April 12, 1960 D. S. CHISHOLM ET AL 2,932,565

METHOD AND APPARATUS FOR MAKING DIE-EXPRESSED METAL SPONGE OF GROUP IV, SUBGROUP A

Filed April 17, 1957 2 Sheets-Sheet 1

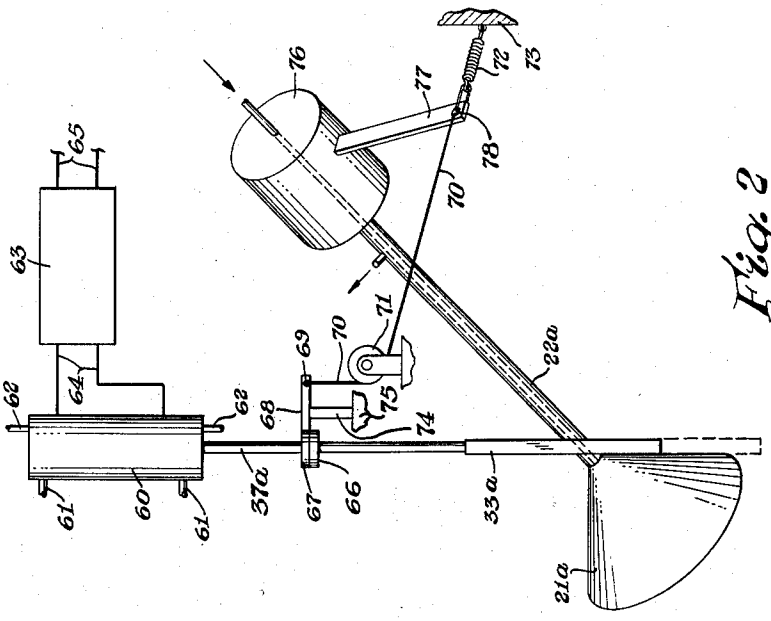


Fig. 2

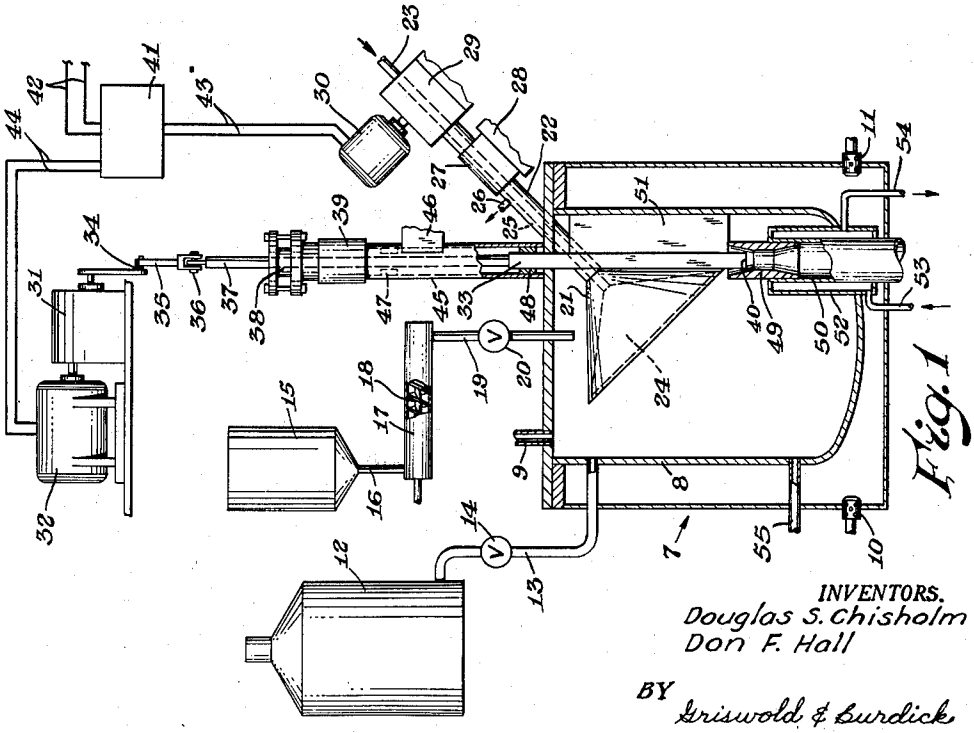


Fig. 1

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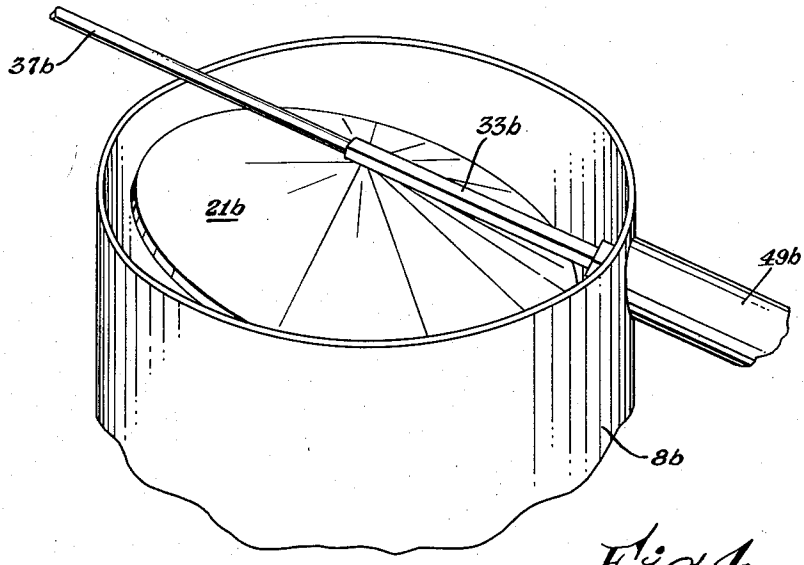


Fig. 4

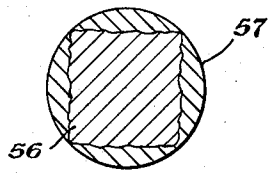


Fig. 3

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METHOD AND APPARATUS FOR MAKING DIE-EXPRESSED METAL SPONGE OF GROUP IV, SUBGROUP A

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Application April 17, 1957, Serial No. 653,391

11 Claims. (Cl. 75—84.1)

This invention is directed to the production of metals of group IV, subgroup a, of the periodic table of elements. More especially it is directed to an improved method of an apparatus for reducing such metals from their salts by the action of a reducing metal to form ingots having a protective sheath thereabout comprising a salt of the reducing metal.

Heretofore, metals of subgroup IVa have been largely produced as a sponge by the reduction of a halide of the metal to be produced, e.g., titanium tetrachloride, by contacting a pool of molten reducing metal, e.g., magnesium, by the halide in vapor form in a reactor. A number of disadvantages are inherent in this practice which limits its usefulness. Among such disadvantages are: The metal produced adheres tenaciously to the walls of the reactor so that the reactor must usually be collapsed or destroyed to release the metal. The reaction also tends to get out of control and cause the reducing metal to vaporize, the resulting vapor then reacting with some of the vaporous halides to produce the reduced metal as dust-like particles. These particles have small value at present since they do not lend themselves well to the formation of metal rods, blocks, or other massive forms. Furthermore, known methods of producing sponge metals of subgroup IVa have not been continuous since the reactive nature of the metal sponge has heretofore required batchwise operation to permit cooling prior to the removal of the metal from the reactor.

In British Patent 734,166 and in our copending U.S. application Ser. No. 315,604, filed Oct. 20, 1952, there is described and claimed a method of an apparatus for reducing a titanium or zirconium halide vapor with magnesium metal at a smoldering temperature to form a sponge of the metal. According to the method therein described, magnesium in the form of particles is deposited upon a supporting surface, such as a steel apron or a circular table, in an atmosphere containing an inert gas and a heated titanium or zirconium halide vapor. The surface is preferably moving and is cooled in relation to the ambient atmosphere containing the halide vapor. The magnesium particles are caused to burn at a smoldering rate by controlling the temperature of the surface where the titanium or zirconium and the by-product magnesium chloride are formed. Some of the magnesium chloride drains from the titanium or zirconium metal and falls to the floor of the reactor while the remainder of the magnesium chloride is entrained in the metal as a part of the reaction product and is removed therefrom later by a suitable means, e.g., vacuum distillation or leaching.

According to one mode of practicing the invention described in British Patent 734,166, the particulate magnesium is deposited on the upper surface of an air-cooled disc which is secured to the lower end of a rotatable hollow driveshaft within a heated reaction vessel containing the vaporous halide of the metal to be reduced. The reaction between the magnesium and the zirconium or titanium halide takes place on the disc forming thereon

magnesium chloride and the titanium or zirconium sponge.

As a method of removing the reaction product comprising titanium or zirconium sponge and some entrained magnesium chloride formed on the rotatable disc according to the British patent, there is described an air-cooled scraper comprising a flat-sided, or preferably somewhat edged, scraper head carried on the end of a reciprocating air-cooled hollow shaft. The shaft is housed in a tube which is affixed to the reaction chamber on one end to a supply of cooling air on the other end. The shaft is reciprocable by means of a crankshaft pivotably attached to an eccentric drive gear. The reciprocable scraper head is positioned to remove the reaction product from the surface of the rotatable disc. The reaction product falls to the bottom of the reaction vessel which contains the magnesium chloride that has drained from the reaction product while on the disc.

The bottom of the reaction chamber shown in the British patent is slanting or hopper-shaped to aid in the removal of the reaction product. The major portion of the magnesium chloride in the reaction product which is a liquid at the temperature of the reaction may be separated from the sponge by the provision of a drain means.

A suggested means for removing the reaction product from the reactor described in the British patent to which reference is made hereinabove comprises a screw conveyor positioned along the slanting bottom of the reactor to carry the reaction product upwardly and outwardly from the body of the magnesium chloride and, by means of an inclosing barrel having an outlet adjacent to the outer end thereof, to drop the reaction product into a receiver through an outlet provided therefor near the outer end of the screw.

Although British Patent 734,166 provides an improved and theretofor novel method of producing titanium and zirconium, the method provided therein for the removal of the reaction product from the reactor is not fully satisfactory where it is desirable that the metal be produced in ingot form or a continuous operation is desired since titanium and zirconium must adequately be protected from air during the production thereof.

There is a desideratum in the art of producing metals of subgroup IVa for a continuous process during which the metal is produced as an ingot protected from the attack of air.

The present invention is predicated on the discovery that a metal of subgroup IVa, viz., titanium, hafnium, thorium, and zirconium produced by the reduction of its halides by a reducing metal on a moving hearth such as for example that described in British Patent 734,166, can be die-expressed to produce an ingot. The preferred embodiment of the invention produces an ingot having a core consisting largely of the produced metal incased in a protective sheath consisting largely of the by-product halide thereby protecting the product from attack and providing a continuous method of operation.

The invention then comprises a method and apparatus for die-expressing a metal of subgroup IVa which is produced on a hearth by reduction thereon of a halide of the metal to be produced by the action of a reducing metal. In the preferred embodiment the die-expressed metal thereby produced is incased in a protective sheath composed largely of the halide of the reducing metal. The accompanying drawing illustrates a preferred embodiment of the invention exemplifying the reduction of titanium tetrachloride by magnesium metal.

Figure 1 of the drawing shows an elevational section of an apparatus of the invention having a reciprocatory ram, rotary cone, and dies associated therewith, the

cone and the ram being driven by alternately operating electric motors. The ram is shown in an advanced position.

Figure 2 shows a modification of the means for obtaining alternate movement of the ram and cone of the apparatus showing the ram in a retracted position.

Figure 3 is a cross-section of an ingot made according to the preferred embodiment of the invention.

Figure 4 is a perspective view with parts removed of a modification of the cone, ram, and die-assemblies of the apparatus of Figure 1 for practicing the invention.

Referring to the drawing and particularly to Figure 1 in greater detail there is shown furnace setting 7 in which is positioned reaction chamber 8. Inert gas is provided by inlet 9. Gas burners 10 and 11 provide heat for reaction chamber 8. Reservoir 12, through feed line 13 having valve 14 therein, supplies titanium tetrachloride to the reaction chamber. Hopper 15, by means of feed line 16, barrel 17 which has screw 18 operating therein and driven by a means not shown, and feed line 19 containing valve 20 therein, supplies the particulated magnesium to reaction chamber 8. The hearth in the form of hollow cone 21 is integrally secured to and is supported by rotatable shaft 22. In shaft 22 is air-cooling channel 23, connected to hollow interior 24 of the cone, and attached to a source (not shown) of incoming cooling air. Annular channel 25 about channel 23 within shaft 22 provides for the return of spent cooling air to air outlet 26. Bearing 27 in bearing support 28 provides a supporting means for the shaft.

Gear box 29, powered by motor 30, rotates shaft 22. Gear box 31, powered by motor 32, reciprocates ram 33 by means of crank 34, connecting rod 35, and wrist-pin 36 at the upper end of rod 37 which passes through stuffing box 38 and guide 39 below which it is secured to the upper end of ram 33. Ram 33 has nose 40 in sliding contact with cone 21. By means of timer 41 connected to a source of current (not shown) by electrical lines 42, and by lines 43 and 44 to motors 30 and 32, respectively, the rotary action of driveshaft 22 and the reciprocatory action of ram 33 are timed to act alternately for predetermined periods of time.

In order that driveshaft 22 and ram 33 have operable clearance, it is necessary that driveshaft 22 be positioned so that it passed ram 33 without interfering with its own action or that of the ram. This clearance may be provided by a number of means among which is that of merely tipping driveshaft 22 slightly so that it is not in the path of ram 33. Although, as the result of such slight tipping, ram 33 does not move exactly radially of cone 21, the practical results obtained by the apparatus for removal of the reaction product from the surface of cone 21 is not affected.

Housing 45 is maintained in an upright position by support 46. Sliding engagement is provided between housing 45 and rod 37 by bearing 47 and between housing 45 and ram 33 by bearing 48.

Elongated die 49 defines a rectangular passageway and enlarged die 50 defines a cylindrical passageway which is aligned with the passageway of die 49 and which leads out of reactor 8. Guide plate 51, having a smooth exposed vertical face, is secured to the wall of reactor 8 so as to extend substantially thereacross in such position that the smooth face is in sliding engagement with that vertical face of ram 33 which is farthest removed from cone 21, and thereby guides ram 33 in its substantially vertical path as well as prevents reaction material, being removed by the ram, from rolling off rectangular nose 40 of ram 33 toward the side of reactor 8 instead of being expressed into die 49.

Cooling jacket 52, having inlet 53 and outlet 54, around die 50 and the lower portion of die 49 provides a cooling means for the dies. A preferred arrangement is to have die 49, the first die, define a square, and die 50, the second die, define roughly a circle having a diameter at least as large as, and preferably slightly larger than, the diagonal of the square defined by die 49. The shape of nose 40 of ram 33 is roughly that of the entrance into the passageway of die 49 with operable clearance for reciprocating therein. However, the ram may merely advance to a position flush with the entrance to die 49 and in such case the nose 40 of the ram need have only the general shape of the die opening. Drain line 55 provides a means for removing molten magnesium chloride from reactor 8.

The practice of the invention will be described according to the embodiment employing titanium tetrachloride and magnesium using the apparatus of Figure 1.

In practicing this embodiment of the invention, pulverulent magnesium of 20 to 200 mesh and preferably from 30 to 100 mesh (U.S. standard sieve series) is placed in hopper 15. A supply of titanium tetrachloride is placed in reservoir 12. By means of gas burners 10 and 11, furnace setting 8 is heated to bring the contents of reactor 8 above the melting point of the magnesium chloride formed but below a temperature which will cause rapid or flaming reaction of the magnesium metal. A temperature between 600° and 900° C. is employed. The recommended temperature is between 708° and 850° C. The magnesium from hopper 15 is caused to fall on cone 21 by operating screw 18 in barrel 17 and titanium tetrachloride is drawn into the reactor through line 13. The reactor chamber 8, thus being heated, the titanium tetrachloride becomes vaporous therein and is disseminated throughout the reaction chamber. The magnesium powder on the cone reacts with the ambient titanium tetrachloride vapors to form the reaction product comprising a reaction mixture of titanium metal and liquid magnesium chloride.

Ram 33, actuated by timer 41, advances downwardly, pushing the reaction product from cone 21 (which is stationary during the action of the ram) into die 49. The ram is caused to begin its movement more or less radially at a point on a relatively short circumference of the cone and to push outwardly toward the cone's periphery, that is, towards the greatest circumference of the cone. The ram thereby pushes the reaction product at predetermined time intervals off the cone. Ram 33 then returns to a retracted position and cone 21 rotates a partial turn as a result of the re-engagement of the driving means for cone 21. The number of degrees of rotation of cone 21 during each partial turn upon its axis and the length of the time interval between each partial rotation during which ram 33 operates are not critical so long as the action of the cone and the inaction of the ram are synchronized and the cone is stationary while the ram moves roughly radially from the cone's center toward its periphery and back again. A suitable arrangement of the apparatus of the invention, for example, is a cone having a circumference of 100 inches which moves through an angle of 7.2° at each partial turn and stops for about 4 seconds for the ram to operate. In other words, the cone stops rotating 50 times during one complete rotation of 360° and the ram makes 15 complete reciprocatory trips along a radius of the cone each minute.

The reaction product which forms on cone 21 is composed essentially of titanium as a metal sponge and magnesium chloride in the molten state. As a result of its molten state, a large portion of the magnesium chloride drains from the titanium sponge on the cone and deposits at the bottom of the reaction chamber where it is removed as desired through drain line 55. An appreciable amount of magnesium chloride, however, remains entrained in the interstices of the titanium sponge. That magnesium chloride which does not drain from the reaction product and is entrained in the titanium sponge is expressed together with the titanium into die 49 by ram 33. Both solidify before leaving die 49 due to cooling jacket 52 and are expressed on into die 50.

The solidified reaction product emerges from die 50 as an ingot comprising predominantly titanium core 56 in-

cased in predominantly magnesium chloride sheath **57** as shown in cross-section in Fig. 3. The core is usually at least 80 percent titanium and the sheath is usually at least 90 percent magnesium chloride.

The formation of the sheath may be explained as follows: The subgroup IVa metal sponge in the reaction product, having interstices therein, is somewhat compressed longitudinally while being expressed through first die **49** by the ram. A substantial portion of the entrained molten salt of the reducing metal, i.e., magnesium chloride in the illustration, is squeezed from the interstices so that it is forced ahead of the titanium metal as it passes through elongated first die **49**. Upon reaching the enlarged cross-section provided by second die **50**, it is forced laterally beyond the periphery of the metal sponge defined by first die **49** and fills the space between the periphery of the metal sponge defined by first die **49** and the confining limits of the extended portion of second die **50**. The somewhat compacted metal sponge moving along the inner portion of the passageway of second die **50** retains the form of first die **49**. Since the dies are provided with cooling means, that salt thus forced into the space about the predominantly metal sponge inner core solidifies in the passageway of die **50** to incase the metal sponge in a protective sheath. An ingot is thus extruded comprising the titanium core and metal halide sheath.

The die-expressed extruded ingot may be cut into convenient lengths by known means, or the operation may be interrupted after predetermined periods of time to provide convenient lengths of the ingot.

A modified means for achieving alternate rotation of cone **21***a*, which is similar to cone **21** of Fig. 1 and reciprocation of ram **33***a*, which is similar to ram **33** of Figure 1, is shown in Figure 2. Hydraulic cylinder assembly **60**, having air-controlled valves therein (not shown), is connected to a source of hydraulic fluid (not shown) by means of lines **61** and **62**. The air-controlled valves therein are timed to admit hydraulic fluid to reciprocate rod **37***a* and ram **33***a* attached thereto by timer **63** connected to cylinder **60** by electric lines **64**. Electric lines **65** lead to a source of electric current (not shown).

To ram **33***a* is secured fixed collar **66**. Adjacent to and supported by fixed collar **66**, when ram **33***a* is in a retracted position, is sliding collar **67** to which is attached arm **68** in which is eyelet **69**. Collar **67**, by means of cable **70** inserted in eyelet **69**, and threaded through pulley **71**, which is under continual tension by a spring **72** secured to bracket **73**, is caused to follow fixed collar **66** when ram **33***a* is advanced, i.e., moved downwardly. Fixed collar **66** is permitted to pass stop **74** which is held in position by support **75**. Sliding collar **67**, however, is prevented from passing stop **74** by arm **68** coming in contact with stop **74**. Shaft **22***a* is operated by a driving mechanism which is inclosed in housing **76** and which is actuated by a conventional over-running clutch (not shown) which is also inclosed in housing **76**. The over-running clutch is attached to the end of arm **77** which extends into housing **76**. In the other end of arm **77** is eyelet **78** into which is made secure the ends of both cable **70** and spring **72**.

When the apparatus of Figure 2 is in operation, cone **21***a* is made to rotate, as by a gear box and a motor similar to those shown in Figure 1, while ram **33***a* and fixed collar **66** are retracted. When ram **33***a* and fixed collar **66** advance by the hydraulic pressure in cylinder **60**, slideable collar **67** also advances due to the tension exerted on collar **67** by spring **72**, but is stopped when arm **68** strikes stop **74**. Collar **67**, being secured by cable **70** to arm **77**, permits spring **72** to move arm **77** counter-clockwise when collar **66** advances, thus causing the over-riding clutch inclosed in housing **76** to disengage the driving mechanism also inclosed in housing **76**. Shaft **22***a*, therefore, stops turning while ram **33***a* continues to advance downwardly, pushing the reaction product from cone **21***a* until the ram has reached an advanced position. Ram **33***a* is then returned to a retracted position by a reversal of hydraulic pressure in cylinder **60** which causes collar **67** to be carried back to its first position by collar **66**. Arm **77** is thus caused to swing in a clockwise arc and again causes the running clutch to engage the drive gear of shaft **22***a*, therefore to cause it to turn until ram **33***a* is again advanced.

Figure 4 shows a portion of a modified apparatus for practicing the invention. Cone **21***b* is shown positioned in reactor **8***b* with cover removed. Cone **21***b* is driven from below by means not shown. Ram **33***b* reciprocates substantially from the center of cone **21***b* to the edge thereof by driving means (not shown) attached to rod **37***b* which is synchronized to operate alternately with the cone-driving means to force reaction product formed on the surface of cone **21***b* into die **49***b*.

Although the practice of the invention has been described according to the drawing for reducing $TiCl_4$ by Mg metal, it is understood that the invention contemplates producing any subgroup IVa metal reducible from its halide by a metal more electropositive than the subgroup IVa metal, e.g., the alkali and alkaline earth metals. It is also understood that the invention contemplates variations of the method described and apparatus shown which fall within the purview of the invention. Instead of a cone, a flat disc or a concavo-convex shaped disc having the convex face upwardly disposed may be employed. When a cone is employed as in the example, the downwardly sloping face adjacent to the ram need not be positioned as shown in the drawing but may be positioned at any desired angle between about 20 and about 90° to the horizontal. The included angle of the cone employed may be any angle of less than 180°, although an included angle of between about 90° and 160° is preferred.

It is necessary that the ram perform a scraping action against the face of the cone with which it is in contact. The contacting faces of the cone and ram need not be exact counterparts of each other, i.e., need not be mirror images of each other, but it is desirable, particularly where a cone having a relatively small included angle is employed, that the cone be contoured into flattened sectors corresponding in angular width equal to the distance the cone is advanced during one rotary movement. Instead of flat sectors, they may be concave resulting in a radially fluted cone surface, and the adjacent surface of the ram be convex to form substantially a mating contacting surface.

Although two concentric dies are described according to the drawing, one die may be employed, thereby forming an ingot of unsegregated subgroup IVa metal and a halide of the reducing metal.

In practicing the invention according to its preferred embodiment there is thus produced convenient length sticks or ingots of a metal extrudate which contains a core of at least 80 percent titanium or other subgroup IVa metal protected by an outer shell or sheath of the by-product halide against corrosion. The sticks of extruded metal thus formed are particularly suitable for use according to our co-pending application Serial No. 649,809, filed April 1, 1957, wherein an ingot thus formed is made a first electrode and fed into an atmosphere of inert gas in which is a second electrode in the form of a rotating rod or disc, which may be either impure titanium, i.e., a cylindrical rotating rod similar to the first electrode or of substantially pure titanium, and striking an electric arc between the nose of the first electrode and preferably the periphery of the rotating electrode to melt the first or non-rotating electrode to form titanium prills intermixed with the halide salt from which the latter can be readily removed.

As an alternative mode of operation, the extruded metal of the present invention need not be cut into lengths, but may be fed, by employing a continuous

means, directly into the apparatus described in the copending application mentioned in the paragraph above.

Having described the invention, what is claimed and desired to be protected by Letters Patent is:

1. In an apparatus for the production of a subgroup IVa metal sponge containing by-product reducing metal halide, having a reaction chamber provided with a heating means and a means for causing a flow of an inert gas therethrough, a means for providing a salt of a subgroup IVa metal and a reducing metal therein, and a rotatable circular surface positioned therein to receive the reducing metal, the improvement comprising a reciprocating ram positioned to move substantially radially outwardly on the face of said surface toward its periphery, a synchronized driving means for rotating said surface and alternately reciprocating said ram, and a die substantially aligned with said ram near the end of its radially outward movement to receive the subgroup IVa metal sponge and by-product halide.

2. The apparatus of claim 1 wherein said die is provided with a cooling means.

3. In an apparatus for the production of a metal of a subgroup IVa, having a reaction chamber provided with a heating means and a means for causing a flow of an inert gas therethrough, a means for providing a halide of subgroup IVa metal and a pulverulent reducing metal therein, and a rotatable circular hearth positioned therein to receive the reducing metal, the improvement comprising a reciprocatory ram positioned to move substantially radially outwardly on the face of said surface toward its periphery to remove reaction product formed on said hearth, a synchronized driving means for rotating said hearth and reciprocating said ram to effect alternate operation thereof, and associated with said ram and substantially aligned therewith a first elongated die opening into a second elongated die, said second die being substantially concentric with and of larger cross-section than said first die.

4. The apparatus of claim 3 wherein a guide plate is secured to the inner wall of said reaction chamber and positioned in sliding engagement with the side of said ram which is opposite to the side in contact with said circular hearth to guide the reaction product into said first die.

5. The apparatus of claim 3 wherein said first die defines a rectangular passageway therethrough and said second die defines a substantially cylindrical passageway therethrough having a diameter at least as large as the diagonal of said rectangular passageway.

6. The apparatus of claim 3 wherein said circular hearth is a cone having its apex upwardly disposed and having an included angle of at least 90°.

7. The apparatus of claim 3 wherein said circular hearth is a concavo-convex disc having its convex side upwardly disposed.

8. The apparatus of claim 3 wherein said circular hearth comprises a series of flattened sectors having an angular width equal to the angular movement of the cone during a single rotary advancement.

9. The apparatus of claim 8 wherein said sectors are concave and the adjacent face of said ram is convex to form substantially mating contacting surfaces.

10. In the method of producing a metal selected from the group consisting of hafnium, titanium, thorium, and zirconium from a halide by means of a reducing metal selected from the group consisting of the alkali and alkaline earth metals wherein the reducing metal is continuously caused to fall on a rotatable surface in an atmosphere comprising an inert gas heated to a temperature not less than the melting point of the halide of the reducing metal being produced to effect a reaction between the reducing metal and the halide in the vapor state on the rotatable surface to produce a reaction product comprising the metal sponge of the metal to be produced and the halide of the reducing metal, the improvement consisting of alternate rotation of the surface and removal of a portion of the reaction product formed thereon, said removal being accomplished by pushing a portion of the thus-produced reaction product radially outwardly to the periphery of the said surface, and die-expressing the reaction product thus removed.

11. The process of claim 10 wherein the halide, from which the metal selected from the class consisting of hafnium, titanium, thorium, and zirconium is produced, is titanium tetrachloride and the reducing metal is pulverulent magnesium.

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