

May 24, 1955

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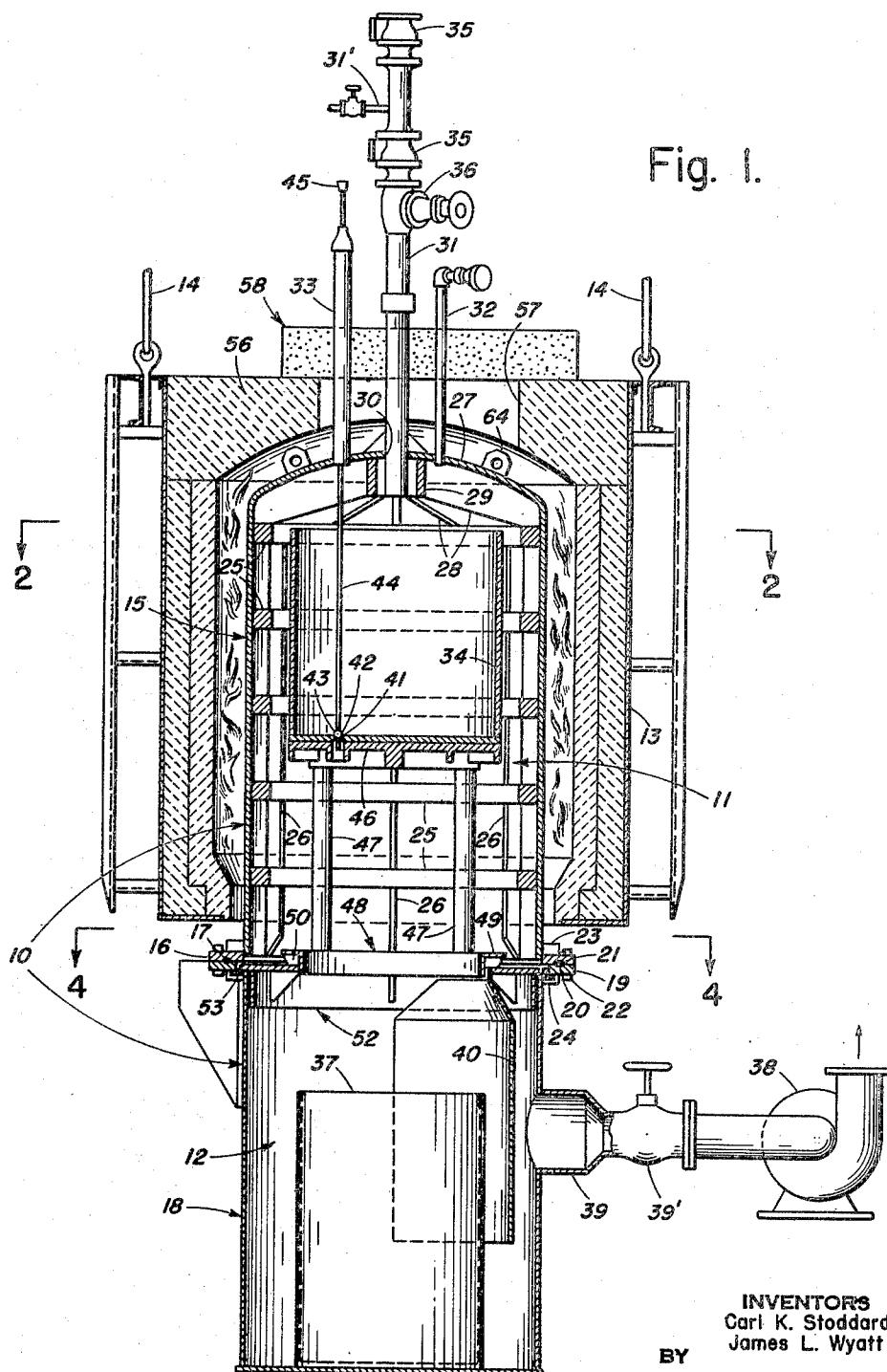
2,709,078

APPARATUS FOR PRODUCTION OF REFRACTORY METALS

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4 Sheets-Sheet 1

Fig. 1.



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Fig. 2.

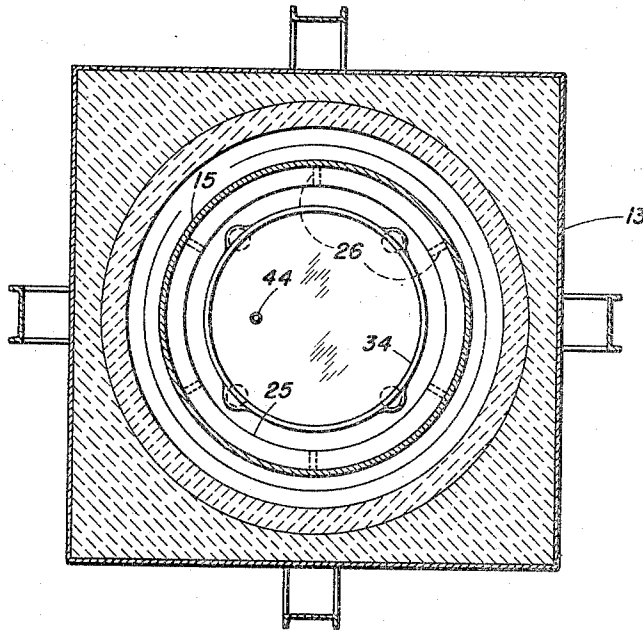


Fig. 4.

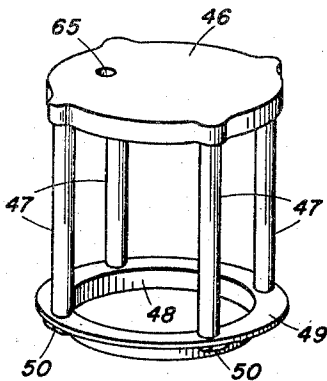
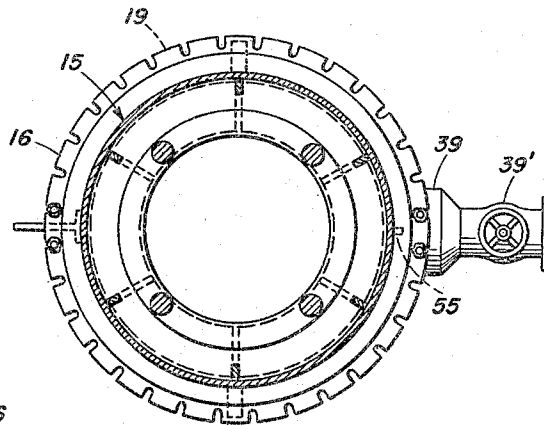


Fig. 5.

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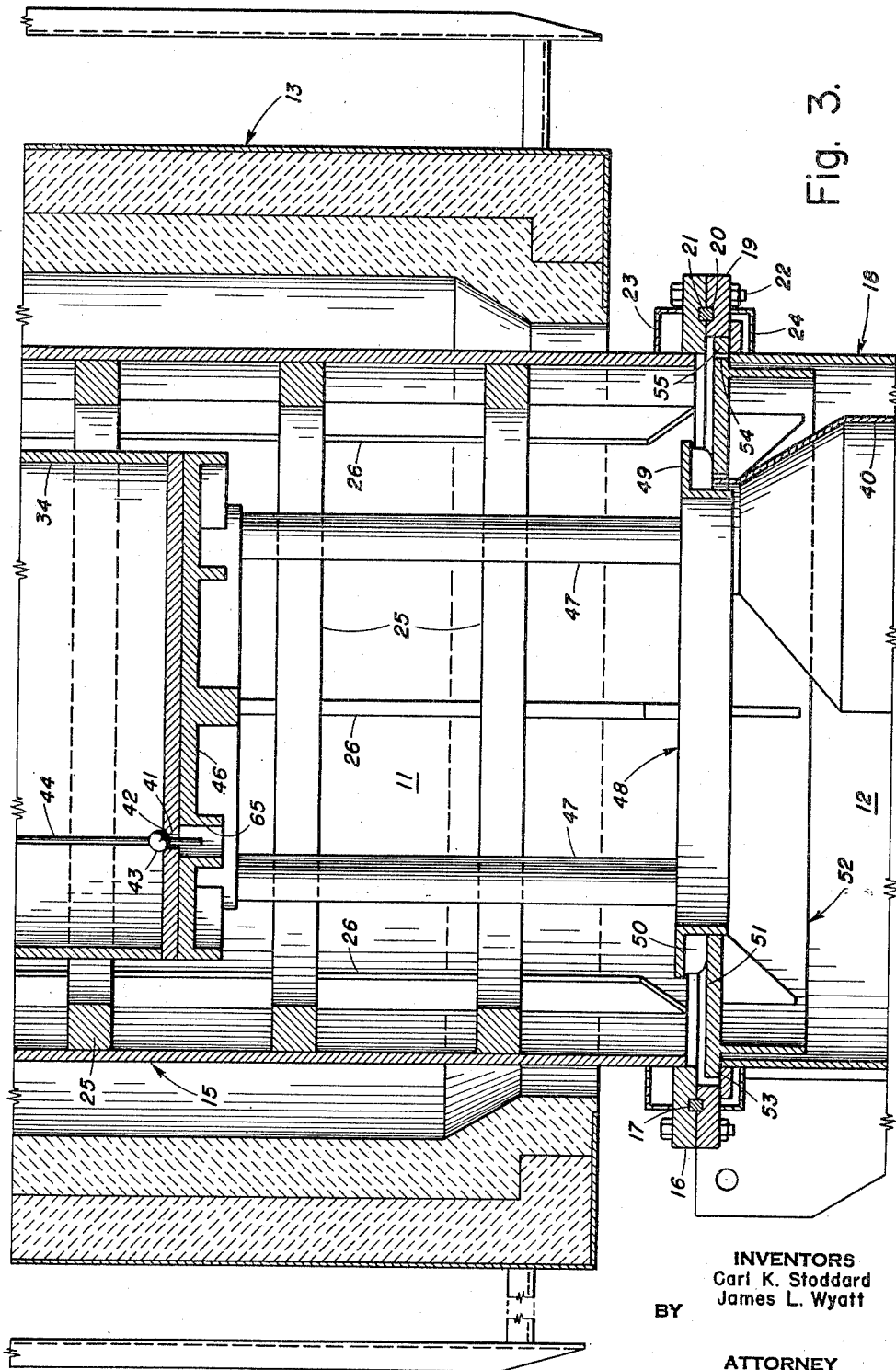
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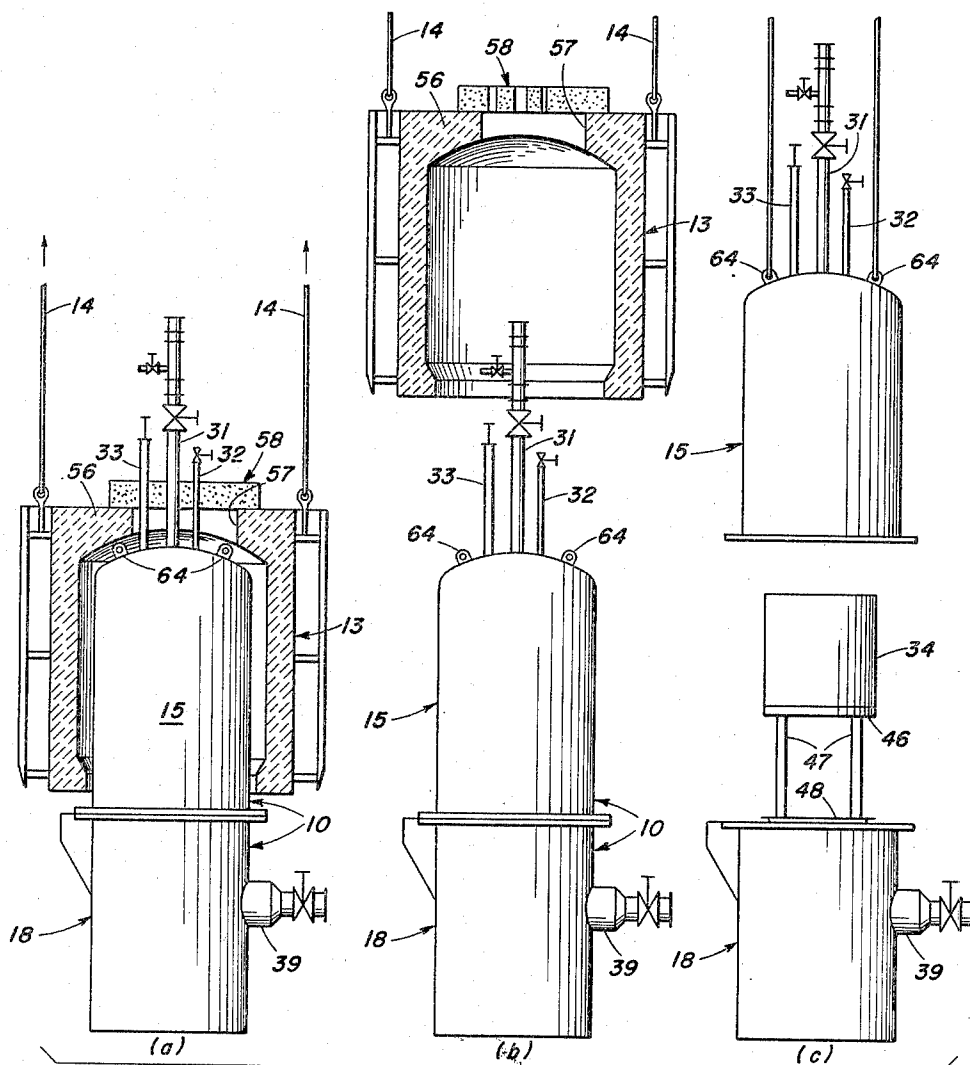


Fig. 6.

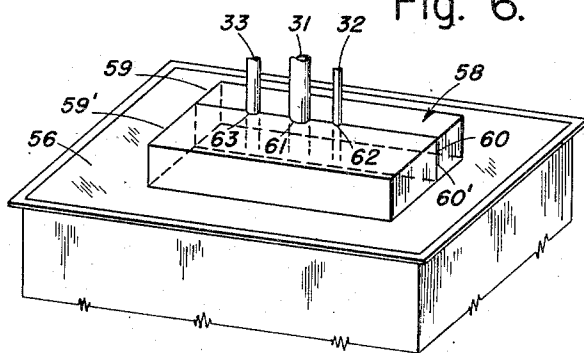


Fig. 7.

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APPARATUS FOR PRODUCTION OF REFRACTORY METALS

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Application July 23, 1952, Serial No. 300,542

2 Claims. (Cl. 266—19)

The present invention relates in general to the production of a refractory metal and more especially to improved apparatus for producing a refractory metal by reacting a halide of a refractory metal with a reactant metal. In particular, the apparatus of the present invention is adapted to the production of titanium metal by reacting titanium tetrachloride with magnesium or sodium but it will be understood that the apparatus may be used for the production of other refractory metals.

The present invention is a continuation in part of the copending application of Carl K. Stoddard et al., Serial No. 164,644, filed May 27, 1950 and issued as U. S. Patent No. 2,663,634, December 22, 1953, which discloses and claims a method for producing titanium metal employing multi-zonal apparatus, the present invention relating to improved multi-zonal apparatus especially suited to the production of titanium metal on a commercial scale.

Many processes have been proposed for producing titanium metal by employing reducing metals such as magnesium and sodium. In most of these processes, however, the titanium metal is formed in a reactor pot in situ with the chlorides of the reducing metal. As a result, these chlorides and the titanium metal form a hard fused mass of material which must be chipped out or otherwise removed in the form of small lumps from the reaction pot and subsequently leached to separate the titanium metal from the chloride of the reducing metal. This process is extremely laborious and costly due to the excessive handling required and the low rate of production. Moreover, a far greater disadvantage of prior methods for forming titanium metal has been the exposure of the metal to the atmosphere prior to the chipping and leaching operations with the result that successive batches of titanium metal are non-uniform, the ductility of the metal, in particular, being low, as a consequence of which the metal has been unsatisfactory for commercial applications.

An object of the present invention is to provide improved apparatus of the multi-zonal type for producing titanium metal in an economical and commercially practical manner.

A further object of the invention is to provide improved apparatus for reacting volatilized titanium tetrachloride with molten magnesium metal to produce a titanium metal sponge free from substantial amounts of magnesium and magnesium chloride.

A still further object of the invention is to provide improved multi-zonal apparatus for reacting volatilized titanium tetrachloride with molten magnesium metal in an oxygen free atmosphere to produce titanium metal sponge and magnesium chloride wherein the latter is continuously or intermittently removed at selected intervals from the reaction pot during the reaction to preclude the inclusion of any substantial amount of magnesium chloride in the titanium metal sponge; any residual molten magnesium metal or included magnesium chloride being

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distilled off from the titanium metal sponge before exposing the latter to the atmosphere.

A still further object of the invention is to provide improved apparatus for producing titanium metal having a multi-zonal reaction unit of improved construction such that the receiving-and-condensing zone of the unit may be disassociated from the reaction zone with ease and dispatch to facilitate recovery of the titanium metal sponge.

These and other objects, features and advantages will become apparent from the following more complete description of the instant invention.

In the accompanying drawings in which certain modes of carrying out the present invention are shown for illustrative purposes:

Fig. 1 is a vertical elevation in section of an embodiment of the improved refractory metal producing apparatus of this invention, including the diagrammatic illustration of a furnace associated therewith;

Fig. 2 is a plan view of the reaction unit of the apparatus on section line 2—2 of Fig. 1;

Fig. 3 is a vertical section of enlarged fragmentary portions of the lower and upper ends respectively of the reactor shell and condensing shell of the reaction unit showing details of the flanges at the interconnected ends thereof and the reaction pot supporting ring;

Fig. 4 is a plan view of the apparatus on section line 4—4 of Fig. 1;

Fig. 5 is a perspective view of the reaction pot supporting cage;

Fig. 6 is a schematic illustration of the apparatus in three stages of its use; and

Fig. 7 is a schematic perspective view of the upper end of the furnace showing the split-cover arranged thereon.

In its broadest aspects the invention relates to superior apparatus comprising a reaction unit, including a reaction pot, heating means for reacting volatile titanium tetrachloride with molten magnesium metal in the pot in a substantially oxygen-free atmosphere to form titanium metal sponge and molten magnesium chloride; flow regulating means for controlling the outflow of molten magnesium chloride from the reaction pot during the reaction; and means for subsequently distilling and condensing off any residual molten magnesium metal and molten magnesium chloride from the titanium metal sponge, the entire operation being conducted in an atmosphere containing substantially no reactive gases other than titanium tetrachloride to insure the production of a substantially pure highly ductile metal.

The apparatus of this invention comprises, in the main, a reaction unit, indicated generally at 10, having an upper zone or chamber, indicated generally at 11, in which the reaction between titanium tetrachloride and molten magnesium is carried out to produce titanium metal sponge and molten magnesium chloride; a lower zone or chamber, indicated generally at 12 in which the molten magnesium chloride is collected; and heating means comprising a heating unit, indicated generally at 13 which serves to heat the upper chamber 11 of the reaction unit to precipitate the reaction between the titanium tetrachloride and magnesium metal.

Pursuant to the objects of this invention the reaction unit 10 is disposed in a substantially upright position normally with the end corresponding to its lower chamber resting on a stationary support, such as, for example, the floor, while the heating unit 13 is supported above the upper chamber 11 of the reaction unit by means of chains or cable 14—14 fastened to an overhead crane (not shown) whereby the heating unit may be raised and lowered respectively from and into operative position with respect to the upper chamber 11 of the reaction unit 10 as and for the purpose hereinafter described.

Referring especially to the reaction unit 10 the latter

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is a composite tubular member comprising the aforesaid upper chamber 11 and the lower chamber 12 the upper chamber 11 being defined by can-shaped member 15, sometimes hereinafter referred to as the reactor shell, formed preferably of heavy gauge stainless steel and arranged with its open end down. As shown especially well in Fig. 3 the open end of the reactor shell 15 is provided with a relatively thick annular outwardly projecting integral flange 16 having an annular sealing groove 17 in its bottom face.

The lower chamber 12 of the reaction unit is also defined by a sheet metal can-shaped member 18, sometimes hereinafter referred to as the condensing-and-receiving shell of the reaction unit, and is formed preferably of heavy gauge sheet steel and arranged with its open end uppermost, its open end being provided with a relatively thick annular outwardly projecting integral flange 19 having an annular sealing groove 20 in its upper face. Referring especially to Fig. 3, the annular flanges 16 and 19 are of substantially the same diameter and are adapted to be detachably secured in sealed relationship by means of an annular sealing gland 21 which is seated in the conjoined sealing grooves 17 and 20 of the flanges; and by fastening means such as, for example, bolts 22 secured in apertures arranged circumferentially in the respective annular flanges 16 and 19.

As a precaution against overheating the sealing gland 21 and the transfer of heat from the reactor shell 15 to the receiving-and-condensing shell 18 each flange is provided with an annular sheet metal cooling chamber 23 and 24 respectively through which a coolant, such as, for example, water, is circulated.

During the operation of the reaction unit the reactor shell 15 is subjected to extreme changes in temperature while at the same time its interior is sometimes below and sometimes above atmospheric pressure. Consequently, the reactor shell is subjected to severe strains. In order to withstand these strains the reactor shell 15 is preferably reinforced on its interior with a skeleton framework which may comprise a plurality of stiff metal rings 25 welded or otherwise secured to the inner walls of the shell in vertically spaced substantially horizontal planes; and a plurality of stiff metal ribs 26, preferably high temperature strength alloy steel, welded to the rings 25 in substantially vertical circumferentially spaced relationship therearound. The top wall 27 of the reactor shell is also reinforced as, for example, by means of a high temperature strength alloy steel spider 28 which is characterized by an annular collar 29 located substantially at the center of the top wall of the shell and in axial alignment with a vertical aperture 30 in which is secured the lower end of a feed pipe 31. Two other apertures are provided in the top wall 27 of the reactor shell on opposite sides of the feed pipe 31 in which are secured a second feed pipe 32 and a guide sleeve 33 respectively. The feed pipe 31 is provided for delivering magnesium metal into a reaction pot 34, hereinafter described, in the upper chamber 11 of the unit, sometimes hereinafter referred to as the reaction chamber, and to this end is provided at its upper end with a pair of vertically spaced full port area valves 35—35 below which is a shut-off valve 36. Intersecting the feed pipe 31 between the valves 35—35 is a valved feed pipe 31' for feeding a non-reactive gas such as, for example, helium or argon into the reaction unit and for purging the portion of the feed pipe above the lower valve 35 of air. In accordance with this construction, successive charges of magnesium metal may be fed into the reaction pot without admitting air into the unit.

The feed pipe 32 is connected to a source of titanium tetrachloride for delivering vaporized or liquid titanium tetrachloride into the reaction chamber of the unit while the fixed sleeve 33 constitutes a guide and sealing gland for slidably supporting the upper end of a ball-valve operating rod hereafter described.

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Supported within the lower chamber 12 of the reaction unit, sometimes hereinafter referred to as the receiving-and-condensing chamber of the unit, is a receptacle 37 for receiving the outflow of molten magnesium chloride from the reaction pot 34. As will be described below, the interior of the reaction unit is adapted to be evacuated to purge the unit of oxygen, and to be maintained at subatmospheric pressure upon completion of the reaction, to distill off residual magnesium metal and magnesium chloride from the titanium metal sponge and to these ends evacuating means such as, for example, a vacuum pump 38 is connected to the interior of the reaction unit by a pipe 39 and valve 39' connected into the wall of the receiving-and-condensing shell 18. As a precaution against drawing the distillate from the interior of the receiving-and-condensing shell 18 into the vacuum pump 38, a semi-cylindrical sheet metal baffle 40 is supported in the receiving-and-condensing chamber with its cylindrical surface arranged opposite the pipe-connection 39 as shown especially well in Fig. 1.

Supported in the reaction chamber of the reactor shell 15 is the reaction pot 34 comprising a can-shaped receptacle formed of relatively thick metal, the bottom of which is provided with flow restricting means preferably in the form of valve means, comprising a valve port 41 having a valve seat 42 and a ball-valve 43.

The valve port 41 of the reaction pot is provided for permitting the egress of molten magnesium chloride from the interior of the reaction pot during the reaction between the volatile titanium tetrachloride and the molten magnesium metal; the outflow of molten magnesium chloride through the valve-port 41 being controlled by the ball valve 43 which is carried on the lower end of a valve operating rod 44. The upper end of the latter extends upwardly through a packing gland at the top of the aforesaid guide sleeve 33 and may be provided at its upper extremity with operating-means such as, for example, a handle 45 for raising and lowering the ball-valve 43 with respect to the valve seat 42 of the valve port 41.

As shown especially well in Fig. 1, the diameter of the reaction pot 34 is appreciably less than the inside diameters of the annular reinforcing rings 25 of the reactor shell, while the vertical dimension of the reaction pot is substantially half the corresponding dimension of the reactor shell as and for the purpose herein-after described. The reaction pot 34 is adapted to be supported in the upper half of the reactor shell and to this end is mounted on a substantially flat circular base plate 46 substantially equal in diameter to the diameter of the pot and provided with a vertical aperture 65 substantially in axial alignment with the valve port 41 of the pot. As shown especially well in Fig. 5 the base plate 46 constitutes the upper platform of a cylindrical cage comprising four leg members 47 seated at their upper ends in sockets in the underside of the base plate 46 and attached at their lower ends at circumferentially spaced points around the rim of a flanged ring 48. Affixed to the under side of the flange 49 of the ring 48 at four substantially equally spaced points therearound are semi-spherical protuberances or lugs 50. The latter are adapted to engage on the upper face of the annular inwardly projecting flange 51 of a supporting ring 52, as shown especially well in Fig. 3, so as to maintain the respective flanges 49 and 51 in vertically spaced substantially parallel planes and hence prevent overheating and warpage of the respective flanges.

The aforesaid flanged supporting ring 52 is provided for removably supporting the pot supporting cage in the reactor shell and to this end its diameter is slightly less than the inside diameter of the receiving-and-condensing shell 18 so as to fit down freely into the open end thereof, the flanged supporting ring 52 being supported, in turn, in the open end of the shell 18 by an annular flange 53 which is an outward extension of the flange 51 to engage on the upper rim of the shell 18. As shown especially

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well in Fig. 3 the outwardly projecting flange 53 of the flanged supporting ring 52 is provided at one point with a vertical aperture 54 adapted to engage over an up-standing lug 55 provided on the flange of the receiving-and-condensing shell 18 to prevent the flanged supporting ring 52 from rotating relative thereto.

In accordance with the above-described construction the reaction pot 34 is removably supported within the reactor shell 15 in annular spaced relationship to the reinforcing rings 25 thereof and in the upper portion of the shell as a consequence of which substantially unobstructed space is provided around the reaction pot for permitting the distillate which rises from the pot into the reaction chamber to be evacuated from the reaction chamber of the reactor shell and drawn downwardly freely through the pot supporting cage and flanged supporting ring 52 into the receiving-and-condensing chamber of the reaction unit by the vacuum pump.

Referring especially to Figs. 1 and 6 the heating unit 13 of the apparatus is shown as a hood-shaped furnace having a substantially cylindrical interior of sufficient dimensions to be lowered over the reaction unit and in particular the reactor shell portion 15 thereof; and to be raised therefrom. To these ends the top wall 56 of the furnace 13 is provided with a vertical aperture 57, the dimensions of which are sufficient to provide clearance for the aforesaid feed pipes 31 and 32 and the valve operating guide sleeve 33 of the reaction unit. During the operation of the reaction unit the furnace is lowered over the reaction unit and the aperture in the top wall of the furnace is closed by means of a split cover, indicated generally at 58. As shown especially well in Fig. 7, the split cover comprises two complementary cover-halves 59—59' slidably mounted on the top wall of the furnace with the meeting edges 60—60' of the cover-halves being provided with vertical semi-cylindrical recesses which, when the meeting edges 60—60' of the cover-halves 59—59' are in abutting engagement form cylindrical apertures 61, 62 and 63 respectively for the feed pipes and valve operating guide sleeve. Suitable locking means (not shown) may be provided for locking the cover-halves in abutting engagement during the reaction. Upon completion of the reaction and preparatory to raising the furnace relative to the reactor shell, the cover-halves are unlocked and drawn apart to provide clearance for the feed pipes and valve operating guide sleeve of the reaction unit.

The operation of the apparatus for producing titanium metal sponge may be described briefly as follows:

Assuming that the reaction unit is assembled as shown in Figs. 1 and 6, i. e. with its pipe connection 39 connected to a vacuum pump 38, with the ball valve 43 seated in the valve port 41 of the reaction pot and with the furnace 13 lowered down over the reactor shell 15 the valve 39' is opened and the vacuum pump is started to evacuate the reaction unit of any air or oxygen. At the same time helium is fed into the reaction unit through the feed pipe 31' to provide a helium atmosphere therein. The furnace is then turned on to preheat the reaction pot to an initial temperature of about 725° C. and thereafter valve 39' in the vacuum pipe 39 is closed, the vacuum pump is shut off and titanium tetrachloride in the form of a liquid or a vapor is introduced into the reaction pot by way of the feed pipe 32 preferably in an amount sufficient to maintain a positive pressure of from 15 to 17 lbs. absolute in the reaction unit. Magnesium metal is then added intermittently to the pot by means of the feed pipe 31, which is purged with helium with each charge of magnesium, the rate of feed of the titanium tetrachloride being about 0.5 lb. per minute and the rate of feed of the magnesium metal being about 1 lb. every 7½ minutes. The solid magnesium metal falls to the bottom of the reaction pot where it is promptly melted and reacted upon by the titanium tetrachloride gas to form titanium metal sponge and molten magnesium chloride. As the reaction proceeds the temperature of the

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reaction zone is held from between 900° C. and 980° C. During any predetermined period of time additions of titanium tetrachloride and magnesium metal are made to the reaction pot and at predetermined intervals the ball-valve 43 is raised from its valve seat 42 to permit the molten magnesium chloride in the pot to flow out of the valve port in the bottom of the reactor pot into the receptacle in the receiving-and-condensing chamber 18 of the unit. In general the ball valve 43 seals the valve port of the reaction pot until such time as the reaction between the titanium tetrachloride and molten magnesium is initiated and thereafter the ball valve may be raised relative to its valve seat to maintain close control over the rate of egress of molten magnesium chloride from the pot, thereby insuring maximum efficiency of operation.

After the capacity of the reaction pot has been reached, the titanium tetrachloride and magnesium metal feed are cut off leaving titanium metal sponge in the reaction pot along with any residual magnesium chloride and unreacted magnesium metal interspersed throughout the titanium metal sponge.

Pursuant to the objects of the present invention, the residual magnesium chloride and unreacted magnesium metal are adapted to be removed from the titanium metal sponge without disturbing the reaction pot or exposing its contents to the atmosphere. To these ends upon completion of the reaction the valves of the feed pipes 31 and 32 of the reaction unit are closed. With the furnace still in position over the reactor shell so as to retain the heat therein, as illustrated in Fig. 6 (a), the vacuum pump 38 is started and the valve 39' opened to release the pressure within the reaction unit and thereafter establish a relatively high vacuum therein whereupon the residual magnesium chloride and unreacted magnesium metal in the titanium metal sponge are distilled off and condensed in the lower chamber of the reaction unit without exposing the titanium sponge to the atmosphere and at a temperature of from about 640° C. to about 950° C., the distillate being drawn upwardly initially out of the reaction pot into the reaction chamber and then downwardly from the reaction chamber by way of the free space between the reaction pot and the walls of the reaction chamber, through the reaction pot supporting cage and into the receiving and condensing chamber where the distillate is collected in the form of a solid condensate. Referring especially to Fig. 6 (b), upon completion of the vacuum distillation and condensing phases of the operation, the connections to the feed pipes 31 and 32 are broken. With the valves of the feed pipes and the valve 39' of the vacuum pipe connection closed the cover-halves 59, 59' of the split cover 58 are moved apart and the furnace is then drawn upwardly relative to the reactor shell 15 to allow the latter and in particular the titanium metal sponge in the reaction pot to cool off.

While it is preferred in the interest of maximum economy in the commercial production of the titanium sponge to move the reaction unit bodily to a cooling station, it will be understood that this technique is not essential and that upon removal of the furnace the reaction unit may be allowed to cool off without moving it to a cooling station. During the cooling off period the vacuum within the reaction unit is preferably replaced by a helium atmosphere. After the termination of a predetermined cooling period, the reactor shell 15 is disconnected from the receiving-and-condensing shell 18 of the reaction unit by unfastening the bolts 22 of the sealed flanges. Cables are then attached to the ears 64 of the reactor shell 15 whereupon the reactor shell is drawn upwardly relative to the reaction pot in the manner illustrated in Fig. 6 (c) to give access to the latter which is then removed to a boring station at which the titanium metal sponge is bored out or otherwise removed from the reaction pot.

After removal of the reaction pot from the reaction pot

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supporting cage, the latter may be dismantled from the flanged supporting ring 52 whereupon the latter is removed from the rim of the receiving-and-condensing shell 18 to give access to the receptacle 37 in which the molten magnesium chloride has collected. The condensed distillate comprising magnesium metal and magnesium chloride will have collected on the side walls of the reactor shell, and in the receiving-and-condensing shell and may be removed by scraping, chipping and similar techniques to prepare the apparatus for another batch operation.

By the improved apparatus of this invention the production of substantially pure titanium metal sponge by reaction of titanium tetrachloride with magnesium metal may be carried out under controlled conditions in the absence of contact with the atmosphere and in a manner to insure maximum volume of titanium metal sponge with each batch operation.

While the invention has been described and illustrated by the apparatus shown in the drawings, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

What is claimed is:

1. In an apparatus for producing a refractory metal by reacting a tetrachloride of a refractory metal with a reactant metal in an oxygen free atmosphere: a sectional air-tight reaction unit comprising an inverted can-shaped reactor shell having an annular flange adjacent its open end, a can-shaped condensing shell arranged with its open end opposite the open end of said reactor shell and provided with an annular flange corresponding to the annular flange of said reactor shell; fastening means on said flanges arranged to detachably secure said flanges in sealing engagement; structural means to reinforce said reactor shell comprising a lattice-like frame secured to the inner walls of said reactor shell; a reaction pot in said reinforced reactor shell; and means to sup-

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port said reaction pot in said reinforced reactor shell comprising a flanged supporting ring mounted in the open end of said condensing shell and a pot supporting cage carried by said flanged supporting ring, said pot bottom having a valve port therein; and manually operated valve means in said valve port arranged to control the egress of molten reacting materials from said reaction pot.

2. In an apparatus for producing a refractory metal by reacting a tetrachloride of a refractory metal with a reactant metal in an oxygen free atmosphere: a sectional air-tight reaction unit comprising an inverted can-shaped reactor shell; a can-shaped condensing shell arranged with its open end opposite the open end of said reactor shell; fastening means constructed and arranged to detachably fasten together the opposed open ends of said reactor shell and said condensing shell; reinforcing means for said reactor shell comprising a plurality of stiff metal ribs secured to the inner wall thereof; a reaction pot in said reinforced reactor shell; and pot supporting means constructed and arranged to be mounted in the open end of said condensing shell and supported by the lower shell, and to support said pot within said reactor shell.

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