

May 29, 1956

S. MELLGREN
FUSED SALT ELECTROLYTIC CELL FOR THE
PRODUCTION OF REFRACTORY METALS

2,748,073

Filed Dec. 11, 1951

4 Sheets-Sheet 1

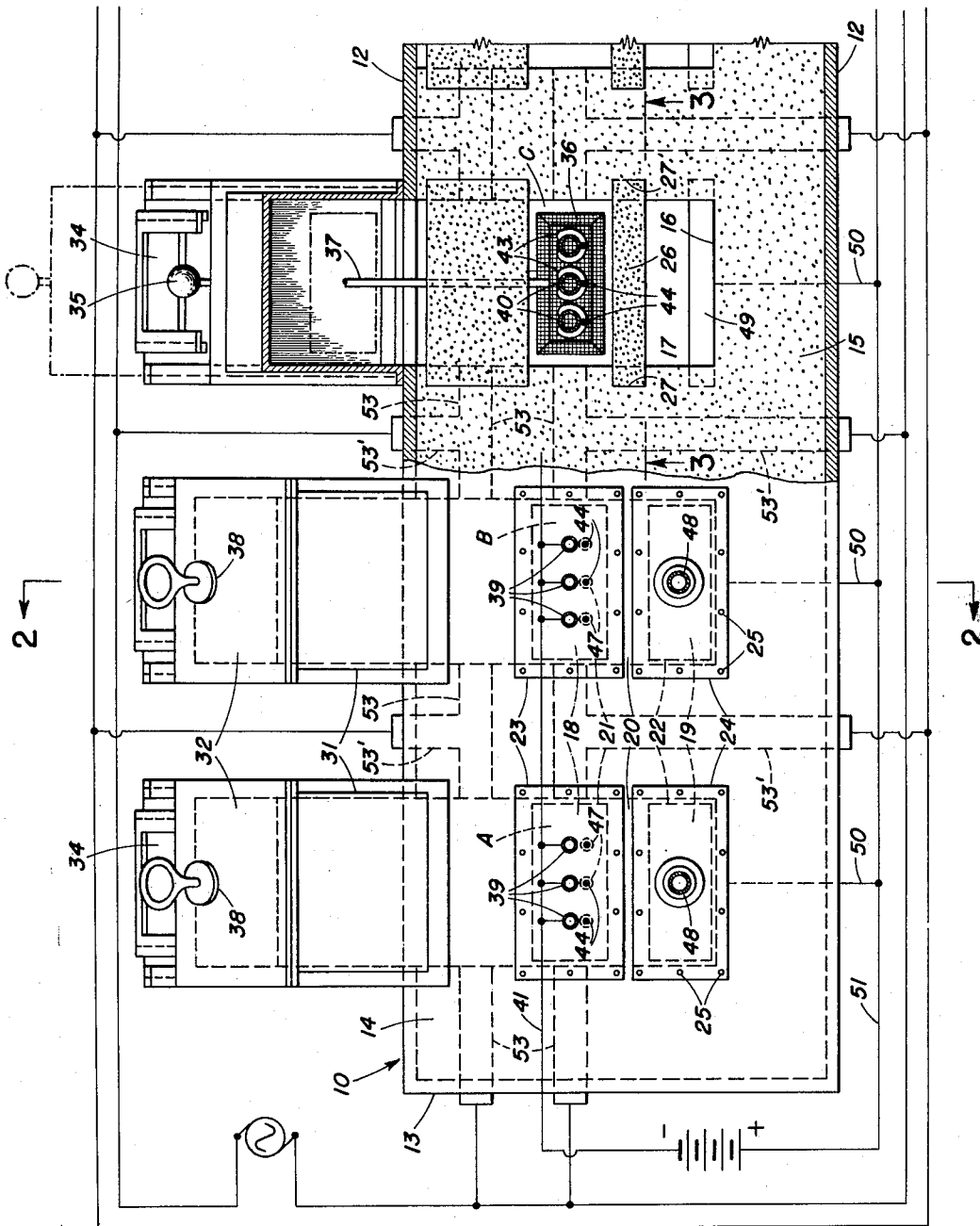


Fig. 1.

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38

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4 Sheets-Sheet 2

Fig. 2.

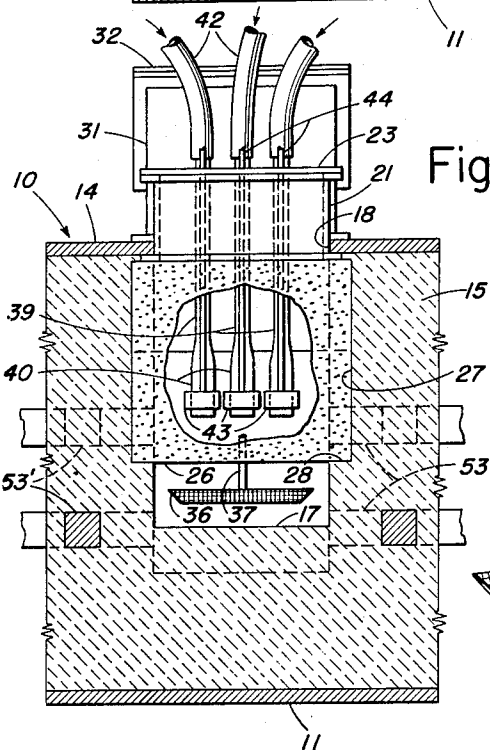
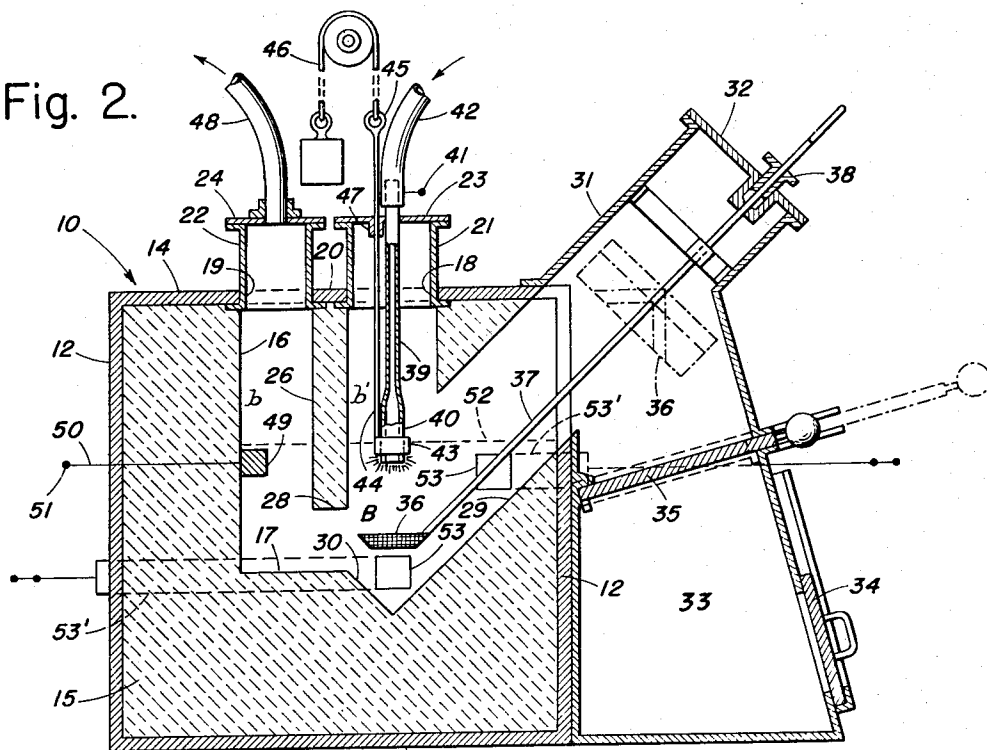


Fig. 3.

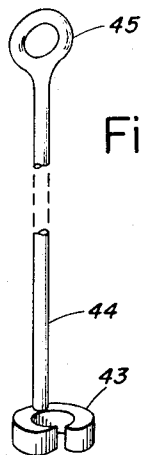


Fig. 4.

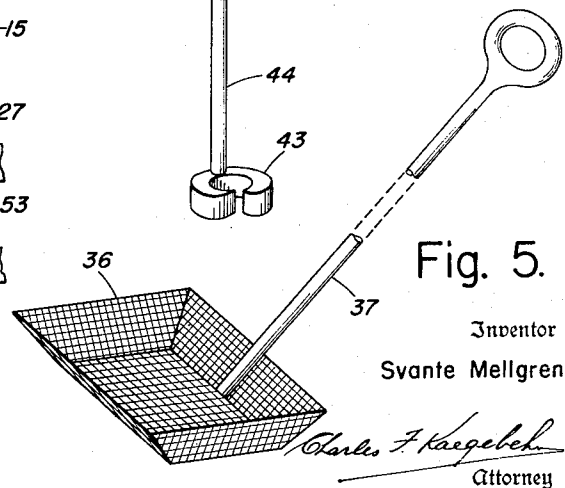


Fig. 5.

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4 Sheets-Sheet 3

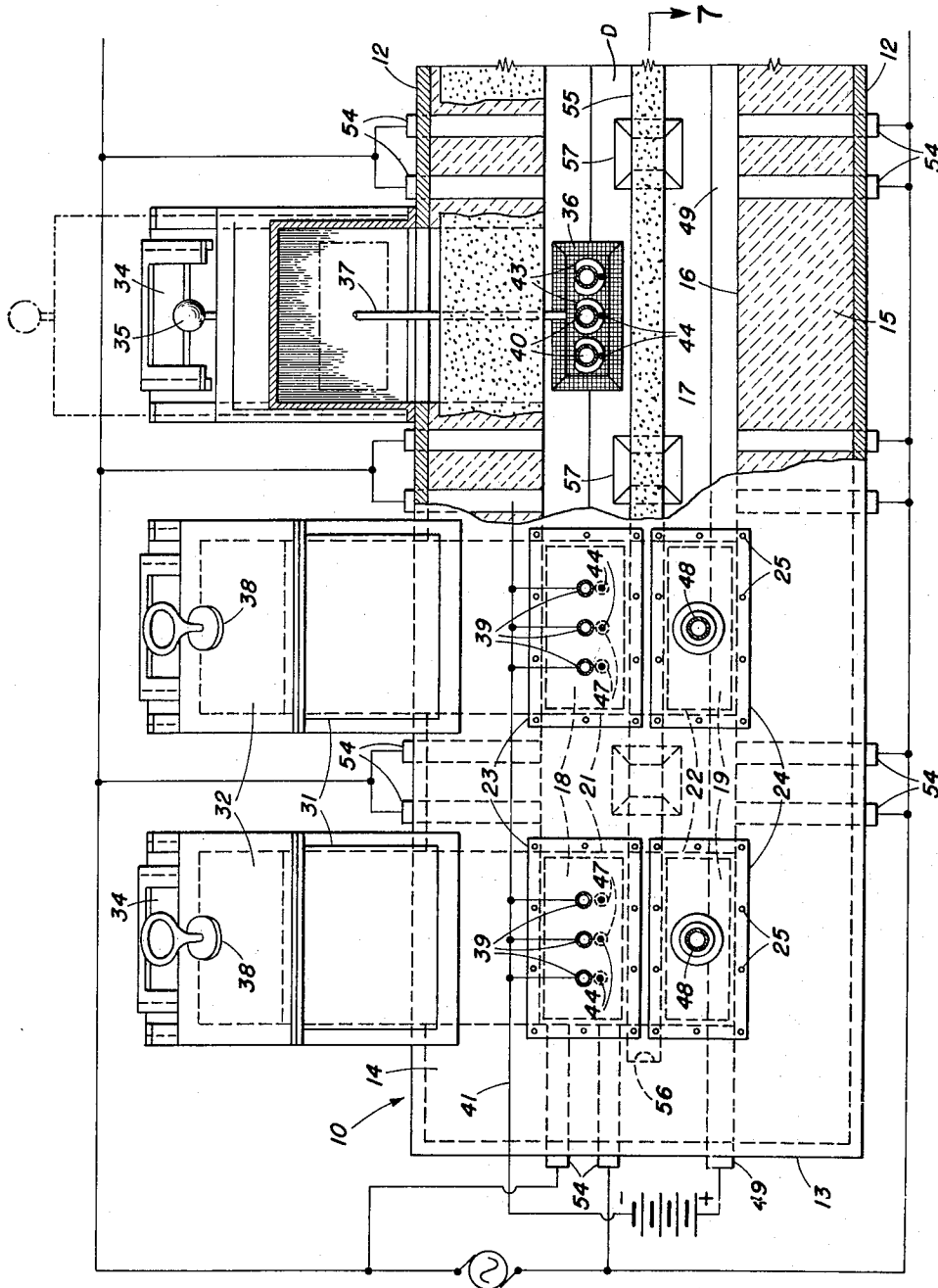


Fig. 6.

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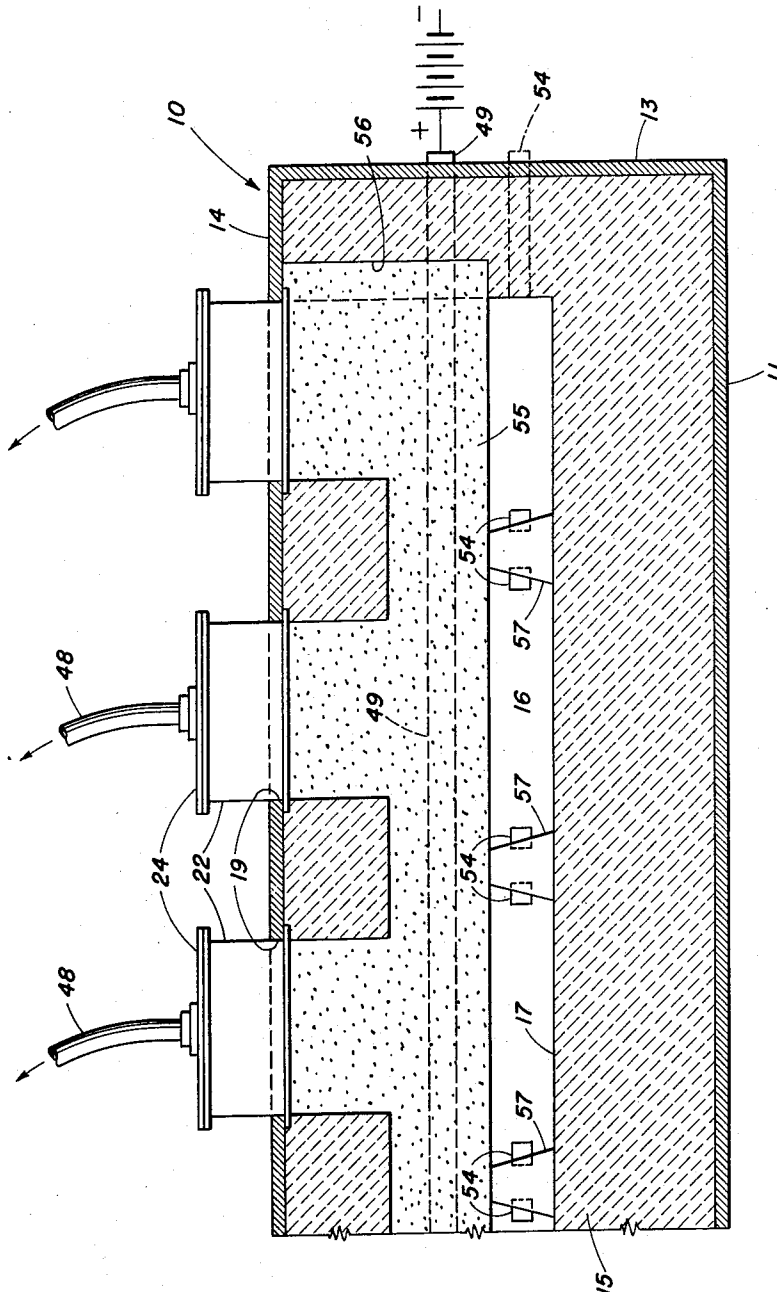
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4 Sheets-Sheet 4



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1

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FUSED SALT ELECTROLYTIC CELL FOR THE PRODUCTION OF REFRACTORY METALS

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Application December 11, 1951, Serial No. 260,961

4 Claims. (Cl. 204—246)

The present invention relates, in general, to the production of refractory metals by electrolytic means, and more especially, to an improved electrolytic cell for the continuous production of refractory metals of high purity from metal halides.

The production of refractory metals by electrolysis has heretofore been carried out, in general, by employing an electrolytic cell having a cathode, an anode and a fused salt electrolyte, and introducing a vaporized halide of a refractory metal into the electrolyte immediately adjacent the cathode while continuously passing electric current through the cell whereby the vaporized metal halide is reduced substantially directly to metal on the cathode.

The refractory metal forms, in large measure, on the bottom or immersed end of the cathode and is a relatively coarse crystalline porous mass which clings precariously to the cathode and is to be distinguished from metals such as, for example, copper or tin which plate out as metal sheets that adhere relatively tenaciously to the cathodes.

Moreover, since oxygen and oxygen-containing gases form oxides which seriously impair the ductility and desirable hardness characteristics of the refractory metals, and, in particular, titanium metal, it is imperative that the electrolytic process be carried out in an inert atmosphere or an atmosphere substantially free from oxygen. It has been customary heretofore to terminate the operation of an electrolytic cell each time an appreciable mass of crystalline metal has accumulated on the cathode and, after waiting for the cathode to cool to a temperature below that at which the oxygen in the atmosphere might react with the crystalline mass of metal on the cathode, to remove the cathode and knock off the crystalline metal. This is known as a batch process and while the production of refractory metals by chemical reduction, direct electrolysis and similar methods by batch processes has achieved some success, these methods are expensive and laborious and the production rate has been so low as to preclude widespread use of the metal in industry.

An object of the present invention is to provide a superior electrolytic cell for the continuous production of highly pure refractory metals.

A further object of the invention is to provide a superior electrolytic cell whereby a refractory metal of high purity and ductility may be produced continuously, economically and at a relatively high rate of production.

A further object of the present invention is to provide a superior electrolytic cell designed to permit continuous production of titanium metal and removal of the metal from the cell for storage without exposing the metal to the atmosphere.

These and other objects and advantages will appear to those skilled in the art from the following description considered in conjunction with the accompanying drawings.

In the drawings in which certain modes of carrying

2

out the present invention are shown for illustrative purposes:

Fig. 1 is a fragmentary partly broken plan view of the improved electrolytic cell of this invention;

Fig. 2 is an elevation in section of the cell on line 2—2 of Fig. 1;

Fig. 3 is a transverse elevation in section of the cell on line 3—3 of Fig. 1;

Fig. 4 is an enlarged perspective view of a cathode stripping ring of the improved cell;

Fig. 5 is a perspective view of the cell collecting-basket;

Fig. 6 is a fragmentary partly broken plan view of a modification of the improved electrolytic cell of this invention, and;

Fig. 7 is a sectional elevation of the modified cell on line 7—7 of Fig. 6.

The showing of Figs. 1 to 5 incl.

The improved electrolytic cell of this invention, as shown in Figs. 1 through 5, is one of a series of identical cells constituting a unitary assembly, each cell of which has its own means for affecting continuous production of a refractory metal. The unitary assembly of individual cells comprises, in general, a rectilinear casing 10 formed of relatively heavy gauge sheet metal and embodying a bottom 11, side walls 12—12, end walls 13—13 and a top 14, the adjoining edges of which are secured together by welded joints to form a rigid fluid tight enclosure. A plurality of individual cells A, B, C, etc. are provided within the metal casing, each cell being formed by refractory material which constitutes a lining for the walls of the metal casing. Since each cell is substantially identical, the description which follows will, in the interest of clarity and succinctness, relate to but one cell.

Referring especially to Figs. 2 and 3, each cell comprises a well as, for example, the well B, formed in the casing 10 by arranging refractory material such as, for example, refractory blocks or fire bricks as indicated at 15, within the metal casing and cementing the refractory blocks together by a suitable cement so as to seal the joints and prevent leakage of the electrolyte from the cell-well. The latter is substantially rectangular in cross section and has substantially vertical side walls 16 and a bottom 17, the upper end of the cell-well being open. The top plate 14 of the casing spans the upper open end of the cell-well and is provided with two substantially rectangular openings 18 and 19 therein separated by a transverse web 20. Secured in each opening of the top plate 14 is a substantially rectangular stack 21 and 22 respectively formed of a refractory metal or metal alloy such as inconel or an equivalent material, each stack being provided at its upper end with a peripheral flange for supporting a cover plate identified at 23 and 24 respectively. Each cover plate is adapted to be detachably secured to its respective flanged stack by suitable fastening means 25 for forming a fluid tight seal.

Mounted within the cell-well immediately beneath the transverse web 20 of the top plate is a substantially vertical gas barrier 26 which comprises a block of refractory material arranged transversely of the cell-well for dividing the upper portion of the latter into two compartments hereinafter identified as the anode and cathode compartments and indicated at *b* and *b'* respectively. As shown especially well in Fig. 2, the lower end of the gas barrier 26 is supported some distance above the bottom 17 of the cell-well and to this end the gas barrier 26 is suspended in the cell-well by engaging the vertical edges of the gas barrier 26 in grooves 27—27 provided in the corresponding side walls of the cell-well, as shown especially well in Figs. 1 and 3, the bottom edge of the gas barrier being supported on the shoulders 28—28 of the grooves.

Pursuant to the objects of the invention, one wall of

the cell-well, hereinafter referred to as the front wall, is intercepted by an inclined aperture or passage indicated at 29 which provides means for removing metal from the cell-well into a suitable collection-and-storage chamber, hereinafter described, without exposing the metal to the atmosphere. To this end, the inclined passage 29 is made substantially rectangular in cross section, its width corresponding substantially to the transverse dimension of the cell-well, as shown in Fig. 3. The inner end or bottom 30 of the inclined passage 29 intersects the bottom 17 of the cell-well to form a sump which is substantially directly beneath the cathode compartment *b'* of the cell as and for the purpose hereinafter described. The outer end of the inclined passage 29 is provided with a stack 31 which extends outside of the cell casing 10 and is preferably formed of inconel or an equivalent refractory metal the outer end of the stack being provided with a cover plate 32 arranged to be detachably secured thereto and to form a fluid tight seal therewith. Extending substantially vertically from the under side of the outer end of the stack 31 and exteriorly of the cell casing 10 is a substantially rectangular casing 33 formed of a refractory metal and constituting the collecting-and-storage chamber of the cell. The bottom of the casing is provided with a detachable or hinged closure member, such as the cover plate 34, which is arranged to form a fluid tight seal therewith. As shown especially well in Fig. 2, an air-lock type gate 35 is provided adjacent the upper end of the collecting-and-storage chamber 33 to close off the lower end of the latter from the cell-well whereby the metal in the bottom of the chamber may be removed without admitting air into the cell-well. Since the collection-and-storage chamber is in a relatively exposed position, air is free to circulate around the chamber and hence cool the metal stored therein so that upon removal of the metal from the chamber the metal will be at a sufficiently low temperature so as not to be adversely affected by the oxygen in the atmosphere.

Operable within the inclined passage 29 of the cell is a metal recovering device which, in the preferred embodiment of the invention, comprises a wire basket 36 adapted to be supported normally in the cell directly beneath the lower ends of the cathodes and to be withdrawn from the cell upwardly in the inclined passage 29 by means of a handle 37 which extends through the cover plate 32 in the outer end of its stack for operating the basket manually exteriorly of the cell-well. A packing gland or similar member 38 is provided on the cover of the stack to insure a fluid tight seal around the basket handle.

Referring more especially to Figs. 2, 3 and 5, the cathode compartment *b'* of the cell is provided with one and preferably a plurality of cathodes indicated at 39 the upper ends of which are permanently secured by fluid tight connections in the cover plate 23 of the corresponding stack; and which depend substantially vertically into the cell-well, the lower ends of the cathodes terminating somewhat above the lower end of the gas barrier 26. In the preferred embodiment of the invention, each cathode is a hollow nickel or tantalum metal tube and is formed at its lower end with a substantially cylindrical enlargement 40. The upper ends of the cathodes extend through the cover plate 23 of the cathode compartment and are connected to a common copper bus bar 41 connected to a direct current source (not shown) by which the individual cathodes are charged with the proper current density for operating the cell. When employing hollow cathodes such as shown herein, the bore of each cathode constitutes a passage for a vaporous halide of a refractory metal which is fed into the upper end of the cathode by suitable feed-means, indicated schematically at 42, and passes down through the cathode to enter the electrolyte immediately adjacent the immersed end of the cathode.

Cooperatively associated with each cathode is means for stripping off the metal which is deposited on the lower end thereof during the operation of the cell. The stripping device is adapted to be operated exteriorly of the cell and this may be done automatically, by any suitable mechanical means, or manually. In the present embodiment of the invention, the cathode stripping devices are adapted for manual operation but it will be understood that other types of operating means are contemplated within the scope of the invention. Moreover, while the preferred embodiment utilizes a stationary cathode and a movable cathode stripper, the invention contemplates any arrangement of elements wherein the cathode and cathode stripper are movable relative to each other.

Referring especially to Fig. 4, each cathode stripper comprises a ring 43 formed of nickel or other suitable metal arranged to embrace the cylindrical enlargements 40 at the lower ends of the respective cathodes and to be movable freely thereover. To facilitate movement of the rings relative to the cathodes, the rings may be split, and since there may be a tendency for more metal to form on the side of the cathode nearest the anodes, each split ring 43 is arranged with its break facing away from the anode side of its respective cathode, as shown especially well in Fig. 1. To actuate the split rings, each ring is provided with an operating rod 44 the lower end of which is secured to one side of the ring and the upper end of which extends through an aperture in the cover plate of the cathode compartment stack. It is preferred to operate each stripping ring individually and to this end the upper end of each operating rod 44 is provided with a handle 45 or similar device by which the stripping ring rod may be actuated for raising and lowering the stripping ring relative to its respective fixed cathode. Since it is desirable to hold the split rings above the enlarged cylindrical portions of the respective cathodes while metal is being deposited thereon, each rod 44 is provided with suitable holding means which, for example, may comprise a counter-weighted cable, indicated generally at 46, secured to the handle 45 of the operating rod and arranged normally to hold the operating rod in a raised position but to allow the latter to be pushed downwardly so as to move its split ring down over the corresponding cathode for stripping the metal deposit therefrom. A packing gland 47 is provided on the cover plate 23 to form a fluid tight seal with the upper end of each operating rod 44 so as to prevent air from leaking into the cell-well. As shown especially well in Fig. 2, the cover plate 24 of the stack of the anode compartment *b* is provided with a fitting 48 for exhausting chlorine gas from the cell during the operation thereof.

Mounted in the anode compartment *b* of each cell-well is an anode 49 provided with a lead 50 which, as shown especially well in Fig. 1, extends through the back wall of the cell casing and is connected in the direct current circuit of the cathodes by a common conductor 51. To operate a cell, the electrolyte therein, indicated at 52, must be maintained at an optimum temperature and to this end each cell is provided with two pairs of graphite heating electrodes 53—53 which, by way of example, are shown in Fig. 1 as extending into opposite sides of the cell, the inner ends of the electrodes terminating substantially flush with the corresponding walls of the cell. For convenience in assembly and economy of design each pair of graphite electrodes 53—53 on opposite sides respectively of each intermediate cell such as, for example, cells B and C, constitute one arm of a T-shaped electrode, the opposite arm of which forms the electrode for the next adjacent cell. The leg 53' of each T-shaped electrode extends out through the wall of the cell and constitutes a common lead for connecting its electrodes 53—53 to an alternating current supply (not shown). It will be understood, however, that the arrangement of the heating

electrodes may be varied depending upon cell design. However, for satisfactory operation, the arrangement of the anodes and heating electrodes must be such that the anodes will not short circuit out through the heating electrodes and to this end the anodes and heating electrodes are preferably arranged so that the cumulative distance between the anode and heating electrodes is at least equal to about one and one-half times the distance between the anodes and the cathodes.

The operation of a single cell of the assembly of cells for the continuous production of a refractory metal such as, for example, titanium, is as follows:

Titanium tetrachloride vapors are passed into the cell through the hollow cathodes, the lower enlarged ends 40 of which are immersed in the electrolyte 52. The latter partially fills the cell-well and comprises a fused salt consisting essentially of a molten halide mixture of an alkali or alkaline earth metal including magnesium, and in particular, the chlorides which may be employed singly or in combination. Mixtures of these halides which form low melting point eutectics are preferred as, for example, mixtures of sodium chloride and strontium chloride or sodium chloride and magnesium chloride. By way of example, the temperature of the electrolyte is maintained between about 700° C. to about 875° C. by means of the graphite electrodes 53—53. An electric current of about 112 amperes at an impressed voltage of approximately 6 volts and equivalent to from about 3.5 to about 5 faradays per mole of $TiCl_4$ is introduced into the cell-well by way of the anode and cathode circuit to maintain an anode current density of about 0.5 ampere per square centimeter and an initial cathode current density of about 3 amperes per square centimeter. The titanium metal which is formed by the reduction of the titanium tetrachloride builds up on the enlarged cylindrical end of each cathode as a relatively large porous mass of coarse crystalline titanium metal. During the initial stages of the operation, the stripping rings of the cathodes are held upwardly above the lower enlarged cylindrical ends of the cathodes by the aforesaid counter-weighted cable 46 until relatively large deposits of porous titanium metal have deposited on the cathode. After a predetermined interval the stripping rings of the cathodes are moved down manually, or by mechanical means, into engagement with the porous masses of titanium metal which, as formed, cling relatively precariously to the cathodes, and strip off the metal. The latter falls downwardly into the baskets which normally are directly beneath the cathodes. The stripping rings are then drawn upwardly to their original positions above the enlarged ends of the cathodes by the counter-weighted cables to allow additional porous metal to be deposited on the cathodes by the electrolytic action of the cell. It will be noted that there is no interruption in the electrolytic reduction of the vaporous titanium tetrachloride during the cathode stripping operation. The baskets are then withdrawn from the cell-well by manual operation of the basket handles to a point opposite the mouth of the collecting-and-storage chamber whereupon the baskets are overturned and the stripped metal falls from the baskets by gravity into the bottom of the chamber where the metal is cooled and stored. Thereafter, when the collecting-and-storage chamber of a cell is nearly full, the air-lock gate of the chamber is closed, and the door in the bottom of the chamber is opened to remove the titanium metal therefrom, the air-lock gate serving to prevent admission of air to the cell-well while the metal is being removed from the storage chamber. The door in the bottom of the collecting-and-storage chamber is then closed, whereupon the air-lock gate in the upper end of the chamber is again opened preparatory to dumping more titanium metal into the storage chamber.

The showing of Figs. 6 and 7

A modification of the electrolytic cell is shown in Fig. 6. In this embodiment of the invention, the casing 10 including the top 14, stack 21 and 22, cathodes 39, and cathode stripping rings 43, are substantially identical to those hereinabove described and hence have corresponding reference numbers. However, instead of providing the casing with a plurality of separate cell-wells, the refractory blocks or bricks which form the lining of the casing are so arranged as to form a single large cell-well which, as indicated at D in Fig. 6, extends substantially the entire length of the casing. The hollow cathodes including the cathode stripping rings may be arranged in groups of two or more at spaced intervals in the cell-well, or may be substantially equally spaced therealong. Suitable provision is also made for supporting the metal receiving wire baskets 36 beneath the cathodes for collecting the stripped metal and depositing it in one or more storage chambers exteriorly of the cell-well.

The anodes of the cell, indicated generally at 49, are connected to the direct current circuit of the cathodes and extend the full length of the cell. The graphite heating electrodes for heating the electrolyte are indicated at 54 and are shown as extending through the cell walls at substantially right angles thereto and at spaced intervals therealong each graphite electrode being connected by a common lead to an alternating current source. As shown especially well in Fig. 7, the gas barrier 55 of the cell is, in this case, a single member which extends longitudinally thereof with its opposite ends engaged in grooves 56—56 in corresponding end walls of the cell. For cells of appreciable length, it is preferred to support the gas barrier with its bottom edge spaced above the bottom of the cell by arranging refractory supporting blocks 57 in spaced relationship along the bottom of the cell.

The operation of the large single cell is substantially identical to the operation of one of the small cells of the plurality of separate cells which form the unitary assembly of cells hereinabove described.

Thus by the superior cell structure of this invention, refractory metals may be continuously produced by an electrolytic process without subjecting the metal to the atmosphere and without removal of the cathode from the cell, the metal deposited on the cathodes being automatically or manually stripped off of the cathodes at predetermined intervals and withdrawn from the cell into a storage chamber, the entire operation being carried out in a simple economical and efficient manner thereby insuring the production of a refractory metal of high purity and ductility at relatively low cost.

The invention may be carried out in other specific ways than those herein set forth without departing from the spirit and essential characteristics of the invention and the present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive and all changes coming within the meaning and equivalency range of the appended claims are intended to be embraced therein.

I claim:

1. In an electrolytic cell comprising a receptacle adapted to contain an electrolyte, the combination including: an anode; a fixed tubular cathode; means for supplying electric current to said anode and cathode; means including said tubular cathode arranged to feed a vaporous halide of a refractory metal into said electrolyte adjacent said cathode to form readily displaceable masses of porous refractory metal continuously on said cathode; cathode stripping means in said cell comprising a member engaged around said cathode and movable relative thereto; means arranged to actuate said stripping member to successively strip masses of porous refractory metal from said cathode; and metal collecting means

comprising an air-tight collecting-and-storage chamber arranged exteriorly of said cell receptacle, a passage sealed from the atmosphere and extending from a point in said cell beneath said cathode to said collecting-and-storage chamber, and a basket movably mounted in said passage, said basket having a handle arranged to be operated from a point exteriorly of said cell to move said basket in said passage to and from a position beneath said fixed cathode, thereby to receive the refractory metal stripped from said cathode and to carry said metal out of said electrolyte into said air-tight collecting-and-storage chamber.

2. In an electrolytic cell comprising a receptacle adapted to contain an electrolyte, the combination including an anode and a fixed tubular cathode; means for supplying electric current to said anode and cathode; means including said tubular cathode arranged to extend into said cell to feed a vaporous halide of a refractory metal into said electrolyte adjacent said cathode to form readily displaceable masses of porous refractory metal continuously on said cathode; cathode stripping means comprising a ring member arranged to embrace said cathode and movable relative thereto; manually operated means arranged to actuate said stripping ring to successively strip masses of porous refractory metal from said cathode; and metal collecting means comprising a collecting-and-storage chamber arranged exteriorly of said cell receptacle and sealed from the atmosphere, a passage sealed from the atmosphere and extending from a point in said cell beneath said cathode to said collecting-and-storage chamber, and a basket movably mounted in said passage, said basket having a handle arranged to be operated from a point exteriorly of said cell to move said basket in said passage to and from a position beneath said fixed cathode, thereby to receive the refractory metal stripped from said cathode and to carry said stripped metal out of said electrolyte into said sealed collecting-and-storage chamber.

3. In an electrolytic cell comprising a receptacle adapted to contain an electrolyte, the combination including an anode; a fixed tubular cathode; a gas barrier between said anode and said tubular cathode; means for supplying electric current to said anode and tubular cathode; tubular means connected to said tubular cathode to feed a vaporous titanium tetrachloride through said tubular cathode to form readily displaceable masses of titanium metal continuously thereon; cathode stripping means comprising a ring member arranged to embrace said cathode and movable relative thereto; manually operated means connected to said ring member and operable exteriorly of said cell to actuate said ring member to successively strip masses of porous titanium metal from said cathode; metal collecting means comprising a collecting-and-storage chamber, said chamber being arranged

exteriorly of said cell receptacle and sealed from the atmosphere, a passage sealed from the atmosphere extending from a point in said cell beneath said cathode to said collecting-and-storage chamber, and a wire basket movably mounted in said passage and arranged to be moved to and from a position beneath said cathode, thereby to receive the titanium metal stripped from said tubular cathode and carry the stripped metal out of said cell into said collecting-and-storage chamber; and manually operable means connected to said wire basket and operable from a point exteriorly of said cell to move said wire basket.

4. In an electrolytic cell comprising a receptacle adapted to contain an electrolyte, the combination including an anode; a plurality of fixed tubular cathodes; a gas barrier separating said anode from said tubular cathodes; means for supplying electric current to said anode and said cathodes; tubular means connected to each of said tubular cathodes to feed vaporous titanium tetrachloride through said tubular cathodes into said electrolyte adjacent the immersed portions of said tubular cathodes to form readily displaceable masses of titanium metal continuously thereon; cathode stripping means comprising ring members arranged to embrace said cathodes and movable relative thereto; manually operable means connected to said ring members and operable exteriorly of said cell to actuate said ring members to successively strip masses of porous titanium metal from said cathodes; metal collecting means comprising a collecting-and-storage chamber, said chamber being arranged exteriorly of said cell receptacle and sealed from the atmosphere, a passage sealed from the atmosphere and extending from a point in said cell beneath said cathodes to said collecting-and-storage chamber, and a wire basket movably mounted in said passage and arranged to be moved to and from a position in said cell beneath said cathodes to receive the titanium metal stripped from said cathodes and to carry said metal out of said cell into said collecting-and-storage chamber; and manually operable means connected to said wire basket and operable from a point exteriorly of said cell to move said wire basket.

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