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F. C. BENNER ET AL
PRODUCTION OF METALS

2,880,156

Original Filed June 23, 1951

2 Sheets-Sheet 1

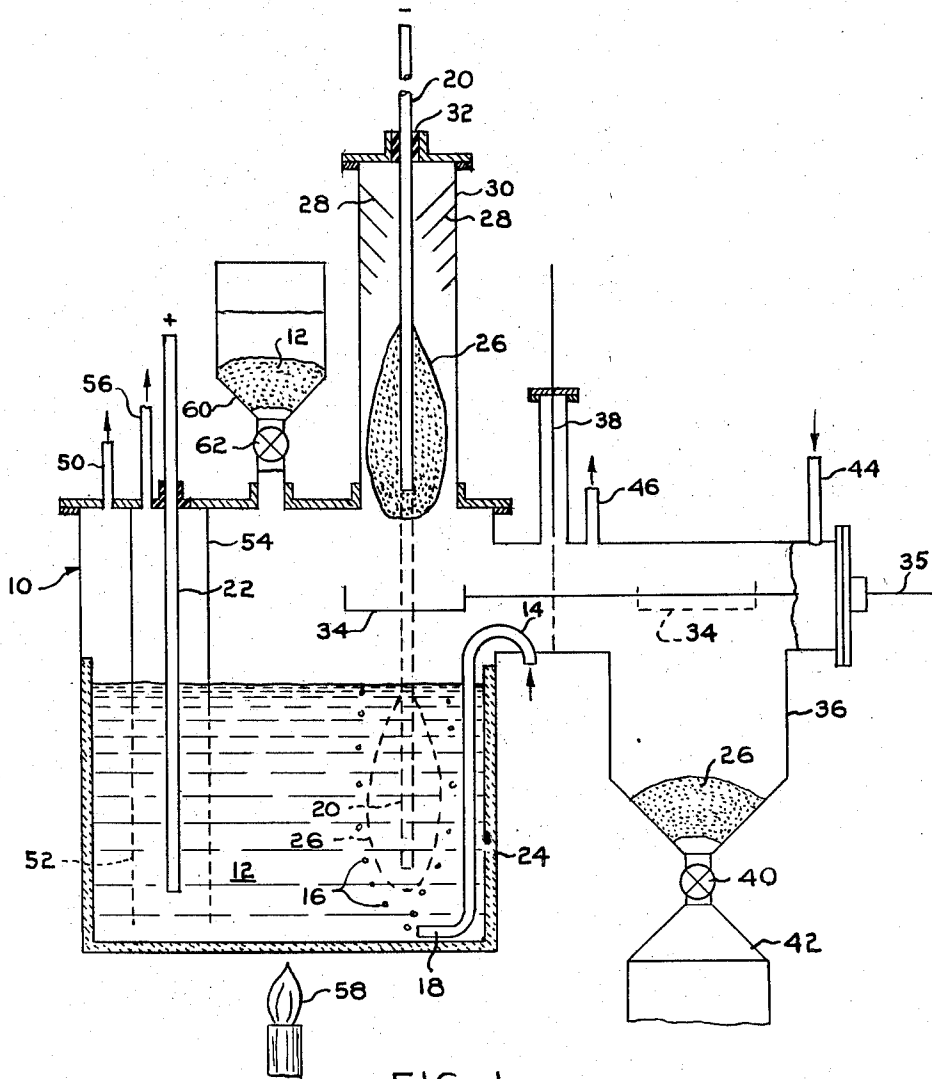


FIG. 1

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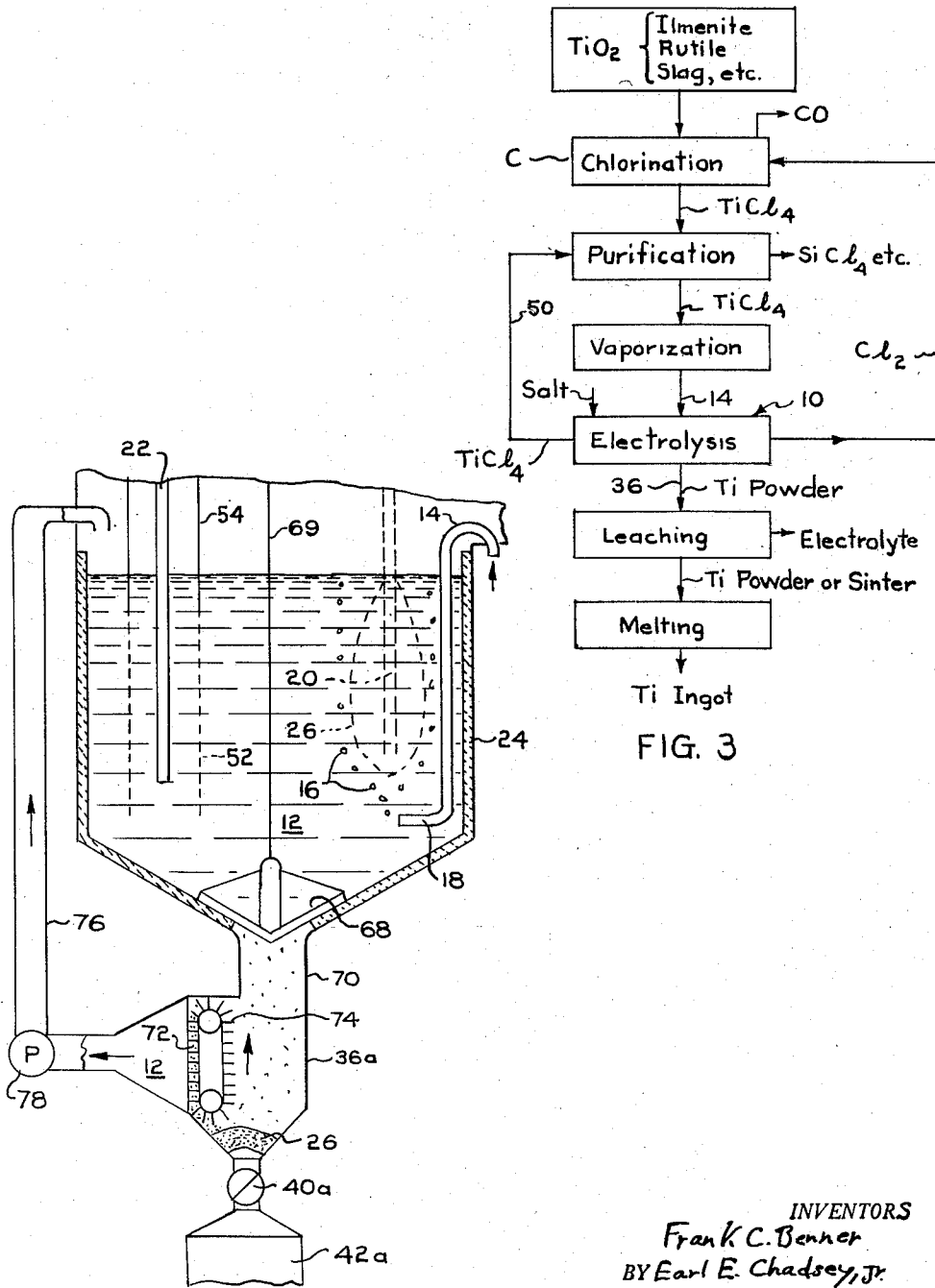


FIG. 2

FIG. 3

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PRODUCTION OF METALS

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Original application June 23, 1951, Serial No. 233,203.
Divided and this application March 26, 1956, Serial
No. 574,027

4 Claims. (Cl. 204—226)

This invention relates to the production of metals and
more particularly to the production of titanium. This
application is a division of copending application Serial
No. 233,203, filed June 23, 1951, in the name of Frank
C. Benner and Earl E. Chadsey, Jr.

A principal object of the present invention is to provide
an improved method for obtaining pure titanium by elec-
trolyzing a compound thereof.

Another object of the invention is to provide such a
process wherein a readily available compound of titanium
is employed and high purity is obtained at the cathode
of the electrolytic cell.

Still another object of the invention is to provide a
relatively low-temperature electrolytic bath in the elec-
trolysis of such a titanium compound.

Still another object of the invention is to provide
techniques which furnish in such processes a maximum
dissolution of relatively insoluble titanium tetrachloride
in fused salt baths.

Other objects of the invention will in part be obvious
and will in part appear hereinafter.

The invention accordingly comprises the process in-
volving the several steps and the relation and the order
of one or more of such steps with respect to each of
the others, and the apparatus possessing the construction,
combination of elements and arrangements of parts which
are exemplified in the following detailed disclosure, and
the scope of the application of which will be indicated
in the claims.

For a fuller understanding of the nature and objects
of the invention, reference should be had to the following
detailed description taken in connection with the accom-
panying drawings wherein:

Fig. 1 is a diagrammatic, schematic, sectional view
showing one form of apparatus embodying the present
invention;

Fig. 2 is a fragmentary, schematic view showing a
modified form of a portion of the apparatus of Fig. 1;
and

Fig. 3 is a flow sheet showing the various steps in
the over-all process.

The production of pure titanium metal has long been
the subject of a considerable amount of research work
on the part of many companies and the U.S. Govern-
ment. Some of the past workers in the art have sug-
gested the electrolysis of titanium compounds, but none
of such suggestions seems to have attained any practical
significance. In the present invention the electrolysis
of a titanium compound is achieved with a starting
material which is readily available, and which can be
obtained in high purity. This electrolysis is accom-
plished under the conditions which furnish a titanium
metal of the highest purity, an essential attribute for
any large-scale use of the metal.

In the present invention the starting material is prefer-
ably titanium tetrachloride which can be readily manu-
factured and purified by known techniques. The electrol-
ysis of titanium tetrachloride is achieved by introducing

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titanium tetrachloride in vapor phase into a bath of a
molten electrolyte, this bath preferably comprising an
oxide-free eutectic mixture of at least two halides from
the class consisting of the halides of the alkali earth
metals and the alkali metals. These halides are, for
reasons of economy, preferably the chlorides and in a
preferred form of the invention the bath comprises a
fused eutectic mixture of the chlorides of the alkali
metals lithium, sodium, and potassium. Such a eutectic
comprises, by weight, 40.4% lithium chloride, 53.2%
potassium chloride, and 6.4% sodium chloride. Since
the titanium tetrachloride has a relatively low solubility
in such a eutectic mixture, the titanium tetrachloride is
preferably introduced adjacent the cathode so that a
maximum permissible concentration of titanium tetrachloride
in the bath is maintained adjacent the cathode. It is also
believed that there may be, coincidentally with the
dissolution of the titanium tetrachloride, either a
compound formation or a partial reduction of the titanium
tetrachloride to a lower chloride which is more soluble
than the titanium tetrachloride in the fused salt bath.

In the operation of the preferred process an atmos-
phere of titanium tetrachloride is maintained above the
bath, this atmosphere being preferably maintained at a
pressure not much in excess of atmospheric pressure.
Chlorine vapor, which is generated at the anode when
chlorides are used for the electrolysis bath, is prefer-
ably separately removed from the region surrounding
the anode so as to prevent contamination of the titanium
tetrachloride atmosphere above the bath, and to prevent
reaction with any lower chlorides of titanium dissolved
in the bath. The process additionally comprises, in a
preferred form thereof, the use of a porous diaphragm
between the anode and the cathode, this porous dia-
phragm appreciably limiting thermal and random diffusion
between the anode and the cathode, and thus permitting
the creation of a maximum concentration of dissolved
titanium tetrachloride, or lower chlorides of titanium,
in the neighborhood of the cathode. The porous dia-
phragm also limits diffusion of chlorine bubbles gener-
ated at the anode. The present invention also contem-
plates the removal of the titanium powder from the cathode
and the transfer of this titanium powder from the elec-
trolytic cell to a leaching chamber where the contained
electrolyte can be removed. Thereafter the powder,
unless of a size greater than about 50 mesh, is heated
at least to its sintering temperature to consolidate the
powder to a nonpyrophoric state before exposure to air.

Referring now to Fig. 1 there is schematically illus-
trated one preferred embodiment of the invention. In
this figure, where like numbers refer to like elements
in the other figures, the electrolysis cell is generally
indicated at 10 and is shown as containing a molten
electrolyte 12. This cell is provided with a pipe 14 for
introducing titanium tetrachloride vapor, this pipe includ-
ing a lower portion 18 thereof which extends under a
cathode 20. The cell also comprises an anode 22 and a
liner 24 which is inert to the electrolyte. The titanium
produced at the cathode 20 collects in the form of a
lump of titanium powder 26, this lump adhering fairly
loosely to the cathode. This cathode lump is removed
from the cathode 20 by means of a scraper, schematically
indicated at 28, which is carried by an extension 30
provided in the top of the electrolysis cell 10. In one
preferred embodiment of the invention this scraper 28
is stationary and the cathode 20 is arranged to be moved
upwardly in a bushing 32 provided in the top of the
extension 30. As the titanium powder 26 is scraped
off the cathode it falls into a collecting tray 34, which
has been moved by a shaft 35 to a position underneath
the cathode after the cathode is raised from the bath,

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The titanium collected in the tray 34 is moved to the right to the dotted line position where rotation of the shaft 35 permits dumping of the collected titanium powder into a bin 36. A valve 38 normally isolates the bin 36 from the electrolysis chamber, this valve being opened to permit movement of the tray 34 between the bin 36 and the electrolysis cell. Located at the bottom of the bin 36 there is a second valve 40 which permits transfer of titanium powder from this collecting bin 36 to a vacuum distillation chamber 42. For maintaining a protective atmosphere over the titanium powder collected in bin 36, there are provided inlet and outlet pipes 44 and 46, respectively, through which argon or other inert gas may be circulated to provide an air-free atmosphere.

The electrolysis cell 10 also preferably includes a pipe 50 through which excess titanium tetrachloride may be removed from above the bath for recirculation to a purifying chamber and refeeding into the electrolytic bath 12 through the feed pipe 14. Surrounding the anode is a porous diaphragm 52, that portion 54 of the diaphragm above, and slightly below, the top of the electrolytic bath 12 being preferably made impermeable so as to prevent the escape of chlorine generated at the anode, and to permit separate removal of this chlorine through a pipe 56. The chlorine generated in the electrolysis cell may be utilized for making titanium tetrachloride by known techniques. In a preferred apparatus an additional feeding means 60 may be provided for holding a predetermined quantity of electrolyte 12, this electrolyte being preferably held in a solid state, and being introduced through a valve 62 when the level of the bath has been decreased below a desired amount. The electrolyte-feeding means preferably is provided with a controlled atmosphere to prevent contamination of the electrolytic bath by the electrolyte which is fed thereto from time to time. This aspect of the invention is particularly important in the event that any of the chlorides fed to the bath are hygroscopic, as is the case with the alkali earth metal chlorides.

In a preferred embodiment of the apparatus described in connection with the discussion of Fig. 1, the walls of the electrolytic cell 10 preferably comprise stainless steel, as do most of the remaining portions of the apparatus. The liner 24, in which the molten electrolyte is confined, preferably comprises carbon or porcelain. The cathode may comprise a rod or sheet of titanium or other inert metal, such as the alloy sold under the trade name "Inconel." The anode 22 may comprise a carbon rod or sheet. The permeable diaphragm 52 surrounding the anode is preferably formed of a porous carbon. Equally, at lower temperatures the diaphragm 52 may be formed of other materials such as sintered Pyrex, or porous refractories such as porous Alundum and porous porcelain. If the diaphragm is conducting it should be insulated from the anode. The upper part 54 of the diaphragm 52 preferably comprises stainless steel which is inert to dry chlorine gas at temperatures below about 800° C.

In the operation of the device of Fig. 1 a sufficient quantity of electrolyte is introduced in solid form into the electrolysis cell 10, this electrolyte preferably comprising the previously mentioned eutectic mixture of the chlorides of sodium, potassium and lithium. When such an electrolyte is employed the electrolysis cell is purged of all air, such as by introducing argon through pipe 44 and removing the argon through pipe 50. The cell is then brought to a temperature of approximately 450° C. by the application of external heat, such as by means of the heater schematically indicated at 58. All water is driven from the electrolyte and any contained oxide is preferably removed by electrolyzing the bath. Titanium tetrachloride is then introduced through pipe 14 at a pressure slightly above atmospheric pressure. With the cathode in the dotted line position, current is passed between the anode and cathode to electrolyze the titanium tetra-

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chloride dissolved in the bath, the titanium depositing as a powder on the cathode. When the anode and cathode are about one inch apart the voltage may be approximately 5 to 5.8 volts with a current density of approximately 5 amps. per square inch of cathode area. Since the solubility of titanium tetrachloride is relatively low in the electrolyte bath, only a minor portion of the titanium tetrachloride is dissolved in the electrolyte 12. Excess titanium tetrachloride escapes through the pipe 50 where it may be led to a condenser or purifier for re-vaporization and recycling. Alternatively, the titanium tetrachloride vapors escaping through the pipe 50 may be compressed and fed back to the pipe 14. After an appreciable lump of titanium powder 26 has been built up on the cathode 20, the creation of this lump taking perhaps an hour or so, the current is stopped and the cathode 20 is lifted from the electrolyte to the full line position in Fig. 1. The valve 38 is opened and the tray 34 is advanced into the full line position below the cathode lump 26. The cathode is now moved upwardly so that the scrapers 28 knock off the titanium powder which falls into the tray 34. The tray 34 is moved to the dotted line position shown in Fig. 1 and the valve 38 is closed. Thereafter the cathode 20 is again lowered to the dotted line position in the electrolytic bath and electrolysis is resumed. During the period when the electrolysis is stopped, the feed of titanium tetrachloride is preferably also stopped so that an undue amount of titanium tetrachloride is not condensed in the collecting bin 36. After the valve 38 has been closed the tray 34 is rotated to dump the contained powder into the bin 36. When a sufficient amount of titanium powder is collected in the bin 36 the valve 40 may be opened and this powder fed to the vacuum distillation chamber 42. This distillation chamber is preferably evacuated, after a supply of titanium powder has accumulated therein, to a free air pressure on the order of 10^{-5} mm. Hg abs., and the titanium powder therein is heated to a temperature on the order of 900–1000° C. to distill all of the contaminating electrolyte 12 from the titanium powder 26. This distilled electrolyte may be condensed on a suitable condenser comprising a part of the vacuum distillation chamber 42, or may be condensed in a separate condenser therefor. Thereafter the vacuum distilled titanium powder can be fed to a melting furnace directly. Alternatively, it can be sintered under a vacuum or protective atmosphere, such as argon, to obtain a nonpyrophoric form of the titanium. The electrolyte in the bath 12 may be replenished from time to time from the supply chamber 60 by suitably manipulating the valve 62. The chlorine generated at the anode 22 is removed through the pipe 56 and passed to a titanium tetrachloride generator where titanium tetrachloride is produced by the reaction of chlorine and carbon on titanium dioxide.

From the above discussion it is obvious that numerous modifications of the present invention may be practiced without departing from the essential features thereof. One such modification contemplates the omission of gate valve 38, condensation of titanium tetrachloride in collecting bin 36 being prevented by maintaining this bin 36 at a temperature of about 150° C. Another modification is shown in Fig. 2 wherein an alternative arrangement is provided for removing the product titanium powder from the electrolytic cell. In this embodiment, which shows only the lower portion of the cell, the titanium powder is suitably scrape from the cathode, such as by means of the scraper 28 of Fig. 1. In this case the cathode may be made stationary and the scraper can be moved downwardly into the bath. This arrangement is particularly desirable when a number of cathodes are placed around a single anode. The use of a stationary cathode and a movable scraper has the additional advantage that the cathode can be scraped very frequently without interrupting the operation of the electrolytic cell. Thus the cathode area may be conveniently maintained

nearly constant, with consequent simplification of the electrical system for maintaining a uniform current density at the cathode.

The titanium powder removed from the cathode is allowed to fall into the electrolytic bath. Since the titanium powder has a higher specific gravity than the electrolyte in the bath, this powder will sink to the bottom of the bath where it may be scraped, by means of a scraper 68 by a shaft 69, into a removal pipe 70. This pipe 70 leads to a collecting and settling chamber 36a, most of the titanium particles 26 settling to the bottom of this chamber 36a. When a sufficiently high concentration of titanium particles is obtained at the bottom of collecting chamber 36a, these titanium particles may be transferred to a vacuum leaching chamber 42a by momentarily opening a suitable valve 40a. If desired, the electrolyte in settling chamber 36a can be filtered through a stainless steel filter 72, the titanium particles 26 collected by the filter 72 being removed therefrom by a suitable scraper, such as that schematically indicated at 74. The electrolyte 12 passing through filter 72 can be recycled to the electrolysis chamber through a pipe 76 by means of a suitable pump 78. This system has the additional advantage that it maintains a steady, and preferably slow, flow of electrolyte through the filter 72, thereby collecting titanium particles from the electrolytic bath even though these particles have not had time to settle by gravity to the bottom of the electrolysis chamber 10. This circulation of the electrolyte also maintains a uniform high temperature in the collecting chamber 36a so that the electrolyte will not freeze therein, an occurrence which would make removal of the titanium particles through valve 40 impracticable.

Referring now to Fig. 3 there is shown a flow sheet which illustrates schematically the processing of titanium ore to obtain a titanium ingot as a final product. As a first step in the process, titanium dioxide in the form of ilmenite, rutile, or slag of high titanium dioxide content is added to a chlorination chamber where it is treated in the presence of carbon with chlorine to convert the titanium dioxide to titanium tetrachloride. This titanium tetrachloride is then purified by known techniques, such as by fractional distillation, to remove impurities such as silicon tetrachloride and iron chloride. The pure titanium tetrachloride is next vaporized and the titanium tetrachloride vapors are fed into the electrolysis chamber 10 through the pipe 14, the excess titanium tetrachloride escaping from electrolysis chamber 10 being returned, if desired, to the purification step by pipe 50. Chlorine generated at the anode in the electrolysis chamber 10 is fed through pipe 56 to the chlorination step. Titanium powder produced at the cathode of the electrolysis cell is transferred to the collecting chamber 36 (Fig. 1) or 36a (Fig. 2) and thence to the vacuum distillation chamber 42 (Fig. 1) or 42a (Fig. 2). The relatively pure titanium from the vacuum distillation step is then transferred to a melting or sintering chamber where it may be compacted by sintering or can be completely melted. The sintering may be accomplished under vacuum or can be accomplished by other techniques, such as the sintering in a calcium bath described in U.S. Patent 2,546,320. Additionally, as pointed out previously, the leaching of the electrolyte carried by the titanium powder may be removed by an acid aqueous leach in the event that the titanium particles are of a size greater than about 50 mesh.

Numerous modifications may be made to the above flow sheet, as will be readily apparent to those skilled in the art. For example, the titanium tetrachloride recycled through the system may, as previously pointed out, be compressed and fed directly into the pipe 14 as a vapor without the necessity of passing through the purification step. Additionally it is apparent that numerous other techniques for the manufacturing of titanium tetrachloride

ride, other than the chlorination step specifically mentioned above, may be practiced.

Numerous modifications can be made in the physical embodiment of the electrolytic cells shown in the drawings. For example, a single anode and a plurality of cathodes surrounding the anode may be used so as to permit replacement of cathodes or removal of collected titanium without completely shutting down the operation of the cell.

Since certain changes may be made in the above process and apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In an electrolytic cell comprising a receptacle adapted to contain an electrolyte, the combination including: an anode; a cathode; means for supplying electric current to said anode and cathode; means to feed a vaporous halide of a refractory metal into said electrolyte adjacent said cathode to form readily displaceable masses of porous refractory metal on said cathode; stationary cathode stripping means in said cell; means arranged to move said cathode into contact with said stationary stripping means 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 the cathode after movement of the cathode into contact with said stripping means 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 the cathode during movement of the cathode into contact with said stripping means, thereby to receive the refractory metal stripped from said cathode and to carry said metal out of said cell receptacle 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; a cathode; means for supplying current to said anode and cathode; means to feed a vaporous halide of a refractory metal into said electrolyte adjacent said cathode to form readily displaceable masses of porous refractory metal on said cathode; stationary cathode stripping means in said cell above said electrolyte comprising at least one scraper to engage around said cathode; means arranged to raise said cathode into contact with said stationary stripping means 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 the cathode when in the raised position 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 the cathode when in the raised position, thereby to receive the refractory metal stripped from said cathode and to carry said metal out of said cell receptacle into said air-tight collecting-and-storage chamber.

3. The electrolytic cell of claim 2 wherein there is included a gas barrier between said anode and said cathode.

4. The electrolytic cell of claim 2 wherein there is included a plurality of cathodes and cathode stripping means.

References Cited in the file of this patent

UNITED STATES PATENTS

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