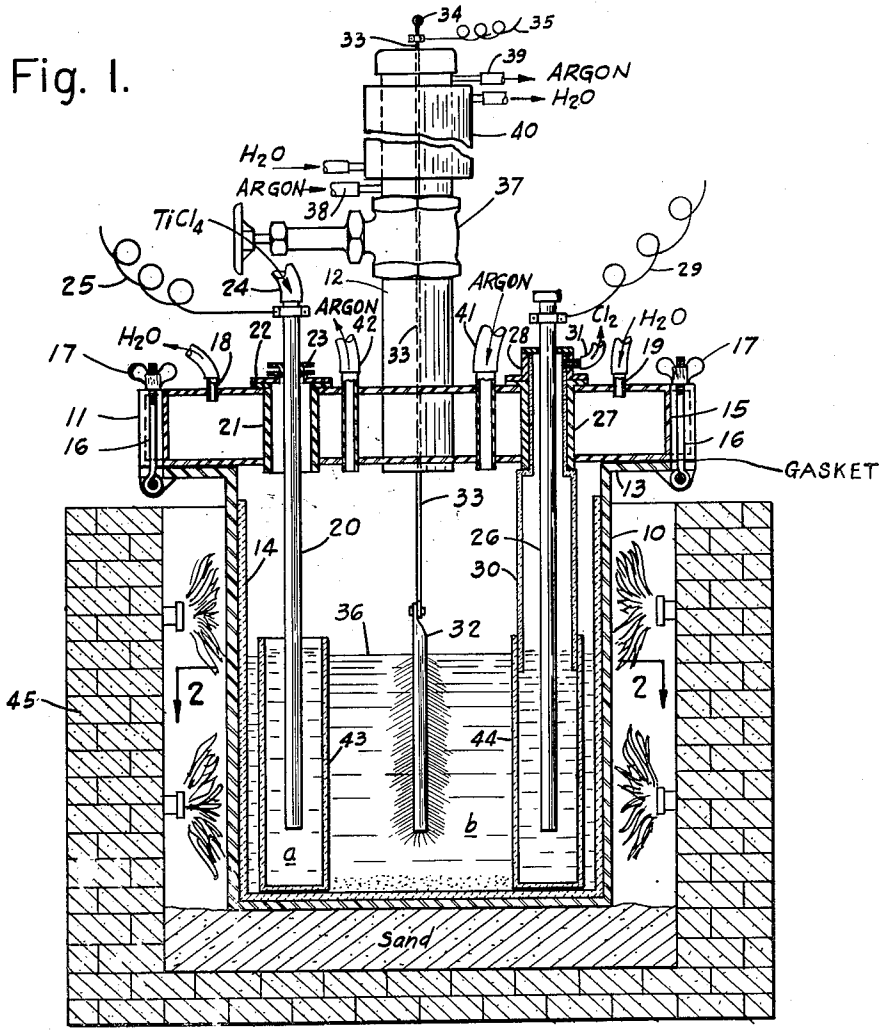
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ELECTROLYTIC CELL OF THE DIAPHRAGM TYPE

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Fig. 1.



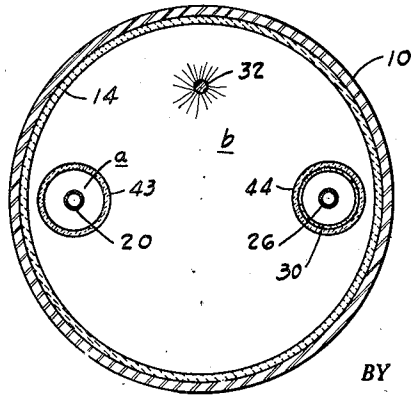


Fig. 2.

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Fig. 3.

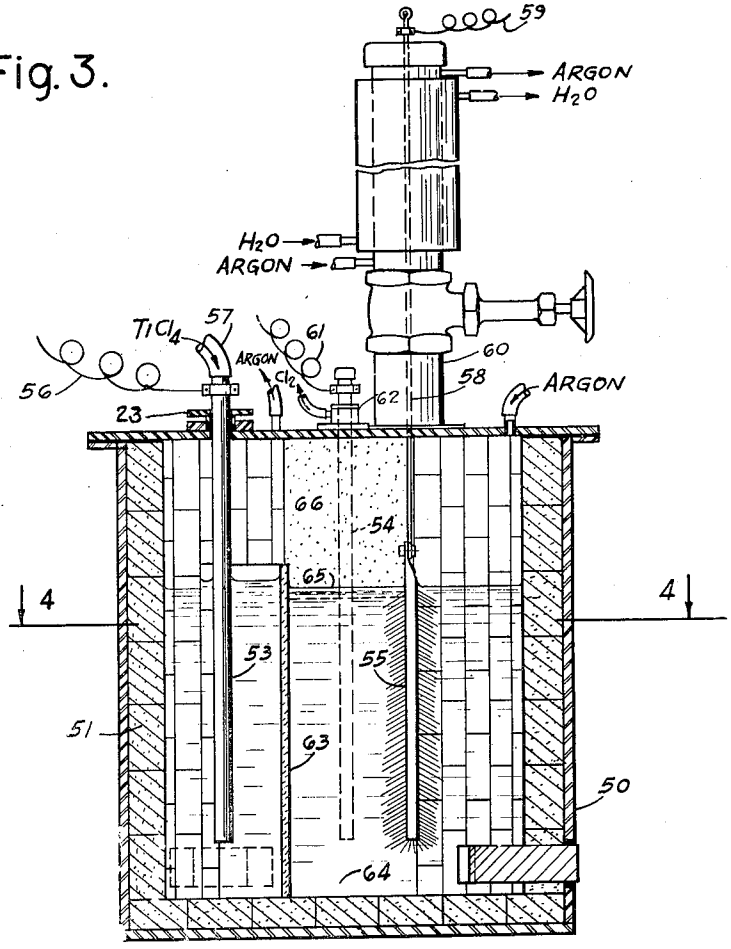
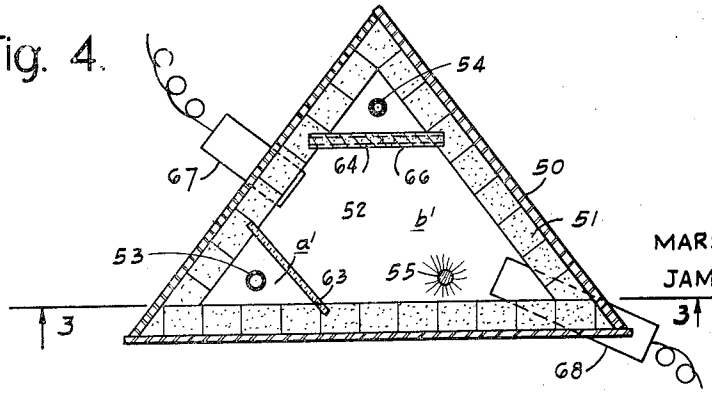


Fig. 4.



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ELECTROLYTIC CELL OF THE DIAPHRAGM TYPE

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Application January 31, 1952, Serial No. 269,288

1 Claim. (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 production of refractory metals of high purity from metal halides.

Electrolytic cells used for producing refractory metals may be classified, in general, as of the diaphragmless type and of the diaphragm type respectively, the latter type of electrolytic cell, and the one with which the present invention is particularly concerned, being characterized by two cathodes separated by one or more diaphragms from an anode.

The development of this type of cell has been based upon the discovery that while certain types of halides of refractory metals and in particular the tetrahalides of titanium are not appreciably soluble in molten salt electrolytes, the tetrachloride of titanium may be converted electrolytically to reduced titanium values i. e. the trivalent and divalent chlorides, sometimes hereinafter referred to as titanium trichloride and titanium dichloride respectively, which are soluble in a molten salt electrolyte. When in solution in the molten salt electrolyte, these reduced titanium chlorides may be readily converted, by electrolysis, to titanium metal. In this connection the cathode which is used to reduce the titanium tetrachloride to titanium dichloride and/or titanium trichloride is termed the "solubilization cathode" while the cathode upon the surface of which the reduced chlorides are deposited as metallic titanium is termed the "deposition cathode."

To insure the successful operation of the diaphragm type of cell, one or more diaphragms are arranged in the cell so that the chlorine which is released at the anode is prevented from contacting either of the cathodes, or the electrolyte in the immediate vicinity of the cathodes (sometimes hereinafter referred to as the catholytes); while the reduced chlorides, which are formed at the solubilization cathode, are prevented from contacting the anode and the chlorine atmosphere surrounding the latter.

In accordance with the present invention it has been found that whereas in this type cell the ratio of the trivalent and the divalent titanium values is fairly low, i. e. of the order of one to four and remains substantially constant during convection from the solubilization cathode to the deposition cathode, it is desirable that a concentration differential of the low valent titanium values be maintained between the catholytes of the solubilization and deposition cathodes respectively within predetermined limits. More particularly, it has been discovered that for optimum results it is essential that a high concentration of reduced titanium values be maintained in the catholyte of the solubilization cathode, and that a low concentration of these values be present in the catholyte of the deposition cathode.

An object of the present invention is, therefore, to provide a superior electrolytic cell of the diaphragm type of economical construction and efficient operation for the

commercial production of refractory metals of superior quality.

Another object of the invention is to provide an improved electrolytic cell of the type hereinabove described having diaphragms of improved design and arrangement whereby a high concentration differential of reduced titanium values may be produced and maintained in the electrolyte.

A still further object of the invention is to provide a superior electrolytic cell of the type hereinabove described wherein the diaphragms of the cell are so designed and arranged relative to each other and to the cell bath that segregated regions of high and low concentrations of trivalent and divalent titanium values may be maintained in the bath thereby insuring high efficiencies and a commercially salable titanium metal.

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 out the present invention are shown for illustrative purposes:

Fig. 1 is a side elevation, partly in section, of the improved electrolytic cell of this invention showing the design and arrangement of the diaphragms of the cell;

Fig. 2 is a plan view of the electrolytic cell on section line 2—2 of Fig. 1;

Fig. 3 is a side elevation, partly in section, of a modification of the cell of Fig. 1; and,

Fig. 4 is a plan view, in section, of the modified cell of Fig. 3.

Referring to Figures 1 and 2 of the drawings, the improved electrolytic cell of this invention is shown by way of example as comprising an outer casing **10** provided with a removable cover **11** having a jacketed stack **12**. The casing **10** may be formed of a corrosion resistant metal such as, for example, Inconel (which is an alloy consisting essentially of nickel, chromium and iron), or a metal having similar properties and is a substantially cylindrical cup-shaped member provided at its upper open end with an annular outwardly projecting flange **13** for supporting the cover **11**. Mounted within the cell casing **10** is a substantially cylindrical cup-shaped lining **14** which may be formed of silica, or an equivalent material.

The cover **11** of the cell is mounted on the flange **13** of the casing, the joint being sealed by a suitable gasket, and comprises, preferably, a hollow substantially disc shaped member provided with a plurality of substantially U-shaped indentations **15** arranged radially in the periphery thereof for accommodating fastening means for detachably securing the cover to the flange of the cell casing. As shown especially well in Fig. 1 the fastening means may comprise bolts **16** hingedly secured at their lower ends to the under side of the cell casing flange **13** and arranged to extend upwardly through the aforesaid indentations **15** of the cover and to be engaged at their upper ends by wing nuts **17**. The cover is made hollow so that it may be cooled during the operation of the cell and to this end the cover is provided with inlet and outlet pipes **18** and **19** by which a coolant may be circulated through the cover.

The solubilization cathode of the cell is indicated at **20** and comprises a metal tube, which may be formed of nickel or an equivalent material adapted to be supported at its upper end in the cover with its lower end extending to a suitable depth into the electrolyte of the cell. The supporting means for the upper end of the solubilization cathode **20** is preferably a metal sleeve **21** secured with a fluid tight fit in vertically aligned apertures in the upper and lower plates of the hollow cover; and provided at its upper end with a cathode supporting cap **22** having a central aperture through which the upper end of the cathode extends. The latter is suitably secured in the

aperture of the cathode supporting cap 22 and is sealed therein against the admission of air by a sealing gland, indicated generally at 23, which also serves to insulate the cathode from the metal casing. Vaporous titanium tetrachloride is adapted to be fed from a supply source (not shown) into the hollow solubilization cathode by means of a feed tube 24 secured to the upper end of the cathode. A conductor 25 is also attached to the upper end of the hollow cathode for connecting the latter to a direct current source.

The anode 26 of the cell is preferably formed of graphite and is supported from the hollow cover of the cell by a sleeve-and-cap assembly, indicated generally at 27 and 28 respectively, designed to insulate the anode from the casing 10. Connected to the upper end of the graphite anode 26 is a conductor 29 of a direct current source. Although not necessary to the successful operation of the cell, the anode may be made hollow, as shown, and in this case is provided with a closure cap which is removable for providing access to the anode chamber of the cell whereby additional salts may be added thereto without removal of the cell cover 11.

In order to prevent the chlorine formed at the anode from migrating to other parts of the cell, and, in particular, into contact with the cathodes, the upper end of the graphite anode is surrounded by a concentric substantially impervious tubular gas-barrier 30, which may be formed of silica or an equivalent material and which extends from within the anode supporting sleeve 27 downwardly into the electrolyte of the cell to a point just below the surface thereof. Thus the chlorine which is evolved at the anode will be confined within the sleeve-like gas barrier and conducted thereby upwardly to an exhaust port 31 adjacent the cap 28.

In the embodiment of the invention shown the anode is supported by its sleeve-and-cap assembly substantially diametrically opposite the solubilization cathode 20 but it will be understood that the position of the anode relative to the cathode is not critical. It is preferable, however, to arrange the two cathodes and the anode in a generally triangular relationship such as shown in Fig. 2 and hereinafter described.

The deposition cathode of the cell may comprise a solid rod 32 formed of nickel or other suitable metal and is adapted to be supported in the electrolytic bath of the cell by supporting means assembled in the aforesaid jacketed stack of the cell. In this respect the jacketed stack 12 of the cover, the aforesaid solubilization cathode 20 and the anode 26 are arranged substantially in triangular relationship, i. e. the solubilization cathode 20, the anode 26, and the deposition cathode 32 (the position of which corresponds to that of the jacketed stack 12) are arranged preferably substantially at the respective apices of an equilateral triangle.

The cathode rod supporting-means is preferably a rod 33 formed of copper or other suitable metal and detachably fastened at its lower end to the upper end of the deposition cathode 32. The upper end of the rod 33 extends upwardly through the jacketed stack 12, from which it is insulated and in which it is guided by centering-means (not shown), and is provided at its upper extremity with an eye or equivalent holding means, indicated generally at 34, by which the deposition cathode 32 may be selectively raised and lowered in the cell. Attached to the upper extremity of the cathode supporting rod is a conductor 35. In its lower position in the cell the deposition cathode 32 is adapted to be immersed in the electrolyte 36 of the cell at a point corresponding substantially to an apex of the equilateral triangle formed by the solubilization cathode 20, the anode 26, and the deposition cathode.

As shown in Fig. 1, the jacketed stack 12 of the cell is provided adjacent its lower end with an air-lock, identified by the valve 37, whereby the jacketed stack may be closed off from the interior of the cell. Thus after a deposit of metal has accumulated on the cathode 32 the latter may be drawn upwardly out of the electrolytic bath 36 into the upper part of the jacketed stack 12, i. e. above the air-lock valve 37. The latter is then closed whereupon the metal deposit on the cathode is allowed to cool in an inert atmosphere which is provided in the upper end of the stack by feed pipes 38 and 39 adapted to circulate an inert gas, such as argon, therethrough. To accelerate the cooling of the metal on the cathode the stack is provided with a concentric jacket 40 having inlet and outlet ports by which a coolant may be circulated through the jacket.

Since nitrogen, oxygen or an oxygen-containing constituent adversely affects the quality of the salt bath and the titanium metal at elevated temperatures it is preferred to carry out the reaction in an atmosphere substantially free of oxygen, water vapour, nitrogen and the like, and to this end the hollow cover 11 of the pot is provided with inlet and outlet pipes 41 and 42 respectively by which an atmosphere of argon or an equivalent inert gas may be maintained above the surface of the electrolyte in the cell. In the embodiment of the invention shown herein the aforesaid inlet and outlet pipes 41 and 42 respectively are located between the jacketed stack of the cover and the anode and cathode respectively but it will be appreciated that any other arrangement may be used.

Pursuant to the objects of the invention the improved cell is provided with superior diaphragm means for obtaining high concentrations of trivalent and divalent titanium values in the vicinity of the solubilization cathode, and relatively low concentrations of these reduced titanium values in the vicinity of the deposition cathode. In general, the total concentration of titanium trichloride and titanium dichloride at the solubilization cathode is preferably from 6 to 8 molal and of the order of from .2 to .4 molal at the deposition cathode, i. e. the concentration of low valent titanium values at the solubilization cathode is from twenty to thirty times that in the remaining portion of the bath. Referring especially to Fig. 2 the diaphragms of the cell are indicated at 43 and 44 respectively, each diaphragm being substantially of the same dimensions and constructed of suitable porous electrically non-conductive material which will withstand the temperature and corrosiveness of the salt bath and will also permit the flow of ions therethrough but retard the mixing, by convection, of different portions of the melt. Satisfactory results have been obtained by the use of fused porous alumina diaphragms.

In the embodiment shown in Figs. 1 and 2 each diaphragm is a substantially cylindrical cup-shaped member the diameter of which is of the order of two-tenths the diameter of the cell, the height of each diaphragm being such as to extend above the level of the electrolyte in the cell. It is evident, of course, that the cylindrical diaphragms of the solubilization cathode and anode respectively serve to segregate corresponding regions of the electrolytic bath and that the volume of electrolyte within each of these segregated regions of the bath is measured approximately by the transverse area of the segregated region times the height of the electrolyte. Thus in the embodiment shown the volume of each segregated region of the bath is substantially one twenty-third the volume of the non-segregated region of the bath. For small installations the cylindrical cup-shaped diaphragms are quite satisfactory but it will be understood that so long as the volume of the portion of the electrolyte segregated by each diaphragm, relative to the volume of the remaining portion of the electrolyte is maintained within the limits specified, the arrangement and configuration of the diaphragms may very depending upon cell size, shape and related factors.

Both diaphragms are supported on the bottom of the cell, the diaphragm 43 being arranged substantially concentric with the solubilization cathode and the diaphragm

44 being arranged substantially concentric with the anode. The diaphragm 43 of the solubilization cathode thus provides a relatively small segregated region in the electrolytic bath in which from 6 to 8 molal of reduced titanium values are initially concentrated. This region is hereinafter identified as the solubilization region *a* of the cell. During the operation of the cell the level of the electrolyte in the region *a* will be raised and maintained higher than the level of the electrolyte in that portion of the cell outside of the cathode diaphragm and hence the concentration of reduced titanium values within the segregated solubilization region *a* of the cell will be urged, by the difference in hydrostatic pressure, to pass through the porous diaphragm 43 into the main portion or non-segregated region of the bath in which the deposition cathode is immersed. This region of the bath is hereinafter identified as the metal deposition region *b* and, as stated above, the volume of this non-segregated region of the electrolytic bath is substantailly twenty-three times the volume of the segregated solubilization region *a*. Thus as the reduced titanium values pass through the diaphragm 43 into the metal deposition region *b* of the electrolytic bath they are widely dispersed and hence the concentration of these reduced titanium values in the bath surrounding the anode diaphragm and the deposition cathode is relatively low, i. e. of the order of 0.2 to 0.4 molal thereby enhancing the deposition of coarse crystalline titanium metal on the lower end of the deposition cathode and precluding titanium tetrachloride losses at the anode.

While the relative diameters of diaphragms and cell specified above have been successfully employed in the electrolytic production of titanium metal it will be understood that the specific relationships given are illustrative only and that other size relationships may be used to obtain a high concentration differential of reduced titanium values in the bath within the range specified herein.

The diaphragm 44 surrounding the anode not only serves to prevent the reduced titanium values in the metal deposition region *b* of the bath from contacting the anode but also, in conjunction with the gas-barrier 30, serves to prevent the chlorine gas, which evolves at the anode, from escaping to either the solubilization or deposition cathode. To this end the upper end of the anode diaphragm fits closely about the lower end of the above-described gas barrier 30 whereby the chlorine gas is carried off by the latter from the cell to a suitable collecting device.

In addition to the above described functions of the diaphragms of the cell, bipolar electrode effects are substantially eliminated by preventing any sludge, i. e. finely divided titanium metal, which may be formed in the vicinity of the solubilization cathode from migrating towards the anode. In fact it has been observed that any sludge which may form at the solubilization cathode is confined to the solubilization area *a* by the diaphragm 43 and is dissolved or partially dissolved upon the subsequent or continuous addition of titanium tetrachloride vapor.

The electrolyte 36 partially fills the cell 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. For optimum operation of the cell, the electrolyte should be maintained at a temperature from about 670° C. to 750° C. and in the embodiment shown the heating means of the electrolyte comprises a furnace indicated generally at 45, in which the cell is mounted. It will be understood, however, that the electrolyte may be heated by other means such as, for example, electrically energized heating electrodes mounted in the cell.

In operating the cell to produce titanium metal, it is preferred to distribute the total of substantially four faradays of current, per mole of titanium tetrachloride introduced into the cell, substantially evenly between the two cathodes, that is to say, substantially two faradays to the solubilization cathode and two faradays to the deposition cathode. Moreover, in order to minimize the formation of sludge at the solubilization cathode due to reduction of a portion of the titanium tetrachloride directly to metallic titanium, it may be desirable to add slightly less than two faradays at the solubilization cathode per mole of titanium tetrachloride so as to insure the presence of some trivalent titanium values in the segregated region *a* surrounding the solubilization cathode. Assuming that the electrolytic bath has been heated to from 670° C. to 750° C. and the vaporous titanium tetrachloride is being introduced into the bath through the hollow cathode, the reduction of titanium tetrachloride through the trivalent and divalent titanium values to titanium metal is accomplished rapidly and efficiently, due to the above described arrangement of diaphragms. Following the accumulation of a relatively large deposit of metal on the deposition cathode, the deposition cathode is withdrawn from the electrolytic bath up into the upper part of the cooling stack whereupon the air-lock 37 is closed and the metal deposit is cooled in an atmosphere of an inert gas such as, for example, argon. After the deposit has cooled sufficiently to avoid embrittlement upon exposure to the atmosphere, the sealed cover of the stack is removed and the deposition cathode is withdrawn from the upper end thereof. A new cathode is then introduced into the upper end of the stack above the air lock, whereupon the upper portion of the stack is closed and purged of air by circulating argon or a similar inert gas therethrough. Thereafter the air-lock is opened and the new cathode is lowered into the electrolyte for the deposition of additional metal thereon.

It has been observed that because of the relatively large deposition area *b* of the electrolyte little or no crust is formed on the surface of the bath and hence inadvertent stripping of metal from the deposition cathode is avoided. Since there will be some removal of the electrolytic bath each time a deposit of metal is withdrawn, the bath should be replenished periodically which may be done by removing the cover or preferably by introducing additional salts into the cell by way of the hollow anode.

While a cell of the design shown in Figs. 1 and 2 is convenient especially for relatively small installations and has produced remarkably large quantities of the highest quality titanium metal, it will be understood that modifications of the cell and its diaphragms are included within the purview of the invention. Thus as shown in Figs. 3 and 4 the invention may be embodied in a cell comprising an outer sealed casing 50 of welded steel construction and lined with refractory brick 51, or an equivalent material to form a cell-well 52 in which the cathodes, anode and diaphragms are mounted. As pointed out above for optimum performance and efficiencies it is preferred to arrange the cathodes and anodes in substantially triangular relationship and hence in this embodiment of the invention the transverse section of the cell is a substantially equilateral triangle. The hollow solubilization cathode 53 is supported by the cover adjacent an apex of the cell-well, the anode 54 is supported by the cover adjacent a second apex of the cell-well while the deposition cathode 55 is located roughly in the region of the third apex of the cell-well in the manner shown in Fig. 4. The structural details of the supporting means for the respective cathodes and the anode may be substantially identical to those hereinabove described and hence a detailed description thereof will be unnecessary. Suffice to say that a conductor 56 and feed tube 57 are attached to the upper end of the hollow solubilization cathode which is supported in the cover by an insulated sleeve 23; the deposition cathode 55 is

supported by an insulated rod 58, having a conductor 59 at its upper end and mounted in a jacketed stack 60 which extends upwardly from the top of the casing and is of the construction shown in Figs. 1 and 2; while the anode is provided at its upper end with a conductor 61, and is supported by a sleeve-and-cap assembly, indicated generally at 62, adapted to carry off the chlorine gas developed at the anode.

The cathode and anode diaphragms of the cell are shown at 63 and 64 respectively each being arranged to segregate the corresponding apex-portion of the cell-well from the remaining portion thereof, the arrangement of the diaphragm 63 of the solubilization cathode being such that the area *a'* segregated thereby from the deposition portion *b'* of the cell-well is substantially one-seventh the volume of the latter whereby a relatively high concentration differential of from twenty to thirty times of reduced titanium values is maintained between the solubilization catholyte and the deposition catholyte.

More particularly the diaphragms 63 and 64 are substantially rectangular plates of refractory electrically non-conductive material supported by their vertical edges in indentations or grooves in corresponding side walls of the cell-well. The lower ends of the diaphragms are shown seated on the bottom of the cell-well with the upper ends of the diaphragms extending above the surface of the salt bath 65. As shown in Fig. 3 the upper end of the anode diaphragm is adapted to engage in a groove in the bottom edge of a gas-barrier 66 which comprises a substantially rectangular plate of an impervious refractory material.

The heating means for the cell is shown as comprising, in this instance, a pair of electrodes 67 and 68 which project through the walls of the cell adjacent the bottom of the cell-well as shown especially well in Fig. 4, the electrode 67 being located in a side wall of the cell substantially midway of the cathode 53 and anode 54, while the electrode 68 extends into the cell-well substantially opposite the electrode 67.

The operation of the modified cell is substantially the same as that of the cell hereinabove described.

The invention may be carried out in other specific ways than those herein set forth without departing from the spirit or 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 claim are intended to be embraced therein.

We claim:

An electrolytic cell for the production of a refractory metal by solubilization and reduction of a refractory metal halide in a fused salt bath, said cell comprising: a casing adapted to contain said bath; a cover on said casing arranged to seal said casing from the atmosphere; an anode; a hollow solubilization cathode, a deposition cathode and means to feed said refractory metal halide through said hollow cathode into said fused salt bath; supporting means carried by said cover and arranged to suspend said anode and said cathodes in said bath in substantially equally spaced triangular relationship in said casing; and electrically non-conductive cup-shaped diaphragms supported in said casing and circumscribing said anode and said hollow solubilization cathode respectively to form a solubilization region in said bath segregated from said anode and from the non-segregated region of said deposition cathode, the volume of said solubilization region being about one twenty-third the volume of the non-segregated region of said bath whereby the concentration of reduced metal halides in the segregated region of said hollow solubilization cathode is of the order of twenty to thirty times greater than the concentration of reduced halides in the portion of the bath surrounding said deposition cathode.

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