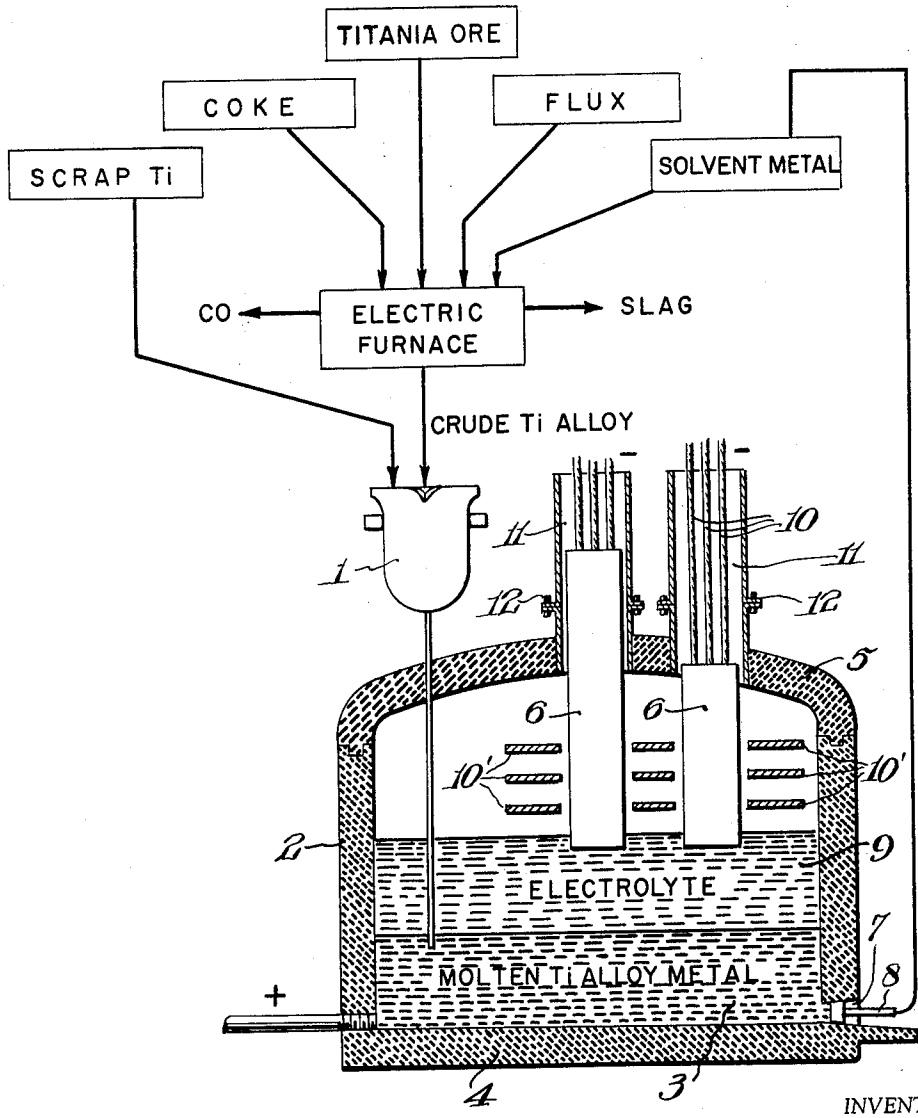
Dec. 15, 1959 C. M. OLSON 2,917,440

TITANIUM METAL PRODUCTION

Filed July 24, 1953 2 Sheets-Sheet 1

Fig. 1.



INVENTOR

CARL M. OLSON

BY

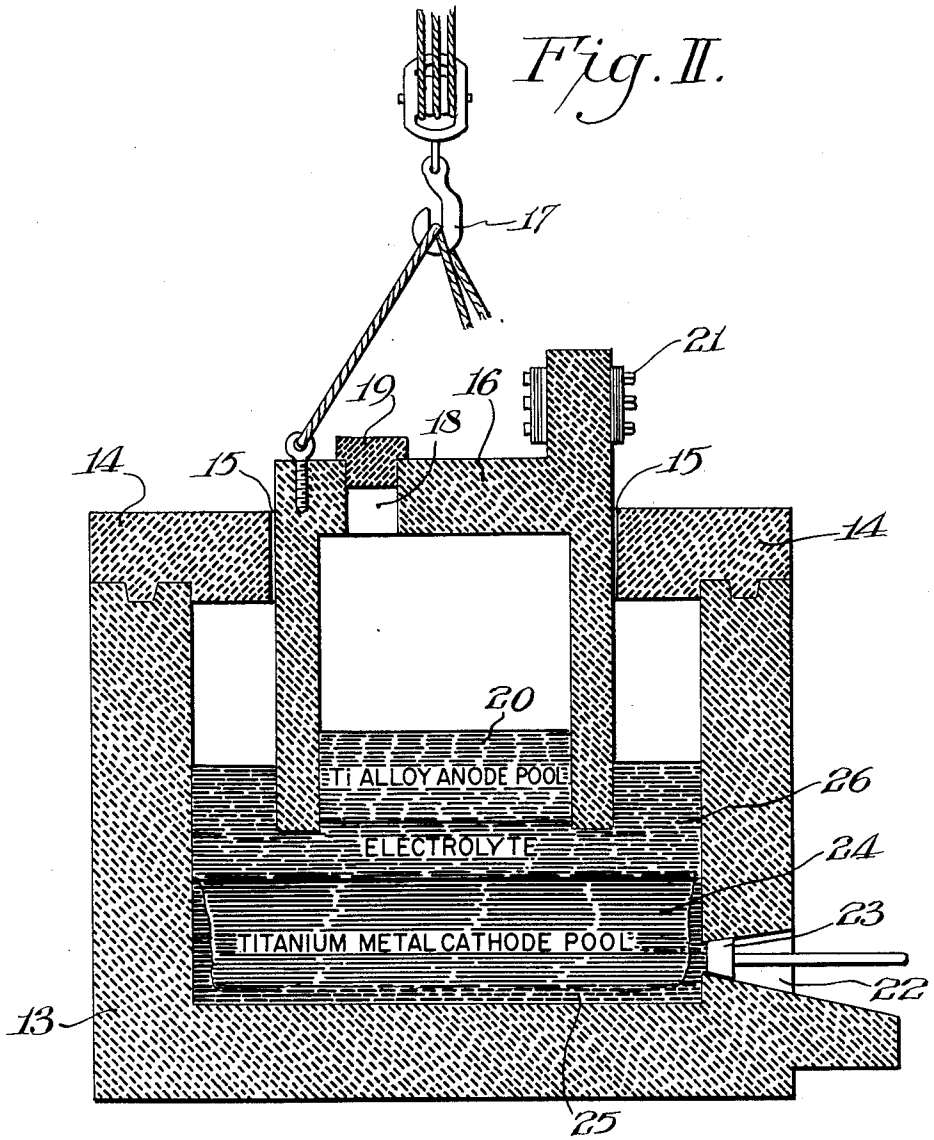
ATTORNEY

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TITANIUM METAL PRODUCTION

Filed July 24, 1953 2 Sheets-Sheet 2

Fig. II.



INVENTOR

CARL M. OLSON

BY

ATTORNEY

United States Patent Office 2,917,440
Patented Dec. 15, 1959

2,917,440

TITANIUM METAL PRODUCTION

Carl M. Olson, Newark, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Application July 24, 1953, Serial No. 370,167

15 Claims. (Cl. 204—64)

This invention relates to the production of titanium metal through electrolytic refining of impure forms of that metal or its alloys, and particularly to its preparation from products such as are obtained from titaniferous sources through high temperature reduction processes.

Titanium metal can be produced commercially by the reduction at elevated temperatures of a titanium halide, such as titanium tetrachloride, with an active reducing metal such as magnesium. The reduction process requires many steps, the raw materials used are expensive to prepare, and great care must be exercised in each of its phases to prevent the entry of contaminating, deleterious impurities into the system. Other reduction processes in which recourse is had to other reducing agents and titanium sources are also known but their successful commercial adaptation has yet to be achieved. These include the reduction of oxides or other compounds of titanium by reducing metals such as those of the alkali or alkaline earth metals (sodium, magnesium, calcium, etc.). Electrolytic processes have also been proposed for this purpose. In these, solutions of titanium halides such as titanium tetrachloride, titanium trichloride and titanium dichloride, in anhydrous molten salts such as lithium chloride, potassium chloride, sodium chloride and the like, or alkali or alkaline earth metal fluotitanate electrolytes, are subjected to electrolysis to produce titanium powders or crystal dendrites. These processes have two distinct disadvantages: (*a*) a pure, anhydrous, oxygen-free cell feed must be prepared and maintained free of all extraneous, readily reducible metals, and (*b*) the gaseous by-products (chlorine or fluorine) which are evolved at the anode prevent use of high current densities.

It is among the objects of this invention to overcome these and other disadvantages characterizing prior titanium metal producing operations and to provide novel, effectually useful procedures for attaining such objects. Particular objects of the invention include the provision of novel electro-refining methods adapted to obviate a pure cell feed requirement; a process wherein high current density is obtainable because gas evolution is minimized; a process wherein the electrolyte serves only as a transfer agent for the titanium values and is not consumed in the electrolytic process, and in which scrap titanium metal or impure metal or alloys can be used as the anode feed to the cell. Further objects are to provide a method in which the titanium metal can be obtained in either liquid state or as a consolidated mass and tedious separation of entrapped salts is not required; and in which the electrolytic cell used is of relatively simple, economical construction. Other objects and advantages will be apparent from the ensuing description and accompanying, diagrammatic drawings, in which

Fig. I is a flow sheet arrangement illustrative of one adaptation of the invention and which also shows a vertical, cross-sectional view of one useful form of electrolytic cell; and

Fig. II is a vertical, cross-sectional view of a modified form of such cell.

The above and other objects and advantages are realized in this invention which comprises subjecting a molten alloy having a melting point below pure titanium, comprising titanium and a metal less electropositive than said titanium, to electrolysis under an inert atmosphere and in an electrolytic cell maintained at a temperature above the melting point of the alloy, employing said alloy as an anode in said cell and a molten anhydrous halide of a metal more electropositive than titanium as an electrolyte, transferring the titanium metal values obtained from the molten alloy anode through said electrolyte to the cell cathode by means of an electrolytic current, and recovering the pure titanium metal product obtained from the electrolysis.

More specifically, the invention comprises separately forming a molten alloy composed of titanium and copper, silicon, iron, or other solvent metal less electropositive than titanium, charging the alloy in molten state into an electrolytic cell wherein it will function as an anode for said cell, employing as an electrolyte for said cell a metal halide, preferably a fluoride, of a strongly electropositive metal such as calcium, and as a cathode for the cell titanium metal, and then transferring through electrolysis the titanium values of said alloy anode to the cathode and recovering titanium metal in pure form from said cathode.

Referring to the drawings, particularly Fig. I, a flow sheet and schematic electrolytic cell arrangement is shown, for preparing a crude titanium alloy and treating it in an electrolytic cell in accordance with the invention to recover its titanium values in pure state. Thus, a crude alloy, such as impure ferro titanium (containing Mn, Ni, Mg, V, Cr, Si, etc., besides traces of O_2 and C), can be prepared in a conventional manner as by separately charging suitable amounts of a titanium ore (ilmenite, rutile, or a suitable slag material), a carbonaceous reducing agent, such as coke, a fluxing agent and an alloying or solvent metal, such as copper, silicon or iron, or reducible compounds thereof, into a high temperature electric or other suitable furnacing means in which desired reduction of a metal oxide to the crude titanium alloy can be effected. Carbon monoxide by-product and slag which form are separately withdrawn from the furnace and system, the slag serving to cover and protect the molten alloy within the furnace and preventing alloy re-oxidation, as well as the formation of nitrides. It also serves to fluidize certain difficultly reducible oxides, such as calcium oxide, in the ore.

The alloy from the reduction furnace is withdrawn in molten state to a ladle or other form of useful dispensing receptacle **1**, wherein titanium enrichment of the alloy can be effected by titanium scrap addition or otherwise, should this be desired or required. The molten alloy can be fed from said receptacle directly to an electrolytic cell **2**, resting in the bottom of the latter to provide a molten titanium alloy anode **3** for the electrolytic system. The cell proper comprises a casing element **4** constructed of graphite blocks or other suitable material, well cemented and sealed in leak-proof relationship and thoroughly baked out. A cover element **5** can be suitably disposed over the cell, if desired, and so placed and sealed that air will be effectively excluded from the cell and inert gas (argon, helium, etc.) use permitted for purging purposes. The cover **5** can be suitably apertured for reception and passage therethrough of a plurality of adjustably suspended masses of titanium metal as cathodes **6**. The alloy **3** is maintained at and can rise to any desired level in the cell, and additional amounts of alloy can be introduced therein from time to time as the titanium values of the anode pool **3** become depleted. Spent alloy formed in the cell can be periodically or continuously tapped from the cell

through the withdrawal outlet 7 having a removable plug 8, and recycled to the primary reduction furnace, via the solvent metal charge, to produce more cell feed alloy. Suitably provided over the molten anode 3 is an electrolyte 9, comprising a halide salt of a strongly electropositive metal. The lower portions of titanium cathodes 6 are immersed in said electrolyte to provide electrical contact therewith. The electrolyte, together with anode 3, forms the two-layer cell system of this embodiment of the invention. Halide salts, preferably fluorides or chlorides, comprise the electrolytes which are most useful herein, examples thereof including those of magnesium, calcium, strontium, barium and cerium fluorides and chlorides. Of these, calcium fluorides, cerium fluoride, calcium chloride, or mixtures thereof, are preferred for use. In selecting the electrolyte, three criteria are observed: (1) the metal ions must be more electropositive than the titanium ions; (2) low volatility is desirable to minimize losses at high temperature; and (3) the cell design and its limitation on the relative densities of salt and metal phases. Suitable thermal radiation shields 10' can be provided within the cell 2 in order to reduce the intense thermal radiation of the molten electrolyte and interior portions of the cell and prevent such radiation from reaching the cover element 5.

In the operation of the cell, a direct current is passed therethrough at a voltage adapted to preferentially dissolve the titanium from the anode pool 3 into the electrolyte 9 for deposition on the cathodes 6. As the titanium metal deposits on the cathodes, they are gradually withdrawn by means of retractible elements 10 into chambers 11 in order to maintain a substantially constant anode-cathode separation distance. Said chambers can be detached, if desired, from the cell at points 12 when the cathode has built up to a desired length. This transfer is not too frequent in a large cell since even with a current density of 10,000 amps. per sq. ft., the increase in length is of the order of about 1 ft. per day. When chambers 11 are disconnected or isolated, suitable metal blanks (not shown) can be inserted at the points 12 to insure against entrance of air or oxidizing contaminants into the cathode sections.

As indicated, charging of the cell with titanium-rich crude metal can be effected from the ladle 1 at the time the cathodes 6 are removed from the cell. If desired, it can be effected by means of a side inlet having an associated trap provided in the cell wall.

While described as applied to a two-layer cell system, use is contemplated of a system wherein three or more layers exist. Thus, in the modification shown in Fig. II, a three-layer system is provided, the operation of which is particularly described in Example II below. This Fig. II cell comprises a casing member 13 provided with a cover element 14 with an opening 15 through which cylindrical, graphite, or other desired form or type of anode "bell" 16 can be raised or lowered, or otherwise adjustably disposed, in the cell as by any means of block and tackle arrangement 17, or otherwise. An inlet 18, having a threadedly secured or otherwise removable plug 19, is provided in the upper part of the bell element, through which opening a suitable molten titanium alloy forming anode pool 20 can be suitably admitted or withdrawn. Suitable electrical contact means 21 are also provided in the bell 16 for connecting it to a source of direct current (not shown). A tap outlet 22 having a removable plug 23 is provided in the lower part of the casing 13 through which titanium metal produced in the cell, which forms as a cathode pool 24 with a crust or skull 25, can be withdrawn under inert conditions into an associated mold or ingot-forming device (not shown). The anode pool 20 is, as will be noted, retained within the confines of bell 16 and the lowermost extremities of the latter as well as said pool are submerged in a layer of electrolyte 26 of the type herein referred to.

To a clearer understanding of the invention, the following examples are given. These are merely illustrative and not in limitation of the underlying scope of said invention:

Example I

A furnace charge, comprising 2400 lbs. of rutile ore, having a TiO_2 content of 96.5%, admixed with 1100 lbs. of aluminum pellets, was placed in the hearth of a three-phase electric arc furnace, together with 720 lbs. of copper scrap, 345 lbs. of titanium alloy (96% Ti) clippings and rejected forgings, and 1800 lbs. of burned lime. An arc was then struck by lowering the three carbon electrodes of the furnace to the scrap metals and then withdrawing them to provide a continuous heating for the batch. Soon thereafter an exothermic reaction took place, causing the batch to emit much heat. After this action had subsided, electrical heating was continued for an additional 95 minutes to effect complete reaction between any solubilized TiO_2 in the slag and residual aluminum in the the molten metal pool. At the conclusion of this phase of the operation the furnace charge had separated into two layers: (*a*) a lower one comprising an impure Cu-Ti alloy (melting at about 1100° C.) and (*b*) an upper protective slag layer comprising a molten calcium aluminate. A large portion of the slag cover was then run off and the Ti-Cu alloy containing about 70% Ti was poured into an associated bottom tapping ladle. From this ladle the alloy was transported to an electrolytic cell of a design essentially that shown in Figure I and previously brought to a temperature of 1600° C. by means of an auxiliary electrode (not shown). The cell hearth was 3 ft. in diameter and the Ti-Cu alloy was introduced therein by pouring from the ladle through a fused CaF_2 electrolyte so that it lay in contact with the graphite bottom of the cell and in electrical contact therewith. Care was taken that no oxide slag was inadvertently introduced during this step. Stubs of two titanium metal electrodes, each one foot in diameter and suspended by heavy water-cooled copper conductors, were lowered through the appropriate chambers until their ends dipped into the cell electrolyte. A direct current voltage was then applied to the cell, a cathode current density of 5000 amps./ft.^{2} drawn at a potential difference of 3 volts being found to exist. The total cathode surface in the cell was about 1½ sq. ft. Electrolysis was continued for a period of six days with 7500 amperes drawn by the cell. During this period the electrodes were gradually withdrawn, and at the end of the six-day period a total of 1300 lbs. of titanium was deposited upon the electrodes. After electrolysis, the Ti concentration in the anode alloy was found to have dropped to 30%, indicating that about 82% extraction of the titanium values had taken place during operation of the cell. The 30% Ti alloy was tapped from the cell and recycled for reuse to the primary electric arc furnace.

Example II

A silicon-titanium alloy containing 52% Si, 38% Ti, and 5.5% Fe as major constituents was prepared in accordance with the disclosure of U.S. Patent 1,019,526. To this alloy sufficient titanium scrap was added to provide a crude alloy charge having a final analysis of 44% Si, 46% Ti, 5.1% Fe, and 0.45% Mn and a melting point of about 1550° C. An electrolytic cell of the design shown in Figure II and comprising a circular container composed of graphite blocks backed up with high temperature refractory was utilized to electrorefine this crude alloy. The internal diameter of the cell was 4 ft. and a tap hole, with a plug stoutly rammed in, was provided in its bottom. Into the cell, while suspended by block and tackle, was inserted a graphite cylinder of 2' I.D. and 2¾' O.D., in the top of which an opening was provided for the admission and removal of the crude silicon-titanium alloy. Suitable means for connecting the cell with a direct current source as well as means

for maintaining an inert atmosphere [noble gas (argon or helium) or hydrogen] within the open space above the electrolyte and the liquid silicon-titanium anode pool was also provided. The furnace lining proper, being the cathode, was connected at several points to the direct current source.

Prior to actual cell operation, the graphite cylinder (herein referred to as the anode "bell") was raised from the cell and three 10-inch diameter graphite rods (connected to a 3-phase A.C. power source) were lowered to the furnace floor. 2300 lbs. of cerous fluoride were poured in around these electrodes and an arc struck between them and the floor. As soon as a portion of the CeF_3 melted, the electrodes were retracted a few inches so that the current path was through the fused salt. During this period a stream of chlorine was introduced into the cell to remove oxygen from the salt. Within a few hours the electrolyte and furnace had reached a temperature of 1800° C. The electrodes were then removed, 200 lbs. of $CeTiF_6$ was added, and the anode "bell" lowered into place, the bottom lip of the "bell" being approximately four inches from the furnace floor. Into the inner portion of the "bell" were poured 470 lbs. of the previously prepared molten silicon-titanium alloy cell feed. The electrolyzing direct current was then applied between the cylinder with its charge of alloy and the furnace proper. A current of 30,000 amperes was maintained at a potential difference of 3.2 volts. Initially, titanium deposited as a solid on the surface of the furnace floor and walls. Later, as the amount of titanium increased, the metal lay as a liquid pool on the cell bottom.

After about six hours of operation the electrolysis was interrupted and a major portion of the titanium-depleted silicon alloy was removed from the anode barrier by means of a graphite dip tube attached to a sealed ladle to which vacuum could be applied. The spent alloy was returned to the alloy preparation area for Ti enrichment. A fresh portion of silicon-titanium alloy was then introduced and the electrolysis continued. This cycle of withdrawing and replenishing the anode alloy was repeated every six hours, an adjustment being made at each cycle of the anode-cathode distance in order to maintain proper separation.

At the end of five days the electrolyzing current was interrupted and the contents of the furnace tapped by piercing through the metal surface plug and crust. 3500 lbs. of Ti metal were tapped into a graphite-lined ingot mold. A small portion of the electrolyte came through also but this immediately rose to the top of the molten metal and served to protect the metal surface from oxidation. At the conclusion of the tapping operation the cell tap hole was again rammed tight in closed relationship and the cell again put back into operation.

It is not necessary to electrolyze the silicon-titanium alloy to complete exhaustion. From a purity angle it is sufficient to go down to a composition of 15% or 10% Ti (remainder silicon and impurities). This affords recovery of about 80% of the titanium values per pass. The remainder of the Ti is not lost but remains associated with the silicon during the enrichment operation on recycling.

Certain phases of the electro-chemistry of the present process are particularly interesting and unusual. Unlike many prior electrolytic procedures in which the bulk of titanium values are added to the cell in the electrolyte, the electrolyte is utilized herein only as a transfer agent for the titanium. For example, in Figure I, when the electrolytic potential is applied to the cell titanium atoms in the molten alloy anode are solubilized in the electrolyte as positively charged ions which migrate to the cathode under the influence of the electric field, by diffusion and by thermal convection, and discharge on the cathode to form titanium metal atoms.

It is critical to the invention that the anode pool remain liquid during the course of the electrolysis in order that the titanium concentration at the anode surface will remain effectively high. If this condition fails to prevail and the anode should freeze, undesired rapid impoverishment of the anode surface with respect to titanium will occur, and disadvantageously the alloying constituent might begin to dissolve in the electrolyte. Hence, it is desirable that the anode alloy have a relatively low melting point, even with a high percentage of titanium content. Several solvent metals are available for use in conjunction with the titanium, and, in order for the selectivity principle to operate, it is necessary that the solvent metal shall be less electropositive than titanium. In practice, this is not restrictive since very few common elements are more electropositive than titanium and these, for example, sodium, calcium, and magnesium, are so volatile that they would not persist in the crude furnacing or final melting steps. Since solvent metals such as iron or copper are also good solvents for other alloying ingredients frequently encountered in titanium technology, it is possible to accommodate titanium scrap or alloy scrap in any proportion simply by adding it to the ladle or furnace prior to the introduction of a charge into the refining cell. I prefer copper as a solvent metal since the melting points of titanium copper alloys are mostly below 1200° C. Other metals non-volatile under the temperature conditions of the furnacing operation can be used, including those of nickel, lead, manganese, iron, silicon, etc., or mixtures thereof.

Since the electrolyte in the cell acts only as a transfer agent, there is little need to remove it from the cell during the electrolysis operation; also, the amount required for a cell charge is relatively small compared with the inventory of anode and cathode metals. Thus, one can employ certain salts which because of cost factors otherwise would be economically unattractive. As already indicated, the electrolyte comprises a molten halide salt of a strongly electropositive metal. Since the electrolysis operation is designed to operate at temperatures up to about 1800° C., it is highly desirable that the vapor pressure of the salts be relatively low. Calcium fluoride fulfills these requirements well, as does cerous fluoride and other alkaline earth and rare earth (cerium, lanthanum, praseodymium, etc.) fluorides. Similarly, the chlorides of these alkaline earth and rare earth metals or mixtures of such fluorides and chlorides can be used. The choice of the molten salt is to a considerable extent dictated by the temperature which will prevail in the electrolytic operation. The density of the molten salt is a matter which must be given consideration in the specific mode of operation being undertaken. In any event, such electrolyte must be free of oxygen, sulfur, and nitrogen since these elements combine readily with titanium metal.

While several modes of operating the present process have been illustrated, it will be readily understood by those skilled in the electrolytic art that various cell anode and electrolyte layer systems as well as one or more titanium cathodes can be resorted to. Thus, a single, solid titanium cathode can be employed in lieu of the plurality utilized in Fig. I. Alternatively, a cell system in which the cathode comprises an upper layer of pure liquid titanium or titanium alloy, the anode a bottom layer of crude liquid titanium alloy between which cathode and anode a layer of electrolyte is interpositioned, can be advantageously used. Similarly, the anode can comprise an upper layer of molten crude titanium-silicon alloy, the cathode a bottom layer of pure liquid titanium, with a layer of CeF_3 or other desired electrolyte interpositioned therebetween. Another type cell comprises one in which the electrolyte, such as CaF_2, floats upon the surfaces of a molten crude titanium alloy anode and pure titanium liquid disposed in divided relationship in the bottom of the cell by means of a dividing or partition-

ing means. This latter barrier type arrangement, though employable, is less preferred for use because the average distance of travel for the titanium ions is large and may impair the electrical efficiency of this type of cell. The density of most fused salts at about 1725° C. is below that of titanium at the same temperature. A possible exception is the fluoride of gadolinium. Certain titanium alloys, however, having a slightly lower density and melting at temperatures below 1725° C. can be supported upon cerous fluoride as in the three-layer cell system comprising, for example, pure liquid titanium alloy as the cathode, crude molten titanium-silicon alloy as the anode, and cerous fluoride as the electrolyte. This has several advantages of which the following dominate: (1) the pure titanium liquid is held below a layer of fused salt to protect it from any oxidizing atmosphere of the cell; (2) the crude titanium-silicon alloy is more readily replenished; and (3) tapping of the fused titanium product is facilitated.

It will be understood by those familiar with the behavior of liquid metals in magnetic fields of high currents that the pools of metals in the cell will have vigorous rotation or agitation. This constant circulation of the liquid metal keeps the anode-electrolyte interface constantly replenished with titanium ions.

Among the various advantages which the electrolytic process of this invention affords over prior processes, the following can be mentioned: The electrolytic cell requires no diaphragm; the titanium values being fed to the electrolytic cell need not be in the pure state and are in the form of a relatively low-melting alloy, say, at about 1200° C.; a substantially constant anode-cathode spacing can exist regardless of the inventory within the cell; the cell serves as the metal production unit and as a reservoir from which metal can be directly poured into ingot form; gas evolution from the cell is held to a minimum (a static protective gas atmosphere is indicated); high current densities can be utilized in the cell due to lack of gas evolution at the anode and the apparent lack of an anode effect; titanium scrap can be directly accommodated for reworking in substantially any ratio, a fact which becomes increasingly important as the titanium industry develops; and the titanium values are added to the cell in a condensed or concentrated phase in the alloy forming an expendable anode pool.

I claim as my invention:

1. A method for preparing pure titanium metal which comprises subjecting to electrolysis a crude molten alloy of titanium with a more noble metal than said titanium and having a melting point below pure titanium, effecting said electrolysis under an inert atmosphere and in an electrolytic cell maintained at a temperature above the melting point of said alloy, employing the latter as an anode in said cell and an electrolyte initially consisting essentially of a molten anhydrous halide of a metal less noble than titanium, transferring by means of an electric current and while maintaining said anode molten the titanium metal values from said molten alloy anode through said electrolyte to a titanium cathode maintained in said cell, and recovering the titanium metal product from said cathode.

2. An electrolytic refining process for obtaining pure titanium metal comprising subjecting a crude, impure, molten alloy of titanium and a metal more noble than titanium to electrolysis within an electrolytic cell maintained under an inert atmosphere and at a temperature above the melting point of said alloy, employing said molten alloy as an anode, an electrolyte initially consisting essentially of a molten, anhydrous fluoride of a metal less noble than titanium and solid titanium metal as a cathode in said cell, transferring while maintaining said anode molten the titanium metal values from said molten alloy anode through said electrolyte to the titanium cathode by means of an electric current, and recovering the deposited titanium metal product from said cathode.

3. A method for preparing pure titanium metal which comprises subjecting under an inert atmosphere a crude, molten alloy of titanium and copper to electrolysis within an electrolytic cell in which said molten alloy is employed as an anode, employing an electrolyte initially consisting essentially of a molten, anhydrous halide of a metal less noble than titanium, transferring by means of an electric current and while maintaining said anode molten the titanium values from said anode to a solid titanium cathode maintained in said cell, and recovering from said cathode the pure titanium metal freed in the process.

4. A method for preparing pure titanium metal which comprises subjecting under an inert atmosphere a crude molten alloy of titanium and silicon to electrolysis within an electrolytic cell in which said molten alloy is employed as an anode, employing an electrolyte initially consisting essentially of a molten, anhydrous halide of a metal less noble than titanium, and recovering the pure titanium metal freed in the process.

5. A process for electrorefining titanium from its alloy with a metal more noble than titanium and having a melting point below pure titanium which comprises subjecting said alloy in molten state and as the anode of an electrolytic cell to electrolysis under an inert atmosphere and at a temperature above the melting point of said alloy, employing as an electrolyte for said cell a molten halide initially consisting essentially of a salt of a metal less noble than titanium metal, transferring the titanium metal by means of an electric current from said anode while maintaining the latter molten through said electrolyte to a solid titanium metal cathode maintained in said cell, and recovering the titanium metal as the product of said cathode.

6. An electrolytic process for refining titanium from an alloy thereof with copper which comprises maintaining said alloy in molten state as an anode in an electrolytic cell, employing as an electrolyte in said cell a molten salt initially consisting essentially of a fluoride of a metal less noble than said titanium and pure solid titanium as a cathode for said cell, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal from said anode by means of an electric current through said electrolyte to said cathode, continuing said transfer until said anode alloy becomes substantially depleted in titanium, interrupting the electrolysis process, removing the depleted alloy from said cell, and charging fresh titanium-rich alloy therein, and then continuing the electrolysis and recovering the refined deposited titanium metal as the cathode product.

7. An electrolytic process for refining titanium from an alloy thereof with silicon which comprises maintaining said alloy in molten state as an anode in an electrolytic cell, employing as an electrolyte in said cell a molten salt initially consisting essentially of a fluoride of a metal less noble than said titanium and pure solid titanium as a cathode for said cell, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal from said anode by means of an electric current through said electrolyte to said cathode, continuing said transfer until said anode alloy becomes substantially depleted in titanium, interrupting the electrolysis process, removing the depleted alloy from said cell, and charging fresh titanium-rich alloy therein, and then continuing the electrolysis and recovering the refined deposited titanium metal as the cathode product.

8. An electrolytic process for recovering titanium in pure condition from an alloy thereof with copper which comprises charging said alloy into an electrolytic cell and maintaining it therein as an anode for said cell in molten state, employing an electrolyte initially consisting essentially of a molten fluoride salt of a metal less noble than titanium for said cell and pure solid titanium metal as a cathode therefor, transferring under an inert atmosphere and while maintaining said anode molten the titani-

um metal from said anode by means of an electric current through said electrolyte to said cathode, and recovering the deposited titanium metal as the cathode product.

9. An electrolytic process for recovering titanium in pure condition from an alloy thereof with silicon which comprises charging said alloy into an electrolytic cell and maintaining it therein as an anode for said cell in molten state, employing an electrolyte initially consisting essentially of a molten fluoride salt of a metal less noble than titanium for said cell and pure solid titanium metal as a cathode therefor, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal from said anode by means of an electric current through said electrolyte to said cathode, and recovering the deposited titanium metal as the cathode product.

10. An electrolytic process for recovering titanium in pure condition from an alloy thereof with copper which comprises charging said alloy into an electrolytic cell and maintaining it therein as an anode for said cell in molten state, employing an electrolyte initially consisting essentially of a molten chloride salt of a metal less noble than titanium for said cell and pure solid titanium metal as a cathode therefor, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal from said anode by means of an electric current through said electrolyte to said cathode, and recovering the deposited titanium metal as the cathode product.

11. An electrolytic process for recovering titanium in pure condition from an alloy thereof with silicon which comprises charging said alloy into an electrolytic cell and maintaining it therein as an anode for said cell in molten state, employing an electrolyte initially consisting essentially of a molten chloride salt of a metal less noble than titanium for said cell and pure solid titanium metal as a cathode therefor, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal from said anode by means of an electric current through said electrolyte to said cathode, and recovering the deposited titanium metal as the cathode product.

12. An electrolytic process for recovering titanium in pure condition from an alloy thereof with copper which comprises charging said alloy into an electrolytic cell and maintaining it therein as an anode for said cell in molten state, employing an electrolyte initially consisting essentially of a fused calcium fluoride for said cell and pure solid titanium metal as a cathode therefor, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal from said anode by means of an electric current through said electrolyte to said cathode, and recovering the deposited titanium metal as the cathode product.

13. An electrolytic process for recovering titanium in pure condition from an impure titanium-silicon alloy which comprises charging said alloy into an electrolytic cell, maintaining it therein in molten state under an inert atmosphere as an anode for said cell, utilizing fused cerous fluoride as an electrolyte for said cell and solid titanium metal as a cathode therefor, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal from said anode by means of an electric current through said electrolyte to the titanium cathode, and recovering the pure deposited titanium metal from said cathode.

14. An electrolytic process for refining titanium-copper alloys containing at least 50% titanium metal comprising charging said alloy into an electrolytic cell and maintaining the same in molten state therein as the anode for said cell, utilizing an electrolyte initially consisting essentially of molten calcium fluoride for said cell and solid titanium metal as a cathode therefor, transferring under an inert atmosphere and while maintaining said anode molten the titanium metal of said anode through said molten fluoride electrolyte to said cathode by means of an electric current, continuing said transfer until the titanium content of said alloy drops to approximately 30% titanium, interrupting the electrolysis and removing said alloy from the cell and introducing therein a fresh charge of molten titanium-copper alloy, recommencing the electrolysis operation and recovering the purified titanium metal as the cathode product of the electrolytic cell.

15. A process for electrolytically refining impure titanium in a fused salt bath comprising the steps of producing with the impure titanium a titanium alloy which is liquid at the temperature of said salt bath and whose other metallic constituents are more noble than titanium, and electrolyzing said liquid titanium alloy as anode of an electrolytic cell having a solid cathode and said fused salt electrolyte initially consisting essentially of at least one halide of a metal less noble than titanium, to deposit refined solid titanium electrolytically on said cathode.

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