April 15, 1958 R. S. HOOD 2,830,940

PRODUCTION OF METALS

Filed March 28, 1952

2 Sheets-Sheet 1

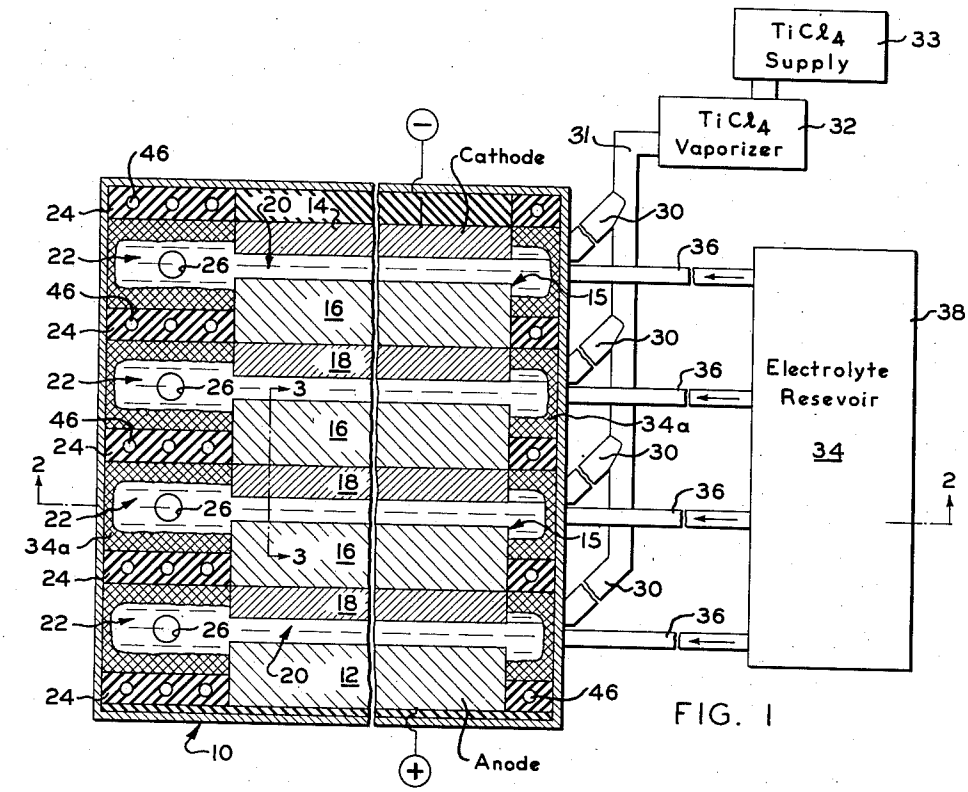


FIG. 1

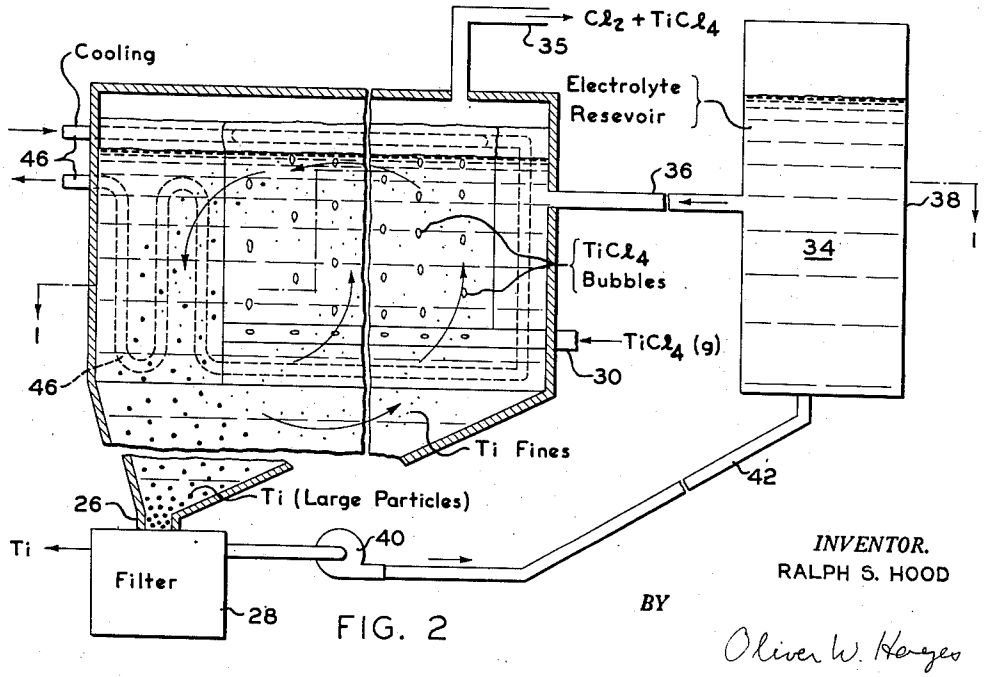


FIG. 2

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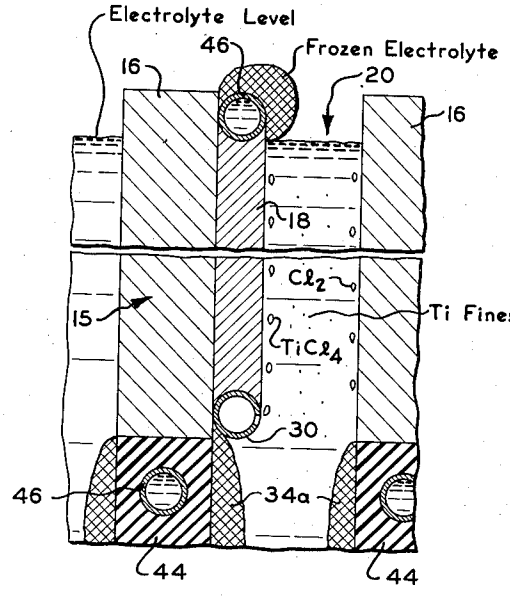


FIG. 3

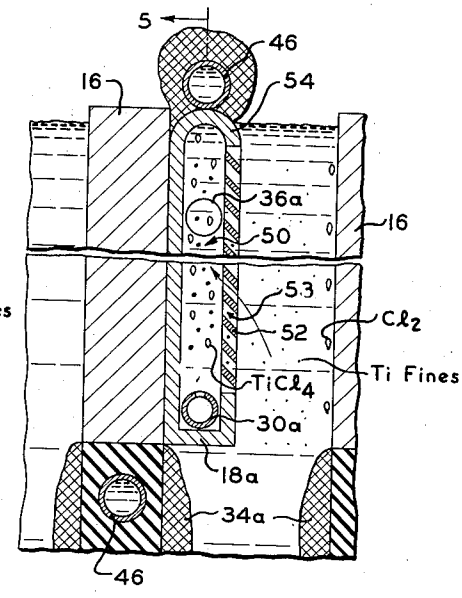


FIG. 4

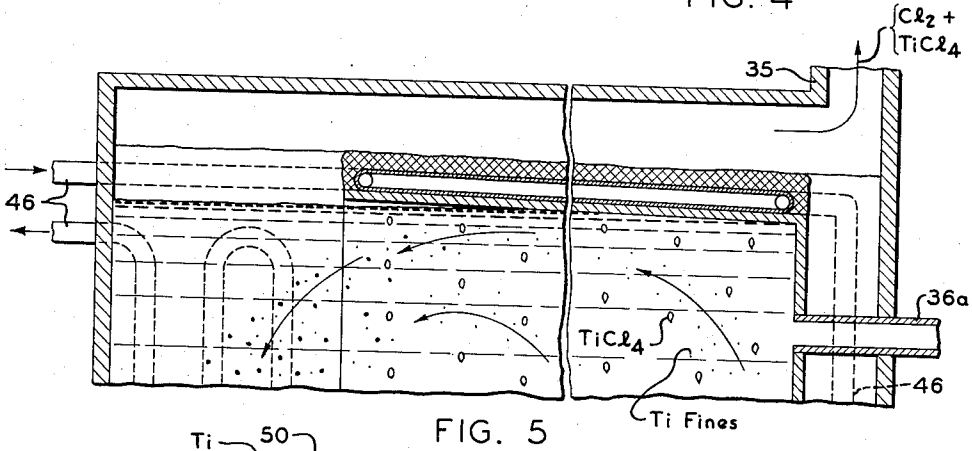


FIG. 5

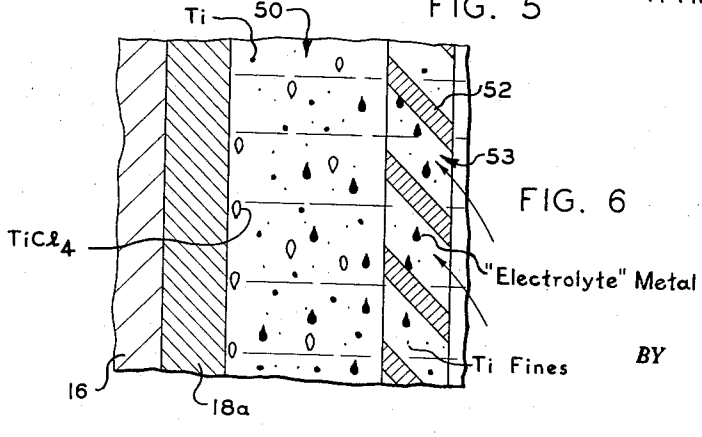


FIG. 6

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2,830,940

PRODUCTION OF METALS

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Application March 28, 1952, Serial No. 279,065

3 Claims. (Cl. 204—64)

This invention relates to the production of metals and more particularly to the production of titanium in an electrolytic cell.

A principal object of the present invention is to provide an improved process and apparatus for producing titanium in an electrolytic cell with a high power efficiency.

Still another object of the invention is to provide such a process and apparatus which permit the use of the principle of bipolar cell operation with a consequent over-all power efficiency.

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

The invention accordingly comprises the process involving 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 arrangement 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 accompanying drawings wherein:

Fig. 1 is a diagrammatic, schematic plan view of one electrolysis cell embodying the invention;

Fig. 2 is a diagrammatic, sectional view of the cell of Fig. 1 taken along the line 2—2;

Fig. 3 is an enlarged sectional view of a portion of the cell of Fig. 1 taken along the line 3—3;

Fig. 4 is a view similar to Fig. 3 showing an alternative type of cathode.

Fig. 5 is a sectional view of the cathode of Fig. 4 taken along the line 5—5; and

Fig. 6 is an enlarged view of a portion of Fig. 4.

In the production of titanium by electrolytic techniques, it is desirable that the titanium manufacture be achieved in each electrolytic cell at the highest possible rate with the highest possible power efficiency. In the present invention these objectives are achieved by a number of features thereof. The cell preferably employs an electrolyte which comprises a molten mixture of halides and particularly the chlorides from the group consisting of the alkali metal chlorides and the alkali earth metal chlorides. To this electrolyte there is fed titanium tetrachloride, and the cell is operated at a sufficiently high voltage so that the cathode potential is above the discharge potential of one of the alkali metal or alkali earth metal ions. In this manner either the alkali metal or the alkali earth metal is liberated at the cathode. For convenience, the alkali metal or alkali earth metal liberated at the cathodes is sometimes hereinafter referred to as the "electrolyte metal." This electrolyte metal serves as a reducing agent which can reduce the titanium tetrachloride in the cell either to titanium metal or to a lower chloride.

In any particular case it is difficult to state whether or not the titanium tetrachloride is completely reduced by

the alkali metal or alkali earth metal to titanium metal, or whether it is only reduced to a lower chloride which has a higher solubility in the electrolyte and which may be further reduced to titanium from solution. In either case much higher production rates are achieved since the electrolyte metal will be completely used up either by forming a more soluble lower chloride or by reducing a titanium chloride to titanium.

Titanium tetrachloride is preferably introduced into the electrolytic bath at a point below the cathode so that it rises in the electrolyte in the form of fine bubbles which pass upwardly into the electrolysis zone between the anode and cathode of the cell. These rising bubbles of titanium tetrachloride serve several important functions. They act as a gas lift which accentuates the gas lift caused by the rising chlorine bubbles from the anode, and thus they cause an upward travel of the electrolyte in the electrolysis zone between the anode and cathode. The cell is preferably arranged so that the electrolyte travels downwardly in a settling zone at a point removed from the space between the anode and the cathode, and is then recirculated upwardly into the anode-cathode space.

The present invention permits utilization of the bipolar principle of electrolytic cell operation with a relatively simple cell construction. This is due to the fact that the reaction between titanium tetrachloride and the electrolyte metal (i. e., alkali metal or alkali earth metal) is highly exothermic. Consequently, considerable heat is generated within the electrolyte due to the presence of this exothermic reaction. Advantage is taken of this excess heat by providing cooling of the salt adjacent the ends of the bipolar plates, this frozen salt serving as an excellent insulation to completely isolate the various pairs of anodes and cathodes. The presence of this extra heat also permits the use of refractory materials in the cell as insulation barriers which are protected by frozen salt layers so that they are not attacked by the fused electrolyte. An additional advantage of the excess heat resides in the freezing of a protective salt layer over any metallic portions of the cathode which extend into the top of the cell where they might otherwise be attacked by chlorine vapor at the high temperature of the cell. The frozen salt can also be used as electrical insulation along the sides and bottom of the cell when these sides or bottom are made of conducting materials such as carbon, metal and the like.

Referring now to Figs. 1, 2, and 3 there is shown one embodiment of the invention as applied to a bipolar cell. In this cell an anode and a cathode are positioned at opposite ends of the cell, and a plurality of bipolar elements are spaced along the cell. During the application of a voltage between the anode and cathode a lesser voltage is applied between the bipolar elements so that there are a plurality of electrolysis zones between the various bipolar elements. One side of each of the bipolar elements acts as an anode, while the other side thereof acts as a cathode. This cell is preferably so arranged that each electrolysis zone between each anode and cathode has a short dimension along the cell so as to cut down the IR drop in the electrolyte.

Titanium tetrachloride is preferably introduced into the cell adjacent the bottom of each cathode so as to cause an upward flow of the electrolyte in each electrolysis zone due to the gas lift of the titanium tetrachloride gas bubbles. The electrolyte flows upwardly within each electrolysis zone, laterally at the top thereof, and then travels downwardly in an enlarged settling zone which is spaced to one side of, and outside of, each electrolysis zone. The downward flow of the electrolyte is in the settling zone where the relatively large particles of titanium settle out of the electrolyte stream

while the titanium fines carried in the stream are recirculated back into the bottom of the electrolysis zone.

In Figs. 1 through 3 the electrolysis cell is generally indicated at **10** and comprises a main anode **12** at one end of the cell, and a main cathode **14** at the other end of the cell. Positioned between the main anode and main cathode is a plurality of bipolar elements, generally indicated at **15**. Each of these bipolar elements comprises an anode **16** and a cathode **18**. As illustrated, there are three of these bipolar elements **15**, the electrolysis zones **20** between each of these elements **15** having a relatively short dimension along the path of current travel through the cell.

In a preferred embodiment of the invention each electrolysis zone **20** is preferably on the order of less than one inch in thickness so as to provide for relatively smaller power loss in the cell. This zone is also preferably free of any mechanical restrictions to current flow between the anode and cathode. Each electrolysis zone **20** is in open communication at one end thereof with a settling zone **22** which is of a considerably larger size so as to provide a relatively slow flow of electrolyte downwardly therethrough. For electrically isolating each settling zone **22** from the adjacent settling zone, there is provided a plurality of insulating barriers **24**. For removing the larger titanium particles which settle downwardly in the electrolyte in each settling zone **22**, there is provided a pipe **26** which leads to a filter **28**.

Titanium tetrachloride is introduced into each electrolysis zone **20** between the anode and cathode defining this electrolysis zone by means of a plurality of pipes **30**. In a preferred embodiment each pipe **30** is connected to a common manifold **31** which leads from a titanium tetrachloride vaporizer **32** which, in turn, is supplied from a titanium tetrachloride storage tank **33**. Each pipe **30** is preferably positioned at the bottom of the corresponding cathode **14** or **18** (see Fig. 3) so that titanium tetrachloride bubbles which escape from the pipe **30** travel upwardly in the electrolyte adjacent the surface of each cathode **14** or **18**. Excess titanium tetrachloride and chlorine gas are removed from the cell through a pipe **35** to a condenser which permits recovery of the titanium tetrachloride with recycling of the titanium tetrachloride to supply **33**.

Electrolyte **34** is preferably introduced into cell **10** by means of pipes **36** from a supply **38** of the electrolyte. In a preferred embodiment, the electrolyte **34** is given a transverse velocity as it enters the cell through the pipe **36** so as to aid in achieving the transverse circulation of the electrolyte in the electrolysis zone **20**. Electrolyte is pumped from the filter **28** by means of a pump **40** through a pipe **42** to the supply **38**. In one preferred embodiment of the invention, the level of electrolyte **34** in the reservoir **38** is maintained higher than the level of electrolyte in the cell **10** so that a continuous feed of electrolyte to the cell is achieved by this difference in pressure.

For isolating the various electrolysis zones **20** from each other, there is preferably provided an insulating member **44** positioned below each anode on each bipolar element **15**. This is particularly illustrated in Fig. 3 where these insulating members **44** are shown as comprising refractory materials within which cooling pipes **46** are provided. The purpose of these cooling pipes **46** is to freeze a layer of electrolyte **34***a* on the surface of the insulating members **44** so as to protect the insulating members **44** from attack by the electrolyte. Similar pipes **46** are also preferably provided at the top of each cathode **18** so as to freeze a layer of salt thereon to protect the tops of these cathodes (which are metallic) against attack by chlorine. The cooling medium may comprise a liquid metal such as sodium-potassium or may be a fluid such as water or oil. Cooled insulating members, similar to those illustrated at **44**, are also provided adjacent the ends of the bipolar elements to serve as insulators adjacent these ends.

In a preferred embodiment of the invention, the walls of the cell **10** are of a suitable material such as carbon, metal or the like which are cooled by cooling coils (not shown) so as to freeze a layer **34***a* of electrolyte adjacent the surface of these walls. This layer of electrolyte is shown in Figs. 1 and 3 and serves as an adequate insulation, due to its low conductivity, and prevents shorting of the cell. Equally, these walls can be made of refractories which are protected from molten salt attack by freezing a layer of salt thereon. The anodes **12** and **16** are preferably formed of elemental carbon, such as carbon, graphite, or mixtures of carbon and graphite, while the cathodes **14** and **18** may be formed of metals, such as titanium, molybdenum, and the like. Suitable thermal insulation (not shown) is provided on the cell and related equipment to prevent undue heat losses. The pipes **36** are made sufficiently long so that the voltage drop in the salt carried thereby is larger than the voltage drop between the bipolar electrodes to permit the cell to operate as a bipolar cell. If the filters **28** are electrically connected, the same applies to pipes **26** and **42**. To the extent that the pipes **36, 30, 26** and **42** are formed of metal, they must include suitable insulation or be sufficiently long to prevent their acting as low resistance shunts to the cell.

In the operation of the cell the circulation of the electrolyte (shown best in Fig. 2) is achieved by three cooperating forces. The first of these is the chlorine gas lift resulting from chlorine generated at each anode. The second is the titanium tetrachloride gas lift resulting from the titanium tetrachloride introduced below each cathode. The third is the flow of electrolyte transversely of each electrolysis zone due to the introduction of electrolyte through the pipes **36**. These forces all cooperate to give a counterclockwise rotation of the electrolyte as shown by the arrows in Fig. 2.

The introduction of titanium tetrachloride adjacent the bottom of each cathode in the bipolar cell, described above, has the very definite advantage that the exothermic reaction of the titanium tetrachloride vapors with electrolyte metal generated at each cathode furnishes extra heat to the cell which provides large excesses of heat over that necessary to keep the electrolyte molten. As a result of this large excess of heat, the walls of the cell may be chilled to permit freezing of the electrolyte, thus furnishing protection to the walls of the cell and providing adequate insulation between the various electrolysis zones.

In one preferred embodiment of the invention the cell is operated under the conditions set forth in Example I.

Example I

Electrolyte composition:		
Lithium chloride	weight percent	40
Potassium chloride	do	60
Temperature of electrolyte	° C	475 to 550
Voltage	volts	6
Cathode to anode spacing	inch	¾
Cathode current density	amps./in.^{2}	7.15
$TiCl_4$ fed to cell	grams/hour	5200
Titanium production	do	100

When the cell is operated in accordance with the conditions set forth in Example I, the titanium tetrachloride is preferably introduced in the form of a vapor by suitably controlling the vaporizer **32**, although a titanium tetrachloride mist may be used if cooling at the bottom of the cell is found to be necessary in any particular case. As is apparent from Example I, approximately a twelvefold excess of titanium tetrachloride (over that necessary for supplying the titanium poduced in the cell) is utilized. This serves to prevent migration of any electrolyte metal over to the anode.

In the preferred embodiment of Example I, which includes potassium chloride in the electrolyte, the top portion of the cell is maintained at approximately 525° C. to 550° C. so as to prevent the formation of a crust which might plug up the chlorine escape line **35**. As described more fully in the copending application of Di Pietro Serial No. 279,160, filed on even date herewith, this crust is believed to be due to the formation of a compound between titanium tetrachloride and potassium chloride. This compound is considered to be unstable at temperatures over about 450° C. to 500° C. and elimination of this crust has been successfully accomplished by maintaining a space immediately above the bath at a temperature somewhat above 450° C. to 500° C. A separate heater (not shown) may be employed for maintaining the desired high temperature at the top of the cell. The total heat balance in the system, however, may be such that this additional heating is not essential, since considerable heat is generated within the cell by the exothermic reaction of the alkali metal or alkali earth metal with the titanium tetrachloride.

The titanium tetrachloride flow into the space forming each electrolysis zone **20** is preferably maintained sufficiently high so as to obtain adequate circulation of the electrolyte upwardly within the zone **20**. As explained previously, this circulation is augmented by the gas lift of the chlorine bubbles rising up the surface of the anodes **12** and **16**. The speed of circulation of the electrolyte is naturally a function of the height of the zone **20** as well as the amount of chlorine and/or other gas rising in this zone **20**. In general, it is desired that sufficient circulation be obtained so that all particles of titanium having a size less than about 300 microns be maintained in suspension in the electrolyte, and be carried back into the zone **20**. However, other considerations, such as heat balance and the necessity for carefully controlling the electrolyte concentration, may dictate different circulation velocities. All titanium particles having a size greater than about 300 microns may be allowed to settle into the pipe **26** at the bottom of the cell **10** where they may be periodically removed to the filter **28**. The titanium tetrachloride gas flow into the cell is made sufficient to move the electrolyte upwardly into the zone **20** with a velocity in excess of about 10 cm. per second. With this velocity the conditions for separation of larger titanium particles from the electrolyte stream are excellent. Since the smaller titanium particles are readily carried in suspension in the electrolyte stream they are readily circulated into the zone **20** while the larger titanium particles, due to their higher mass, readily settle out of the electrolyte stream and collect in the pipe **26** at the bottom of the cell.

The electrolyte and titanium particles in the pipe **26** are fed to the filters **28** where gross quantities of the salt are removed from the titanium particles and the salt is returned to the cell. The remainder of the electrolyte salt may then be removed from the titanium by vacuum-distilling or by washing with a low-melting-point salt, such as aluminum trichloride, as described more fully in the above identified Findlay et al. application, Serial No. 252,564. The thus purified titanium powder is then preferably vacuum-distilled to remove the aluminum trichloride, and may be consolidated in accordance with usual techniques, such as by melting in an arc furnace to form an ingot.

In connection with the operation of the cell, it is extremely important that all oxides and nitrides be kept out of the electrolyte and that no air be permitted to contact the electrolyte during the operation of the cell. If there are any impurities in the salts comprising the electrolyte, these salts should be purified by known techniques prior to production of titanium in the cell.

In still other embodiments of the invention the conditions of operation of the cell are preferably the same as described in connection with the discussion of Example I. However, in these cases the electrolyte compositions and temperatures may be as set forth in the following examples.

Example II

Electrolyte ---------- 35 mole percent NaCl, 45 mole percent $MgCl_2$.
Temperature ---------- Above M. P. of 430° C.

Example III

Electrolyte ---------- 67 mole percent KCl, 33 mole percent $MgCl_2$.
Temperature ---------- Above M. P. of 430° C. preferably above 500° C.

Example IV

Electrolyte ---------- 35 mole percent $BaCl_2$, 65 mole percent LiCl.
Temperature ---------- Above M. P. of 510° C.

Example V

Electrolyte ---------- 50 mole percent $SrCl_2$, 50 mole percent NaCl.
Temperature ---------- Above M. P. of 565° C.

Referring now to Figs. 4, 5, and 6, there is shown a modification of the bipolar cell of Figs. 1 through 3 wherein each cathode **18***a* is formed of a hollow metallic member, to the inside **50** of which the titanium tetrachloride is introduced by pipe **30***a*. The hollow space **50** inside of the cathode **18***a* serves as a reduction zone in which the introduced titanium tetrachloride is reduced to titanium particles by the electrolyte metal liberated in the electrolysis zone adjacent that surface of the cathode **18***a* closest to the anode **16**. This surface of the cathode is preferably provided with slotted members **52** which slant upwardly and inwardly to provide openings **53**. The electrolyte metal generated on these slanting members **52** is guided through the openings **53** into the interior of the cathode where it reacts with the titanium tetrachloride vapor bubbling up inside of the cathode. The electrolyte returned to the cell is preferably introduced into space **50** by pipe **36***a* so as to provide lateral flow of the electrolyte within the cathode space **50**. The curved top **54** for the cathode **18***a* serves to carry the vapors in the cathode space laterally to the end of the cathode **18***a*. In other respects, the operation and construction of the cell may be identical to that shown in Figs. 1 through 3.

In connection with the operation of the Figs. 4–6 embodiment of the invention, it should be pointed out that the circulation of the electrolyte may additionally include flow of electrolyte from the electrolysis zone **20** through the openings **53** in the cathode **18***a*. This allows the titanium to be carried back into the reduction zone **50** inside of the cathode.

While preferred embodiments of the invention have been described in considerable detail above, numerous modifications can be achieved without departing from the spirit of the invention. For example, the circulation of the electrolyte may be assisted by the use of an inert gas lift or by pumping the electrolyte out of and into the cell near the bottom thereof. This modification is quite useful when relatively low electrolyte velocities are encountered in the settling zones and the bottom of the cell. Such low velocities may permit too much collection of titanium fines, but this can be prevented by such additional stirring or circulation as mentioned above.

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. A process for producing titanium which comprises the steps of providing a closed electrolytic cell having a

plurality of bipolar electrodes to provide a plurality of cathodes and anodes, pairs of said cathodes and anodes defining electrolysis zones therebetween, providing in said cell an electrolyte bath composed of a molten mixture of halides from the group consisting of the alkali metal and the alkaline earth metal halides, introducing titanium tetrachloride below the surface of the electrolyte into the space between an anode and a cathode in said cell, said titanium tetrachloride being introduced in the form of fine gas bubbles adjacent the bottom of said cathode, electrolyzing said molten mixture by passing an electric current therethrough, circulating said electrolyte upwardly in each electrolysis zone and laterally into a settling zone in communication with said electrolysis zone, and freezing said electrolyte adjacent the edges of each settling zone, thereby electrically isolating said zones.

2. A process for producing titanium which comprises the steps of providing a closed electrolytic cell containing an electrolyte bath composed of a molten mixture of halides from the group consisting of the alkali metal and the alkaline earth metal halides, providing within said cell a plurality of bipolar electrodes which provide a plurality of cathodes and anodes, pairs of said cathodes and anodes defining electrolysis zones therebetween, said zones being separated by frozen electrolyte barriers, introducing titanium tetrachloride below the surface of said electrolyte into the space between an anode and a cathode in said cell, said titanium tetrachloride being introduced in the form of fine gas bubbles adjacent the bottom of said cathode, electrolyzing said electrolyte by passing a current therethrough, circulating said electrolyte upwardly in each electrolysis zone by introducing said gas bubbles into the bottom and laterally into a settling zone in communication with said electrolysis zone by introducing said electrolyte into the side of said cell, and freezing said electrolyte adjacent the edges of each settling zone, thereby electrically isolating said zones.

3. In a process for the production of titanium within an electrolytic cell provided with an electrolyte bath composed of a molten mixture of chlorides from the group consisting of alkali metal and alkaline earth metals, an anode and a cathode forming an electrolysis zone essentially free of any mechanical restrictions to electrical currents passing therebetween, the steps which comprise introducing titanium tetrachloride in the form of fine bubbles below the surface of the electrolyte into the space between the cathode and the anode of said cell adjacent the bottom of said cathode, electrolyzing said electrolyte by passing a current therethrough, circulating said electrolyte upward through the electrolysis zone between said cathode and anode and transversely into the collection zone adjacent the end of said electrolysis zone and then back to said electrolysis zone by introduction of said electrolyte into the electrolysis zone at a point opposite said collecting zone, thereby removing the titanium formed within said electrolysis zone to said collection zone wherein the larger particles of said titanium are separated out for collection and the fine particles of said titanium remain suspended in said electrolyte and are returned to the electrolysis zone.

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