Dec. 16, 1958 H. L. SLATIN 2,864,749

PROCESS FOR THE PRODUCTION OF TITANIUM METAL

Filed May 9, 1951 4 Sheets-Sheet 1

Fig. 1

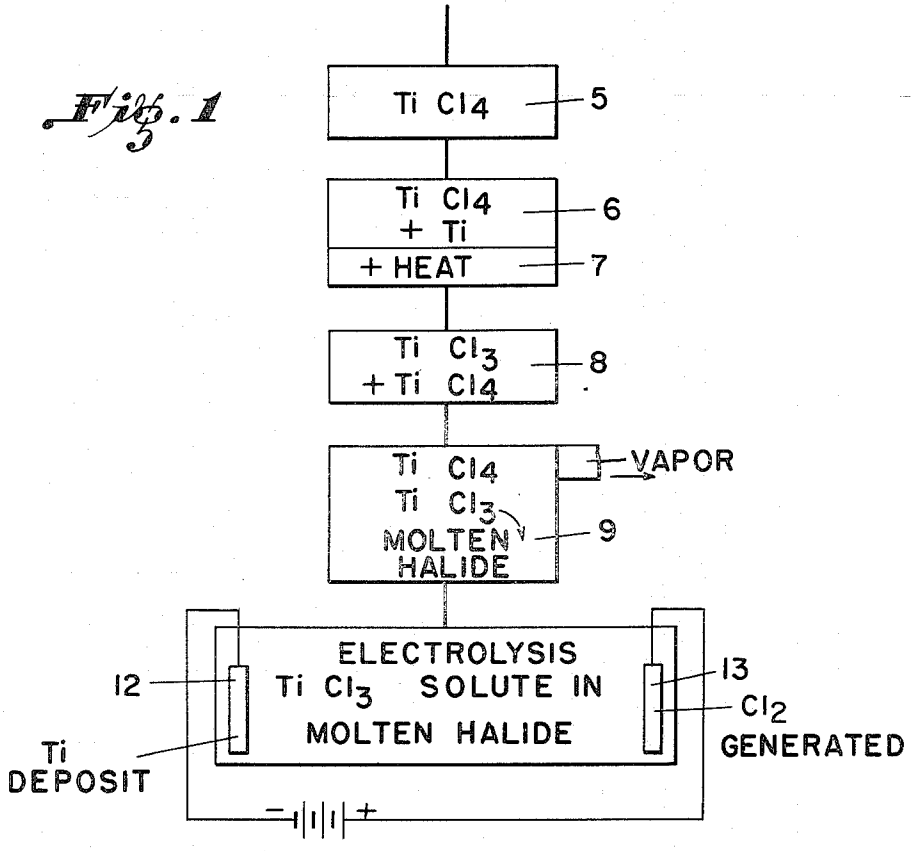
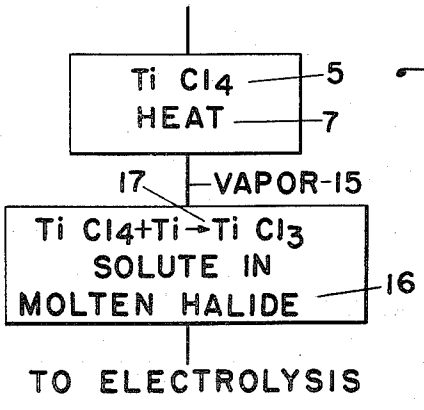


Fig. 2



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PROCESS FOR THE PRODUCTION OF TITANIUM METAL

Filed May 9, 1951 4 Sheets-Sheet 2

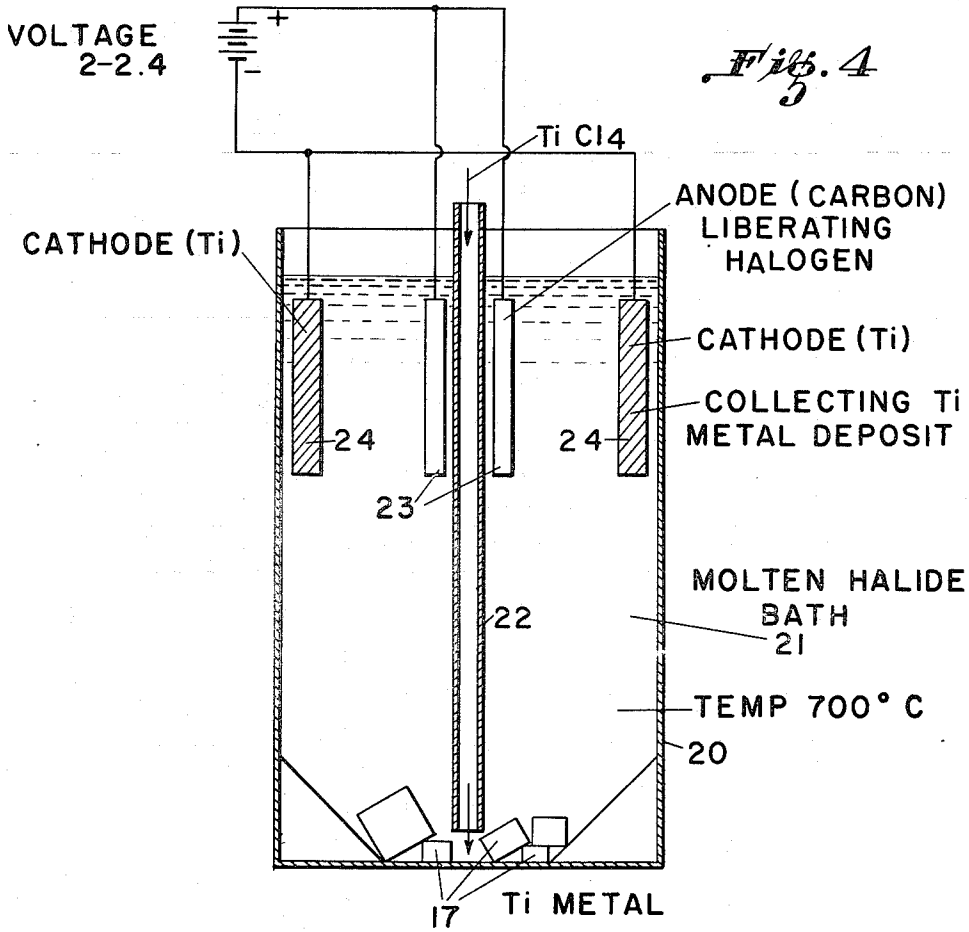

Fig. 4

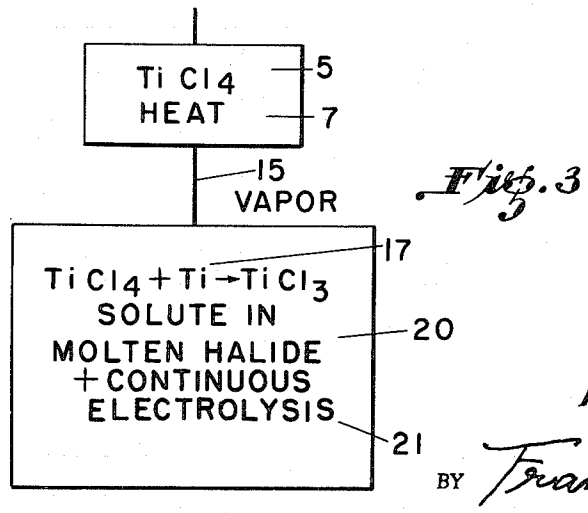

Fig. 3

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PROCESS FOR THE PRODUCTION OF TITANIUM METAL

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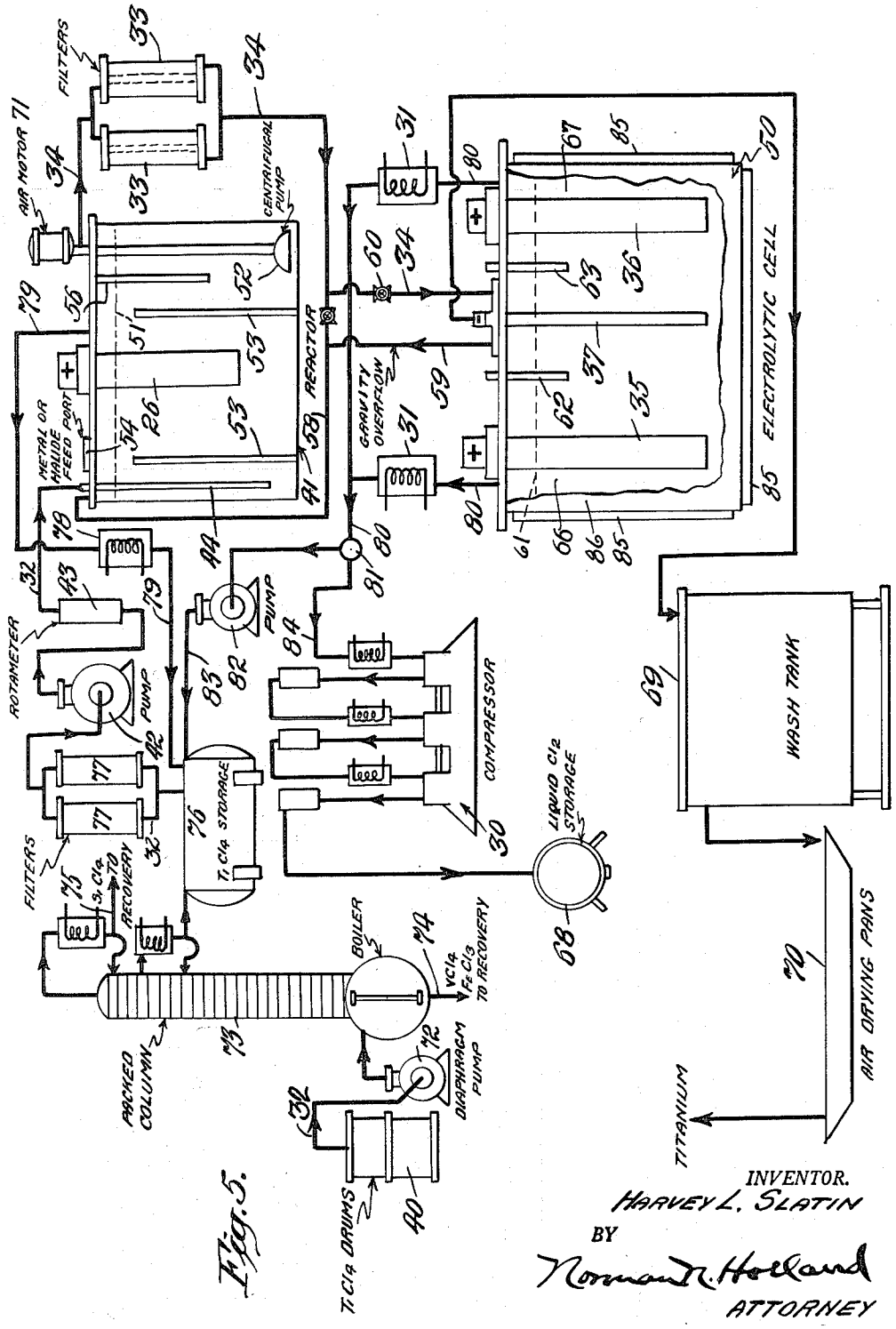

Fig. 5.

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PROCESS FOR THE PRODUCTION OF TITANIUM METAL

Filed May 9, 1951 4 Sheets-Sheet 4

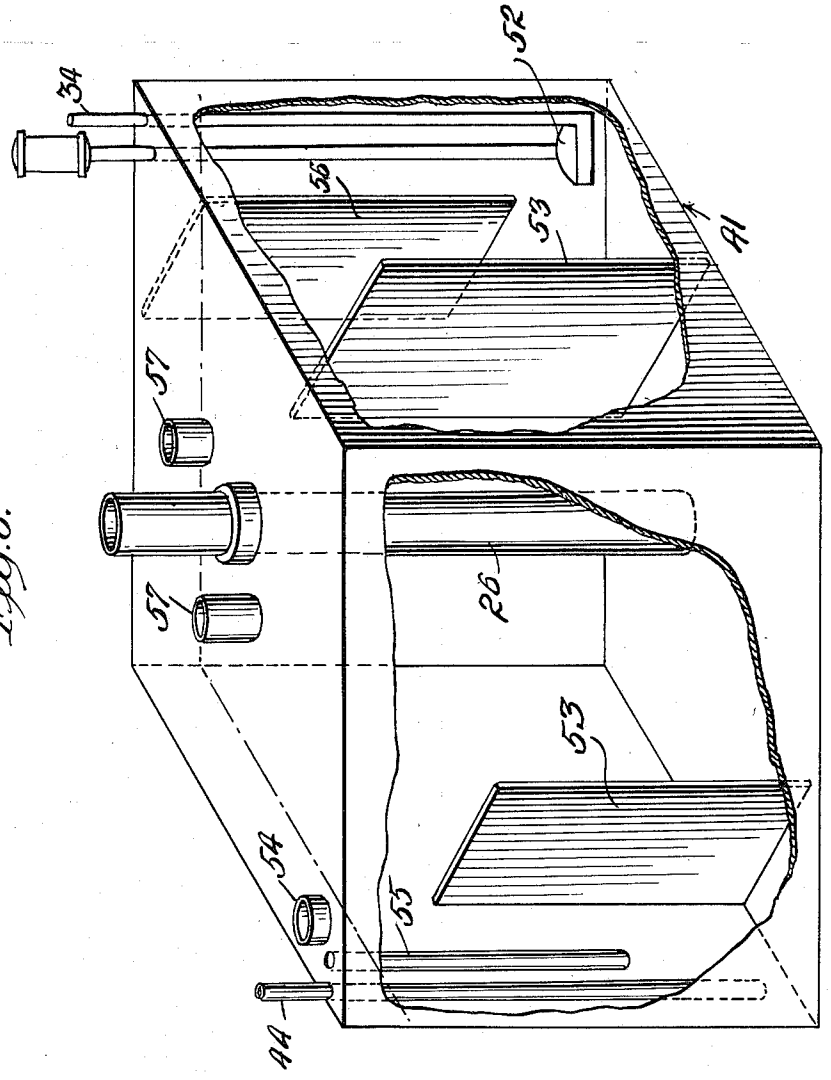

Fig. 6.

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United States Patent Office

2,864,749

Patented Dec. 16, 1958

2,864,749

PROCESS FOR THE PRODUCTION OF TITANIUM METAL

Harvey L. Slatin, New York, N. Y., assignor to Timax Corporation, Wilmington, Del., a corporation of Delaware

Application May 9, 1951, Serial No. 225,375

8 Claims. (Cl. 204—64)

This invention relates to the production of titanium metal and similar metals such as zirconium and hafnium.

The object of the invention is to provide a system for the supply of these metals by electrolysis.

A further object of the invention is to condition the electrolysis to produce the metals in the form of relatively large crystalline aggregates resistant to oxidation.

Further objects of the invention, particularly in the special procedures for developing the metal salt solute of the electrolytic bath in economical and effective manner, will appear from the following specification applying more specifically to titanium and to be taken in connection with the accompanying drawing in which:

Fig. 1 shows a typical flow sheet outlining the main features and steps involved;

Figs. 2 and 3 are similar showings of modified procedures;

Fig. 4 is a diagrammatic sectional view of an electrolytic cell illustrating a typical operation of the process of Fig. 3;

Fig. 5 is a flow sheet of a modified system, and

Fig. 6 is a diagrammatic view of a reactor shown in Fig. 5.

In order to industrially electrodeposit titanium metal, it is important to satisfy these desiderata:

(*a*) The molten solvent must have cations whose decomposition potentials are higher than that of titanium. In addition, the said potentials must be sufficiently higher at normal concentrations used to obviate co-deposition with titanium resulting in alloy deposition or reduction in purity.

(*b*) A titanium compound to serve as an electrolyte must have appropriate properties of stability at the operating temperature, chemically and physically, ionizability with the deposition of metal, availability commercially, conductivity, and freedom of oxides and oxygen compounds.

(*c*) The cell should provide for continuous operation, withdrawal of cathodes, and adequate separation of anolyte and catholyte as well as anode and cathode products and embody materials of construction suitable for long use without impairing production or purity of deposited titanium.

(*d*) The conditions of electrolysis should insure adequate crystal growth with maintained purity, so as to assure the practicability of the process.

(*e*) The preconditioning of the electrolyte and feed should exclude contaminants and provide for the purity of the product in a continuous process.

Electrolyte solvent

The solvent that must be used under criterion (*a*) can consist of alkali and alkaline earth chlorides usually. In the case of aluminum, however, the decomposition potentials of titanium and aluminum are so similar at lower temperatures that separation of the metals by electrolysis is impractical. Sodium, potassium, calcium, magnesium, lithium and barium, for instance, are satisfactory cations in the solvent and at reasonable titanium chloride concentrations will not adversely affect the purity of the titanium deposited. The specific compounds of these alkali and alkaline earth metals that can be used are rigorously restricted to their halides, and for overall convenience and cheapness, to their chlorides. These compounds, as NaCl, LiCl, $MgCl_2$, $CaCl_2$, KCl and $BaCl_2$, may have water of crystallization or water bound in their formation. These compounds also tend to hydrolyze in the presence of water to form their respective oxides, as follows

$$2LiCl+H_2O=Li_2O+2HCl$$
$$MgCl_2+H_2O=MgO+2HCl$$

On fusion these chlorides undergo decomposition, as

$$2LiCl+\tfrac{1}{2}O_2=Li_2O+Cl_2$$

These oxides react with titanium metal and titanium chlorides to form oxides or oxychlorides which do not produce metal of high purity and usually do not electrolyze directly to deposit metal, for instance

$$Ti+Li_2O=TiO+2Li$$
$$TiCl_4+MgO=TiOCL_2+MgCl_2$$
$$TiCl_3+K_2O=TiOCl+2KCl$$

Oxygen and oxygen compounds are impossible impurities to tolerate in the presence of titanium metal. If they are present in the bath, the resultant metal deposited will be contaminated. The oxygen compounds of all metals including titanium itself must be eliminated. The method for removing the water and oxides from the solvent bath may be (*a*) fusion of the salts in a dry HCl atmosphere, (*b*) electrolysis of the salts after fusion to decompose the oxides preferentially, (*c*) precipitation of the oxides chemically and separation mechanically, and (*d*) preparation of the chlorides from oxide free metal.

The fusion of the halide salts in a HCl atmosphere does not insure the complete absence of oxides, but does avoid the accumulation of large percentages of oxides in the bath. In the electrolysis of the oxides, the time required for the complete removal of the oxide by electrolytic decomposition is infinitely long, and even reduction of the oxide to a tolerable limit of a few thousandths of a percent is largely due to the recombination of the anode and cathode products and the co-deposition of chlorine with oxygen. Despite these objections, this method may be used in the process described.

Electrolyte solute

The compounds of titanium that can be used satisfactorily under criterion (*b*) in electrodeposition of titanium metal are limited. The oxides are unsuitable due to limited solubility in common solvents such as chlorides, failure to readily ionize and conduct, and ability to react with titanium metal at reasonable temperatures to form the lower oxides. Oxychlorides are equally bad for the same reasons. The halides are useful and acceptable. They can be separated from their oxides readily and can be maintained after purification. In considering the halides $TiCl_4$ is a liquid with limited solubility in fused salts, does not conduct and ionize well, and is a non-polar compound. Other halides of titanium are expensive to prepare such as the iodides. Although these and the bromides and fluorides can be used, the chlorides are preferred. The trivalent chlorides are preferred over the divalent principally due to the ease of preparation. Both satisfy the conditions of electrolysis. $TiCl_3$ is a polar compound. It forms a stable complex salt with the solvents described and ionizes to produce ions that yield metal on electrolysis. In solution the trichloride is thermally stable at all temperatures tested in electrolysis, 350–1100° C. It does not have an ob-

jectionably high vapor pressure under these conditions and is a good conductor of electricity. Its decomposition potential is of the order of 1.6 volts and lower than that of the solvent salts. It can be prepared by reacting the tetrahalide with H_2, alkali and alkaline earth metals, or other metals as zinc, cadmium and titanium for instance. For convenience in subsequent processing, lithium, magnesium and titanium are preferred; in order to save subsequent purification of the trivalent halide, titanium metal is most preferred, for instance

$$3TiCl_4+Ti=4TiCl_3$$

This reaction has a favorable reaction rate at 500° C., but at 700° C. the rate is better and preferred. It is carried out by bubbling $TiCl_4$ through a bed of titanium metal in a fused salt bath of proper eutectic composition at 500° C. to 700° C. The bath 6 (Fig. 1) is maintained at temperature by auxiliary heat as required. The heat of reaction and the rate of feed are not sufficient to maintain the desired temperature and desired composition unless a number of cells are used.

Electrolyte cell

The cell that is used under criterion (*c*) to carry on the electrolytic process must be constructed of such material that it will not be attacked by hot chlorine gas discharged at the anode nor liquid lithium or magnesium at the cathode, and not add impurities to the cathode deposit in any way. Refractory oxides, silicates, and other ceramic materials must be immediately abandoned as they are attacked by titanium metal and are slightly soluble in the solvent. Nickel has resistance to attack of dry chlorine, but is soluble in liquid lithium or magnesium. Iron can be used with these metals, but is rapidly attacked by hot chlorine. Carbon or graphite is usable, but tends to form objectionable carbides, which on decomposition fill the bath with finely divided carbon, a source of cathode impurity to be avoided. The problem is solved by electrolyzing in a frozen crust of the bath. The cell must also be compartmentalized to prevent the anode product, $TiCl_4$, CO, O_2, or Cl_2, from contaminating the deposited cathode metal and to prevent a contamination of the Cl_2. With improperly prepared graphite anodes, graphite undergoes some disintegration with the separation of fine particles of graphite. Titanium deposits would be contaminated with carbon if these particles came in contact with the titanium metal. The cell can not be completely diaphragmed as there are no available materials that can be used. A metal baffle, protruding above the solution level, and extending partially into the solution is effective in separating the anode and cathode products. The baffle is made of steel as is the cell and is prevented from being a bipolar electrode by a frozen layer, maintained by jackets on the cell cooled with water or other coolant material. Titanium compounds can be di-, tri-, or tetravalent. At the cathode, the trivalent titanium is reduced to metal. At the anode, trivalent chlorides may be oxidized to tetravalent chlorides electrolytically or by secondary oxidation by the chlorine. These anode processes are not rapid at the temperatures used, a surprising observation, but the baffle apparently contributes to prevent excessive loss of the trichloride by restricting diffusion. The diffusion rate is not affected much by temperature and the ion migration is slow due to the size of the ion. The baffle, then, also serves to increase the anode efficiency. The cathode efficiency in a pure bath is 100%, a predictable fact based on the wide difference in discharge potentials, elimination of secondary reactions at the cathode, and non-existence of dischargeable ions below titanium in the bath. The anode efficiency has not been determined with precision but is greater than 90%, i. e., some of the voltage and current used oxidizes trichloride to tetrachloride. As the trichloride is depleted in the vicinity of the anode, the lower diffusion rate is dominant and the anode efficiency is increased.

Conditions of electroylsis

The conditions of operation under criterion (*d*) are largely predetermined. In purifying the bath and its ingredients free of all oxygen and oxygen bearing compounds, the electrolyte contains only the following and nothing else: Solvent salt-LiCl—KCl or $MgCl_2$—NaCl, etc. pure and oxide free, and pure $TiCl_3$ yielding pure titanium metal. The physical nature of this metal is dependent on the conditions of electrolysis.

The purity of the metal is affected by composition only in the lower concentrations $TiCl_3$, where magnesium, for instance may co-deposit. At low concentrations, too, the crystal size of the deposit is reduced due to rapid depletion of titanium electrolyte at the cathode. At higher concentrations, the larger particle sizes are deposited. It is possible to have secondary chemical reaction between the trichloride and titanium at higher concentration with a reduction in a particle size, as follows:

$$T+2TiCl_3=3TiCl_2$$

At concentrations of 5–30% $TiCl_3$ by weight, acceptable particle sizes are attained. The drag-out loss is higher at the higher concentrations, holding the high concentrations desirably to 20–30%. The preferred concentrations are 15–25%, although concentrations of trichloride from a few tenths to 70% have been used successfully.

The temperature of operation is determined by the melting point of the tertiary salts and the eutectic temperature. Operation at 50–100° C. above the melting point is a reasonable minimum temperature. Electrolytic cells have been operated from 375–1100° C. The particle size is not appreciably affected by temperatures in the low ranges, 350–700° C. but above the transformation temperature, where titanium is cubic rather than hexagonal close packed, the particle size is considerably increased. In order to deposit bright dense plates, temperatures of above 880° C. are desirable. However, difficulties in materials of construction, deposition, and side reactions are experienced at the higher temperatures, usually resulting in lower current efficiencies. But, in this case, where a solid frozen crust essentially serves as the cell wall or container and the baffle surfacing, no difficulties are experienced. The conductivity is increased, the decomposition potential is decreased, and the efficiency is not impaired. Hence, for good crystal sized deposits, the higher operating temperatures are preferred. Adequate protection of the cathode product is essential during removal above 650–700° C. It is possible that physical sintering of the metal product occurs simultaneously with deposition; nevertheless, the process of crystal growth is inherently bound by the self-same phenomena and principles. The preferred temperature range for largest crystal growth and adherence is 880–1050° C., although 375–1100° C. range has worked effectively. Excellent continuous operation was attained at 500° C.–650° C.

The cathode current density affects crystal growth in the same way. At lower current densities, the size is larger and remains so at intermediate densities. At higher densities, the particle size is reduced. There exists a wide range where little difference in particle size is determined by current density. If lower densities are used, the number of cells and cell size must be increased to impracticably large sizes and huge numbers. This is not economically feasible nor reasonable. The higher current densities must be avoided as well, although they are compromisable and tolerable. Anode current densities are preferably kept low to restrict side reactions and destruction of the anode. Current densities of from a fraction of an ampere per square inch to 20 amperes per square inch have been used and a pre-

ferred range is of the order of 0.5–5 amperes per square inch.

The cathode metal that is used is important. Metals such as tungsten, molybdenum, nickel, iron and copper, stainless steels, monel, and carbon have been tested but the preferred material is titanium. No impurity can thereby be introduced and the deposited metal can easily follow the base structure of the cathode. This increases crystal size and affords better adherence. Lower temperature operation is possible.

The adherence of the metal deposit is important in reducing recovery losses and affording simplicity and ease of cathode operation. In a clean oxide free bath of this invention with no foreign metallic impurities, at reasonable concentrations, temperatures and current densities, the adherence to a solid cathode is perfect with 100% recovery of deposit.

Preconditioning of electrolyte

The electrolyte is best prepared under criterion (*e*) by fusing a eutectic mixture of 59 mol percent of lithium chloride and 41 mol percent of potassium chloride in a nickel or nickel clad tank **41** (Fig. 5). The salts are heated to 500–650° C. and maintained fluid until all of the excess water has distilled out of the melt. At this point, the bath has deleterious oxides of the alkali metals and some water dissolved in it. A graphite anode **26** is lowered into the bath, the cell sealed to the atmosphere, and electrolysis begun to decompose the oxides electrochemically to oxygen gas which passes out of the vent. Periodic analyses are made on the discharging gases until the concentration of O_2 and CO in the Cl_2 is a minimum, about 0.2%.

System of Figs. 1, 2, 3 and 4

Passing for a moment these specific aspects of the solution and electrolyte, the process to which my invention relates is exemplified in the embodiment illustrated in Fig. 1 where the tetrachloride **5** is not suited for electrolysis and must be reduced to the trichloride or dichloride, for example by heating in contact with titanium metal, designated **6** in the drawing as follows:

$$3TiCl_4+Ti+heat=4TiCl_3$$
$$TiCl_4+Ti+heat=2TiCl_2$$

Some $TiCl_4$ remains with the $TiCl_3$ in the form of vapor and liquid giving a mixture of trichloride and tetrachloride, designated **8**, also containing some dichloride.

Separation of the desired trichloride and dichloride from the tetrachloride is accomplished by carrying over the mixture **8** into contact with the surface of a molten mass, preferably a halide such as sodium chloride, as indicated at **9** in the drawing. On contact the tetrachloride is vaporized and passes off at **10** while the trichloride and dichloride are received and dissolved in the molten mass, this procedure being continuous and accumulating the trichloride and dichloride as a solute in the solution.

This molten solution of titanium trichloride and dichloride is then passed into a cell where it is subjected to electrolysis by potential applied across cathode **12** and anode **13**, the concentration, temperature and current density being regulated to give a desired formation of the titanium deposit on the cathode **12**, with chlorine liberated at the anode. The solution may be reinforced from time to time with additional trichloride and/or dichloride and the electrodes **12**, **13** may be removed and replaced, making the electrolysis continuous in its production of the titanium metal.

The chlorine may, of course, be reclaimed and used, for instance, in the production of the tetrachloride from the ore.

The preferred concentration of the trichloride and dichloride in the molten bath is of the order of 20% to 30% by weight on an equivalent trichloride basis. Concentrations within the range of 12% to 43%, have been electrolyzed. Too high a concentration results in unnecessary loss of trichloride and dichloride of titanium by adherence to the cathode with the titanium. Too low a concentration will lower the efficiency and capacity of the cell. These are the controlling factors so far as concentration is concerned. The temperature range is 400° C. to above 1050° C. with best results at 700° C. to 800° C. for large crystalline aggregates of good bright metal. At low temperatures the tendency is toward titanium deposits in granulated or powdery form.

The cathode current density is from a fraction of an ampere per square inch to about 20 amperes. The most effective range for larger metal particles is 0.1 to 0.5 ampere per square inch. At lower and higher densities the particle size of the deposit decreases, the larger crystals being characteristic of the intermediate current densities. The voltage across the cell terminals is normally 2.0 to 2.4 volts which is above the decomposition potential of the titanium compounds, and may range from 1.5 volts minimum up to 5 volts depending, for instance, on temperature and other factors.

Good results with large crystals and favorable weight distributions with most of the metal in large masses have been obtained at 2.4 volts, 1.5 amperes (equivalent to 0.3 ampere per square inch at the cathode), 28% $TiCl_3$ equivalent and at 850° C. to 710° C. The chloride is desirably separated from the cell rapidly by appropriate baffling.

The cathode material **12** can be any conducting metal which remains solid at the temperature of the bath during electrolysis. Titanium is preferred and copper, nickel, iron, stainless steel, and tungsten have been used. The anode **13** is preferably of graphite or electrocarbon. Carbon and graphite have been used, titanium may be used when desirable to maintain a constant concentration of the solute titanium salt, and at low temperatures and current densities tungsten may be used.

In general the electrolytic process deposits the titanium metal on the cathode by electrolytic reduction of the soluble chloride, and a convenient method for control of the trichloride concentration in the cell is to compare the color of the solution with previously prepared samples.

When the trichloride and dichloride are dissolved in the bath they do not decompose even though the temperature of the bath is above their disproportionation temperatures because as solute they are stabilized. The titanium trichloride or dichloride may be dissolved in the molten halide of any metal more electropositive than titanium. Potassium chloride has been used as have mixtures such as (*a*) lithium and potassium chlorides and (*b*) sodium-lithium-potassium chlorides and (*c*) sodium-potassium chlorides and (*d*) sodium-potassium-barium chlorides, (*e*) sodium-calcium chlorides and (*f*) sodium-potassium-calcium chlorides. Potassium fluoride (10–20%) in a sodium-potassium electrolyte has given a bright deposit of titanium.

The procedures outlined in the flow sheet of Fig. 1 leading to the final electrolytic bath may be simplified and improved by effecting the reduction of the titanium tetrachloride by the titanium metal in a molten halide bath, thus combining steps designated 2, 3 and 4 as diagrammed in Fig. 2. The reduction of the tetrachloride and the solution of the trichloride and dichloride in the molten halide is then attained in a single step. This is accomplished by vaporizing the tetrachloride, as shown at **15** in Fig. 3, and by bringing the tetrachloride vapors into contact with the molten mass of the halide **16** containing titanium metal **17** which acts as a reducing agent. The tetrachloride fed to the body of the molten halide is reduced by the titanium metal and the supply is controlled to avoid excess of tetrachloride and give the desired concentration in the molten halide bath. This may be the concentration desired for electrolysis or further

blending or additions to bring it into condition for electrolysis may be required.

A further simplification of the operations is diagrammed in Fig. 3 which combines the reduction and electrolysis in a single reaction vessel **20** as illustrated in outline (Fig. 4). The titanium tetrachloride (preferably in liquid form) is continuously fed to the bottom of the molten electrolyte 21, where it vaporizes, through flow tube **22** and onto the titanium metal pieces **17** at such rate as to maintain a constant trichloride equivalent concentration in the bath. The container may be of iron, the inner surface being coated with solid salt within which the molten electrolyte is kept fluid by the heat of the electrolysis.

The tetrachloride vapor impinges on the metal maintained at the temperature of electrolysis of about 700° C. as above indicated. The gas aids in stirring the fused salt **21** and in the distribution of the trichloride and dichloride. The D. C. potential across the anode **23** and cathode **24** deposits metallic titanium at the cathode, the voltage being maintained at about 2.4 volts. The cathode **24** may be periodically removed for recovering of the adhered titanium crystals, and replaced for subsequent deposition.

The temperature of reduction of the tetrachloride by the titanium metal may be in the neighborhood of 400° C. to 500° C. and other reducing agents may be used for this reduction step, namely hydrogen, zinc, cadmium, iron, nickel, aluminum, magnesium, or titanium carbide. Instead of the titanium trichloride the dichloride may be substituted in the electrolysis in the molten bath and in the reduction of titanium dichloride, titanium, and hydrogen and some of the other reducers above listed may be employed.

System of Figs. 5 and 6

The flow sheet, Fig. 5, depicts the process with accessory preconditioning and controls. The titanium tetrachloride is stored in drums **40** and fed by pump **72** via pipe **32** to column **73** where the titanium tetrachloride is separated from the higher boiling impurities such as VCl_4 drawn off at **74**. The lower boiling $SiCl_4$ is separated at reflux condenser **75**. If the tetrachloride is not contaminated with sulfur compounds, then the purification of the tetrachloride can be made in the tri-generator **41**, where the $SiCl_4$ is separated from the excess tetrachloride and Cl_2 by distillation, and the metallic impurities are precipitated as metals and retained in the generator. The tri-generator or reactor **41** is shown in detail in Fig. 6. A diaphragm pump or piston pump **42** is preferred to pass the tetrachloride to the reactor. The tetrachloride dip-leg **44** is made of nickel but carbon can be used.

The purified titanium tetrachloride is collected and stored in tank **76**. The titanium tetrachloride is withdrawn from storage tank **76** by pump **42** through pipe **32** and filters **77**, metered by rotameter **43**, and fed through pipe **32** and through dip-leg **44** in reactor **41**. Excess titanium tetrachloride gas returns to the storage tank **76** through pipes **79** and condenser **78**. The reactor **41** contains an anode **26** and baffles **53** and **56** which restrict the flow of the fused electrolyte whose level is indicated at **51**. A metal and halide feed port is shown at **54**. The molten electrolyte is recycled by centrifugal pump **52** driven by air motor **71** via pipes **34** through filters **33** and can be returned to reactor **41** or sent to the electrolytic cell **50** through valve **60** and pipe **34**. The level of the electrolyte in the cell is indicated at **61**. The cell **50** is compartmentalized by baffles **62** and **63** into a central catholyte chamber and two anode chambers **66** and **67** containing anodes **35** and **36**. A cathode **37** is shown immersed in the electrolyte. The titanium metal deposited on cathode **37** is washed in tank **69** and dried in pans **70**.

The walls of the cell **50** are cooled by jackets **85** to form a solid electrolyte crust shown at **86**. The electrolyte overflows by gravity through pipes **59** and **58** to reactor **41**. The anode gases pass through pipes **80** through coolers **31** to separator **81** from which the condensed titanium tetrachloride, if present, may be passed by pump **82** and pipe **83** to storage **76**. The non-condensed chlorine is passed via pipe **84** to compressor **30** and the liquid is stored in tank **68**.

The chlorine compressor system shown generally at 30 is a standard piece of equipment common to the industry. The separation of the tetrachloride vapor from the chlorine gas of the anode chamber is readily achieved by use of a condenser **31**. It is not necessary to freeze the tetrachloride for adequate separation.

All fittings for the tetrachloride lines **32** can be steel, but stainless steel is preferred. The pump packing and rotameter packing should be Teflon. The hot chlorine lines can be stone ware, but nickel or chlorometal alloy is recommended at high temperatures. If the chlorine is dry and oxygen free, carbon or graphite is acceptable. The electrolytic cell is protected by the frozen salt from corrosion. The trigenerator, which is run hot and not protected from the bath or gases, must be made of a resistant material. In this case, cast iron is recommended. It may be carbon lined for added protection.

The filter **33** in the salt line **34** should be sintered nickel.

The anodes **35**, **36** are electro-graphite or carbon normally used in the electrochemical industry. The cathodes **37** are nickel. The electrodes are preferably equipped with internal resistance heaters in order to hold the fluid bath at operating temperature by supplying auxiliary heat to that generated in the electrolysis. The heaters are nichrome wound sheathed heaters. They are limited to an operating temperature of about 1000° C. if properly protected. Other means of heating are possible, as superimposing A. C. across the electrodes, but are not as convenient and attractive.

The electrolytic cell **50** is jacketed and water cooled. The thickness and temperature of the solidified salt crust is regulated by controlling the rate of water feed. The exit hot water is used for washing the salts from the deposited metal on the cathodes.

It is important to have a continuous precise control of the life blood of the system—the electrolyte solution with its titanium chlorides as solute and this control is mainly effected in the operation of the reactor or generator **41** and begins with the initial conditioning of the materials involved.

During this period of purifying the salts, Li metal deposits on the cathode wall, which is the tank **41** itself. The electrolysis is halted, and $TiCl_4$ is pumped into the bath via the nickel dip-leg **44**. The tetrachloride reacts with the Li metal and is reduced to trichloride with the formation of lithium chloride. The residual oxide that remains reacts with the tetrachloride or the trichloride to form insoluble oxide or oxychloride. When all of the lithium has been redissolved, the concentration of trichloride may be increased by adding lithium or titanium metal to the path and adding more $TiCl_4$, or by electrolyzing the titanium out, stripping the bath, making more metal and chewing the metal with tetrachloride. In this first deposition, the impurities tend to concentrate at the cathode 41 and this is a means of purifying the bath. It is preferred, however, to filter the prepared bath into the electrolytic cell **50**. A suitable filter **33** is made by sintering nickel powder on a nickel plate, properly designed, in a hydrogen atmosphere at 1100–1200° C. for 10–20 hours. The nickel powder used is —320 mesh, but is not restricted to this particle size. The filter is welded into a suitable pipe and will separate fine insolubles from the electrolyte. The filtered salts are cast into the electrolytic cell **50**, where a solid crust

is formed on the cool walls. The bath is kept molten and at temperature by the heat of electrolysis and auxiliary A. C. heat supplied to the bath by immersion heaters or electrode-imbedded heaters. Auxiliary heaters are used to hold the temperature during stand-by conditions. In operation, while the electrolysis is in operation, spent electrolyte overflows into the generator tank **41**, and is replenished with enriched trichloride and pumped thru the filter **33** back to the electrolytic cell. This recycling system requires little supervision; all adjustments are predetermined and controlled electronically.

Another way that is used to start up the cell plant, and is preferred as a time and equipment saver that produces the same results, consists of fusing sodium chloride in the generator tank **41** equal to 31.5% of the total salt weight finally needed. The oxide and water content of sodium chloride is much lower than lithium and is quickly reduced to a minimum. Magnesium metal is added to the melted salt equivalent to a Mg—Cl_2 concentration of 38.5%. Tetrachloride is pumped in until the Mg is consumed. The resultant trichloride concentration is 65% by weight. The salts are filtered hot at **33** and frozen in the crust in cell **50**. When the solution is up to level in cell **50**, electrolysis is started in the cell and titanium deposited. The feed rate is curtailed until the concentration is brought down to 20–30% trichloride. This eutectic melts at about 450° C., but the melting point of the 65% trichloride is about 100% C. higher. This insures a solid lining in the cell **50** and is easily accomplished. The concentration of trichloride is conveniently kept above 5% to prevent the codeposition of Mg.

The pump **52** that can be used to transfer salts hot from the trigenerator **41** to the electrolytic cell **50** is similar to those used in magnesium and aluminum metal transfer. The total dynamic head is low and the volume of enriched solute required for continuous operation, agitation, etc. is low and consequently simple submerged centrifugals can be used. The pressure drop across the filter **33** is equivalent to 1 pound or so per sq. in., a slight impedance to flow. However, screw pumps are equally as good. The baffles **53** are used to retain the scrap titanium metal in place, immediately accessible to the tetrachloride. The metal can be aded from time to time thru port **54** provided for in the cover to provide a bed of titanium as illustrated, for instance, at **17** in Fig. 4. If required, the tri-generator **41** can be used to furnish its own reductant, but as a matter of simplicity and saving of materials of construction, the generator does not have to be used as an auxiliary electrolytic cell. The generator can be used to feed a large number of cells; its capacity is great enough to handle that without overworking. The baffles **53** in the generator **41** are arranged to separate the heavy solids and sludge formed by precipitation of the metal impurities and prevent them from entering the pump **52**. The fine oxide and metal that reaches the pump will be removed by the filter **33** on the discharge side of the pump.

The tri-generator and baffles can be made of nickel, or nickel clad. However, cast iron has been recommended and used. If steel were used, carbon lining may be advisable. Cast iron pots are the most inexpensive and practical.

The pump **52** on the salt feed line **34** is powered by an air motor in order to save on over heating by conduction from the cell.

The tri-generator **41** can be gas fired or heated electrically. The outer walls are protected from oxidation and scaling by cement and brick. Electrical heating is more convenient on this scale operation, as it can be thermostatically controlled simply. The tri-generator is started up by filling the reactor about a third full with NaCl. The salt is fused and dehydrated. The cover is not closed, which involves simply the closing of the feed ports and attachment of the vent lines **57**, until the salts are water free. The generator **41** is then closed with the dip leg **44**, thermowells **55**, pump **52**, baffles **53**, **56** (Fig. 6) discharge lines, vents **57**, return salt lines **58**, **59** (Fig. 5) in place. The temperature of the salt at this time is about 800° C. The equivalent magnesium metal is added (actually it is added in portions, requiring 8–10 additions before the total metal has been consumed) to the reactor. Titanium tetrachloride is pumped slowly into the cell thru the dip leg **44**, at a rate consistent with maintaining the temperature at 800–825° C., until the level in the bath has increased by 50%. More Mg and $TiCl_4$ are added, and the temperature allowed to fall gradually to 700° C. by the end of the run, where it is maintained constantly. The metal and tetra feeds are continued until the required metal has been added and decomposed by the tetrachloride. The temperature should be kept within the temperatures above noted, to avoid reduction of the tetrachloride directly to metal. If some of the tetrachloride is reduced to metal, it will be consumed by the tetrachloride later, but the reaction should be controlled to keep this from going excessively in such direction. The solution level will rise as the concentration of trichloride is increased. When the level reaches 6 inches from the top, the pump **52** is started and the electrolyte cell **50** is filled with electrolyte. The electrolyte is richer in trichloride than is desired or required by optimum operating practice. By electrolyzing the salts in the cell **50**, however, the concentration can be brought down and reduced to reasonable concentrations. The tri-generator **41** can be refilled and replenished with fused salts as required.

When the tri-generator **41** is in operating stage, the temperature is maintained thermostatically at 700° C. and tetra feed to the scrap titanium added to the generator as required, at a rate consistent with the depletion of the trichloride in the cell. The rate of feed is balanced with the rate of deposition in time so that eventually the concentration in the electrolytic cell remains quite constant. This may be helped by regulating the control feed valve at the filter **33**. The salt feed lines **34**, **58** are so constructed that salts are recycled in the tri-generator continuously. In the event of pump failure, the lines are self-draining. The line **34** runs from the pump outlet or discharge side thru the filter **33** and back into the salt return line **58**. This line is tapped in the down leg side and valve-regulated at **60** to feed the electrolytic cell **50**. The rate of recycling to the cell is determined by the pump speed and the aperture in the valve **60**. The cell overflows by gravity feed to the return salt line **59** in the tri-generator. The system described provides for constant stirring and replenishment of the salts. The solution is constantly in flow from the reactor section in the tri-generator **41**, over the solution baffle **53**, into the settling section, over the sludge baffle **53** and under the vapor and gas baffle **56** into the pump inlet; thence, thru the filter **33** and return **58** back to the reactor section. Some of the trichloride salts are deflected into the electrolytic cell **50** where they sweep past the cathode **37** by gravity and overflow into the return line **59** to the reactor section. All lines are provided with insulated nichrome winding thermostatically controlled at 650–700° C. Safety devices to prevent filling the cell are installed. The generator itself is properly regulated by safety devices. The pump speed is controlled by a regulating valve on the input side and has wide ranges of flow. This method of preparing the salts and starting up the cells is fast and requires simple equipment and design. The time in starting is one day.

Operation of electrolytic cell 50

The electrolytic cell **50** is baffled at **62**, **63** to separate the cathode and anode compartments. It is vital to keep oxygen out of the chlorine. Small concentrations of oxygen contained in the chlorine render it useless for

tetra production. The anodes 35, 36 are 4" in diameter graphite, 40 inches long and are immersed in the solution for 24–26 inches. They have a central cavity for immersion heaters and thermowells. They are removable and replaceable without disturbing the electrolytic process. Two banks of four anodes 35, 36 are used to reduce the anode current density and limit the oxidation of trichloride. The two sections can be reversed, permitting two cathodes 37, but little advantage is gained by this. The cathode 37 is heated internally as desired and can be split to facilitate handling. The temperature of operation is 500° C.–950° C. The concentration in the bath is controlled to 25% $TiCl_3$ and may vary ±5% without affecting the nature of the electrolysis. The current density for so small a cell is about 1500 amps./sq. ft., for 500 pounds of metal a day. This is a rather high current density; a better rate would be 300 amps./sq. ft.

When the salts from the tri-generator 41 are cast into the cell, the water in the jackets is on. The rapid heating of the water and heat transfer is not excessive and can be controlled by the rate of solution feed to the cell. The electrodes are in place during the casting operation and the temperature of the salts is permitted to fall to the freezing point of the eutectic along the walls. As the solution level rises to the operating level, the rate of flow is cut to approximately the operating rate and adjusted to a final rate later. The heaters and D. C. current are turned on to bring the salts to the desired temperature, and the water flowing through the jackets regulated to maintain a crust of a few inches on the walls and baffles. A safety device controls the bipolarity positively. The main current voltage is 5 to 8 and the flow of salt to the cell is continued, the concentration determined by the color of the salts and rapid chemical analysis. The cathodes 37 are changed from time to time and deposited titanium metal removed by scraping and washed free of adherent salts. The cathode 37 is dried after cleaning and readied for reuse in the cell. The high initial composition of trichloride in the bath permits the operation of a higher crust temperature without fear of rupturing the frozen solid and inducing bipolarity. The crust can fluctuate in thickness without adding impurities to the bath. The initial electrodeposits that are removed will be contaminated with the residual oxide and metallic impurities in the bath. As each new cathode is removed, the metal deposited becomes purer and purer. The cell is then in continuous operating condition and is prepared for final operation.

The rate of deposition is determined by the number of ampere-hours put thru the cell per hour, within limitations. The cathode 37 then must be changed every 2–4 hours, although in a 500 pound a day cell every 8 hours would be satisfactory. In such a unit, the D. C. input is of the order of 200 kva., and the use or need of auxiliary A. C. heaters is questionable. The resistance of such a unit is 0.0011–0.00035 ohm, where the cathode-anode separation is 20 inches and the effective area is 1800–600 sq. inches. The throwing power of the bath is good. A thickness of 2 ins. might be built up on the cathode 37, with an apparent density of 2; the weight of deposit would be 250 pounds.

The anode current carrying capacity is adequately satisfied by the use of 8 4 in. diameter graphite electrodes 35, 36. In the absence of air and oxygen, the anodes will not require replacement.

The anode compartments 66, 67 are vented to a condenser 31 which separates the tetrachloride from the chlorine gas, and is joined to a compressor 30 which liquifies and stores the chlorine at 68. The Cl_2 can be used for making tetrachloride from the ores.

The titanium metal is washed free of salts before subsequent processing as indicated at 69. The adherent deposit is removed by scraping or stripping and flushed with water. All the salts in the deposit are water soluble, and by keeping the temperature of the wash water below 50° C., hydrolysis is prevented and contamination avoided. The salts may be recovered if valuable. The metal can be air dried in shallow pans 70. There is no reason to filter or centrifuge the product; decantation is satisfactory. The metal can be briquetted, or melted, or used as is.

The metal exposed to air at 700° C. or above has a tendency to absorb oxygen and nitrogen. Consequently, the cathodes are not pulled from the bath at temperatures in excess of 650° C.

The titanium tetrachloride stored in drums 40 may be of comercial composition making it desirable to interpose a purification in advance of reactor 41. The $TiCl_4$ from drums 40 is fed to rectifying column 73 by diaphragm pump 72. The reflux ratio in this column is adjusted to give a good separation of silicon tetrachloride at 75. Vanadium tetrachloride and ferric chloride are tapped off the bottom of the column at 74. The titanium tetrachloride so purified is stored at 76 and drawn through filter 77 by pump 42 for positive delivery to the reactor 41. Gases from the top of the anode chamber of the reactor 41 are bled off by pipe 79, condensed at 78 and passed to the titanium tetrachloride storage tank 76. Similarly the gases from the anode chamber of cell 50 are passed through condensers 31 by piping 80 and carried to the separator 81 from which pump 82 draws the condensed $TiCl_4$ and delivers it to the reservoir tank 76 by pipe 83, while the chlorine gas passes by pipe 84 to the compressor 30.

While the specification has been confined to the treatment of titanium salts and the production of titanium metal it equally applies to the similar salts of zirconium and hafnium for the electrolytic production of zirconium and hafnium metals.

The system of this invention thus provides for the production of metallic titanium and also zirconium and hafnium by electrolytic action. The process involves a cumulative purification of the materials reducing contaminants to negligible traces and rendering the metal usable in all fields. Yields of 99.99 titanium, zirconium and hafnium are attained with only the expenditures directly applied to the purification and electrolysis. The apparatus required is capable of efficient embodiment in a group of cells supplied for common reactor and purification units and is adaptable to a wide range of installations.

I claim:

1. A process for the production of a molten salt solution free of oxygen and oxygen compounds and containing a solute formed by at least one of the group consisting of the dichloride and trichloride of titanium comprising fusing an electrolyte solvent of the group consisting of the alkali and alkaline earth halides and combinations thereof, electrolyzing said molten solvent to decompose halides and contaminating dissolved oxides and to deposit metal components therein, continuing said electrolysis until the oxygen content of the evolved gases has been reduced substantially to zero, and then passing titanium tetrachloride through said cleansed electrolyte in contact with said deposited metal, reacting said tetrachloride with said deposited metal and reforming the electrolyte solvent and producing lower valent titanium chloride in the bath, said reaction being conducted below about 825° C.

2. A process for the production of a solution of titanium dichloride and titanium trichloride in a molten salt comprising providing in a bath of molten salt a bed of metal selected from the group consisting of sodium, lithium, magnesium and titanium, said molten salt being selected from the group consisting of the halides of the alkali and alkaline earth metals, feeding titanium tetrachloride to said molten bath so as to contact with said metal therein at about 825° C. and at a rate and in an amount consuming said metal and any titanium formed thereat and converting the tetrachloride to at least

one of the group consisting of titanium dichloride and trichloride within said molten salt bath as a solute therein.

3. A process for the production of a solution of titanium dichloride and titanium trichloride in a molten salt comprising providing a bed of titanium metal in a bath of molten salt selected from the group consisting of the halides of the alkali and alkaline earth metals; feeding titanium tetrachloride to said molten bath so as to contact and react with said titanium metal therein and reduce said tetrachloride and form at least one of the group consisting of titanium dichloride and trichloride therefrom within said molten salt bath and as solutes in said bath, and drawing off from said bath a supply of the resulting molten salt solution of said titanium dichloride and trichloride.

4. The process of preparing and supplying a solution of titanium compounds for electrolytic production of titanium comprising providing a molten electrolyte solvent bath of the group consisting of the alkali and alkaline earth halides and combinations thereof and containing titanium metal, feeding into said solvent bath fluid titanium tetrachloride in contact with said metal, reacting said metal with said tetrachloride to reduce said titanium tetrachloride to a chloride of lower valence and dissolving and dispersing the resulting titanium chloride of lower valence in said solvent bath, and circulating a supply of said solvent electrolyte and lower valent titanium chloride solute free of titanium to a separate electrolytic cell acting to electrolytically deposit titanium from said electrolyte with return of depleted electrolyte from said cell to said bath for replenishment and recirculation to said cell.

5. A process for the continuous electrolytic production of titanium metal, comprising supplying to an electrolytic cell a molten electrolyte consisting of a solvent of the group consisting of the alkali and alkaline earth halides and combinations thereof and a solute formed by at least one of the group consisting of the dichloride and trichloride of titanium and transferring a part of the said electrolyte to a reactor, supplying titanium metal to said reactor and causing said electrolyte to flow over and through a bed of said titanium metal, simultaneously bubbling titanium tetrachloride through said bed of said titanium metal immersed in said electrolyte in said reactor to produce dichloride and trichloride of titanium as solute, transferring said enriched electrolyte to said electrolytic cell, electrolyzing said electrolyte to deposit titanium, and returning the electrolyte depleted in solute to said reactor for enrichment with said solute.

6. A process for the continuous electrolytic production of titanium, comprising supplying to an electrolytic cell a molten electrolyte consisting of a solvent of the group consisting of the alkali and alkaline earth chlorides and combinations thereof and a solute formed by at least one of the group consisting of the dichloride and trichloride of titanium, electrolyzing said electrolyte to deposit titanium, transferring a part of said electrolyte depleted in titanium chloride to a reactor containing a molten solvent of the group consisting of the alkali and alkaline earth chlorides and combinations thereof and containing at least one metal of the group consisting of the alkali and alkaline earth metals and titanium, bubbling titanium tetrachloride through said solvent and electrolyte and in contact with said metal and supplying said tetrachloride to said metal at a rate and in an amount and at a temperature reducing said tetrachloride to at least one chloride of the group consisting of the dichloride and trichloride of titanium, said reaction being below about 825° C., thus enriching said molten solvent with said titanium chloride of reduced valence as solute therein, and supplying to the electrolyte of said cell a portion of said enriched molten solvent to reinforce said electrolyte for electrolytic deposit of titanium therefrom.

7. A process for the continuous electrolytic production of titanium metal within a fused electrolyte of the group consisting of the alkali and alkaline earth metal halides and combinations thereof and a solute formed by at least one of the group consisting of the dichloride and trichloride of titanium comprising providing a supply of titanium metal within said fused electrolyte and passing titanium tetrachloride into said electrolyte so as to contact with and react with said titanium metal at a temperature and at a rate and in an amount thereby reducing said tetrachloride to at least one of the group of the dichloride and trichloride of titanium and enriching said electrolyte with said lower valence chloride of titanium, and electrolyzing said enriched electrolyte to deposit titanium on a cathode immersed therein.

8. A process for the continuous electrolytic production of titanium comprising electrolyzing a fused bath consisting of at least one chloride of the group of alkali and alkaline earth metal chlorides to deposit said metal therein, passing titanium tetrachloride into said fused bath so as to contact and react with the said deposited metal at about 825° C. and at a rate and in an amount reforming the metal chloride and producing an electrolyte solution of at least one chloride of the group consisting of the dichloride and trichloride of titanium as a solute in said fused bath, and electrolyzing said electrolyte solution to produce titanium metal at a cathode immersed therein.

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