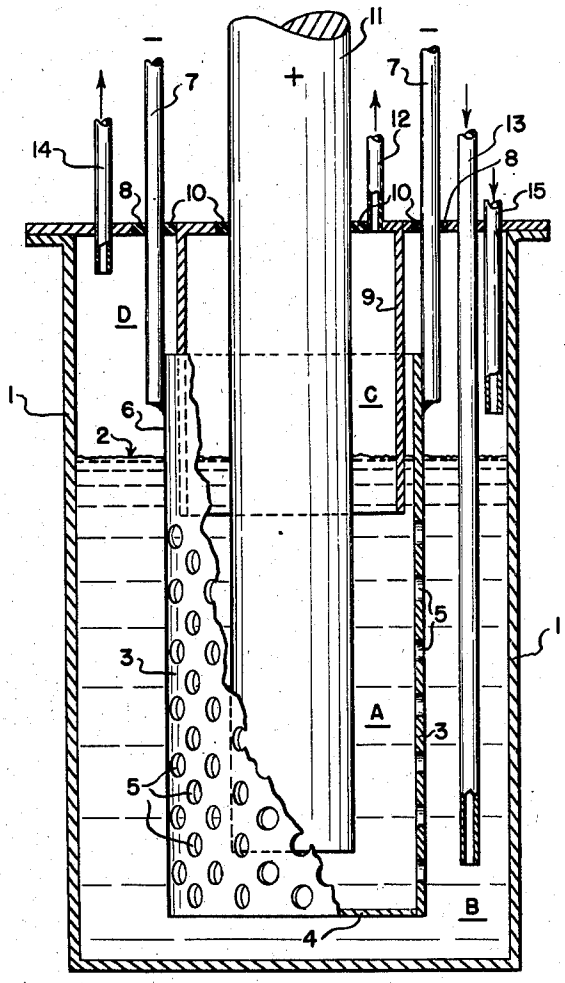
Oct. 13, 1959 C. E. BARNETT 2,908,619

PRODUCTION OF TITANIUM

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PRODUCTION OF TITANIUM

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This invention relates to the production of titanium and, more particularly, to the electrowinning of metallic titanium by fused salt electrolysis.

In the fused salt electrolysis of a titanium chloride in a diluent chloride salt bath, it is a well established fact that these chloride salts should be as free as possible of water and other oxygen-containing compounds in order to obtain a metallic titanium deposit free from oxygen. In spite of this precaution, which in itself accomplishes the desired result, the subsequent leaching of entrained salts from the electrodeposited titanium metal, or handling of the salt-free metal, or both, results in surface oxidation of the metal. Because the surface-to-volume ratio of fine titanium particles is greater than that of the coarser particles, surface oxidation is lessened, and purity of the metal is correspondingly increased, as the coarseness of the deposit is increased. Consequently, it is presently preferred practice to produce a titanium deposit of as coarse crstal size as possible and to discard the fine particles which carry the maximum amount of contaminating oxygen.

An electrolytic operation which is particularly characterized by the production of relatively coarse electrodeposited metallic titanium is one wherein the titanium is deposited on that surface of a cathode which is distal with respect to an anode in direct bath-communication with one another. That is, a fused chloride salt bath containing titanium trichloride and titanium dichloride is electrolyzed between the anode and cathode while titanium tetrachloride is introduced into the bath, the anode and cathode being in direct communication with one another through the bath uninterrupted by any physical barrier other than a pervious deposit of metallic titanium on the cathode. The electrolytic conditions are so maintained between the electrodes, and the bath composition is so maintained adjacent that surface of the initially perforate cathode which is distal with respect to the anode, that metallic titanium is deposited predominantly on this distal surface of the cathode. The successful operation of such a cell depends on the rapid deposition of a layer of titanium metal on the cathode before any significant diffusion of titanium ions into the anolyte can occur. For small cells, the deposition of a layer of titanium metal on the cathode takes place rapidly and this layer formed during the early part of the run with low current and low rate of feed of titanium tetrachloride remains on the cathode all through the operation preventing diffusion of titanium ions into the anolyte. For larger cells, and particularly for deep cells of commercial or near commercial size into which at the beginning of a run titanium tetrachloride is substantially continuously introduced for periods ranging up to several hours in duration, the layer of titanium metal deposited on the cathode during the early part of the run is not readily maintained on the cathode, as evidenced by the fact that lower titanium chlorides diffuse into the anolyte portion of the bath and cause titanium tetrachloride to be evolved with the chlorine at

the anode. This condition represents loss of control of the operation.

In spite of the fact that it has previously been established that re-suspension of sludge in the bottom of the cell by introduction of titanium tetrachloride close to the bottom of the cell is detrimental to cell operation and to cathode deposit quality, I have now found that the introduction of oxygen-containing metallic titanium fines from a previous cathode deposit facilitates the rapid and substantially uniform establishment of the necessary layer of titanium metal on the entire cathode before significant diffusion into the anolyte can occur. Thus, the improvement in the aforementioned operation which characterizes the present invention comprises introducing titanium tetrachloride into the portion of the bath which is in direct contact with the aforesaid distal cathode surface, the titanium tetrachloride being introduced into the lower portion of the bath but above the level of any sludge in the bottom of the bath, and introducing finely-divided oxygen-containing cathodically-deposited metallic titanium into this portion of the fused salt bath in such amount that metallic titanium is formed on the distal surface of the cathode sufficiently rapidly and permanently as to substantially completely prevent the development of titanium tetrachloride in the portion of the bath adjacent the anode.

The metallic titanium which is introduced into the cell bath pursuant to the present invention must be only the finely divided portion of a previous cathode deposit in order to facilitate its assimilation into the bath by reaction with the incoming titanium tetrachloride. This assimilation is particularly efficient when the particle size of the added titanium is not significantly greater than about 74 microns. Its oxygen content ranges between 0.5 and 2% by weight, an oxygen content of this order of magnitude generally being characteristic of the relatively high oxygen-content fines which are separated from cathodically deposited titanium metal in the selection of a high purity component of such a deposit as described, for example, in United States Patent No. 2,821,468.

The amount of finely-divided oxygen-containing metallic titanium added to the cell bath pursuant to the present invention should not exceed about 15% by weight of the total expected amount of the cathode deposit. As little as 1.0% of this added metal has a significant effect in increasing the rate of establishing the desired metallic titanium deposit on the perforate cathode, and a progressive improvement in control is obtained by still greater quantities of the added metal up to the aforementioned amount of about 15%.

The finely-divided oxygen-containing metallic titanium is added, advantageously above the surface of the bath, to that portion of the fused salt bath which is in direct contact with the distal (deposition) surface of the cathode. There, instead of being included in or otherwise contaminating the cathode deposit, the added metal reacts with the incoming titanium tetrachloride to form titanous chlorides. It will be seen, accordingly, that the addition of the fine extraneous metallic titanium, in spite of its oxygen content, permits control of deep molten salt titanium cells and promotes rapid attainment of the optimum conditions for forming and maintaining the metallic titanium deposit on the cathode which prevents diffusion of the lower titanium chlorides from the catholyte portion to the anolyte portion of the bath.

The molten salt baths which are useful in practicing the invention comprise one or more of the halides of the alkali metals and alkaline earth metals. Thus, the chlorides, bromides, iodides and fluorides of sodium, potassium and lithium as well as the same halides of calcium, magnesium, barium and strontium may be used with

advantage. However, in the interest of simplifying the recovery of the halogen which is liberated at the anode during electrolysis, I presently prefer to use only the chlorides of these metals. Although an individual halide may be used as a single constituent bath, I now prefer to use a combination of these halides inasmuch as such combinations are characterized by relatively lower melting points than the individual salts. It is particularly advantageous, when using a combination of the aforementioned halides, to mix these halides in proportions approximating a eutectic composition in order to obtain baths with low melting points. For example, I have used with particularly satisfactory results a eutectic mixture composed of 5 mol percent of sodium chloride, 40 mol percent of potassium chloride and 55 mol percent of lithium chloride, the resulting mixture having a melting point of about 350° C. Other useful eutectic mixtures are represented by the mixture composed of 48.5 mol percent of sodium chloride and 51.5 mol percent of calcium chloride having a melting point of 505° C. and by the mixture composed of 24 mol percent of barium chloride, 35 mol percent of sodium chloride and 41 mol percent of potassium chloride having a melting point of 552° C. Of course, as in all other molten salt electrolytic methods for the production of metallic titanium, the bath should be as completely anhydrous as possible and should be compounded of salts of high purity.

The titanium tetrachloride is advantageously supplied to the bath by introducing it directly into the molten bath either with or without a carrier gas such as argon. The cell atmosphere should, of course, be compartmented to maintain separation between the atmosphere above the portion of the bath into which the titanium tetrachloride is introduced and the portion of the bath from which the chlorine is evolved at the anode. Moreover, the cell is advantageously tightly closed in order to control the cell atmosphere.

The cell electrodes should be constructed of material which will not introduce extraneous elements into the fused bath. Thus, a nonmetallic anode such as graphite or carbon should be used, graphite having been found in practice to be wholly suitable for this purpose. Cathodes of nickel, and preferably of corrosion-resistant nickel base alloys, are useful in practicing the invention. At the prevailing cell temperature, the aforementioned cathode materials have been found not to contaminate the deposited metallic titanium to any significant degree and may be used in solid or foraminous form.

The relative position between, and the arrangement of, the anode and cathode within the molten salt body should be such that (*a*) chlorine evolved at the anode will rise in the body of molten bath without entering the body of molten bath adjacent the distal surface of the cathode, (*b*) the body of molten bath between the anode and the proximal cathode surface and the body of molten bath adjacent the distal surface of the cathode are in communication with one another through a multiplicity of passages, and (*c*) the distance between the anode and the proximal cathode surface, and hence the resistance of the bath between these surfaces, is sufficiently small to permit electrolytically induced depletion of the titanium content of the molten bath between these surfaces.

A number of arrangements of anode and cathode will assure these conditions, and a variety of such arrangements is shown in the drawings in the copending application of Reimert and Fatzinger, Serial No. 441,324, filed July 6, 1954, now Patent No. 2,848,397. However, a presently preferred cell arrangement for practicing the invention is shown in the accompanying drawing in which the single figure is a partial sectional elevation of the cell.

As shown in the drawing, a closed cell **1** is provided with a fused salt bath **2** in which a cylindrical cathode is nearly but not completely immersed. The deposition cathode comprises a cylindrical side wall body portion **3** closed at its lower end with an impervious bottom wall **4** but open at its top end. The side wall portion **3** is composed advantageously of sheet material having a large number of small openings **5** punched in an area of the cylinder which is confined to an upper border below the level of the bath and above the bottom wall **4**. The impervious bottom wall **4** and upper side wall portions **6**, as well as the perforate central portion of the cathode, are constructed of sheet metal composed of a corrosion-resistant nickel-base alloy. This deposition cathode structure is secured to supporting rods **7** which project into the cell through the cell roof and which thus provide an electrical connection from an external source to the cathode structure positioned within the cell. The supporting rods are mounted in insulating material **8** as they pass through the cell cover. The cathode assembly thus encloses an inner body portion A of the fused salt bath **2**.

The anode assembly for the cell comprises a brick-lined metal dome **9** extending downwardly into the interior of the side walls **3** of the cathode assembly, the lower extremities of the dome being immersed in the fused salt bath **2**. The dome is secured to the cover of the cell by insulating portions **10** which also support a graphite anode **11** extending into the cell and downwardly into the interior of the cylindrical cathode assembly. The roof of the cell is provided with a port **12** to permit escape of chlorine gas from the surface of the bath within the dome **9**, and the cell roof is also provided with a titanium tetrachloride inlet line **13** so as to supply the tetrachloride, either with or without an inert carrier gas such as argon, to the lower portion of the main body portion B of the fused salt bath **2**.

In the cell arrangement just described, the chlorine evolved at the anode **11** leaves the surface of the bath within the confines of the dome **9** which thus define a compartment C in the cell atmosphere containing the evolved chlorine. The portion of the cell atmosphere exterior of this chlorine compartment defined by the cell walls comprises a compartment D into or through which titanium tetrachloride is introduced. It will be seen, accordingly, that the titanium tetrachloride is absorbed by the body portion B of the bath and is assimilated only in that portion of the bath which is in contact with the distal surface of the deposition cathode. The body portion A of the bath, on the other hand, is maintained substantially completely depleted of titanium ions by control of the electrolyzing conditions. Any unabsorbed gas is withdrawn from compartment D through an exit line **14** in the cell roof. The metallic titanium fines are introduced into the cell through a charging line **15** which also extends through the cell roof.

The electrolyzing condition which assures the maintenance of titanium-depletion in the body portion A of the molten bath between the anode and the proximal cathode surface comprises the use of a voltage sufficiently high to strip the body portion A of the bath of its titanium chloride content. When the body portion A is effectively stripped of its titanium chloride content, thus leaving essentially only the aforementioned eutectic bath composition composed of lithium, sodium and potassium chlorides, the back electromotive force of the cell, when measured across the anode and cathode upon opening of the exterior cell circuit, has a magnitude of about 2.6 volts or more when operating with a bath temperature of about 550° C. A back electromotive force below about 2.4 volts is an indication of the presence of titanium chloride in the body portion A. As the upper limit of about 3.4 volts is exceeded, and particularly as the back electromotive force reaches about 3.5 volts, decomposition of the non-titaniferous bath components such as the alkali metal chlorides begins to occur. It must be understood that, as appreciated by one skilled in the art of fused salt electrolysis, the maximum back electromotive force will be influenced by the bath composition, by the electrode compositions and by the bath tempera-

ture, but in general it can be stated that under most conditions the presently preferred upper limit for the back electromotive force is about 3.4 volts. The back electromotive force is maintained within the aforementioned range either by control of the cell voltage, so as to maintain appropriate depletion of titanium ions in the body portion A of the bath, or, as described in the copending application of Earl W. Andrews, Serial No. 628,117, filed December 13, 1956, now abandoned, by controlling the rate at which the titanium tetrachloride is delivered to the cell for assimilation by the molten bath. Measurement of the back electromotive force at intervals of 15 minutes is generally sufficiently frequent to permit the maintenance of a substantially uniform back electromotive force to within about one-tenth of a volt.

Control of the cell operation by the practice of this invention is shown by the following example:

An electrolytic cell, similar to that shown diagrammatically in the drawing and having an internal diameter of 42 inches and a depth of 5½ feet, was partially filled with 3000 pounds of a eutectic salt mixture composed of 53.2% potassium chloride, 41.6% lithium chloride and 5.2% sodium chloride and heated by external means to 600° C. After sealing the cell and flushing it with argon, titanium tetrachloride was fed below the melt in the catholyte compartment. At the same time current was applied at a rate of 2 faradays per mol of titanium tetrachloride being fed. The extent to which the amperage (and the feed) could be increased was governed by periodic measurements of the cell back E.M.F. This was maintained at about 2.6 volts. It had been planned to feed enough titanium tetrachloride to attain a concentration of 1.75% Ti in the catholyte but after 6 hours had elapsed and the concentration of Ti was about 1%, the cell back E.M.F. dropped to 2.3 volts and lower chlorides began to diffuse through the cathode-diaphragm into the anolyte compartment. When this occurs the cell is said to be out of control. Titanium tetrachloride boils out of the anolyte compartment and the run must be terminated. Any metal harvested from such a run is worthless, as it was in this instance.

Several days later a similar run was scheduled but in this instance fines were added while titanium tetrachloride was being fed to the catholyte. At the start of the run the applied amperage was 1500 amperes. Current was gradually increased and had risen to 6000 amperes when the Ti concentration had been built up to 1.75%. The extent to which the amperage (and the feed) could be increased was governed by periodic measurements of the cell back E.M.F. This was maintained at about 2.6 volts. In addition to feeding 43 liters of titanium tetrachloride during this period, 20 pounds of fine oxygen-contaminated titanium powder was added to the catholyte compartment in four hourly increments of five pounds each. During this period no titanium tetrachloride issued from the anolyte and the cell operation was completely under control.

I claim:

1. In the electrolysis between an anode and a cathode of a fused halide salt bath containing titanium trichloride and titanium dichloride wherein titanium tetrachloride is substantially continuously introduced into the bath, metallic titanium is deposited on the cathode and chlorine is evolved at the anode, the anode and the cathode being in direct communication with one another through the bath uninterrupted by any physical barrier other than a pervious cathode deposit of metallic titanium on the cathode, the titanium metal being deposited predominantly on that surface of an initially perforate cathode which is distal with respect to the anode, the improvement which comprises rapidly establishing and maintaining the formation of the metallic titanium deposit on the distal surface of the cathode by introducing titanium tetrachloride into the portion of the bath which is in direct contact with the aforesaid distal cathode surface, the titanium tetrachloride being introduced into the lower portion of the bath but above the level of any titanium sludge in the bottom of the bath, and introducing finely-divided oxygen-containing cathodically-deposited metallic titanium having a particle size not significantly greater than 74 microns into the upper portion of the bath adjacent the distal surface of the cathode in such amount that metallic titanium is formed on the distal surface of the cathode sufficiently rapidly and permanently as to substantially completely prevent the development of titanium tetrachloride in the portion of the bath adjacent the anode, the amount of added finely-divided titanium being not greater than about 15% by weight of the total expected cathode deposit and the oxygen content of the added titanium being within the range of 0.5 to 2% by weight.

2. In the electrolysis between an anode and a cathode of a fused halide salt bath containing titanium trichloride and titanium dichloride wherein titanium tetrachloride is substantially continuously introduced into the bath, metallic titanium is deposited on the cathode and chlorine is evolved at the anode, the anode and the cathode being in direct communication with one another through the bath uninterrupted by any physical barrier other than a pervious cathode deposit of metallic titanium on the cathode, the titanium metal being deposited predominantly on that surface of an initially perforate cathode which is distal with respect to the anode, the improvement which comprises rapidly establishing and maintaining the formation of the metallic titanium deposit on the distal surface of the cathode by introducing titanium tetrachloride into the portion of the bath which is in direct contact with the aforesaid distal cathode surface, the titanium tetrachloride being introduced into the lower portion of the bath but above the level of any titanium sludge in the bottom of the bath, and introducing finely-divided oxygen-containing cathodically-deposited metallic titanium into the upper portion of the bath adjacent the distal surface of the cathode in such amount that metallic titanium is formed on the distal surface of the cathode sufficiently rapidly and permanently as to substantially completely prevent the development of titanium tetrachloride in the portion of the bath adjacent the anode, the amount of added finely-divided titanium being not greater than about 15% by weight of the total expected titanium cathode deposit.

3. In the electrolysis between an anode and a cathode of a fused halide salt bath containing titanium trichloride and titanium dichloride wherein titanium tetrachloride is substantially continuously introduced into the bath, metallic titanium is deposited on the cathode and chlorine is evolved at the anode, the anode and the cathode being in direct communication with one another through the bath uninterrupted by any physical barrier other than a pervious cathode deposit of metallic titanium on the cathode, the titanium metal being deposited predominantly on that surface of an initially perforate cathode which is distal with respect to the anode, the improvement which comprises rapidly establishing and maintaining the formation of the metallic titanium deposit on the distal surface of the cathode by introducing titanium tetrachloride into the portion of the bath which is in direct contact with the aforesaid distal cathode surface, the titanium tetrachloride being introduced into the lower portion of the bath but above the level of any titanium sludge in the bottom of the bath, and introducing finely-divided oxygen-containing cathodically-deposited metallic titanium into the upper portion of the bath adjacent the distal surface of the cathode in such amount that metallic titanium is formed on the distal surface of the cathode sufficiently rapidly and permanently as to substantially completely prevent the development of titanium tetrachloride in the portion of the bath adjacent the anode, the amount of added finely-divided titanium being not greater than about 15% by weight of the total expected

cathode deposit and the oxygen content of the added titanium being within the range of 0.5 to 2% by weight.

4. In the electrolysis between an anode and a cathode of a fused halide salt bath containing titanium trichloride and titanium dichloride wherein titanium tetrachloride is substantially continuously introduced into the bath, metallic titanium is deposited on the cathode and chlorine is evolved at the anode, the anode and the cathode being in direct communication with one another through the bath uninterrupted by any physical barrier other than a pervious cathode depost of metallic titanium on the cathode, the titanium metal being deposited predominantly on that surface of an initially perforate cathode which is distal with respect to the anode, the improvement which comprises rapidly establishing and maintaining the formation of the metallic titanium deposit on the distal surface of the cathode by introducing titanium tetrachloride into the portion of the bath which is in direct contact with the aforesaid distal cathode surface, the titanium tetrachloride being introduced into the lower portion of the bath but

above the level of any titanium sludge in the bottom of the bath, and introducing finely-divided oxygen-containing cathodically-deposited metallic titanium into the upper portion of the bath adjacent the distal surface of the cathode in such amount that metallic titanium is formed on the distal surface of the cathode sufficiently rapidly and permanently as to substantially completely prevent the development of titantium tetrachloride in the portion of the bath adjacent the anode, the particle size of the added titanum being not significantly greater than 74 microns and the amount of the added titanium being not greater than about 15% by weight of the expected titanium cathode deposit.

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