

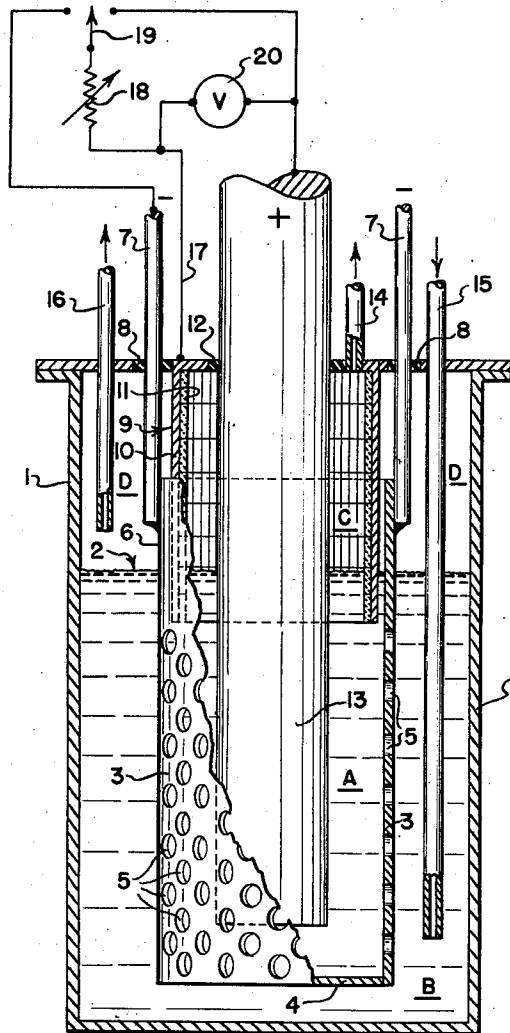
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G. E. SNOW

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PRODUCTION OF TITANIUM

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INVENTOR.

BY George E. Snow

ATTORNEYS

Pennic, Edwards, Morley, Barrow & Taylor

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PRODUCTION OF TITANIUM

George E. Snow, Palmerton, Pa., assignor to The New Jersey Zinc Company, New York, N.Y., a corporation of New Jersey

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This invention relates to the production of titanium and, more particularly, to the electrodeposition of metallic titanium on the surface of a cathode which is distal with respect to an anode, the anode and cathode being in direct bath-communication with one another within a fused salt bath.

In the aforementioned distal cathode deposition operation, a fused chloride salt bath containing titanium trichloride and titanium dichloride is electrolyzed between the anode and cathode while titanium tetrachloride is substantially continuously introduced into and assimilated by the bath, the anode and cathode being in direct communication with one another through the bath uninterrupted by a physical barrier. The electrolytic conditions are so maintained between the electrodes, and the bath composition is so maintained adjacent that surface of the cathode distal with respect to the anode, that metallic titanium is deposited predominantly on this distal surface of the cathode. Concomitant with the deposition of titanium at the cathode, chlorine is liberated at the anode. In order to prevent this chlorine from escaping to the entire cell atmosphere, where it could re-enter the bath and react with the lower chlorides and thus oxidize these chlorides back to the tetrachloride form, a refractory-surfaced wall is provided to define an anode dome within which the chlorine is collected as it is liberated from the anode. The walls of the chlorine dome extend below the surface of the cell bath, and the dome is provided with an outlet line so that the collected chlorine can be recovered outside of the cell.

The chlorine dome is advantageously constructed of corrosion-resistant metal such as nickel lined with a still more corrosion-resistant surface of refractory brick. In the course of operating a cell with such a chlorine dome, it has been repeatedly observed that sometimes the nickel structure has been seriously corroded, particularly at the bath surface level, and that at other times the refractory brick lining has been sufficiently corroded to loosen the bricks. Although these varying types of corrosion of the chlorine dome have occurred while the dome was electrically isolated from both the anode and the cathode, I have found that the type of corrosion of the chlorine dome is related to the attained value of the open circuit back electromotive force measured between the dome and the anode during the operation. That is, I have observed that when this back electromotive force falls below about 2 volts the metallic structure of the chlorine dome is attacked exteriorly of the chlorine atmosphere and that when the back electromotive force rises above about 2.4 volts the refractory lining of the dome adjacent the chlorine atmosphere is attacked. However, I have discovered that if the chlorine dome is made anodic or cathodic, as the operation may require, so that the open circuit back electromotive force between the chlorine dome and the anode is maintained within the range of about 2 to about 2.4 volts, there is no significant corrosion either of the metallic structure or of the refractory lining of the chlorine dome. The chlorine dome back

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electromotive force is maintained within this range, pursuant to my invention, by electrically connecting the chlorine dome to the cathode when the back electromotive force falls below 2 volts and by electrically connecting the chlorine dome to the anode when the back electromotive force rises above 2.4 volts. In each instance, the electrical connection is made to supply a sufficient current to the dome for a sufficient period of time to restore the back electromotive force to and maintain it within the aforesaid range.

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, it is presently preferred to use only the chlorides of these metals. Although an individual halide may be used as a single constituent bath, I 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, and the cell is advantageously tightly closed in order to control the cell atmosphere. 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, and this compartmentation is advantageously provided by a chlorine dome such as that previously described. The chlorine dome should, of course, be formed of a material, such as refractory brick and the like, which is normally resistant to attack by the chlorine and titanium tetrachloride. For practical purposes, however, the refractory is usually mechanically reinforced with a metal grid or other structure enclosed within or backing the refractory structure, and this metallic structure may be used advantageously for making an electrical contact to the chlorine dome pursuant to the present invention.

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 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. 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 pervious 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 chlorine 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 chlorine dome 9 is advantageously constructed of a corrosion-resistant metal such as nickel in the form of a main frame 10 with an inner lining 11 of alumina brick held in place with refractory cement. The dome is secured to the cover of the cell by insulating portions 12 which also support a graphite anode 13 extending into the cell and downwardly into the interior of the cylindrical cathode assembly. The roof of the cell is provided with a port 14 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 15 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 13 leaves the surface of the bath within the confines of the chlorine 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 argon is withdrawn from compartment D through an exit line 16 in 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 proximate 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 an 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. The maximum back electromotive force will, of course, be influenced by the bath composition, by the electrode compositions and by the bath temperature, 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, 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.

The back electromotive force between the chlorine dome 9 and the anode 13 is maintained within the necessary range pursuant to my invention by means of the electrical connections schematically indicated in the drawing. Thus, a line 17 connects the chlorine dome with a variable resistance 18 which in turn is connected to a switch 19. The poles of the switch are connected to the anode and cathode so that the circuit including the variable resistance 18 and the chlorine dome 9 may be connected either to the anode or to the cathode. A voltmeter 20 is connected between the anode and the line 17 so as to measure the open circuit back electromotive force between the chlorine dome and the anode. Thus, when the back electromotive force between the chlorine dome and the anode falls below about 2 volts, the switch 19 is operated to connect the dome to the cathode and the variable resistance 18 is adjusted to supply sufficient current to the dome to restore its back electromotive force to the necessary range; when the back electromotive force between the dome and the anode rises above about 2.4 volts, the switch 19 is operated to connect the dome to the anode, and again the variable resistance 18 is adjusted to supply sufficient current to the dome to restore its proper back electromotive force. Whether the chlorine dome is connected to the anode or to the cathode, or is electrically free of both, the value of the back electromotive force between the dome and the anode is measured at appropriate intervals, generally at intervals of about 15 minutes, to determine whether the prevailing anodic or cathodic bias, or absence of any bias, should be changed or whether the prevailing bias current value should be changed.

The effectiveness of the method of my invention for protecting the chlorine dome will be readily apparent from the following example in which operations with a dome back electromotive force above and below the proper range are compared with an operation embodying the invention. The operations were carried out in an eleven-inch diameter cell, similar to that shown in the drawing, partially filled with a eutectic salt mixture composed of 53.2% KCl, 41.6% LiCl, and 5.2% NaCl and heated by external means to 600° C. After sealing the cell and flushing it with argon, TiCl_4 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 TiCl_4 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. The cylindrical nickel cathode (3) was 5 inches in diameter with $\frac{3}{8}$ inch diameter holes (5), and the graphite anode (13) was 2 inches in diameter. The chlorine dome (9) consisted of a nickel tube 4 inches in diameter and 8 inches long and was lined with vertical strips of alumina refractory $\frac{7}{8}$ inch wide and $\frac{1}{4}$ inch thick held in place with refractory cement. In each run, metallic titanium of high quality was electrodeposited on the outer (distal) surface of the cathode.

The duration of one run was 45 hours and the average cell current was 134 amperes. No attempt was made to control the dome back E.M.F. (i.e. the open circuit voltage between the chlorine dome and the anode), but it was measured at intervals with a voltmeter. During the first 12 hours of the run the dome back E.M.F. was 1.4 volts, but then it rapidly rose to 2.5 volts and gradually increased to 2.9 volts during the remaining 33 hours of the run. At the end of the run the alumina lining was severely cracked at the melt level, and some of the cement had fallen out. Both the cement and the alumina were highly alkaline.

The duration of the next run was 42 hours and the average cell current was 139 amperes. Again, no attempt was made to control the dome back E.M.F. and it stayed within the range of 0.9–1.3 volts throughout the run. At the end of the run the alumina and refractory cement were both in perfect condition, but there were deep grooves corroded into the nickel backing at the melt level. At one point below the melt level, there was a $\frac{3}{16}$ " diameter hole completely corroded through the nickel.

The duration of a third run was 46 hours and the average current was 142 amperes. The dome back E.M.F. was maintained at 2.2 volts throughout the run by using a bias current pursuant to the invention. During most of the run, a cathodic bias current of 1 to 10 amperes was required, but during a $\frac{1}{2}$ -hour period an anodic current of 9 amperes was necessary. At the end of the run the dome lining was in perfect condition, and there was no corrosion of the nickel backing.

I claim:

1. In the electrolysis between an anode and a cathode

of a fused halide salt bath containing a titanium lower chloride wherein titanium tetrachloride is substantially continuously introduced into and assimilated by the bath and metallic titanium is deposited on the cathode, the anode and cathode being in direct communication with one another through the bath uninterrupted by any physical barrier, the titanium metal being deposited predominantly on the surface of the cathode distal with respect to the anode, the chlorine evolved at the anode being collected in and discharged from a confined space defined by a refractory-surfaced metallic conductor-containing wall extending below the surface of the bath and normally electrically isolated from both the anode and cathode, and the titanium tetrachloride being delivered to the portion of the bath in contact with the distal surface of the cathode, the improvement which comprises maintaining the open-circuit back electromotive force between the refractory-surfaced wall and the anode within the range of 2 to 2.4 volts by electrically connecting the wall to the cathode when the back electromotive force falls below said range and by electrically connecting the wall to the anode when the back electromotive force rises above said range, the electrical connection being made in each instance to deliver a sufficient current to the wall for a sufficient period of time to restore the open-circuit back electromotive force to and maintain it within said range.

2. In the electrolysis between an anode and a cathode of a fused halide salt bath containing a titanium lower chloride wherein titanium tetrachloride is substantially continuously introduced into and assimilated by the bath and metallic titanium is deposited on the cathode, the anode and cathode being in direct communication with one another through the bath uninterrupted by any physical barrier, the titanium metal being deposited predominantly on the surface of the cathode distal with respect to the anode, the chlorine evolved at the anode being collected in and discharged from a confined space defined by a refractory-surfaced metal wall extending below the surface of the bath and normally electrically isolated from both the anode and cathode, and the titanium tetrachloride being delivered to the portion of the bath in contact with the distal surface of the cathode, the improvement which comprises maintaining the open-circuit back electromotive force between the refractory-surfaced wall and the anode within the range of 2 to 2.4 volts by electrically connecting the wall to the cathode when the back electromotive force falls below said range and by electrically connecting the wall to the anode when the back electromotive force rises above said range, the electrical connection being made in each instance to deliver a sufficient current to the wall for a sufficient period of time to restore the open-circuit back electromotive force to and maintain it within said range.

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