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ELECTRODEPOSITION OF TITANIUM

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This invention relates to the production of metallic titanium. More particularly, it relates to the production by the electrolytic decomposition of titanium monoxide in a fused salt diluent bath of titanium metal which can be recovered in a form substantially free from embrittling contaminants.

Pure titanium metal possesses many unique properties which are making titanium of increasing commercial importance. The valuable properties of titanium may be impaired, however, if the metal is contaminated with even small amounts of impurities such as oxygen, nitrogen or carbon which embrittle the metal to such an extent as to render it virtually impossible to cold work. Considerable investigation has been directed to the problem of developing a satisfactory process for the production of titanium metal substantially free from these embrittling contaminants. Some of the processes which have been developed have resulted in the production of a satisfactory product but for economic or practical reasons do not appear to be wholly satisfactory from a commercial standpoint.

Among the most promising proposals for the production of titanium metal are electrolytic processes in which titanium monoxide is electrolyzed in fused salt baths. For example, the electrodecomposition of titanium monoxide in a fused salt bath composed of an alkali metal halide has resulted in the production of a metallic titanium deposit on the cathode. The metal produced, however, is in such finely divided form, and the efficiency of the process so low, as to make this process commercially unacceptable. It has also been proposed to electrolyze titanium monoxide in a fused bath consisting of an alkaline earth halide with or without the addition of an alkali metal halide. The titanium metal deposited on the cathode in this process is exceptionally pure if certain conditions of operation are observed. For example, the optimum temperature range within which the electrolysis must be carried out is from about 800° to 850° C. If the electrolysis is carried out much below 800° C. the primary product at the cathode is metallic calcium, and if the temperature of the bath rises much above 850° C. the titanium metal is dispersed throughout the bath, thereby making it necessary to wash the entire bath in order to recover the titanium.

Furthermore, although exceptionally pure titanium metal is deposited on the cathode within the optimum temperature range of the last mentioned process, it is obtained in such finely divided form that great difficulty is encountered in washing the metal particles free from entrained salt without oxidizing the surface of the metal to an undesirable extent. Rather rigorous washing of the finely divided metal product with warm water and dilute acids is required to remove all the entrained salt therefrom. During the washing procedure the extremely small particles of titanium metal become coated with a film of oxide which, because of the high ratio of surface area to weight of these particles, contaminates and embrittles the titanium to such an extent as to render a metal ingot produced therefrom unworkable in the cold. The production of a coarsely crystalline titanium metal by the electrolysis of titanium monoxide would be an important development in this art. The larger particles would be more readily washed free from entrained salt and would have a smaller surface area to weight ratio which, in turn, would tend to reduce the likelihood of excessive oxide contamination.

I have made an important improvement in the process of producing titanium metal by the electrolysis of titanium monoxide whereby such coarsely crystalline titanium can be readily produced. This improvement comprises using as the fused salt diluent bath a mixture composed of at least one alkali metal halide other than an alkali metal fluoride and from 2 to 30% by weight of at least one alkali metal fluotitanate. The titanium monoxide feed and the constituents of the bath preferably should be substantially anhydrous and of high purity. The metallic product of the electrolysis is substantially pure crystalline titanium metal most of which has a particle size greater than that which will pass through a 200 mesh screen (Tyler standard) and among which are single crystals up to 0.5 inch in length. In my improved process the oxide component of the electrolytically decomposed titanium monoxide combines with carbon from a carbonaceous anode with the concomitant evolution of carbon monoxide gas at the anode. The carbonaceous anode, therefore, is one of the reactants in my process. My invention may be practiced within a relatively wide range of operating temperatures and permits the fused salt diluent bath to be used indefinitely without becoming dominated by decomposition products which would eventually necessitate discarding the bath.

The major constituent of the diluent bath of my invention is at least one alkali metal halide other than the fluoride, preferably sodium or potassium chloride, or mixtures of these two salts. It is important that the alkali metal chloride, bromide or iodide, or mixtures thereof which are used in the practice of my invention, be pure and substantially completely anhydrous. Both sodium and potassium chloride are available in commercial quantities in a state of purity sufficient for use in my process.

The alkali metal fluotitanate constituent of the bath may be either sodium fluotitanate (Na_2TiF_6) or potassium fluotitanate (K_2TiF_6), or mixtures thereof, potassium fluotitanate being preferred because of its ease of handling. Although fluotitanates of commercial grade may be used, I have found it advantageous to use a purified form of these salts. Moreover, I have found that the anhydrous form of the fluotitanate leads to further improved results. Fluotitanates of the purity preferred for the practice of my invention may be readily obtained by recrystallizing the salt once from water followed by filtration and washing, and all moisture associated with the salt may be removed by drying under vacuum of about 1 millimeter of mercury or less at a temperature in the range of about 160° to 200° C. The alkali metal fluotitanate may, if desired, be formed in the bath itself by placing in a molten bath of alkali metal halide a suitable amount of potassium or sodium fluoride and by then introducing anhydrous titanium tetrafluoride into the bath, preferably in the vaporized form.

The diluent bath composed of the aforementioned alkali metal halide and alkali metal fluotitanate may be prepared either by mixing the pure anhydrous constituents together prior to fusion, or by introducing the crystalline fluotitanate into an already fused bath of the alkali metal halide, or by forming the fluotitanate in a fused bath of the alkali metal halide in the manner outlined hereinbefore. The bath should contain from about 2 to 30% by weight of the alkali metal fluotitanate, and preferably from about 7 to 20% of the fluotitanate, the balance of the bath consisting of one or more of the aforementioned alkali metal halides. Of course, the over-all composition of the bath changes somewhat upon the introduction of titanium monoxide and after electrolysis has commenced. However, under normal operating conditions the alkali metal fluotitanate and the alkali metal halide constituents of the bath do not appear to be appreciably affected by the electrolysis or to become excessively dominated by the products of decomposition thereof and therefore do not interfere with sustained continuous or incremental additions of the titaniferous source material to the bath.

The primary source of the titanium which is deposited on the cathode during the electrolysis is the titanium monoxide introduced into the aforementioned bath. Carbon monoxide, which is formed at the carbonaceous

anode, is removed from the bath as a gaseous effluent. Consequently, the bath may be used continuously and apparently indefinitely with only the introduction of additional titanium monoxide thereinto to make up for the titanium metal deposited at the cathode.

The titanium monoxide (TiO) used in my process should be anhydrous and free from any higher oxides of titanium. That is, it should have no significant content of such higher oxides as Ti_2O_3, Ti_3O_5 or TiO_2. If the titanium monoxide is contaminated with higher oxides, the electrolytic product at the cathode will be contaminated with an amount of oxygen approximately equivalent to the amount of higher oxide contaminant in the titanium monoxide feed. Titanium monoxide of the required purity may be obtained by the process described in the copending patent applications of Messrs. Wainer, Steinberg and Topinka, S. N. 206,712, filed January 18, 1951, now U. S. Patent 2,681,847; Messrs. Wainer and Sibert, S. N. 202,805, filed December 26, 1950, and Messrs. Sibert and Carlton, S. N. 289,878, filed May 24, 1952, now U. S. Patent 2,681,849, and may be supplied directly to the diluent salt bath without intermediate treatment.

The titanium monoxide is advantageously introduced into the molten bath as a finely divided powder added to the bath continuously or incrementally throughout the operation of the process, although it may be effectively added in the form of relatively coarse granules which dissolve relatively slowly in the bath so that only comparatively infrequent additions of titanium monoxide need be made. The rate at which the titanium monoxide dissolves in an unsaturated bath depends largely upon the available surface area of the monoxide particles, and therefore the rate of dissolution of the monoxide in the bath may be controlled by the use of monoxide particles of predetermined size.

Both of the aforementioned procedures for the addition of titanium monoxide to the diluent salt bath are suitable for maintaining therein an effective amount of the monoxide for electrolysis. All amounts of the monoxide up to its limit of solubility in the bath are effective in the practice of my invention, although higher concentrations within this range lead to higher outputs. However, if the titanium monoxide is added as aforementioned in a manner which leaves some of the monoxide undissolved in the bath, care should be taken that the amount of any finely divided monoxide physically suspended in the bath does not exceed about 3% by weight of the bath for otherwise mechanical occlusion of the monoxide in the cathode deposit is encountered.

The electrodeposition of titanium monoxide may be carried out in the fused salt bath of my invention within a relatively wide range of temperatures, voltages and current densities. The temperature of the diluent bath should be maintained within the range of about 550° and 950° C. and preferably between about 600° and 800° C. In order to reach the lower temperatures of operation, eutectic mixtures of sodium and potassium halides are generally required, the lowest temperature at which any specific diluent bath may be operated depending largely upon the melting point and fluidity of the mixture of fused salts used therein. The maximum temperature at which the bath may be operated depends upon the temperature at which the components of the bath commence to decompose or volatilize and the tendency of carbon monoxide to combine with titanium metal at temperatures upwards of 850° C. to form titanium carbide. The voltage at which the electrolysis is carried out must be sufficient to electrolytically decompose the dissolved titanium monoxide while at the same time the electrolytic decomposition of the alkali metal halide and alkali metal fluotitanate constituents of the diluent bath is minified. Due regard must also be paid to the physical dimensions and internal resistance of the cell. With the type of cell I have employed in my process, and described further hereinafter, I have found that a cell voltage in the range between about 3 and 7 volts is satisfactory to meet these requirements. The current density at the cathode does not appear to be critical within very wide limits. Thus, I have found that the current density may vary between about 10 and 500 amperes per square decimeter. If the above temperature and current density conditions are observed, crystalline titanium metal of high purity is deposited on the cathode with the concomitant evolution of carbon monoxide at the anode without the formation of extraneous products of decomposition which would tend to build up in and to dominate the diluent bath.

As in other processes for the electrolytic production of titanium metal from a fused salt bath, precautions must be taken to avoid contamination of the bath and of the titanium metal deposited on the cathode. Thus, the electrolysis should be carried out in a closed electrolytic cell under an inert atmosphere. The inert atmosphere may be maintained and the gaseous products of decomposition removed therefrom by sweeping the atmosphere in the cell with a purified inert gas such as argon or helium, or the inert atmosphere may be provided by a vacuum, the vacuum being maintained and the gaseous products of decomposition being removed from the cell by active vacuum pumping throughout the process. The metallic titanium deposited on the cathode must similarly be protected from contact with air until it has been cooled well below the bath temperature, advantageously by maintaining it in an inert atmosphere until it has been cooled to approximately room temperature.

I have used a variety of electrolytic cells in carrying out my process. The cell may consist of a simple graphite container or crucible which serves as the anode and a cathode of iron or similar metal disposed centrally within the cell. The upper portion of the iron cathode is advantageously provided with a graphite sleeve which sheathes the cathode at the salt line and in the region above the molten bath to protect it from the corrosive effects of the gaseous products of decomposition of the bath. In such a simple electrolytic cell, carbon monoxide is formed all over the inner surface of the anode including the bottom thereof. A portion of the carbon monoxide thus formed passes over the surface of the metal on the cathode and, if the temperature of the bath is too high, there is some tendency for the hot carbon monoxide to combine with the metallic titanium deposit to form titanium carbide. This tendency may be minimized, however, by maintaining the temperature within the cell below about 800° C. throughout the electrolysis. The efficiency of a simple electrolytic cell such as this is quite high, the current efficiency being about 70 to 90% and the metal recovery efficiency being in excess of 95%.

Any tendency for titanium carbide to form at the cathode and for the deposited titanium metal to become contaminated with suspended titanium monoxide may be overcome through the use of a compartmented cell, that is, a cell divided by an interior partition into anode and cathode compartments. The interior partition may be made of graphite or other suitable material. The partition may be porous to facilitate communication between the anode and cathode compartments, or such communication may be provided in the case of an imperforate partition by submerging the partition in the liquid bath so that there is a space of 1 or 2 inches above or below the partition for the flow of liquid between the compartments. In such compartmented cells a solid anode of graphite is used in the anode compartment and an iron cathode is advantageously used in the cathode compartment. Titanium monoxide feed is introduced into the anode compartment and is confined therein until it dissolves in the fused salt bath. Carbon monoxide, resulting from consumption of the graphite anode, is evolved within the anode compartment. Thus the titanium metal deposits on the cathode in a region free from both undissolved suspended titanium monoxide and evolved carbon monoxide gas. For continuous operation of the cell, the region immediately above the cathode should be provided with an air lock arrangement whereby the cathode with its deposit of titanium metal may be removed and a new cathode inserted into the cell without affecting the inert atmosphere above the cell.

Another advantageous form of compartmented cell comprises a graphite crucible which serves as the anode and which has an inner false wall within the crucible spaced about one-half inch therefrom. The false wall may advantageously be made of thin graphite bored full of minute holes. To avoid having carbon monoxide form on and evolve from the bottom of the crucible within the circular false wall, the bottom may be covered with a sintered block of titanium monoxide. Because the electrical conductivity of titanium monoxide is appreciably less than that of graphite, the majority of the cell current passes into the fused salt bath from the wall of the crucible without affecting the sintered block of titanium monoxide

which covers the bottom thereof. Titanium monoxide feed is introduced into the fused bath in the annular space between the wall of the crucible and the interior false wall. The cathode, which may advantageously be an iron rod, is located in the bath centrally within the false wall and thus in a region free from undissolved suspended titanium monoxide and evolved carbon monoxide gas.

Still another form of cell which I have found to operate satisfactorily has disposed therein a hollow graphite anode of thick wall section made porous by drilling a number of small holes in it. The cathode is located within the cell an appreciable distance from the anode but is not separated therefrom by an interior partition or false wall. Titanium monoxide is fed into the interior of the hollow anode where it is retained until it passes into solution. The carbon monoxide formed during the electrolysis is vented from the cell directly in the area of the anode.

The following examples are illustrative but not limitative of my invention:

Example I

A furnace was provided in which the electrolysis could be carried out in an inert atmosphere. The furnace was equipped with an air lock arrangement to permit access to the interior of the furnace without affecting the inert atmosphere therein. A graphite crucible which served as the anode of the electrolytic cell and also as the bath confining part thereof was placed within the furnace beneath the air lock. The cathode was not placed in the cell at this stage of preparation for electrolysis. The cathode comprised an iron rod encased at its upper end in a graphite tube which, when the bath was in operation, served to shield the iron rod from any gaseous products of decomposition of the bath. An inert atmosphere was established within the furnace by passing through the furnace argon gas substantially free of nitrogen, oxygen and water vapor. The furnace was heated to 800° C. and then 200° parts (as used in this and the succeeding examples, parts refers to parts by weight of the diluent bath) of chemically pure sodium chloride were added to the graphite crucible. The heating was continued until the sodium chloride became molten after which 200 parts of potassium fluotitanate were added thereto. The potassium fluotitanate had been purified by recrystallizing the salt once from water and thereafter vacuum-drying the salt at 180° C.

After the molten diluent bath was prepared 5 parts of titanium monoxide were added thereto. The substantially completely pure and anhydrous titanium monoxide was in the form of minus 325 mesh (Tyler standard) particles. About five minutes thereafter, the iron cathode was inserted into the bath so that the bath completely covered the bare iron rod at the lower end thereof and electrolysis was thereupon initiated.

The electrolysis was carried out at 750° C. and at a current density of 350 amperes per square decimeter. The initial voltage was approximately 4.2 volts. However, as the electrolysis continued, the voltage rose gradually to about 5.1 volts at which it leveled off after about one hour of operation. During the initial stage of operation a noticeable odor of chlorine developed. After the first five or ten minutes, however, the odor of chlorine died down rapidly. Throughout the electrolysis pure titanium monoxide was added to the bath in increments of 5 parts every 3 minutes and carbon monoxide evolved from the bath and was removed from the furnace by sweeping the furnace atmosphere with purified argon gas. After about an hour of operation the electrolysis and the addition of titanium monoxide were stopped and the cathode was raised above the surface of the bath. The molten salt was allowed to drain from the cathode and then the cathode was raised into the chamber of the air lock where it was allowed to cool to room temperature.

Upon the removal of the first cathode a second cathode was inserted into the bath as before. The electrolysis was recommenced and 5 parts of minus 325 mesh titanium monoxide were again added to the bath every 3 minutes. The bath was maintained at 750° C. and the voltage leveled off at approximately 5 volts almost at once. Electrolysis was again continued for about an hour and was then stopped. The second cathode was removed, drained of fused salt and allowed to cool in an inert atmosphere and a fresh cathode was inserted into the bath as before. Thereafter the electrolysis was continued under substantially the same conditions with the fresh third cathode and so forth for a number of successive runs.

After washing and drying the product of the first cathode a yield of 60 parts of pure titanium metal was obtained. About 65% of the metal product was in the form of plus 200 mesh particles and a portion of the plus 200 mesh material was in the form of granules considerably coarser than 10 mesh. The recovery of titanium metal on the first cathode was approximately 50% on a metal basis of the titanium introduced into the bath during the first period of operation and was produced at a current efficiency of about 45%. A yield of 75 parts of titanium metal was obtained after washing and drying the product on the second cathode. This was equivalent to a metal recovery efficiency of over 60% of the titanium introduced into the bath during the second period of operation and represented a current efficiency of over 60%. About 110 parts of titanium metal were recovered from the third cathode, a yield equivalent to a metal recovery efficiency of 85% at a current efficiency of 91%. Substantially all of this metal was coarser than 20 mesh and over half of the product was in the form of single crystals approximately 0.2 inch in length. Metal recovery efficiencies on cathodes used subsequent to the third cathode varied between 80 and 100% at current efficiencies of the order of 70 to 90%. The coarseness of the metal product remained at substantially the same level as that reported for the third cathode and the bath was quiet in operation with consistently uniform results.

Example II

The electrolytic cell and the mode of operation were substantially the same as reported in Example I. The diluent bath consisted of 2000 parts of potassium chloride and 200 parts of potassium fluotitanate. The electrolysis was carried out at 780° C., while voltage and amperage conditions were approximately the same as in Example I.

Pure titanium monoxide having a particle size of minus 325 mesh was added to the bath at the rate of 3 parts every 5 minutes. Fresh cathodes were placed in the bath about every hour. The yield of titanium metal, current efficiency and particle size of titanium metal product were approximately the same as those reported in Example I.

Example III

The electrolytic cell and mode of operation were the same as set forth in Example I. The diluent bath consisted of 1000 parts of sodium chloride, 1000 parts potassium chloride and 200 parts of potassium fluotitanate. The electrolysis was carried out at 650° C. and the cell voltage varied between 3 and 5 volts. In all other respects the conditions of operation were substantially the same as described in Example I. The metal recovery efficiency, current efficiency, and particle size of the titanium metal product were all substantially the same as those obtained at corresponding stages in Example I.

Example IV

The electrolytic cell and the mode of operation were the same as set forth in Example I. The bath consisted of 2000 parts of sodium chloride and 50 parts of potassium fluotitanate. For the first two one-hour periods of operation, during which titanium metal was deposited on the first and second cathodes, titanium monoxide was added at the rate of about 2.5 parts every 3 minutes. Thereafter, for all cathodes subsequent to the first and second, the bath was operated under the same charge conditions as set forth in Example I. In each operating period subsequent to the third period the metal recovery efficiencies were substantially the same as for the corresponding periods in the operation described in Example I.

Example V

A compartmented electrolytic cell was used in place of the simple electrolytic cell of the prior examples. The interior of the cell was divided into anode and cathode compartments by a partition made of graphite which was submerged to a depth of two inches below the bath level. The anode was made of graphite and was centrally disposed within the anode compartment. The cathode was an iron rod encased at its upper end in a protective graphite sheath and was disposed centrally

within the cathode compartment so that the level of the molten bath completely covered the bare iron lower portion of the cathode. The cell was placed within the furnace so that the cathode could be removed therefrom and a new cathode inserted therein through the air lock of the furnace.

The bath composition was the same as that reported in Example I, that is, 200 parts of sodium chloride and 200 parts of potassium fluotitanate. About 300 parts of titanium monoxide, in the form of minus 100 mesh particles, was initially added to the bath in the anode compartment and no further additions of the monoxide were made during the operation of the cell. The bath in the anode compartment was stirred occasionally to facilitate the dissolution of the titanium monoxide therein.

The bath was maintained at approximately the same temperature, i. e., 750° C., as in Example I. The cell voltage ranged between 6 and 7 volts and the current densities were substantially the same as those reported in the previous examples. The metal recovery and current efficiencies were approximately the same as those encountered in the corresponding operation stages of the simple cell of Example I subsequent to the third period.

Example VI

A heavy-walled graphite crucible was used which was concentrically divided by an inner false wall into an annular anode compartment and a central cathode compartment. The bottom of the inside of the crucible was covered by a heavily sintered slab of titanium monoxide about one-quarter inch thick. The inner false wall was spaced about one-half inch from the wall of the crucible and was made of thin graphite pierced approximately every half inch with 1/16 inch holes. The relatively heavy walls of the graphite crucible served as the anode of the cell and an iron cathode was disposed centrally within the central cathode compartment. The cell was placed within the furnace so that the cathode could be removed from and a new cathode introduced into the cell through the air lock of the furnace.

The composition of the bath was the same as reported for Example I. A relatively large quantity of pure titanium monoxide in the form of minus 325 mesh particles was introduced into the annular space between the graphite crucible and the porous graphite false wall and no further additions thereof were made during the operation of the cell. The bath temperature, voltage, and current density conditions and results were substantially the same as those reported in Example I.

Through the use of the fused salt diluent bath of my invention in the electrolytic decomposition of titanium monoxide, I have found that I can obtain an exceptionally pure titanium metal in coarsely crystalline form. Titanium is deposited on the cathode in the form of single crystals which frequently weigh as much as one gram and measure up to one-half inch in length. These crystals of titanium are readily washed free of entrained salt without excessive oxidation thereof so that an ingot of titanium substantially free from embrittling contaminants may be produced therefrom. Furthermore, under normal operating conditions, the fused salt diluent bath is not adversely affected by the electrolysis of the titanium monoxide nor does the bath become contaminated with injurious by-products of the electrolytic decomposition thereof. Moreover, the diluent bath of my invention makes possible the use of a wide range of operating temperatures and current densities which heretofore have been found impossible to attain.

I claim:

1. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, introducing substantially pure titanium monoxide into the said fused electrolyte to form a fused salt cell bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, and recovering the resultant cathodically deposited titanium.

2. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 7% and 20% by weight of at least one alkali metal fluotitanate, introducing substantially pure titanium monoxide into the said fused electrolyte to form a fused salt cell bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, and recovering the resultant cathodically deposited titanium.

3. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, introducing substantially pure titanium monoxide into the said fused electrolye to form a fused salt cell bath, maintaining the bath temperature between 550° C. and 950° C. while passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, and recovering the resultant cathodically deposited titanium.

4. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, progressively introducing substantially pure titanium monoxide into the said fused electrolyte to form a fused salt cell bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, the rate of introduction of the titanium monoxide being substantially equivalent to the rate of electrolytic decomposition of the titanium monoxide and recovering the resultant cathodically deposited titanium.

5. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, introducing substantially pure titanium monoxide into the said fused electrolyte in an amount greater than will dissolve in the said electrolyte and thereby forming a fused salt cell bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, progressively dissolving the undissolved titanium monoxide in said fused bath at a rate substantially equivalent to the rate of electrolytic decomposition of the titanium monoxide, and recovering the resultant cathodically deposited titanium.

6. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, introducing substantially pure titanium monoxide into the said fused electrolyte to form a fused salt cell bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, continuing the introduction of substantially pure titanium monoxide into the fused bath at a rate which maintains the amount of undissolved suspended titanium monoxide in the bath below a concentration of about 3% by weight of the bath and recovering the resultant cathodically deposited titanium.

7. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, progressively introducing substantially pure titanium monoxide into the said fused electrolyte to form a fused salt cell bath, progressively

dissolving said titanium monoxide in said bath at a rate substantially equivalent to the rate of electrolytic decomposition of the titanium monoxide while maintaining any undissolved suspended titanium monoxide in the bath below a concentration of about 3% by weight of the bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, and recovering the resultant cathodically deposited titanium.

8. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, introducing substantially pure titanium monoxide into the said fused electrolyte to form a fused salt cell bath, passing an electrolyzing current through the fused bath between a carbonaceous anode and a cathode in contact with said bath, and recovering the resultant cathodically deposited titanium.

9. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt bath in a compartmented cell which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal halide from the group consisting of alkali metal chlorides, alkali metal bromides and alkali metal iodides and between 2% and 30% by weight of at least one alkali metal fluotitanate, introducing substantially pure titanium monoxide into the

fused electrolyte in the anode compartment of the cell to form a fused salt cell bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, and recovering the resultant cathodically deposited titanium.

10. A process for electrodepositing titanium metal in the form of a coarse crystalline electrodeposit from a fused salt both which comprises: preparing a fused electrolyte consisting essentially of between 98% and 70% by weight of at least one chloride from the group consisting of sodium chloride and mixtures of sodium chloride and potassium chloride and between 2% and 30% by weight of at least one fluotitanate of the group consisting of sodium fluotitanate and potassium fluotitanate, introducing substantially pure titanium monoxide into the said fused electrolyte to form a fused salt cell bath, passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath, and recovering the resultant cathodically deposited titanium.

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