United States Patent Office 2,722,509 Patented Nov. 1, 1955

2,722,509

PRODUCTION OF TITANIUM

Eugene Wainer, Cleveland Heights, Ohio, assignor, by mesne assignments, to Horizons Titanium Corporation, Princeton, N. J., a corporation of New Jersey

No Drawing. Application November 12, 1952, Serial No. 320,113

14 Claims. (Cl. 204—64)

This invention relates to the production of titanium metal and, more particularly, to the electrolytic deposition of metallic titanium from a fused salt bath.

There has been developed heretofore a method of producing metallic titanium by electrolysis of titanium monoxide contained in a fused salt diluent bath. A requisite condition for the successful practice of this method is that the titanium monoxide be chemically pure, that is, it must be completely free of uncombined carbon and of any oxides of titanium higher than the monoxide. It is also a characteristic of the aforementioned method that the oxygen component of the titanium monoxide must have free carbon available for reaction therewith in the diluent bath with a resulting liberation of carbon monoxide at the anode, and this characteristic has necessitated the provision of a consumable carbonaceous anode in cells wherein the monoxide is electrolyzed.

I have now discovered that when a mutual solid solution of titanium carbide and titanium monoxide is used as the titaniferous material which is electrolyzed in a fused salt bath the special requirements of the titanium monoxide-electrolysis method may be eliminated. That is, I have found that when a solid solution of titanium carbide and titanium monoxide is electrolyzed in a fused salt diluent bath, the titanium metal deposited at the cathode is of as high purity as that obtainable by electrolysis of the highest purity titanium monoxide. Moreover, the sole decomposition product of the electrolysis, other than the desired metallic titanium, is carbon monoxide, and thus there is no necessity for a consumable carbonaceous anode to sequester the oxygen of the titanium monoxide component of the mutual solid solution as the latter undergoes electrolytic decomposition.

Accordingly, my present invention comprises an improvement in the electrolytic production of metallic titanium by electrolysis of a titanium compound in a fused salt bath, the improvement residing in the use as this titanium compound of a mutual solid solution of titanium carbide and titanium monoxide in which the molar ratio of the carbide to the monoxide does not exceed 1.

The titanium compound which is electrolyzed in a fused salt diluent bath pursuant to my present invention must be, as pointed out hereinbefore, a mutual solid solution of the titanium carbide and titanium monoxide as distinguished from a mere physical mixture of these components. Inasmuch as titanium carbide and titanium monoxide have the same cubic structure and space grouping and nearly the same lattice size, they are capable of forming a continuous series of solid solutions ranging from pure titanium carbide to pure titanium monoxide. When the individual components are intimately mixed and subsequently heated to an appropriate elevated temperature in an inert atmosphere, even though the temperature is below that at which fusion occurs, the two components form a mutual solid solution which has a single crystal structure and therefore behaves as a single compound (i. e. as TiC·TiO), and it is only this solid solution which has utility in the practice of my present

invention. When the two components are merely mechanically admixed, the resulting mixture, regardless of the degree of intimacy of admixture, behaves during electrolysis in a fused salt bath precisely like the individual components. As a result, a mere physical mixture of these two components simply provides titanium monoxide and titanium carbide which are independently electrolyzed in the bath with resulting formation of free oxygen and free carbon in the bath. Contrasted with the formation of these contaminants for titanium metal by the electrolysis of a mere physical admixture of the monoxide and the carbide, the aforementioned mutual solid solution of the monoxide and the carbide yields only carbon monoxide which is not a troublesome contaminant for the electro-deposited titanium metal.

The aforementioned mutual solid solution of titanium carbide and titanium monoxide may be formed by either a solid state or fusion procedure. For example, a mixture of finely divided pure titanium carbide and finely divided pure titanium monoxide will yield, when heated to a temperature of 2000°–2100° C. for about one hour in a vacuum or other inert atmosphere such as argon or helium, a lusterless mass of fine particles composed of the desired mutual solid solution of the initial components. When a somewhat higher temperature is used so as to effect vitrification of the particles, the resulting mass of the vitrified mutual solid solution has a somewhat brighter appearance. Heating a mixture of the carbide and monoxide by exposure to an electric arc in a similar inert atmosphere will yield a bright silvery fused mass of the desired mutual solid solution. The solid solutions of titanium carbide and titanium monoxide produced by any of the aforementioned procedures function equally effectively in the practice of my invention. Although I presently prefer to use the pure carbide and the pure monoxide as starting materials for making the desired mutual solid solution of these components, the carbide and the monoxide may be somewhat impure without impairing the effectiveness of the solid solution in the practice of my invention. For example, the carbide may contain some titanium oxide and the monoxide may contain some residual carbon or titanium carbide. Moreover, the solid solution may be prepared directly as the product of a reducing operation in which titanium monoxide, titanium sesquioxide or titanium dioxide is heated with carbon under rigidly controlled temperature conditions. Regardless of the source of the components for the final product of such methods, the product will be suitable for use in practicing my present invention if it consists of a mutual solid solution of titanium carbide and titanium monoxide.

The molar proportions of titanium carbide and titanium monoxide in the mutual solid solution of these two components may vary considerably provided the molar ratio of the carbide to the monoxide does not exceed 1. Such a composition can be represented by the formula

$$TiC \cdot nTiO$$

wherein "n" is at least 1. That is, the mutual solid solution should contain a sufficient amount of oxygen in the form of the monoxide component to combine with all of the carbon content of the carbide component with the resulting formation of carbon monoxide. Thus, the titanium monoxide used as the source of this component in the mutual solid solution need not be completely free of higher oxides inasmuch as these higher oxides will be reduced to the monoxide by the carbide when the mixture of these components is heated sufficiently to form the aforementioned mutual solid solution. As a result, the presence of any higher titanium oxides in the titanium monoxide used in preparing the carbide-monoxide solid solution will somewhat lower the carbide content

of the solid solution and the solid solution will therefore have a carbide content never in excess of that corresponding to the carbide and monoxide contents of the starting materials. When the molar proportion of the carbide to the monoxide in the mutual solid solution exceeds 1, there is introduced into the bath during electrolysis of the solid solution a significant amount of free carbon, resulting from decomposition of this excess titanium carbide, and the fine degree of subdivision of this carbon promotes its suspension in the bath and its ultimate occlusion in the titanium metal cathode deposit. A molar excess of titanium monoxide in the mutual solid solution tends to introduce unconsumed titanium monoxide into the bath, but inasmuch as titanium monoxide is decomposed electrolytically in the bath preferentially to the titanium monoxide-titanium carbide mutual solution any free titanium monoxide thus formed will be promptly reduced to titanium metal. However, if a significant molar excess of titanium monoxide is present in the solid solution of the two components, I have found it advisable to have present in the electrolytic cell a consumable carbonaceous anode to facilitate the electrolytic decomposition of such excess titanium monoxide. On the other hand, when a substantially equal molar ratio of titanium carbide to titanium monoxide is established in the mutual solid solution, the solid solution is effectively electrolyzed as a single compound without contaminating or complicating the bath composition and its treatment and without need for a consumable carbonaceous anode.

The fused salt diluent baths in which the mutual solid solution of titanium carbide and titanium monoxide may be electrolyzed may comprise one or more alkali metal or alkaline earth metal simple or complex halides (to wit, the simple and complex chlorides, bromides, iodides and fluorides of sodium, potassium, lithium, calcium, magnesium, strontium and barium). Thus, the bath may be composed of one or more alkali metal halides or alkaline earth metal halides, or mixtures thereof in all proportions, or it may be composed of a mixture of one or more alkali metal halides and a minor or a major proportion (i. e. from 2 to 80% by weight) of one or more alkali metal fluotitanates such as the sodium or potassium double fluorides of titanium known as the corresponding alkali metal "fluotitanates." When it is desired to deposit the titanium metal from such a bath in the form of finely divided metal suitable for pyrophoric purposes or the like, then there should be used as the diluent bath either one or more alkali metal halides or one or more alkaline earth metal halides, or mixtures thereof. However, when it is desired to deposit the metallic titanium in a relatively coarse form so as to facilitate melting down the deposit into ingot form, a formation of such a coarse deposit is enhanced by the presence in the bath of an alkali metal fluotitanate. Inasmuch as it is generally preferred to separate the cathode deposit from entrained bath by washing with water or with dilute acid, the alkali metal fluotitanates are preferably used with the alkali metal halides and not with the alkaline earth metal halides whose fluorides are highly insoluble and therefore difficult to remove by washing. However, the alkaline earth metal fluorides may be used alone or with the alkali metal halides or fluotitanates when the entrained salt in the titanium metal cathode deposit is removed by a procedure other than washing, i. e. by vacuum evaporation or the like.

The fused salt bath used for the electrolysis of a solid solution of titanium carbide and titanium monoxide pursuant to the invention should be completely anhydrous. This result can be obtained by vacuum drying the constituents of the bath at elevated temperatures not exceeding about 350° C. under a vacuum of 1 millimeter of mercury or less. These conditions may be used effectively for dehydrating the bath constituents either individually or when admixed with one another preparatory to melting down into the fused form. It is generally unnecessary to dehydrate the alkali metal halides, but the alkaline earth metal halides must be dehydrated, advantageously at temperatures of about 300°–350° C. under a vacuum of less than 1 millimeter of mercury. The alkali metal fluotitanates can be effectively dehydrated at lower temperatures within the range of 160°–200° C. under a similar vacuum.

Electrolysis of a mutual solid solution of titanium carbide and titanium monoxide pursuant to the invention should be carried out in an inert atmosphere in order to maintain the anhydrous condition of the bath and to prevent its contamination by contact with the ambient atmosphere. For this purpose I have found it advantageous to maintain an atmosphere of pure anhydrous argon in contact with the upper surface of the bath within a closed cell. However, other inert gases such as helium may be used, or, if desired, the inert atmosphere may be insured simply by maintaining a vacuum of 1 millimeter of mercury or less on the bath.

When the temperature of the diluent salt bath is maintained within proper limits during electrolysis of the mutual solid solution of titanium carbide and titanium monoxide, the products of electrolysis will be substantially exclusively titanium metal and carbon monoxide. If the temperature of the bath falls appreciably below the optimum operating range, there is a pronounced tendency for titanium tetrachloride to be formed and liberated from the bath, and if the temperature of the bath exceeds the optimum range a free halogen such as chlorine is formed as a result of decomposition of one or more of the diluent bath constituents. For all of the diluent baths referred to hereinbefore, the optimum operating temperature of bath covers a range of about 100° C. although the lower and upper limits of this optimum range are somewhat different for different diluent baths. For example, the optimum operating temperature of diluent baths composed of one or more alkali metal halides ranges between 500° and 850° C., the more complex mixtures having the lower operating temperatures. The optimum operating temperature of diluent baths composed of one or more alkaline earth metal halides ranges between 700° and 850° C. For diluent baths composed of a mixture of one or more alkali metal halides and one or more alkaline earth metal halides, the optimum operating temperature ranges between 600° and 800° C., and this same optimum temperature range prevails for diluent baths composed of a mixture of one or more alkali metal halides and an alkali metal fluotitanate. In each instance, a bath having a melting point at or below the lower limit of the optimum temperature range for that type of bath may be obtained by complexing, that is, by the use of a mixture of constituents within the class of compounds from which the bath is composed. Regardless of the composition of the diluent salt bath, the optimum operating temperature may be readily ascertained by operating at a temperature at which the bath is molten and at which no significant amount of either titanium tetrachloride or free halogen is liberated into the cell atmosphere above the molten bath. Throughout the entire operating temperature range of 500° to 850° C. for the aforementioned baths, the actual temperature appears to have no significant effect upon the electrolysis provided the temperature is an optimum one for the bath composition being used.

Within the aforesaid optimum operation temperature ranges, each of the various bath compositions referred to hereinbefore functions effectively in the practice of my invention. None of these baths requires any further treatment other than that necessary to insure its anhydrous condition, and each anhydrous bath, once it is brought to a proper operating temperature, permits immediate deposition of metallic titanium when the solid solution of the carbide and monoxide is subjected to electrolyzing conditions in the bath. In the case of diluent baths composed of one or more alkali metal halides or of one or more alkaline earth metal halides, or mixtures thereof, the immediate rate of deposition of metallic titanium is

its optimum ultimate rate. In the case of diluent baths composed of an alkali fluotitanate and one or more alkali metal halides, on the other hand, the initial rate of formation of metallic titanium is lower than its ultimate optimum value, a conditioning period corresponding to about 300 ampere-hours of operation being required to bring the bath up to its maximum yield rate.

The electrical conditions for electrolysis of a mutual solution of titanium carbide and titanium monoxide in the aforesaid diluent salt baths pursuant to my invention are not critical. The cell voltage need only be sufficient to deposit metallic titanium at the cathode and should not be so high as to effect any significant decomposition of the diluent bath constituents. In general, cell voltages within the range of 3 to 7 volts are wholly satisfactory, most operations being effectively carried out within the more limited range of 4 to 5 volts. Current densities are also not critical, current densities varying from 10 to 500 amperes per square decimeter having been used effectively in the practice of the method of my invention. However, current densities in excess of about 500 amperes per square decimeter promote polarization at the anode, although such polarization can be readily counteracted by scraping the anode surface with a graphite rod or by decreasing the current density below 500 amperes per square decimeter, or by a combination of both expedients.

The cell design is also not critical but it should be such as to maintain the evolved carbon monoxide out of contact with the cathode deposit. For this purpose, I have found it advantageous, if the mutual solid solution of titanium carbide and titanium monoxide is not used as the anode per se, to maintain the charge of this solid solution in a restricted zone near the anode so as to permit retention of the evolved carbon monoxide adjacent the anode. It will be apparent, accordingly, that the cell design is largely dependent upon the manner in which the mutual solid solution of titanium carbide and titanium monoxide is supplied for electrolysis. For example, the solid solution of the carbide and monoxide may be sintered at an elevated temperature in an inert atmosphere, such as that described hereinbefore, in the form of a rod or plate which can be used directly as the anode of the cell. When the solid solution is thus used as the anode, the cell should be provided with means for feeding the rod progressively into the fused diluent salt bath at the rate it is consumed. In such a case, I have found it advantageous to maintain a protective sleeve, advantageously of graphite, about that portion of the anode rod exposed to the cell atmosphere above the bath. When one length of rod is nearly consumed, another length may be threaded onto the exposed end of the nearly consumed rod. On the other hand, the mutual solution of the carbide and monoxide may be introduced into the diluent salt bath either in the form of relatively small lumps or of coarse powder, and in this case a conventional cell anode of graphite or the like is used. The solid solution of carbide and monoxide thus introduced into the bath may be contained within a perforated inert vessel within the molten bath, a suitable vessel for this purpose comprising a hollow graphite tube closed at its lower end and provided with a number of small holes which permit the path to make contact with the carbide-monoxide solid solution within the tube. When the anode of the cell comprises a graphite crucible which contains the fused diluent salt bath, the carbide-monoxide solid solution may be introduced into a space defined by the crucible and a perforated graphite diaphragm which prevents the solid solution from coming into physical contact with the cathode. In each of these expedients, an iron cathode may be used advantageously although there may be used other materials, such as molybdenum, stainless steel, and the like, which do not contaminate the metallic titanium deposited thereon.

The following examples are illustrative of the practice of my invention:

Example I

Equimolar amounts of finely divided chemically pure titanium carbide and finely divided chemically pure titanium monoxide were intimately admixed and heated to a temperature of about 2000° C. for a period of about 1 hour in a pure argon atmosphere. The resulting mutual solid solution of equimolar proportions of titanium carbide and titanium monoxide was then compacted in the form of a rod and was heated in an inert atmosphere to an elevated temperature sufficient to effect sintering of the particles. The resulting rod, one-half inch in diameter, was then used as the anode and as the sole source of titanium cathodically deposited from a fused salt bath. The chemical analysis of the rod composition was 77.1% titanium, 12.5% oxygen, 9.5% carbon, and 0.9% miscellaneous impurities.

The fused salt bath in which electrolysis of this anode rod was carried out was prepared by first vacuum drying anhydrous calcium chloride at a temperature of 350° C. and by subsequently raising the temperature of the anhydrous salt to 850° C. in a closed graphite crucible placed within a furnace. The rod of titanium carbide-titanium monoxide solid solution was then inserted into the bath as the anode of the cell, and the cathode comprised an iron rod similarly inserted in the bath. The temperature of the bath was then lowered to about 800° C. and was maintained at this temperature while electrolyzing with a cell voltage of 3.5 volts and a total cell current of 100 amperes. The lower 3-inch portion of the anode rod was exposed to the bath, the upper portion being protected by a surrounding graphite tube. At 1-hour intervals the cathode was removed from the bath into the chamber above the bath but within the cell atmosphere and another cathode was moved into place in the bath. The hourly rate of deposition of titanium metal corresponded to a current efficiency of 72% and a metal recovery efficiency of 87% based upon the amount of the anode composition consumed during cell operation. The deposits formed on the cathodes, after being cooled to ambient temperature without exposure to air, were removed from the cathodes, were washed by soaking in cold water and were subsequently washed on a filter first with cold water and then with a 3% formic acid solution. After further washing of the acid from the metallic deposit, followed by filtering and vacuum drying, a fine black metallic powder was obtained. The operation of the cell was made continuous for a number of periods by continuously feeding the titanium carbide-titanium monoxide solid solution anode into the bath as rapidly as it was consumed and by the successive use of a plurality of cathodes. The only loss of the diluent bath comprised that which was mechanically entrained in the cathode deposit removed from the cell.

Example II

The operation described in Example I was repeated with only two departures from that operation, to wit, the use as the diluent salt bath of a mixture of equal parts by weight of calcium chloride and sodium chloride and the maintenance of a bath temperature of 725° C. throughout the electrolysis. The washed metallic titanium deposit obtained in this operation was somewhat coarser than that obtained in the operation described in Example I.

Example III

The operation described in Example I was repeated with the single deviation of using anhydrous sodium chloride as the sole component of diluent salt bath.

Example IV

The operation described in Example I was repeated in a different type of cell. In this case, the anode comprised the graphite crucible and the cathode was the same

as that used in Example I, to wit, an iron rod of which all but the lower 3 inches within the bath was enclosed in a graphite sleeve. The cell was provided with a cylindrical diaphragm extending to about ½ inch above the bottom of the crucible and having a multiplicity of 1/16 inch diameter holes below the top of the bath level. In this operation, the titanium carbide-titanium monoxide solid solution was supplied in the form of ⅛ inch diameter particles fed into the annular space between the diaphragm and the side walls of the crucible. Each cathode was used for 90 minutes of operation, and in each of a series of such periods the cathode deposit on each electrode weighed about 100 grams. The cell current was 100 amperes, as in the operation described in Example I, but the cell voltage was slightly higher, i. e. between 4 and 5 volts.

Example V

The operation described in Example I was repeated with the same cell, the same anode material and the same electrical conditions as described in that example. The deviation from the conditions recited in Example I comprised the use, as the diluent salt bath, of a vacuum dried mixture of 5 parts of sodium chloride to 1 part by weight of potassium titanium fluoride (K_2TiF_6). Electrolysis was carried out at a bath temperature of 750° C. In the first hour of operation the cathode deposit totaled 35 parts by weight of metallic titanium which, when washed, had a particle size within the range of 60 to 100 mesh (Tyler Standard Screen). The cathode deposit for the second hour of operation amounted to 55 parts by weight and had a particle size within the range of 20 to 60 mesh, and the cathode deposit in the third hour of operation increased to 70 parts by weight most of which was coarser than 60 mesh and a substantial portion of which was in the form of crystals ranging between 0.2 and 0.5 inch in cross-section. In the fourth and successive hourly periods of operation, the cathode deposit weighed approximately the same and had approximately the same particle size as that obtained in the third hourly period.

Example VI

A mutual solid solution of titanium carbide and titanium monoxide was electrolyzed in a cell comprising a graphite crucible which served as the anode. The cell was provided with a centrally positioned iron cathode all but the lower 3 inches of which within the fused salt bath was covered with a graphite protection tube. The fused salt bath consisted of an anhydrous mixture of 20 parts of sodium chloride to 1 part by weight of potassium titanium fluoride. Electrolysis was carried out in this cell with a cell voltage ranging between 4 and 5 volts so as to maintain a cell current of about 100 amperes, and the bath temperature was maintained at 750° C. The aforementioned solid solution of titanium monoxide and titanium carbide, having a chemical analysis of 76.1% titanium, 16.9% oxygen, 6.2% carbon, and 0.8% incidental impurities, ground to minus 325 mesh, was added in small amounts once every 5 minutes. During the first hour of operation, the washed and dried cathode deposit of metallic titanium amounted to about 40 parts by weight whereas the product of the second hour of operation increased to 50 parts and that for the third hourly period and all successive periods ranged between 70 and 80 parts by weight. The metallic titanium obtained during the third and subsequent hourly periods represented a metal recovery efficiency of 92% (based upon the amount of titanium consumed in the form of the aforementioned titanium carbide-monoxide solid solution) and had a degree of coarseness considerably greater than the product obtained during the first hourly period.

It will be seen, accordingly, that my novel method of electrolytically producing metallic titanium is characterized by its amenability to continuous operation without degeneration or contamination of the diluent salt bath composition. Titanium metal is produced by this method with current efficiencies of at least 75%, with titanium metal recoveries upwards of 75%, and in a substantially pure form containing a maximum of 0.3% of impurities. And because of the unusual physical characteristics of the mutual solid solutions of titanium carbide and titanium monoxide used in the practice of the method of my invention, including its susceptibility to sintering or fusing to massive forms and its high electrical conductivity (greater than that of graphite), there is now available for the first time an electrolytic method for the production of metallic titanium in which the titaniferous source material can be supplied solely in the form of a consumable anode.

I claim:

1. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; maintaining the bath in a fused state at a temperature between 500° C. and 850° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; introducing into the fused electrolyte a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

2. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; maintaining the bath in a fused state at a temperature between 500° C. and 850° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; introducing into the fused electrolyte a mutual solid solution of equimolar proportions of TiC and TiO; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

3. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; maintaining the bath in a fused state at a temperature between 500° C. and 850° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; introducing into the fused electrolyte a consumable anode comprising a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; passing an electrolyzing current through the fused bath between said anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

4. The method of producing metallic titanium in an electrolytic cell which comprises preparing an anhydrous fused electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; maintaining the bath in a fused state at a temperature between 500° C. and 850° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; introducing into the fused electrolyte a consumable anode comprising a mutual solid solution of equimolar proportions of TiC and TiO; passing an electrolyzing current through the fused bath between said

anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

5. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one chloride salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; introducing into the fused electrolyte a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; maintaining the bath in a fused state at a temperature above that at which titanium tetrachloride is produced and below that at which a free halogen is evolved under an atmosphere which is inert to the bath components, the cell components and the electrolysis products while passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

6. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one chloride salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; introducing into the fused electrolyte a mutual solid solution of equimolar proportions of TiC and TiO; maintaining the bath in a fused state at a temperature above that at which titanium tetrachloride is produced and below that at which a free halogen is evolved under an atmosphere which is inert to the bath components, the cell components and the electrolysis products while passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

7. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; introducing into the fused electrolyte a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; maintaining the bath in a fused state at a temperature between 700° C. and 800° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

8. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, and mixtures of at least one alkali metal halide with at least one alkali metal fluotitanate; introducing into the fused electrolyte a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; maintaining the bath in a fused state at a temperature between 700° C. and 800° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

9. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, and mixtures of at least one alkali metal halide with at least one alkali metal fluotitanate; introducing into the fused electrolyte a mutual solid solution of equimolar proportions of TiC and TiO; maintaining the bath in a fused state at a temperature between 700° C. and 800° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

10. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkali metal halides, alkaline earth metal halides and mixtures of same with at least one alkali metal fluotitanate; introducing into the fused electrolyte in close proximity to the anode, a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; maintaining the bath in a fused state at a temperature between 500° C. and 850° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

11. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of alkaline earth metal halides and mixtures of at least one alkaline earth metal halide with at least one alkali metal fluotitanate; introducing into the fused electrolyte a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; maintaining the bath in a fused state at a temperature between 500° C. and 850° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

12. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused electrolyte consisting essentially of a mixture of at least one alkali metal halide and at least one alkaline earth metal halide; introducing into the fused electrolyte a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; maintaining the bath in a fused state at a temperature between 600° C. and 800° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

13. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of sodium chloride, calcium chloride and mixtures of same with at least one alkali metal fluotitanate from the group consisting of sodium fluotitanate and potassium fluotitanate; introducing into the fused electrolyte a mutual solid solution of TiC and TiO in which the molar ratio of the carbide to the monoxide does not exceed one; maintaining the bath in a fused state at a temperature between 600° C. and 800° C. under at atmosphere which is inert to the bath components, the cell components, and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

14. The method of producing metallic titanium in an electrolytic cell which comprises: preparing an anhydrous fused salt electrolyte consisting essentially of at least one salt from the group consisting of sodium chloride, calcium chloride and mixtures of same with at least one alkali

metal fluotitanate from the group consisting of sodium fluotitanate and potassium fluotitanate; introducing into the fused electrolyte a mutual solid solution of equimolar proportions of TiC and TiO; maintaining the bath in a fused state at a temperature between 600° C. and 800° C. under an atmosphere which is inert to the bath components, the cell components and the electrolysis products; passing an electrolyzing current through the fused bath between an anode and a cathode in contact with said bath and recovering the resultant titanium as a cathode deposit.

References Cited in the file of this patent

UNITED STATES PATENTS

2,302,604	Dolbear	Nov. 17, 1942
2,636,856	Suggs et al.	Apr. 28, 1953

FOREIGN PATENTS

334,475	Germany	Mar. 14, 1921