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PRODUCTION OF METALLIC TITANIUM

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This invention relates to the production of metallic titanium and, more particularly, to improvements in the electrolytic production of metallic titanium.

The esteemed qualities of titanium metal are predicated upon its availability in malleable or workable state and the latter can be attained only when the metal is produced substantially free of contained oxygen. The principal sources of oxygen in electrolytically deposited titanium are oxygen or water vapor in the atmosphere above the electrolytic bath from which the metal is deposited and moisture contained in the salts which are used as the electrolytic bath. It is a common and effective practice to exclude air from the atmosphere above the bath by sweeping this atmosphere with an inert gas such as argon, helium, or the like, and substantially all traces of moisture can be removed from the bath by electrolysis under conditions which will effect dissociation of any contained water without deposition of any significant amount of titanium metal. These expedients are effective in preventing contamination of the cathodically deposited titanium by oxygen, but subsequent handling of the deposited metal for its recovery in the form of an ingot or other useful shape tends to introduce a substantial amount of extraneous oxygen into the metal. This contamination is caused by the necessity of freeing the deposited metal from entrained salts when it is removed from the cell, such separation being generally effected by washing the deposited metal with water and with dilute acid. Of necessity, washing and leaching to remove entrained salts is sufficiently drastic to cause some surface oxidation of the particles of titanium metal. When these particles of surface-oxidized metal are subsequently melted in an inert atmosphere, it is generally found that the resulting titanium ingot contains such an amount of oxygen that it is brittle and unworkable. Accordingly, in order to lower the ratio of surface area to volume of such particles and thus lower the oxygen contamination of the resulting ingot, it is advantageous to produce the metal particles in the largest size possible.

In the production of metallic titanium by electrolysis of an alkali metal fluotitanate in a diluent bath composed of one or more alkali and alkaline earth metal halides, it has been found possible heretofore to deposit the titanium metal in the form of particles 60 to 80 microns in average size provided that an inert cell atmosphere is maintained and that the bath is subjected to pre-electrolysis at a decomposition potential below that of the titanium salt but sufficient to insure decomposition of all free or combined water in the bath components. However, at least 30% of the particles so produced have a size less than about 45 microns and only a small percentage of the particles are as large as 100 to 150 microns. The purity of the metal ingot produced from such particles is only about 99% Ti, the balance being predominantly oxygen.

We have now discovered that the particle size of the cathodically deposited titanium produced by the aforementioned electrolysis of an alkali metal fluotitanate in a fused diluent salt bath can be markedly increased by controlling the maximum amount of certain impurities which are normally introduced into the bath as impurities indigenous to the fluotitanate. The impurities which we have found to be critical in this regard are aluminum, chromium, iron and vanadium, these elements normally being present in the trivalent form in such a fused salt bath. We have found that when the total amount of these trivalent elements in the bath is maintained below 0.1% by weight of the titanium content of the bath, the average particle size of the cathodically deposited metal is much larger than could be obtained heretofore.

Accordingly, our present invention represents an outstanding improvement in the production of metallic titanium by electrolysis of an alkali metal fluotitanate in a diluent bath composed of one or more alkali and alkaline earth metal halides. Our improvement comprises maintaining the total bath content of aluminum, chromium, iron and vanadium below 0.1% by weight of its titanium content with the resulting production of titanium metal in greater yield and in the form of particles at least 90% of which are larger than 325 mesh and the average size of which is at least about one-quarter inch. Control of the amount of these trivalent impurities in the fused salt bath is attained by using as the fluotitanate an alkali metal fluotitanate purified to the extent that its total content of aluminum, chromium, iron and vanadium is less than 0.02% by weight, with the result that the massive titanium metal produced from the cathode deposit invariably exeeds 99.5% titanium and less than 0.1% oxygen.

The alkali metal fluotitanates from which titanium metal may be obtained by electrolysis in a fused salt bath are sodium and potassium fluotitanate, Na_2TiF_6 and K_2TiF_6, respectively. Pursuant to the present methods of producing these salts, the salts are obtained in the form of an aqueous solution thereof and recovery of the salt is obtained by simple crystallization from the solution. The sodium and potassium fluotitanates thus produced are of high purity by normal commercial standards and it has not been realized heretofore that these salts contain any impurity in such amount as to deleteriously affect the quality of the metallic titanium cathodically deposited therefrom. Thus, the sodium and potassium fluotitanates obtained as described hereinbefore, and which generally contain a total of about 0.5% of aluminum, chromium, iron and vanadium as tolerable impurities, yield upon electrolysis metallic titanium substantially free of these impurities. Although the metallic titanium produced from the purified fluotitanates used in the practice of our present invention contains even less of these impurities, the most valuable improvement resulting from the use of the purified fluotitanates resides in the increased particle size of the deposited metal.

Purification of the alkali metal fluotitanates for use in the practice of our invention should be such as to reduce the total content of the normally trivalent impurities aluminum, chromium, iron and vanadium at least to 0.02% by weight of the salt. Although the method of purification of the salt is not critical, we have found that the most simple and effective purification procedure is to recrystallize the salt. Thus, the commercial grade of alkali metal fluotitanate is dissolved in such an amount of hot water as to form a saturated solution at a temperature of about 90° C., whereupon cooling of the solution to ambient temperature results in recrystallization of the fluotitanate. The recrystallized fluotitanate so obtained may be removed readily from the mother liquor by any conventional filtering device and is readily amenable to drying in pan driers and the like at temperatures of about 120° C. The resulting dried product will then contain not more than 0.02% by weight of aluminum, chromium, iron and vanadium, inclusive. Additional recrystallization steps may be performed if desired, but we have found that the major improvement is obtained by the aforementioned single recrystallization of the initially crystallized product.

The salts useful in forming the diluent bath are the conventionally used alkali metal and alkaline earth metal halides. Either one or a mixture of such halides may be used in the practice of our invention inasmuch as the control of the impurities in the fluotitanate pursuant to our invention leads to consistently better results with any given diluent bath composition. Accordingly, sodium chloride may be used as the sole component of the diluent bath or mixtures of the aforementioned halides, such as a eutectic mixture of sodium chloride and potassium chloride, may be used where it is desired to obtain a lower melting point bath. However, sodium chloride alone forms a diluent bath which permits electrolysis within a temperature range of about 700° to 1000° C. and is so relatively inexpensive and of such high purity that we presently prefer to use this salt as the diluent bath component. Where other alkali metal and alkaline earth metal halides are used in making up the diluent bath composition, they should be obtained in a sufficiently high state of purity as to not introduce any significant amount of the aforementioned trivalent impurities into the bath.

The amount of alkali metal fluotitanate which is incorporated in the diluent salt bath in practicing our invention is not critical within the range of 0.5 to 35 mol per cent of the diluent bath component, but within this range we have found it advantageous to use between 10 and 25 mol per cent of the fluotitanate.

Although it has heretofore been considered necessary to remove moisture from the cell bath not merely to the extent possible by vacuum drying but to the much greater extent possible by pre-electrolysis of the bath, we have found that such pre-electrolysis is not essential to the quality of particle size of the electrodeposited titanium metal obtained by the practice of our invention. Thus, we have found it to be wholly satisfactory to subject the bath components merely to vacuum drying at temperatures up to about 200° C., a vacuum of the order of one millimeter of mercury or less being sufficient for this purpose. When the bath components are thus vacuum dried, they may be used directly in the operation of an electrolytic cell in the practice of our invention.

The practice of our invention does not necessitate any modification in the cell geometry or operating conditions which have been previously ascertained to be useful in the electrolysis of the unpurified fluotitanates heretofore. Thus, the cell voltage should be such as to provide the necessary decomposition voltage for the alkali metal fluotitanate while nevertheless being below the decomposition voltage of the diluent bath components. Current densities up to about 400 amperes per square decimeter are also not critical inasmuch as with any specific current density up to that limit an improvement in the particle size of the deposited titanium is noted when the purified fluotitanate is used in accordance with our invention as compared with the particle size previously obtainable under identical conditions with the unpurified fluotitanate. Within the aforementioned range, current densities of the order of 200 to 400 amperes per square decimeter are particularly useful and lead to commercially acceptable current efficiencies of at least 50%. We have ascertained, however, that the maximum improvement in particle size of the deposited titanium obtained at any cell voltage and current density used in practicing our invention is obtained when the voltage gradient between the cell anode and cathode is at least one volt per centimeter. For example, with a cell voltage of about 6 to 8 volts, we have found it advisable to maintain all portions of the anode and cathode immersed in the fused bath within a maximum mutual spacing of 2 inches. It must be understood, however, that the increase in particle size obtainable by adopting the aforementioned optimum values of current density and voltage gradient are cumulative with respect to the increase in particle size obtained simply by the use of a purified fluotitanate according to our invention. Thus, under all cell conditions which result in the electrodeposition of metallic titanium from an unpurified fluotitanate, the use of a purified fluotitanate pursuant to our invention will, under the same cell conditions, effect a substantial increase in the particle size of the electrodeposited titanium. Adoption of the other optimum cell conditions recited hereinbefore merely accentuates this increase in particle size and therefore they are not essential conditions but merely optimum conditions of cumulative value.

The products of the electrolysis consist of titanium metal deposited at the cathode and chlorine gas evolved at the anode. No fluorine is evolved and consequently the concentration of fluorides in the bath is progressively built up by successive additions of the alkali metal fluotitanate. We have found it generally advisable to continue electrolysis of the alkali metal fluotitanate in the aforementioned diluent bath only until the molar ratio of potassium fluoride to sodium fluoride in the bath reaches a value of about 2:1. At this point, we have found it desirable to replace the diluent bath, the spent bath being appropriately treated for recovery of its potassium and fluorine components.

The following specific examples are illustrative but not limitative of the practice of our invention:

Example I

Commercial grade potassium fluotitanate was mixed with a sufficient amount of water to form a saturated solution at 90° C. A further addition of about 1% by weight of potassium fluoride was added to the mixture in order to enhance subsequent crystallization of the fluotitanate from the saturated solution by virtue of the common ion effect. Upon cooling to room temperature, crystals of potassium fluotitanate were formed and these crystals were separated from the mother liquid by filtering, were given a single wash with pure water and were then pressed dry on the filter. The resulting purified potassium fluotitanate contained by chemical analysis a total of less than 0.1% by weight of aluminum, chromium, iron and vanadium, less than one-fifth of the total content of these elements in the initial commercial grade fluotitanate. The purified salt was then vacuum dried at a pressure of about one millimeter of mercury for a period of 12 hours at a temperature of 170° C.

An electrolytic cell was heated to a temperature of 850° C. in a dry argon atmosphere and thereupon chemically pure sodium chloride was charged to the cell and heating was continued under the argon atmosphere until the sodium chloride was fused. At this point, the aforementioned vacuum dried purified potassium fluotitanate was transferred to the fused sodium chloride bath in such manner as to minify exposure of the salt to the ambient atmosphere. The amounts of these charge components were 380 units of the purified fluotitanate and 1800 units by weight of the sodium chloride. An iron cathode was then inserted in the bath to a depth of 2 inches and spaced from the anode a maximum of 1.5 inches. The cell temperature was promptly lowered to 750° C. and electrolysis of the fused bath was then carried out at this temperature under an argon atmosphere while maintaining a cell voltage within the range of 4.8 to 6.1 volts. The current density during the electrolysis period of 92 minutes varied between 300 and 400 amperes per square decimeter. At the conclusion of the electrolysis, the bath was cooled so that the cathode could be removed at a temperature sufficiently low to insure against oxidation of the sponge-like cathode deposit of titanium metal. The titanium was separated from the cathode, was washed with dilute sulfuric acid, and was then washed with water and dried in a vacuum. The yield of titanium metal was determined to be 54 parts by weight and represented a yield efficiency of 80% at a current efficiency of approximately 50%. The titanium metal product was coarsely crystalline in appearance and was subjected to sizing tests which established that 12.5% by weight of the product had a particle size of less than 325 mesh and that the remainder of 87.5% had a substantial proportion of crystals which were approximately ½ inch in diameter. Analysis of the coarse crystalline product was as follows:

Ti	99.9+
Si	0.001
Fe	0.005
Mg	Less than 0.001
Mn	Less than 0.001
Al	0.007
Mo	Less than 0.001
V	Less than 0.001
Cu	Less than 0.0005
Zr	0.01
Pb	Less than 0.002
O	Less than 0.04
N	0.009
C	0.01

Example II

The operation described in Example I was repeated with identical amounts of materials, tempertaures and electrical conditions but with a single variation in that recrystallization and vacuum drying of the potassium fluotitanate were omitted. Under these conditions, the yield of titanium metal from the cathode deposit was only 50 parts by weight, representing a 46% current efficiency and a 74% yield efficiency. The screen analysis of the cathode deposit was 74% minus 325 mesh and only 26% coarser than 325 mesh, and the over-all product was so fine that it was difficult to wash. The product contained approximately 98% titanium and 0.2% oxygen.

Example III

Commercial grade potassium titanium fluoride was recrystallized and vacuum dried as described in Example I. Simultaneously, chemically pure sodium chloride was similarly vacuum dried. The two products were then thoroughly mixed at room temperature in the same amounts as described in Example I and the mixture was subjected to further vacuum drying for an additional 2 hours. The electrolytic cell was heated to 850° C. in an argon atmosphere, and the vacuum dried mixture of potassium fluotitanate and sodium chloride was then added quickly to the cell. A vacuum was promptly applied to the cell and heating was continued until the mixture of salts was molten. Thereupon, the cell vacuum was replaced with a dry argon atmosphere, and electrolysis of the molten salt was carried out under the same conditions as described in Example I. The electrodeposited titanium metal was composed of 60 parts by weight of relatively coarse metal product representing a 56% current efficiency and an 89% yield efficiency. Screen analysis of this product showed that only 6% of it was minus 325 mesh, that 94% of it was coarser than 325 mesh, and that the plus 325 mesh portion consisted predominantly of flakes ranging from 0.25 inch to 1.0 inch in length.

It will be seen, accordingly, that the purification of the alkali metal fluotitantae prior to electrolysis in a diluent fused bath in accordance with our present invention results in a remarkable increase in the particle size of the electrodeposited titanium metal. The use of purified potassium fluotitanate according to our invention thus results in the electrolytic production of titanium metal capable of being converted to ingot form with only such a minute amount of oxygen that the ingot metal is malleable and amenable to cold working. A further advantage resides in the fact that the practice of our invetnion eliminates the necessity of subjecting the fused salt bath to pre-electrolysis and therefore contributes to the art a substantial saving in the power requirements heretofore considered necessary for the electrolytic production of metallic titanium. It has been observed heretofore that at bath temperatures sufficiently high to maintain fused salt conditions, and thus establish condiitons making possible pre-electrolysis of the bath, moisture in the bath tended to cause hydrolysis of the titanium salt. Such hydrolysis results in the combination of the oxygen component of the water with the titanium salt to form a titanium-oxygen compound which is not decomposed prior to the titanium electrolysis, and consequently hydrolysis of the titanium salt has in the past resulted in significant oxygen-contamination of the electrodeposited titanium. This tendency toward hydrolysis is eliminated by the practice of our invention inasmuch as it makes possible adequate dehydration of the bath components by simple vacuum drying at temperatures not substantially in excess of 200° C., and in this additional respect our invention offers a further contribution to the advancement of the art of titanium production.

We claim:

1. A method of producing metallic titanium in the form of particles substantially all of which are larger than 325 mesh which comprises: forming an anhydrous fused salt electrolyte consisting essentially of at least one salt of the group consisting of alkali metal halides and alkaline earth metal halides, maintaining the fused salt bath at an elevated temperature and under an inert atmosphere, providing an alkali metal fluotitanate containing more than a total of 0.02% by weight of the trivalent impurities: aluminum, chromium, vanadium and iron, purifying the alkali metal fluotitanate to the extent that its total content of aluminum, chromium, iron and vanadium is less than 0.02% by weight, introducing an amount of the purified alkali metal fluotitanate into the fused salt bath sufficient to form a mixture containing between 0.5 and 35 mol percent of the fluotitanate, electrolyzing the so-formed mixture and recovering the titanium as an electrodeposit consisting of particles substantially all of which are larger than 325 mesh.

2. A method of producing metallic titanium in the form of particles at least 90% of which are larger than 325 mesh and the average size of which is at least about one-quarter inch which comprises: forming an anhydrous fused salt electrolyte consisting essentially of at least one salt of the group consisting of alkali metal halides and alkaline earth metal halides, maintaining the fused salt bath at an elevated temperature and under an inert atmosphere, providing an alkali metal fluotitanate containing more than a total of 0.02% by weight of the trivalent impurities: aluminum, chromium, vanadium and iron, purifying the alkali metal fluotitanate to the extent that its total content of aluminum, chromium, iron and vanadium is less than 0.02% by weight, introducing an amount of the purified alkali metal fluotitanate into the fused salt bath sufficient to form a mixture containing between 0.5 and 35 mol percent of the fluotitanate, electrolyzing the so-formed mixture under a cell voltage gradient of at least one volt per centimeter between anode and cathode and with a current density not in excess of 400 amperes per square decimeter and recovering the titanium as an electrodeposit consisting of particles substantially all of which are larger than 325 mesh.

3. A method of producing metallic titanium in the form of particles substantially all of which are larger than 325 mesh which comprises: forming an anhydrous fused salt electrolyte consisting essentially of at least one alkali metal chloride, maintaining the fused salt bath at an elevated temperature and under an inert atmosphere, providing an alkali metal fluotitanate containing more than a total of 0.02% by weight of the trivalent impurities: aluminum, chromium, vanadium and iron, purifying the

alkali metal fluotitanate to the extent that its total content of aluminum, chromium, iron and vanadium is less than 0.02% by weight by recrystallizing the impure alkali metal fluotitanate from an aqueous medium, introducing an amount of the purified alkali metal fluotitanate into the fused salt bath sufficient to form a mixture containing between 0.5 and 35 mol percent of the fluotitanate, electrolyzing the so-formed mixture and recovering the titanium as an electrodeposit consisting of particles substantially all of which are larger than 325 mesh.

4. A method of producing metallic titanium in the form of particles substantially all of which are larger than 325 mesh which comprises: forming an anhydrous fused salt electrolyte consisting essentially of at least one salt of the group consisting of alkali metal halides and alkaline earth metal halides, maintaining the fused salt bath at an elevated temperature and under an inert atmosphere, providing an alkali metal fluotitanate containing more than a total of 0.02% by weight of the trivalent impurities: aluminum, chromium, vanadium and iron, purifying the alkali metal fluotitanate to the extent that its total content of aluminum, chromium, iron and vanadium is less than 0.02% by weight by recrystallizing the impure alkali metal fluotitanate from an aqueous medium, drying the recrystallized purified fluotitanate, introducing an amount of the dried purified alkali metal fluotitanate into the fused salt bath sufficient to form a mixture containing between 0.5 and 35 mol percent of the fluotitanate, electrolyzing the so-formed mixture and recovering the titanium as an electrodeposit consisting of particles substantially all of which are larger than 325 mesh.

5. A method of producing metallic titanium in the

form of particles substantially all of which are larger than 325 mesh which comprises: forming an anhydrous fused salt electrolyte consisting essentially of at least one alkali metal chloride, maintaining the fused salt bath at an elevated temperature and under an inert atmosphere, providing an alkali metal fluotitanate containing more than a total of 0.02% by weight of the trivalent impurities: aluminum, chromium, vanadium and iron, purifying the alkali metal fluotitanate to the extent that its total content of aluminum, chromium, iron and vanadium is less than 0.02% by weight by recrystallizing the impure alkali metal fluotitanate from an aqueous medium, drying the purified fluotitanate under a vacuum at least as low as one millimeter of mercury at an elevated temperature up to about 200° C. prior to electrolysis, introducing an amount of the dried purified alkali metal fluotitanate into the fused salt bath sufficient to form a mixture containing between 0.5 and 35 mol percent of the fluotitanate, electrolyzing the so-formed mixture and recovering the titanium as an electrodeposit consisting of particles substantially all of which are larger than 325 mesh.

References Cited in the file of this patent

UNITED STATES PATENTS

1,815,054	Driggs	July 21, 1931
1,835,025	Driggs et al.	Dec. 8, 1931
1,874,090	Driggs	Aug. 30, 1932

OTHER REFERENCES

"Journal of Applied Chemistry" (U. S. S. R.), vol. 13 (1940), pages 51 thru 55.