

May 19, 1959

R. D. BLUE ET AL

2,887,443

ARC-CATHODE PRODUCTION OF TITANIUM

Filed Feb. 15, 1957

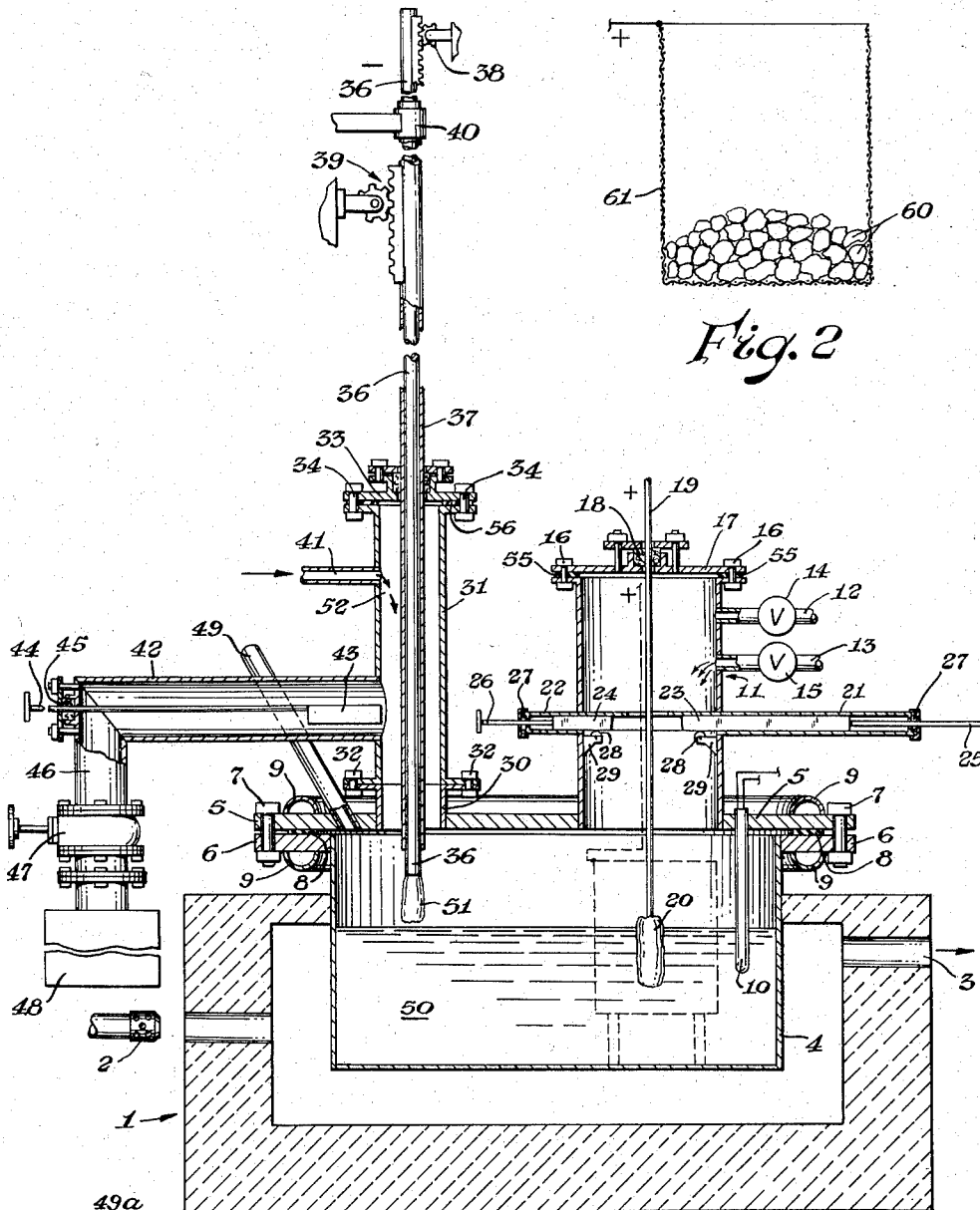


Fig. 2

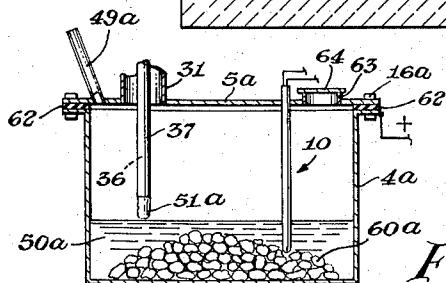


Fig. 3

Fig. 1

INVENTORS.  
Robert D. Blue  
Marshall P. Neipert

BY  
Griswold & Burdick  
ATTORNEYS

1

2,887,443

## ARC-CATHODE PRODUCTION OF TITANIUM

Robert D. Blue and Marshall P. Neipert, Midland, Mich.,  
assignors to The Dow Chemical Company, Midland,  
Mich., a corporation of Delaware

Application February 15, 1957, Serial No. 640,556

10 Claims. (Cl. 204—64)

The invention pertains generally to the production of titanium metal. It pertains more particularly to a method of and apparatus for the electro-deposition of titanium metal on a retractable arc-producing cathode from an impure titanium source.

Titanium metal has been produced largely by the chemical reduction of a titanium halide particularly titanium tetrachloride by metals more electropositive than titanium, e.g., magnesium. Titanium has also been produced in limited quantities by the thermal dissociation of a titanium halide, particularly titanium tetraiodide.

Some progress has been made in the production of titanium at a conventional submerged cathode by electrolysis of a fused electrolyte comprising a halide or mixed halides of alkali or alkaline earth metals containing a lower halide of titanium. Neither a substantially pure halide nor the mixed halide salt, however, has been fully successful. When a bath of a single fused salt, e.g., NaCl, is employed as the electrolyte, temperatures of at least about 850° C. are required. Steel parts are clearly weakened when subjected to temperatures in that range. Therefore, any means for removing the titanium which employs moving steel parts requires elaborate cooling means. Cooling systems employing water as a cooling medium are usually employed. Such cooling systems are costly to design, construct, and maintain. Furthermore, the employment of a readily vaporizable material such as water in the proximity of hot titanium is very dangerous and definitely not recommended for commercial production.

Mixed fused salts are not a satisfactory bath when employed in a conventional electrolytic cell having a submerged cathode because when mixed fused salts are thus employed in proportions which permit lower temperatures, the titanium is produced at the submerged cathode as a highly pyrophoric powder. Such highly pyrophoric material has but very small commercial value and constitutes a serious hazard to safety.

An object of the present invention is to provide an improved method of producing massive titanium metal electrochemically in a fused salt bath of mixed alkali or alkaline earth halides at lower temperatures than those heretofore found necessary.

Another object is to provide a method of producing titanium electrochemically in a fused salt bath of a substantially pure alkali or alkaline earth halide which permits the removal of the titanium thus produced by a continuous operation which does not require water-cooling means.

Another object is to provide a method of producing titanium employing a consumable anode of impure titanium in a bath of a fused alkali or alkaline earth halide or mixtures thereof containing a lower halide of titanium.

Another object is to provide a method of recovering substantially pure titanium by electrolysis on an arc-producing retractable cathode at the surface of the electrolyte.

A further object is to provide a method of producing ductile titanium metal by first reacting  $TiO_2$  with carbon

2

and thereafter recovering the titanium from the thus-prepared carbon-containing source by electrolysis in a fused salt bath.

A still further object is to provide a continuous method of producing titanium from a source containing at least 90 percent titanium by depositing the titanium in a compact flake form on a retractable cathode and periodically loosening and carrying away the thus-deposited titanium.

The method of attaining these and related objects is described and illustrated hereinafter.

The invention comprises consuming an impure titanium anode by electrolyzing lower-valence halides of titanium, e.g., titanium trichloride or titanium dichloride, in a fused salt bath and recovering the titanium in a comparatively purified state by accretion on a retractable cathode which is maintained at such a distance above the bath that an arc is formed between the cathode and the surface of the bath. The cathode is gradually retracted as the accretion of titanium grows at the end thereof.

Fig. 1 of the drawing shows an elevational section of an apparatus suitable for practicing the invention.

Fig. 2 and Fig. 3 are modifications of portions of Fig. 1 showing alternative means for providing impure titanium for the electrolysis.

The fused salt bath consists essentially of an alkali or alkaline earth halide or a mixture thereof, e.g., NaCl or the eutectic mixture of KCl and NaCl. The eutectic salt mixture offers the advantage of low temperature operation. On the other hand, a substantially pure salt bath of NaCl, offers the advantage of providing a better formed and more nearly pure Ti accretion at the cathode. Either a divalent halide or a trivalent halide must be present in the bath as the titanium halide, the chlorides being the preferable halides to employ. Available sources of the lower chlorides of titanium usually consist of mixtures of the tri- and dichlorides. The dichloride is preferred to the trichloride because it results in greater current efficiency and a purer titanium recoverable at the cathode. After a convenient size titanium accretion, referred to hereinafter as a carrot, has formed on the cathode, it is further retracted, and the carrot is loosened by impact, vibration, or rod-sleeve arrangement, described hereinafter, and caused to fall from the cathode. An improved embodiment of the invention is to have a boat or pan which slides beneath the cathode end at the time that the carrot is loosened therefrom to catch the carrot and carry it to a place of storage.

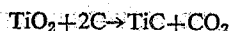
The titanium may be provided by any source of titanium containing not less than 90 percent titanium and preferably not less than 95 percent titanium. It may be in the form of an elongated stick or as a lump secured to a steel rod which serves as the positive terminal of the cell as shown in Fig. 1. On the other hand, it may be in comparatively small pieces confined in a basket of porous, perforated, or interwoven conducting material which is not itself affected by the electrolysis connected to a positive source of electricity; or the pot of the cell may be made the anode and pieces of impure titanium merely dropped into the pot.

A particularly useful embodiment of the invention is to prepare a carbon-containing titanium anode by an adaptation of known methods and thereafter to electrodeposit the titanium, from the anode in a fused salt bath containing a lower halide of titanium, on an arc-producing retractable cathode according to the invention.

Titanium occurs plentifully as its oxide. A common method of winning metals from their oxides is by reacting the oxide with a reducing agent such as carbon. When titanium oxide is reacted with carbon, however, titanium carbides, particularly  $TiC$ , together with some crystallized carbon in the form of graphite, and traces of other materials are present with the titanium metal. A work-

able and economically feasible method of winning the titanium from the carbide either alone or in admixture with graphite has been a long-felt need in the art of titanium production. On embodiment of the present invention provides such a method.

A carbon-containing titanium anode suitable for this embodiment of the invention may be prepared by one of several known methods. A particularly suitable method of preparing the anode for use in the invention is that described by H. Moissan in *Compt. Rend.*, v. 117, pp 423-425, v. 120, p. 1393 and v. 125, p. 839. Sixteen parts of titanium dioxide and seven parts of carbon by weight are reacted in an electric arc for 10 minutes or longer. The principal reaction may be represented by the equation:



The presence of a flux, e.g., up to 10 percent of  $\text{CaF}_2$  by weight, with the carbon and  $\text{TiO}_2$  causes the reduction of  $\text{TiO}_2$  to proceed smoother and faster giving a better product. The carbon-containing titanium product may be formed in a desired shape to serve as an anode or the anode may be in the form of pieces which may be placed in a basket composed of a conducting material as explained hereinabove.

Titanium dichloride and titanium trichloride suitable for practicing the invention may be prepared according to known methods such as those set out in *Titanium* by Barksdale, pp. 81 to 82 (1949).

Titanium dichloride and titanium trichloride may also be prepared according to our copending application, Serial No. 659,253, filed May 15, 1957, wherein a gaseous halogen compound such as  $\text{TiCl}_4$ ,  $\text{HCl}$ ,  $\text{HBr}$ , or  $\text{Cl}_2$  is reacted with Ti sponge, or carbon-titanium alloys or  $\text{TiC}$  to produce  $\text{TiCl}_2$  and  $\text{TiCl}_3$ .

The molten salt bath should have a melting point below about  $700^\circ\text{C}$ . The  $\text{KCl-NaCl}$  bath and particularly the eutectic mixture is preferred because of its lower melting point. The following melting point values for  $\text{KCl-NaCl}$  mixtures are given in molal percentages:

| KCl in Molal percent | NaCl in Molal percent | Melting Point, $^\circ\text{C}$ |
|----------------------|-----------------------|---------------------------------|
| 100                  | none                  | 776                             |
| 80                   | 20                    | 736                             |
| 70                   | 30                    | 720                             |
| 60                   | 40                    | 665                             |
| 50                   | 50                    | 600                             |
| 40                   | 60                    | 686                             |
| 30                   | 70                    | 697                             |
| 15                   | 85                    | 760                             |
| none                 | 100                   | 798                             |

The above table illustrates the lower operating temperatures possible when mixtures of  $\text{KCl}$  and  $\text{NaCl}$  between 70 percent  $\text{KCl}$ -30 percent  $\text{NaCl}$  and 30 percent  $\text{KCl}$ -70 percent  $\text{NaCl}$ , molal quantities, are used.

The  $\text{TiCl}_2$  or  $\text{TiCl}_3$ , or mixture thereof, is added to the bath in such amount that the titanium fraction of the trichloride and/or dichloride comprises between 8 and 16 percent and preferably about 16 percent by weight. By the titanium fraction is meant that portion of the titanium chloride which would be titanium if quantitatively analyzed. To provide the bath with 16 percent of titanium by adding  $\text{TiCl}_3$ , about 51 percent of the weight of the bath of  $\text{TiCl}_3$  is added.

The current density employed at the cathode is based upon that necessary to attain the desired deposition temperature which is between  $850^\circ\text{C}$ . and  $1400^\circ\text{C}$ . The temperature may be satisfactorily ascertained by employing an optical pyrometer. A cathode current density of between 40 and 350 amperes per square inch of cathode area at the arc is usually employed.

The voltage employed, as measured across the termi-

nals of the anode and cathode, is not critical but is generally between 8 and 15 volts, although higher voltages may be employed. The amperage for a given voltage will vary according to the resistance offered. The resistance depends upon such conditions as the area and spacing of the electrodes and amount, type, and temperature of the electrolyte.

Referring to Fig. 1 in greater detail there is shown furnace setting 1. Heat is provided by gas burner 2. Outlet 3 provides for the escape of combustion gases. Pot 4, adapted to contain the fused bath to be electrolyzed, is positioned in the furnace setting. Pot 4 is provided with removable cover 5 which is secured to flanged rim 6 of the pot by means of electrically insulated bolts 7. Gasket 8 of electrically insulating material provides a seal between the cover 5 and rim 6. Water jackets 9 on the outside of cover 5 and rim 6 above and below the gasket encircle the cell near bolts 7 to prevent the heat in that area from damaging the gasket and insulated bolts. Thermocouple 10 provides a continuous means of ascertaining the temperature of the bath. Anode chamber 11 is integrally secured in an upright position above the opening provided therefor in cover 5. Anode chamber 11 is equipped with evacuating line 12 and inert gas line 13 containing valves 14 and 15, respectively. The upper end of chamber 11 has secured thereto, by means of electrically insulated bolts 16, removable cover 17 having a stuffing box 18 therein through which is inserted anode rod 19 to which is secured impure titanium piece 20. Gasket 55 of insulation material prevents electrical contact between cover 17 and the walls of chamber 11. Projecting at right angles to chamber 11 are side-wall housings 21 and 22 in which gates 23 and 24 respectively, which have opposed mating slightly beveled edges, are moved by handles 25 and 26 to provide a closure means against air contamination through chamber 11 when adding impure titanium to anode rod 19. Housings 21 and 22 project also laterally into chamber 11 sufficiently to provide a rectangular opening therethrough when gates 23 and 24 are open. Packings 27 provide tight fits for handles 25 and 26. Gates 23 and 24 are rotatably positioned in brackets 29 and provide a means for forcing the forward portions of the upper faces of gates 23 and 24 against the upper face of housing 21 and 22 to prevent passage of gases between the gates and the side-wall housings when the gates are closed. The beveled edges of the gates provide good contact between the mating edges when the forward ends of the gates are tipped slightly upward.

Flanged nipple 30 is integrally fixed about the opening provided therefor in cover 5. Cathode chamber 31, having its lower edge flanged to mate with flanged nipple 30, is secured in an upright position to nipple 30 by means of bolts 32. Chamber 31 is provided with removable cover 33 secured by electrically insulated bolts 34 and electrically insulated therefrom by gasket 56 of insulation material. Cover 33 has an opening therein which permits the insertion therethrough of sleeve 37 in which cathode rod 36 is slidably positioned. Cathode rod 36 is provided with rack and pinion assembly 38 for advancing or retracting rod 36 independently of sleeve 37. Sleeve 37 is equipped with rack and pinion assembly 39 for raising or lowering sleeve 37. Cylindrical guide 40 provides a sliding support for sleeve 37. Inlet 41 is provided in cathode chamber 31 for admission of inert gas. Extending from cathode chamber 31 is auxiliary chamber 42 which contains boat 43 provided with handle 44 extending horizontally through stuffing box 45 of auxiliary chamber 42. Extending downwardly from auxiliary chamber 42 is drop chamber 46 having valve 47 therein and a flanged bottom edge. Attached to the flanged bottom edge is receiver 48 for receiving the contents of chamber 42 when valve 47 is opened.

Sight glass 49 extending through cover 5 enables an operator to observe the operation of the cell.

In practicing the invention, using the apparatus illustrated by the drawing for example, the cell is charged with a suitable alkali or alkaline earth halide salt, as described hereinabove, to form electrolyte 50 which is maintained in the molten state. Inert gas is introduced through inlet 41 and exhausted at outlet 12 to flush the system.

Rod 19 is retracted so that its lower end is above housings 21 and 22. Gates 23 and 24 are then closed and inert gas introduced through line 13 and exhausted through line 12. Cover 17 is then removed and titanium bearing chunk 20 is secured thereto. Cover 17 is then replaced and, while continuing to introduce inert gas, gates 23 and 24 are opened and chunk 20 is immersed in bath 50 as shown in Fig. 1. The upper end of rod 19 is connected to the positive terminal of a source of D.C. electricity.

The negative terminal of the source of D.C. is connected to cathode 36 of the cell. Cathode 36 is then lowered into electrolyte 50 and slowly retracted until it emerges from the surface of the electrolyte whereby an arc is struck between the cathode tip and the electrolyte. Cathode 36 is then withdrawn slowly to maintain the arc at the desired temperature. Since the di- and trihalides dissociate in solution into titanium and halide ions, at the instant the electric arc forms across the gap between the cathode and the electrolyte titanium begins to accrete on the tip of the cathode at the arc. The halide ions react with unrefined or unpurified titanium metal at the anode to form more di- and trihalides. The cathode is then slowly retracted or withdrawn so as to continue to maintain the arc as the titanium continues to accrete thereon forming a massive accretion or carrot of a generally cylindrical shape on the end of the cathode. As the titanium carrot forms at the end of the cathode, the thus-formed carrot serves as a part of the cathode itself.

The size of the gap between the cathode tip and the surface of the salt is governed according to the temperature desired in the arc. The optimum temperature of the arc is that which results in the most consistent and uniform deposition or accretion of the titanium on the cathode and is usually between 900° and 1200° C.

The gradual withdrawal of the cathode is referred to as rise-rate. When the gap between the surface of the bath and the cathode is widened by increasing the rise-rate of the cathode, the resistance and the temperature are increased. An increase in resistance is accompanied by an increase in potential or voltage across the gap. A temperature between 850° and 1400° C. is easily maintained by regulating the gap between the cathode and the surface of the electrolyte.

When a suitable arc has been formed, it is desirable to maintain a more or less constant gap. The gap may be manually controlled or it may be controlled by automatic means, e.g., rack and pinion assembly 38 may be operated by a motor which is actuated by a relay system which transposes and amplifies an electrical impulse formed in response to a change in the voltage across the gap according to known means. For example, when the voltage across the gap has decreased to a predetermined value by the accretion of titanium on the cathode, the motor is actuated and moves cathode 36 upward to widen the gap.

The length of the titanium carrot permitted to accrete on the cathode is not critical but carrots of ½ to 2½ inches long are convenient lengths in a small-scale operation. Cross-sectional dimensions of a carrot depend largely upon the shape and size of the cathode where deposition takes place. The cross-section of the carrot depends also on certain operating conditions such as the current density of the electrolyte and the temperature of the arc. As a general rule the carrot will ex-

ceed the cross-section of the cathode to some extent, such extent being somewhat greater when the rise-rate is relatively slow. A cathode which results in a carrot of ½ to ¾ inch across its largest cross-sectional dimension is usually employed when producing carrots of the length suggested above.

After producing the desired size of titanium carrot, the cathode is withdrawn sufficiently to break the circuit, and the carrot dislodged from the cathode and removed from the apparatus. This may be accomplished by moving sleeve 37 downwardly with reference to cathode 36. The lower end of the sleeve 37 then pushes off the carrot from the cathode. A recommended mode of recovering the carrot is to move boat 43 beneath the cathode tip, at the time the carrot is dislodged, to receive it. As shown, boat 43 containing the dislodged carrot is withdrawn by means of handle 44 to a position. While above chamber 46 in this position the boat is inverted to drop the carrot into chamber 46. By opening valve 47 the carrot may be dropped into receiver 48 without admitting air to the system.

The invention will be better understood by the following example.

#### Example

A rod-shaped ingot of carbon-containing titanium material was prepared by arc-melting TiC and metallic titanium. The titanium material thus prepared showed the following analysis in weight percent for the elements for which an analysis was made, the balance being essentially titanium:

| C   | Al   | Fe  | Mn   | Mg   | Ni  | Si  | Zr  | V   |
|-----|------|-----|------|------|-----|-----|-----|-----|
| 4.0 | .023 | .11 | .056 | .002 | NHl | .08 | .20 | .09 |

A cell similar to that shown in Fig. 1 was charged with the eutectic mixture of sodium chloride and potassium chloride, i.e., 50 molal percent NaCl and 50 molal percent KCl. This is a weight percentage of 56 percent KCl and 44 percent NaCl. The salt mixture was melted by means of gas burner 2 as shown. TiCl<sub>3</sub> was then added in an amount equal to about 50 percent by weight of the molten KCl-NaCl bath. Air was flushed from the apparatus by admitting inert gas 52 through inlet 41. A cylindrical piece of the carbon-containing titanium thus prepared was secured to rod 19 to form anode 20 and placed in bath 50. Rod 19 was connected to the positive terminal of a source of D.C. electricity. Cathode rod 36 having a diameter of about ½ inch was connected to the negative terminal of the D.C. source. At the tip of the cathode an arc was struck with the surface of bath 50 whereby a complete circuit was set up with a potential of 10 volts across the arc and a current of 41 amperes. The current density of the cathode was 350 amperes per square inch of cathode area involving the arc. Titanium metal began to accrete at the end of the cathode to form carrot 51. As the titanium continued to accrete, the cathode was retracted slowly at an average rate of about 0.12 inch per minute. The temperature of the arc was about 900° C. as determined by an optical pyrometer. As titanium carrot 51 accreted on the cathode, it formed an extension of the cathode itself. The spacing was gauged by positioning the cathode relative to the electrolyte surface at a height producing the most consistent and uniform-shaped titanium carrot.

Carrot 51 formed thereby was between ¾ and 1½ inch in diameter. When it was about 2 inches long, it was removed from the cathode by raising cathode 36, together with sleeve 37, so that carrot 51 was at a height greater than that of boat 43 thereby also breaking the circuit across the gap. Boat 43 was advanced by means of handle 44 to a place beneath the carrot and the car-

rot was dislodged by manual operation as explained hereinabove.

The means employed for removing the carrot need not be manually operated but may be operated by a synchronized mechanism, not shown. The mechanism may be operably geared to an electric motor which is energized when a contact switch is tripped by cathode 36 at a predetermined height or when the resistance through the carrot has increased to a predetermined value. The sequence of steps thus automatically operated are substantially the same as those in the manual operation above.

The titanium metal deposits formed on the cathode were separated from adhering salt by volatilizing off the salt under a vacuum according to known practice. The titanium then contained the following elements in percent by weight for which an analysis was made, the balance being titanium containing not more than 0.001 percent of other impurities:

| C    | Al   | Fe   | Mn   | Mg    | Ni  | Si   | Zr   | V   |
|------|------|------|------|-------|-----|------|------|-----|
| .016 | .021 | .120 | .060 | <.001 | Nil | .002 | <.01 | .11 |

The example illustrates but one mode of practicing the invention. Any titanium source containing at least 90 percent metallic titanium may be employed as the anode. Other modes of practicing the invention are illustrated in Figures 2 and 3. Figure 2 illustrates the use of fragments 60 of impure titanium which are placed in basket 61 of a conducting material which is not affected by the electrolysis. Basket 61 is made the anode of a suitable cell as indicated by the dotted outline in Fig. 1 below the anode chamber. The titanium is recovered from the fragments on subjecting them to electrolysis in the molten electrolyte employing the principle of the invention. In practicing the invention in this manner, a steel basket, for example, is connected to a positive lead-in line as indicated by the dotted line passing upward to and through stuffing box 18 in place of rod 19.

Fig. 3 illustrates a mode of practicing the invention wherein steel pot 4a is shown directly connected to a positive source of electricity and titanium particles 60a are added directly to the molten salt bath 50a in the pot. Particles 60a together with pot 4a serve as the anode of the cell. In the modification shown in Fig. 3, cover 5a is completely insulated from the body of pot 4a by insulation 62 and secured thereto by electrically insulated bolts 16a. Opening 63, having cover 64 thereon, provides a means for adding impure titanium particles 60a. No anode chamber is required in this modification.

As a further modification, lower-valence halides of titanium may be fed directly into the electrolyte during operation of the cell to maintain a source of titanium instead of the lower-valence halides being provided, after operation has begun, as hereinabove described from an impure titanium anode reacting with halide ions in the bath.

These and other modifications of the invention will be construed as falling within the purview of the invention as defined by the claims.

A number of advantages in the art of producing titanium are realizable from a practice of the invention. Among such advantages are: the production of titanium metal in a cohesive massive form, in contrast to pyrophoric powder, at a temperature of not over about 700° C., eliminating the need for cooling systems to cool moving mechanical parts and the accompanying explosion hazard; a method of continuous electrolysis of lower halides of titanium in a fused salt bath to produce titanium metal from which the bath may be subsequently

easily separated by sublimation and the titanium thereafter melted into ingots; a means of utilizing carbon-containing titanium anodes which are made by reacting carbon and  $TiO_2$ , thereby rendering such extensive sources of titanium as rutile, Sorel titaniferous by-product slag, and ilmenite more readily utilizable as direct sources of titanium metal.

Having thus described the invention, what is claimed and desired to be protected by Letters Patent is:

1. The method of producing ductile titanium which comprises charging an electrolytic cell with a halide salt bath mixture consisting of a halide salt selected from the class consisting of the halides of alkali and alkaline earth metal halides and mixtures thereof and with lower-valence titanium halides in an amount between 8 and 16 percent by weight of the titanium fraction provided by said titanium halides based on the weight of said bath, making the anode of said chamber an impure titanium metal consisting of at least 90 percent titanium and the cathode a retractable conductor, creating an arc between the surface of said salt mixture and the retractable cathode, collecting ductile titanium on the cathode, gradually retracting the cathode while maintaining the arc, and thereafter recovering the titanium thus collected.
2. The method according to claim 1 wherein the salt bath comprises a mixture of potassium chloride and sodium chloride in substantially eutectic proportions.
3. The method according to claim 1 wherein the halide of said salt bath is the chloride and the lower-valence titanium halide is predominantly the dichloride.
4. The method according to claim 1 wherein the anode of the cell is a chunk of titanium-bearing material containing at least 90 percent titanium.
5. The method according to claim 1 wherein the source of titanium is fragmented titanium sponge confined in a conducting basket, having openings therein, which serves as the anode of the electrolytic cell.
6. The method according to claim 1 wherein the electrolyte container of the cell is made an anode of the cell and the source of titanium is fragments of titanium-bearing material containing at least 90 percent titanium unconfined in the fused salt electrolyte and in direct contact with said container.
7. The method of producing titanium metal from an oxide of titanium which comprises reacting the oxide with carbon to form a carbon-containing titanium solid shape, containing at least 90 percent titanium, making said shape an anode in a molten salt electrolyte consisting essentially of halides of alkali and alkaline earth metals and at least one lower-valence halide of titanium in sufficient amount to yield between 8 and 16 percent by weight of the titanium fraction, positioning a cathode at the surface of said electrolyte to form an arc therebetween, collecting titanium metal on said cathode, gradually withdrawing said cathode and the thus collected titanium metal while maintaining said arc, continuing to collect titanium on said cathode, and removing the thus collected titanium therefrom.
8. The method of producing titanium metal from an oxide of titanium which comprises reducing the oxide with carbon to form carbon-containing titanium solid pieces, containing at least 90 percent titanium, placing said pieces in a basket of conducting material, making said basket an anode in a molten salt bath selected from the class consisting of an alkali halide, an alkaline earth halide, and mixtures thereof, and containing at least one lower-valence halide of titanium, forming an arc between a retractable cathode and the surface of the molten salt bath, so as to produce a deposit of titanium on the cathode while gradually retracting the cathode so as to maintain the arc as the deposit forms, periodically withdrawing the cathode having the titanium thereon sufficiently to break the arc, and dislodging said titanium.
9. The method according to claim 8 wherein the salt bath is substantially the eutectic mixture of potassium

chloride and sodium chloride containing a mixture of titanium dichloride and titanium trichloride in an amount sufficient to provide between 8 and 16 percent by weight of the titanium fraction of said chlorides at a temperature of not over 700° C.

10. The method according to claim 7 wherein the salt bath is sodium chloride containing a mixture of the lower valence chlorides of titanium, said mixture comprising predominantly titanium dichloride.

5

# References Cited in the file of this patent

## UNITED STATES PATENTS

|           |                      |               |
|-----------|----------------------|---------------|
| 2,734,855 | Buck et al. -----    | Feb. 14, 1956 |
| 2,734,856 | Schultz et al. ----- | Feb. 14, 1956 |
| 2,741,588 | Alpert et al. -----  | Apr. 10, 1956 |
| 2,748,073 | Mellgren -----       | May 29, 1956  |
| 2,813,069 | Raynes et al. -----  | Nov. 12, 1957 |

## OTHER REFERENCES

10

Journal of Metals, September, 1956, pages 1162-1168.