Aug. 25, 1959 R. S. DEAN ET AL 2,901,410

ELECTRO-REFINING TITANIUM

Filed Aug. 2, 1956 2 Sheets-Sheet 1

Fig. 1.

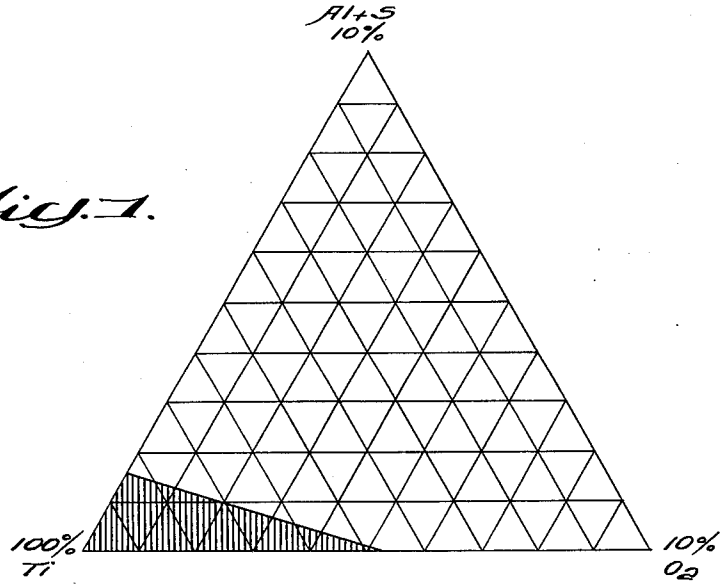
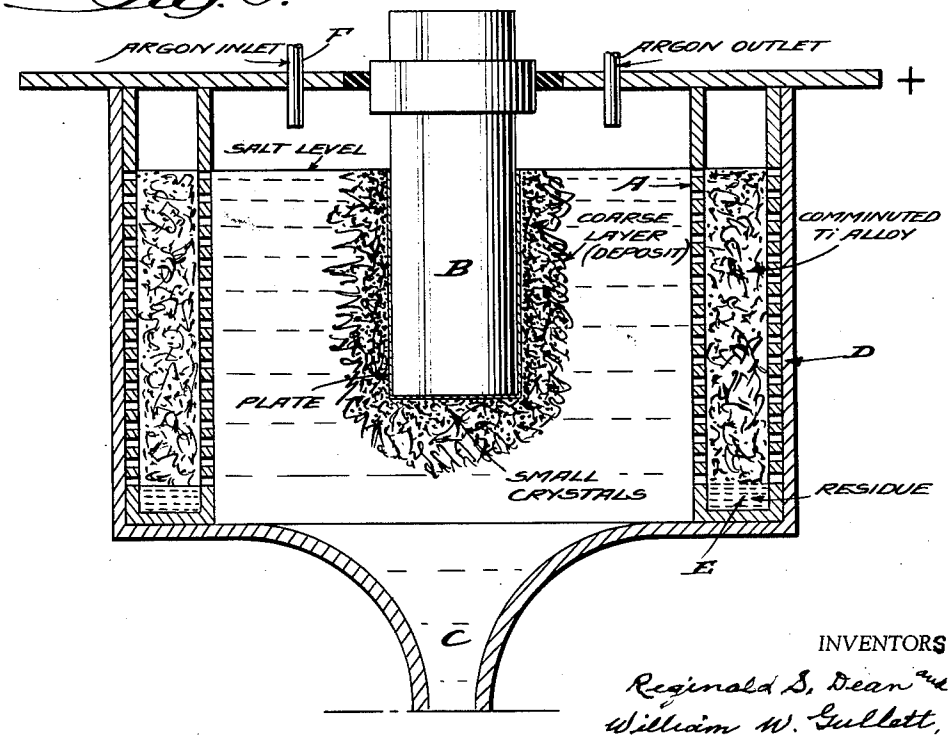


Fig. 3.



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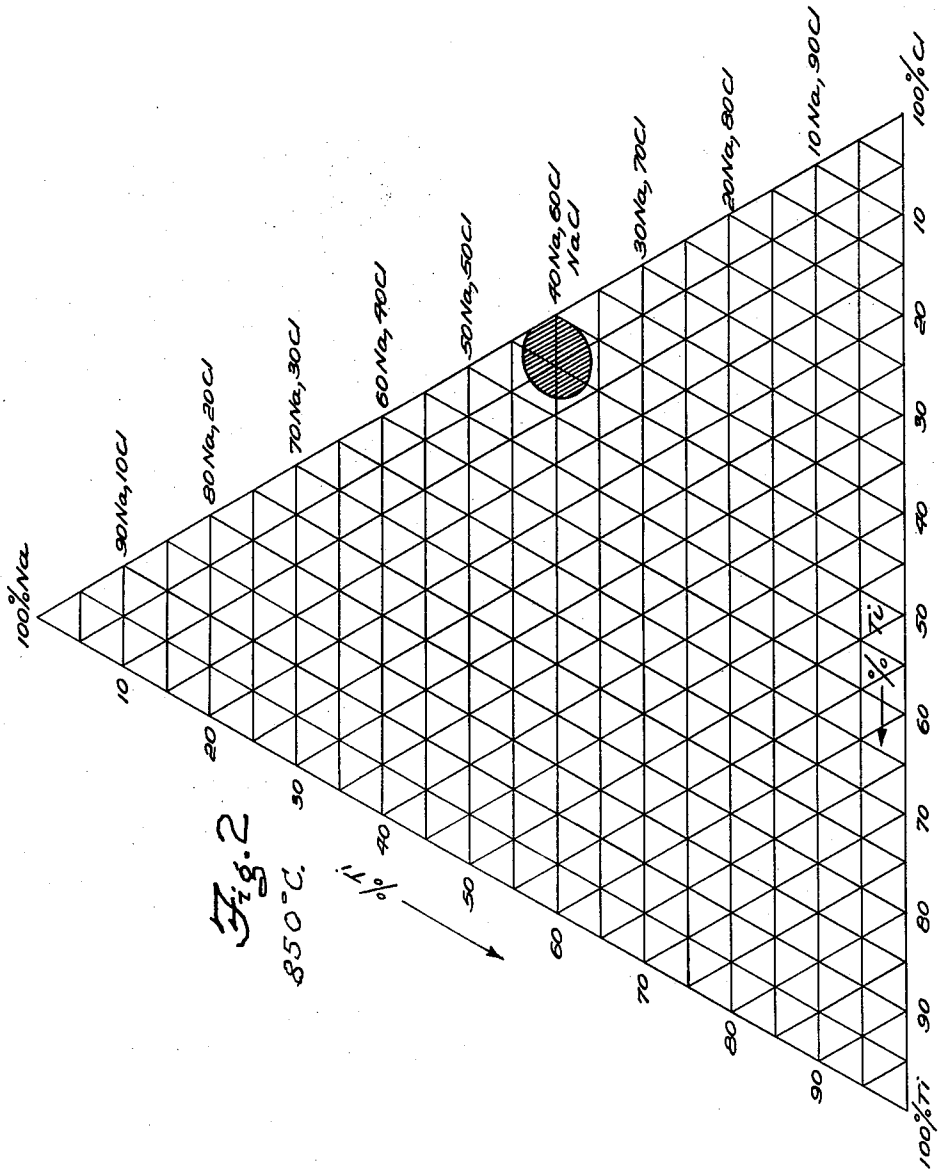


Fig. 2

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2,901,410

ELECTRO-REFINING TITANIUM

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Application August 2, 1956, Serial No. 601,705

1 Claim. (Cl. 204—64)

The invention relates to the production of highly pure titanium from crude titanium alloys or metallic titanium-containing materials by electro-refining; and more particularly the invention relates to a procedure and correlated series of steps by which large crystals of highly pure titanium may be formed on a commercial scale at the cathode of an electrolytic cell having a molten cell bath therein.

The manufacture of increasing quantities of titanium and titanium alloy products is producing increasing quantities of scrap material either as an incident to the fabrication of such titanium products, or as a result of the production of material which does not meet specifications, or for other reasons.

Other titanium-containing materials also exist, such as titanium ore and materials formed incident to the manufacture of titanium sponge. These materials also have a titanium content which would be valuable, provided that the titanium content can be economically separated from other associated elements and produced in the form of large crystals.

Accordingly, there is an existing need for an economical and practical procedure for reclaiming titanium in a highly pure large crystal form from metallic titanium-containing materials.

Various methods have been proposed from time to time for electro-depositing titanium in an electrolytic cell, but for one reason or another such proposals have not been adapted for the satisfactory and economical commercial production of highly pure titanium in large crystal form.

The structure of the desired form of cathode product having large highly pure titanium crystals is shown in the copending application of W. W. Gullett, entitled Titanium Group Metal Deposits and Methods of Making Same, filed June 20, 1956, Serial No. 592,543. Suitable molten salt cell baths which can be controlled to produce titanium in large crystal form are described in the copending application of W. W. Gullett entitled "Refining Titanium Alloys," filed March 23, 1956, Serial No. 573,336 (now Patent No. 2,817,631); in the co-pending application of W. W. Gullett, entitled Electrorefining Titanium, filed April 10, 1956, Serial No. 577,227; and in the copending application of R. S. Dean, entitled Compositions in the System Titanium-Alkalinous Metal-Chlorine, filed June 18, 1956, Serial No. 592,089, now abandoned. Dean Serial No. 592,089 discloses the cell bath and Gullett Serial No. 577,227 discloses one manner in which the cell bath may be prepared.

Accordingly, it is a general object of the present invention to provide a new method and a correlated and coordinated series of steps for practically and economically commercially producing highly pure titanium in large crystal form.

Furthermore, it is an object of the present invention to provide certain correlated and coordinated steps concerning the preparation and location of the desired metallic tianium-containing material in a cell operating with a cell bath such as disclosed in said aplications Serial Nos. 577,227 and 592,089, as well as to provide the operating

conditions for such cell and the procedure to be followed after large crystals have been formed, for the commercial production of high-purity titanium in large crystal form preferably having the structure disclosed in application Serial No. 592,543, such that the resultant high-purity titanium crystals produced may be used in place of or blended with selected titanium sponge for the production of titanium and titanium alloys.

Finally, it is an object of the present invention to solve the stated problems, to eliminate difficulties heretofore encountered in refining titanium or reclaiming highly pure titanium from metallic titanium-containing materials, generally to improve refining procedures, and to obtain the foregoing advantages and desiderata in an effective, satisfactory, economical and simple manner.

These and other objects and advantages, apparent to those skilled in the art from the following description and claim, may be obtained, the stated results achieved, and the described difficulties overcome by the methods, steps, operations and procedures and by the apparatus, combinations and arrangements which comprise the present invention, the nature of which is set forth in the following general statement, preferred procedures and examples of which—illustrative of the best modes in which applicants have contemplated applying the principles—are set forth in the following description and shown diagrammatically in the drawings, and which are particularly and distinctly pointed out and set forth in the appended claim forming part hereof.

The nature of the discoveries and improvements of the present invention in our new method for the electro-production of pure titanium may be stated in general terms as preferably including the following steps:

(1) Selecting a desired metallic titanium-containing anode material which can be readily comminuted.

(2) Preparing the selected material in desired comminuted form.

(3) Providing a cathode preferably formed of material inert with respect to the cell bath when acting as a cathode.

(4) Locating the comminuted anode material in spaced relation with respect to the cathode, for example, by surrounding the cathode with an anode material support such as a foraminous conductive anode basket.

(5) Forming the anode support of a material which is not attacked by the cell bath while in operation.

(6) Maintaining the spaced relation between the cathode and anode as close as possible while permitting a maximum volume of titanium to form at the cathode under efficient operating conditions.

(7) Providing a molten cell bath which can be maintained at selected composition by anodic solution of titanium alone at selected current densities.

(8) Providing a current density at the cathode surface of a magniude to effectively and continuously produce large crystals of titanium at the cathode without changing the cell bath composition. For example, the cathode current density may be from 100 to 2,000 amperes per sq. ft. of original cathode surface.

(9) Providing a current density at the surface of the consumable anode material of a magnitude such as to maintain the titanium concentration of the cell bath, but insufficient to bring about anodic solution of impurities. For example, the anode current density may be from a few amperes per sq. ft. up to 50 amperes per sq. ft. of consumable anode surface, depending upon the nature of impurities present in the consumable anode material.

(10) Passing direct current between anode and cathode at selected amperage to establish the optimum current density at the anode.

(11) Continuing to pass current until titanium crystals in desired amount have been formed adherent to the cathode.

(12) Separating the titanium crystals from the molten cell bath, for example, by draining the molten cell bath from the cathode and its adherent crystals, or by removing the cathode and its adherent crystals from the cell bath.

(13) Maintaining a controlled preferably inert atmosphere such as argon in the cell during cell operation and cooling the cathode and adherent titanium crystals in such controlled atmosphere.

(14) Separating the titanium crystals from plate on a cathode and from bath salts and contained fine titanium particles formed around and adherent to the cathode, for example, by breaking the crystals from the cathode and washing and screening the crystals to remove salt and titanium fines, or by washing and then breaking the crystals from the cathode.

(15) Removing anode residue from the cell.

(16) Replenishing the supply of consumable anode material and cell bath in the cell.

Certain features of our invention are illustrated diagrammatically in the drawings in which:

Fig. 1 is a portion of a ternary diagram of the system having components of Ti—O_2—(Al plus Si);

Fig. 2 is a portion of a ternary diagram of the system having components of Na—Ti—Cl, at about 850° C.; and

Fig. 3 is a diagrammatic sectional view of the operation of the improved cell.

Similar reference characters refer to similar parts throughout the drawings.

In the practice of our invention it is necessary to provide anode material which will dissolve as uniformly as possible and from which the metallic titanium content can be effectively removed by solution at the anode, leaving the impurities as anode residue. It is further important in the production of pure titanium at the cathode that the anode material be free from elements which dissolve with titanium at the anode and deposit with titanium at the cathode under the operating conditions maintained. Manganese is one element which requires carefully controlled conditions.

Copper and iron may be present in the anode up to 10%, either singly or in combination.

Nitrogen, carbon, oxygen, chromium, aluminum, vanadium, and silicon may be singly present in the anode up to 5%. It has, however, been found that presence of combinations of certain of these latter elements result in failure of the anode to dissolve properly. When oxygen is present, the amount of aluminum and silicon which can be tolerated is substantially reduced.

In Fig. 1 the cross-hatched area defines the preferred composition range or relationship in the titanium-containing anode material of the elements aluminum, silicon and oxygen with titanium for the production of a satisfactory anode.

It is necessary in the practice of our invention to supply the anode material to the cell in comminuted form, that is, broken up into pieces of desired size. Preferably, the anode material should have a size such that its specific surface available for contact with the molten cell bath is at least 1 sq. ft. per lb. of material. The anode material may be provided in comminuted form by any convenient means. One way of providing the anode material in comminuted form is to add oxygen to scrap titanium alloy material so as to make it brittle and then break up the brittle material into pieces of the desired size with a hammer, press or other suitable equipment.

Another procedure for providing the anode material in comminuted form is to melt scrap titanium alloy and pour the molten material into a bath of molten sodium chloride to granulate the titanium-containing material.

The comminuted anode material may be located in spaced relation with the cathode by surrounding the cathode with an anode material support. This support may take the form of a basket A, illustrated diagrammatically in Fig. 3, which provides electrical contact with the comminuted anode material and permits diffusion of the dissolved titanium into the portion of the cell D containing the cathode B. A simple perforated steel basket is adequate. The bottom of the basket should be imperforate so as to retain anode residue until removed, as illustrated at E in Fig. 3. A basket formed of steel is inert with respect to the cell bath when acting as an anode support. The basket A also maintains a spaced relationship between a cathode B and the consumable anode material during cell operation. Also, the basket forms a convenient receptacle to charge and establish electrical contact with anode material in comminuted form.

A steel rod or bar is satisfactory as a cathode, such material being inert with respect to the cell bath when acting as a cathode. The size or diameter of the cathode B is selected so as to provide the desired original cathode surface area immersed in the molten cell bath with respect to the total surface of the consumable anode material, such that the desired current density at anode and cathode surfaces can be maintained while permitting a maximum volume of titanium crystals to form at the cathode during cell operation. The cathode surface should be as close as possible to the surrounding anode basket to permit a high current density to be maintained at the cathode surface, yet the cathode surface must be spaced sufficiently from the surrounding anode basket to permit a maximum volume of titanium crystals to form at the cathode under efficient operating conditions while maintaining the current density of the anode surface sufficiently small as to prevent anodic solution of impurities in the consumable anode material.

We prefer to use a cell bath whose composition is described by a point within the cross-hatched area of Fig. 2, which is a portion of the ternary diagram for the system having components of Na—Ti—Cl at about 850° C. The cell bath is maintained molten at from 1500° F to 1650° F. during operation by external heating means.

A convenient method of analyzing the cell bath for control purposes is the determination of total soluble titanium by dissolving a sample of the cell bath in dilute sulphuric acid and titrating with standard dichromate. Another sample is then dissolved in acidified ferric sulphate in a fermentation tube and gas evolution noted, and ferric sulphate reduction is determined by titration with standard dichromate.

The gas evolution corresponds to sodium present, each ml. of H_2=2 mg. Na. The average valence of titanium is determined by the formula:

$$4-\frac{\text{ml. dichromate for ferric sulphate}}{\text{ml. dichromate for sulphuric acid}}$$

The composition of the cell bath of our invention is conveniently specified in terms of percent soluble total titanium, average valence of soluble titanium and percent free sodium determined by hydrogen evolution. The cell bath of our invention dissolves titanium from titanium alloys, but under suitable conditions does not dissolve the other elements present. The foraminous steel anode basket is completely unattacked in this cell bath.

Important features of our invention are the provision of a proper cell bath to provide anodic refining of the selected titanium alloy, of a cell bath to which cell bath make-up material may be readily added, of a cell bath which will not attack the basket, and of a cell bath which will produce large crystals adherent to the cathode. A suitable cell bath is disclosed in said Dean application Serial No. 592,089, and such cell bath may be prepared as disclosed in said Gullett application Serial No. 577,227.

In operation, using an anode of the composition and structure described, and a cell bath of the composition indicated, large crystals of pure titanium form at the cathode adherent thereto. Provided that the current

density on the cathode is properly selected, we believe that such current density forms an initial plate of titanium containing a small percentage of sodium on the cathode, and that a titanium-poor layer is then formed which diffuses outward from the cathode and in which large crystals of highly pure titanium are soon formed. The structure of such titanium crystal formation is disclosed in said Gullett application Serial No. 592,543.

In accordance with the invention, the highly pure titanium crystal formation at the cathode will have most of the titanium in the form of large crystals when the cathode current density is 100 to 2,000 amperes per sq. ft. of original cathode surface. In order to obtain maximum density of the titanium crystals and a maximum proportion of large crystals, we prefer to start cell operation at a low cathode current density, say, 100 amperes per sq. ft., and increase the current density regularly as the crystal formation increases in thickness so that at the end of a run the cathode current density is about 1,000 amperes per sq. ft. of original cathode surface. Under such operating conditions of cell bath and current density, the cell bath composition does not more than transiently change during cell operation.

The separation of the titanium crystals formed at the cathode from the cell bath without exposure to the air is another element of our invention. This depends on the structure of the formed titanium crystals. The structure is composed of coarse filamentary particles in bundles from which the cell bath drains readily so as to leave only 5 to 10% of the cell bath material in the form of salt, adhering to the crystals if properly drained. Not all of the crystals are filamentary but they are aggregated into filaments like rock candy grown on a string. We prefer to drain the cell bath from the cell, thus permitting complete drainage of cell bath material from around the formed titanium crystals. This may be accomplished simply by removing the cell bath material from the bottom of the cell through outlet C by introducing argon under pressure into the cell at inlet F.

The cathode B with the titanium crystals adherent thereto alternatively may be lifted from the cell, drained and removed through suitable locks. Separation of the cell bath by draining from the cell, however, has the additional advantage that any fine anode slime is also removed from the cell with the cell bath material and may conveniently be settled or filtered from the cell bath material before returning cell bath material to the cell. Cell bath make-up may be added to the cell bath material when returned to the cell.

After draining the cell, the formed crystals adhering to the cathode B are cooled therein in an argon atmosphere. Following cooling, the cell may be opened to remove the cathode and adherent titanium crystals, and at this time residue E may be removed from the basket and additional comminuted anode material may be added to the basket.

After the cathode B with titanium crystals adherent thereto is removed from the cell, the crystals may be broken away from the cathode and washed and screened to remove salt formed from the cell bath material and titanium fines, and to provide highly pure titanium in large crystal form. Alternatively, the crystals may be washed while adhering to the cathode and then broken away from the cathode.

Several examples of the operation of the improved method are given below:

EXAMPLE I

In this example titanium alloy scrap was melted in an induction furnace in a graphite crucible, provided with a loosely sealed graphite cover. The melted scrap was cast by bottom pouring into a graphite mold protected from air. The composition of the melted scrap was:

	Percent
Iron	1.5
Chromium	2.5
Oxygen	3.5
Nitrogen	1.8
Carbon	0.8

The cast ingot was brittle and was broken with a hammer into pieces which pass a two mesh screen. This product has a specific surface of about one (1) square foot per pound of consumable anode material. We placed this comminuted crude titanium alloy in a foraminous steel basket, such as disclosed in R. S. Dean's copending application, entitled Electrorefining of Metals, filed November 23, 1954, Serial No. 470,610, and illustrated in Figure 3. This basket A may hold 100 lbs. of comminuted metal per foot of depth, thereby providing 100 sq. ft. surface area of anode material per foot of depth. The immersion of the basket was 3 ft. so that the specific surface of the anode is 300 sq. ft. The cathode B in the cell Figure 3 was 12 inches in diameter so that its immersed surface was about 9 square feet. We passed a current between anode and cathode of 5,000 amperes, which is 550 amperes/sq. ft. on the cathode and 16 amperes/sq. ft. on the anode.

The cell bath used contained 5% total soluble titanium. Average valence 2.3 to ferric sulphate with sodium corresponding to 5 ml. hydrogen per gram in acidified ferric sulphate. This cell bath is disclosed in the Dean copending application, Serial No. 592,089. We prepared this cell bath as set forth in the Gullett copending application, Serial No. 577,227, namely, by reacting sodium and $TiCl_4$ at 450° C., then adding this reaction mixture to molten sodium chloride and electrolyzing at a low current density with a titanium anode until the desired composition was obtained.

Under these conditions, the titanium alloy anode dissolves at the same rate titanium is formed at the cathode. The anode residue falls to the bottom of the foraminous basket and may be removed periodically. Analysis of the anode residue showed:

	Percent
TiO_2	34.0
Fe	7.0
TiN	27.2
TiC	16.1
Cr	12.0

Balance metallic titanium and SiO_2, Al_2O_3, etc.

The structure of the cathode deposit was that disclosed in Gullett copending application, Serial No. 592,543. That is, a plate about .003 inch thick formed on the cathode, then a zone of salt and fine crystals ¼ inch thick formed on the plate, and the balance, 95.6%, was made up of filamentary particles of titanium having individual crystals .25 mm. average diameter. Crystals having an average diameter of .25 mm. and larger are termed herein large or coarse crystals. When the cell was drained by removing the molten cell bath salt through the aperture C in the bottom of the cell, the large crystal formation adherent to the cathode contained 6.2% salt and had a bulk density of 2.2.

The analysis of the coarse crystalline formation was:

	Percent
Oxygen	.004
Nitrogen	.003

Balance substantially all titanium.

The hardness of a button melted under argon from these crystals was 89 Brinell.

EXAMPLE II

In this example crude titanium was prepared from Sorel slag by magnesium copper alloy reduction and solution of the magnesium oxide in acid. This titanium was melted

in an induction furnace, cast, and comminuted as in Example I. The analysis of the comminuted anode was:

	Percent
Copper	10
Iron	6
Silicon and aluminum	2
Oxygen	2
Nitrogen	1
Carbon	1

Balance substantially titanium.

This comminuted crude titanium alloy was placed in a basket having fine perforations at the bottom through which fine anode residue could be discharged. This basket was placed in a cell having a cell bath of the composition:

	Percent
Soluble titanium	5
Average valence	2.1

Sodium corresponding to 2.4 ml. H_2 per gram.

A rotating cylinder cathode was provided above the basket as disclosed in the R. S. Dean copending application, entitled Plating Titanium and Other Metals, Serial No. 513,759, filed June 7, 1955. The cathode was so immersed as to provide a cathode current density of 1,000 amperes/sq. ft. Under these conditions the anode current density was about 50 amperes/sq. ft.

The cathode cylinder was rotated and provided with a doctor blade which removed only the outer layer of coarse crystals which formed. In this way the plate on the cathode and thin layer of fine crystals which initially formed were not disturbed. The crystals were removed from the cell and leached with dilute hydrochloric acid. The leached and dried crystals were melted in an argon atmosphere, and the button had a hardness of 85 Brinell.

EXAMPLE III

In this example we proceeded as in Example I except that the alloy to be refined was mechanically comminuted to provide chips. A smaller cell was used than in Example I, and individual baskets were spaced concentrically around the cathode.

The log of the operation in Example III follows:

Current during operation

Time from Start	Amperes	Ampere Hours	Volts	
			Closed Circuit	Open Circuit
1 hour	20	20	.25	.04
2 hours	30	30	.27	.05
3 hours	40	40	.30	.05
4 hours	50	50	.28	.00
5 hours	50	50	.27	.00
6 hours	60	60	.27	.00
7 hours	70	70	.28	.00
8 hours	80	80	.28	.00
9 hours	80	80	.25	.00
9½ hours	80	40	.25	.00
		520		

Anode specifications:
- Composition—
  - O_2—.144%
  - Cr—2.74%
  - C—.06%
  - Fe—1.34%
  - N_2—.021%
- Character—Chips, 10 lbs.
- Immersed area—3.0 sq. ft.
- Current density (avg.)—1.82 amps./sq. ft.
- Location—In perforated steel containers 3 inches from cathode in concentric circle.

Cathode specifications:
- Composition—Mild steel
- Size—¾" diameter rod
- Immersed area—18.85 sq. in.
- Current density—407 amperes/sq. in.

Cell bath:
- NaCl+5.05% soluble Ti
- Average valence of Ti to ferric sulphate 2.2
- Hydrogen evolution in ferric sulphate; 2.4 ml./gram

Temperature of operation: 850° C.

Deposit:
- Plate, .003 inch thick
- Salt layer, .015 inch thick
- Crystals, 1.0 inch thick
- Total weight of deposit, 465 grams
- Weight of large crystals, 397 grams
- Weight of salt, 58 grams
- Weight of fine crystals, 10 grams
- Density large crystal deposit, 2.2

Analysis:
- Plate, 98% Ti, 2% Na
- Fine crystals, 99.8% Ti
- Large crystals, 99.99% Ti
- Brinell hardness large crystals melted in argon 85

EXAMPLE IV

In this example a series of 10 consecutive runs like that in Example III were made. The data given below establishes that the composition of the electrolyte remains unchanged in the electrorefining, and that coarse crystals of pure titanium are obtained over a large number of consecutive operations.

The log of these runs is shown in the following table:

Run No.	Electrolyte Composition			Cathode Current Density	g.Ti per Amp. Hr.	Size of Crystals
	Sol. Ti, Percent	Ave. Valence	H_2			
1	4.2	2.5	2.2	200-800	.75	95%+10 mesh.
2	4.3	2.3	1.9	200-300	.85	¼" Avg. Dia.
3	5.0	2.2	2.2	250-700	.70	95%+10 mesh.
4	4.3	2.3	3.0	200-750	.70	Do.
5	4.4	2.2	2.4	200-750	.70	Do.
6	4.5	2.4	2.2	200-800	.70	90%+10 mesh.
7	4.4	2.3	2.5	200-600	.75	95%+10 mesh.
8	4.3	2.2	2.7	200-750	.70	Do.
9	4.4	2.3	2.4	200-750	.70	Do.
10	4.5	2.2	2.4	200-750	.70	Do.

In every case the titanium crystals analyzed more than 99.90% titanium and when melted in argon showed a hardness of less than 100 Brinell. The length of all runs was 500 ampere hours.

Accordingly, the present invention provides a new procedure and apparatus for the manufacture of highly pure titanium from metallic titanium-containing material adapted for the satisfactory and efficient commercial production of large titanium crystals analyzing more than 99.90% titanium; obtains the many new results hereinabove described; and overcomes many prior art difficulties and solves long-standing problems in the art.

In the foregoing description certain terms have been used for brevity, clearness and understanding, but no unnecessary limitations are to be implied therefrom beyond the requirements of the prior art, because such terms are utilized for descriptive purposes herein and not for the purpose of limitation and are intended to be broadly construed.

Moreover, the description of the improvements is by way of example and the scope of the present invention is not limited to exact details described, or to the particular examples set forth.

Having now described the features, discoveries and principles of the present invention, the operations, procedures, coordinated steps and controls therefor, the characteristics of the highly pure titanium produced, and the advantageous, new and useful results obtained thereby; the new and useful apparatus, methods, steps, operations, procedures, discoveries, principles, elements, com-

binations and subcombinations, and mechanical equivalenst obvious to those skilled in the art, are set forth in the appended claim.

We claim:

In an electrolytic method of producing pure titanium according to which comminuted metallic titanium-containing material having a specific surface of at least one square foot per lb. of material and containing at least one impurity selected from the group consisting of oxygen, nitrogen, carbon, iron, chromium, copper, vanadium, aluminum, and silicon, is made the anode in an electrolytic cell having a cell bath material therein consisting essentially of oxygen-free molten sodium chloride containing titanium 3–7% as dilute acid soluble titanium having an average valence of 2.0–2.5 and metallic sodium as determined by hydrogen evolution in ferric sulphate solution of 1–7 ml. H_2 per gram, said cell having a cathode inert with respect to the cell bath when acting as a cathode, the improvement which consists in locating the comminuted anode material in a steel basket having a foraminous wall thereof between the anode material and the cathode in the cell bath in spaced relation with and substantially surrounding the cathode; connecting the

conductive foraminous steel basket and the cathode with a source of direct current; and passing direct current at a current density of 100–2000 amperes per sq. ft. of original cathode surface between the comminuted anode material and the cathode to form substantially only coarse titanium crystals adherent to the cathode and to maintain the cell bath without change in composition by solution of titanium only from the comminuted anode material in electrical contact with the foraminous steel wall between the anode material and the cathode.

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