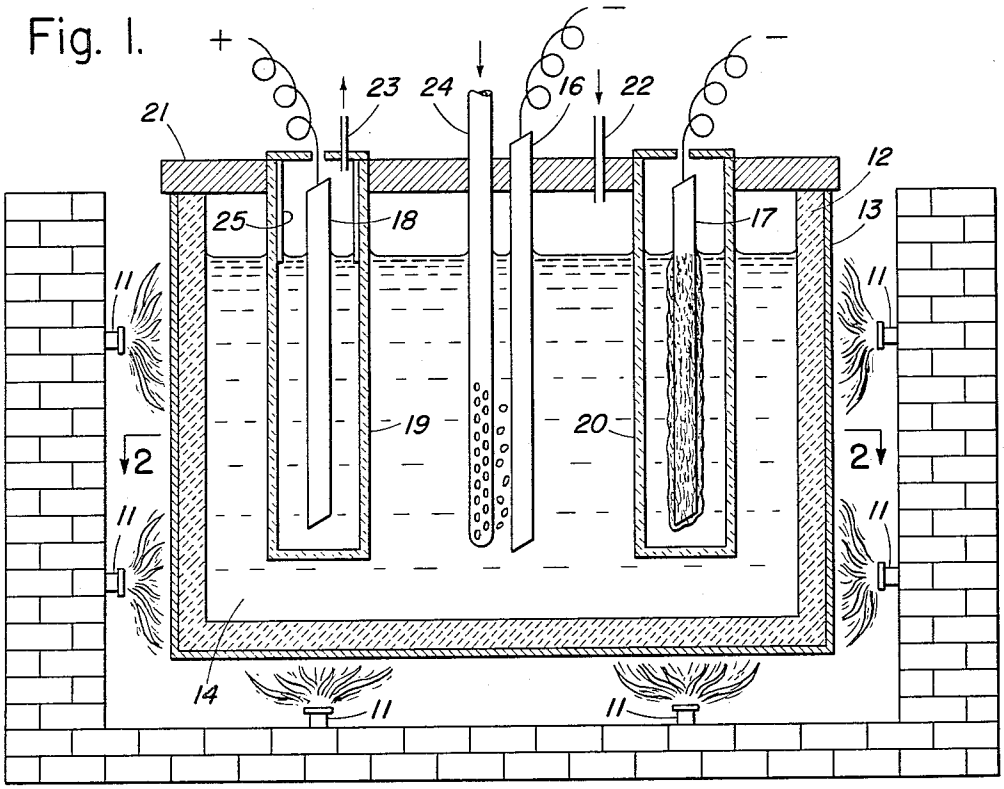
April 10, 1956 M. B. ALPERT ET AL 2,741,588

ELECTROLYTIC PRODUCTION OF TITANIUM METAL

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Fig. 1.



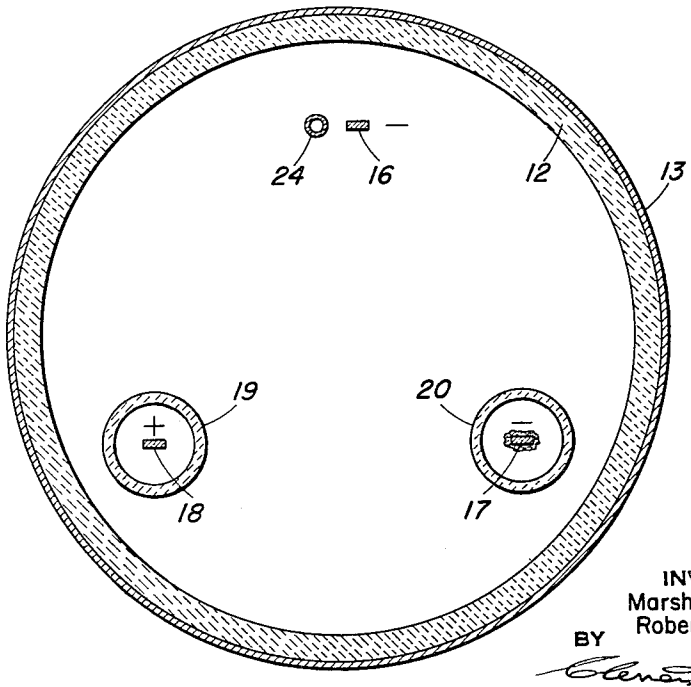


Fig. 2.

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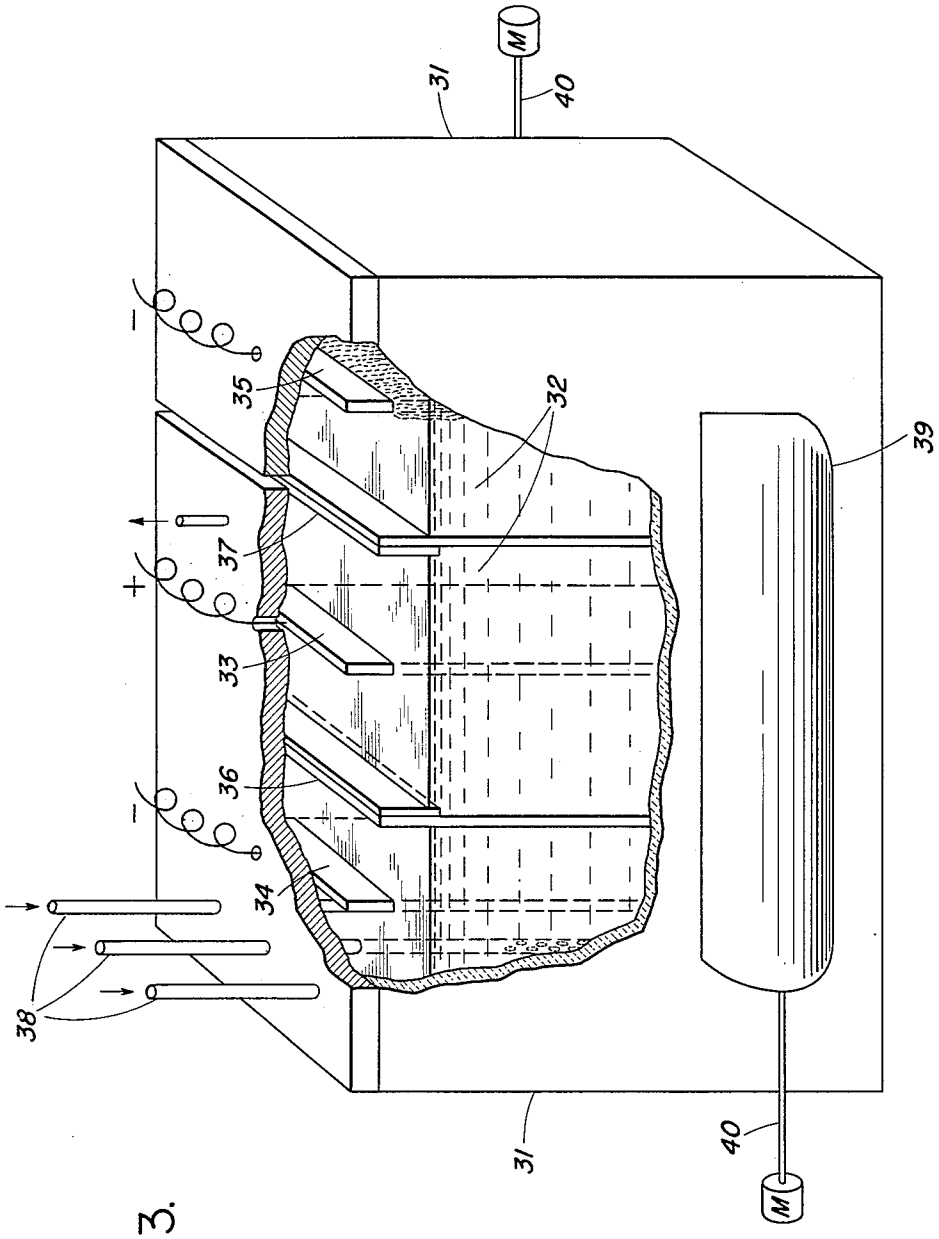


Fig. 3.

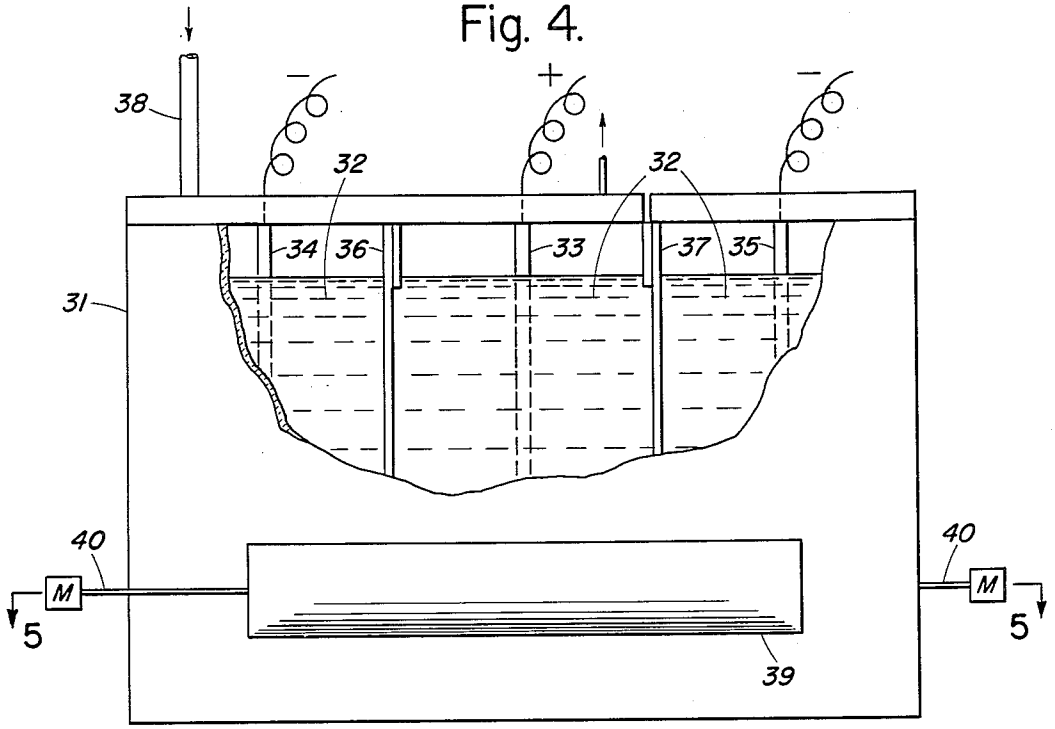
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ELECTROLYTIC PRODUCTION OF TITANIUM METAL

Filed Oct. 5, 1951 3 Sheets-Sheet 3

Fig. 4.



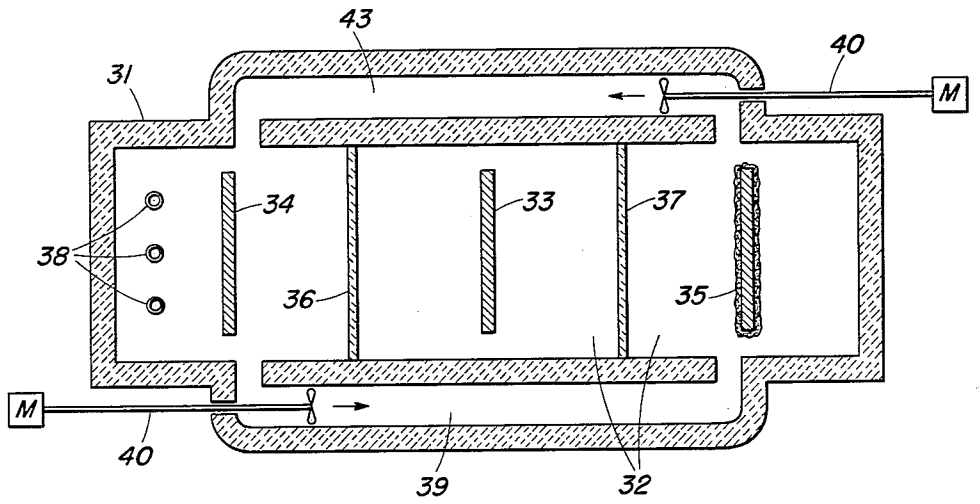


Fig. 5.

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2,741,588

ELECTROLYTIC PRODUCTION OF TITANIUM METAL

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Application October 5, 1951, Serial No. 249,958

4 Claims. (Cl. 204—64)

This invention relates to the production of titanium metal and more particularly to production of high purity ductile metal by an electrolytic method. More specifically, it relates to an electrolytic method for producing titanium metal of high purity from titanium tetrachloride.

Titanium metal has heretofore been reduced from a salt, for instance the tetrachloride, by direct chemical reduction employing a metallic sodium or metallic magnesium reducing agent. Such methods are described in the literature, for instance the Hunter Process in Journal of The American Chemical Society, volume 32, page 330 et seq. in 1910, and the Kroll Process in U. S. Patent No. 2,205,854. While these methods have produced metallic titanium, they suffer from a fundamental economic disadvantage in that the cost of the metallic sodium or metallic magnesium is relatively high and the processes are expensive to operate. Actually the reducing agent must generally itself be first reduced to metallic form by an electrolytic process from either an oxide or a chloride and this in turn used for reduction of titanium tetrachloride. The total processing cost is therefore considerably greater than if the titanium itself were reduced electrolytically from a titanium salt.

Titanium tetrachloride is a non-conductor and cannot be electrolyzed. Therefore the use of a suitable electrolytic medium is necessary. The electrolysis of aqueous solutions of titanium tetrachloride has to date produced only thin films of impure titanium metal on the cathode and has been very unsatisfactory. The use of a molten salt electrolyte has been considered but titanium tetrachloride of itself is not soluble in such a medium. According to the present invention however, the titanium tetrachloride is easily converted electrolytically to reduced titanium chlorides which are soluble in the molten salt electrolyte. These reduced chlorides include titanium dichloride and titanium trichloride. It has further been found that these reduced titanium chlorides may be readily reduced by electrolysis to titanium metal. In this way it is possible to produce titanium metal by a continuous electrolytic process.

It is a principal object of this invention to provide a method whereby titanium metal of high purity may be produced electrolytically. A further object of this invention is to provide a method for electrolytic production of titanium metal in convenient form for re-melting. A further object is to provide an economical direct method for electrolysis of titanium tetrachloride. A still further object is to provide a process which may be employed for continuous production of titanium metal. These and other objects will become apparent from the following more complete description of this invention.

This invention in its broadest aspects contemplates a method for electrolytically producing titanium metal which comprises providing a fused salt electrolyte in an electrolytic cell having an anode and two cathodes. For convenience the two cathodes are referred to as the solubilization cathode and the deposition cathode. By the term "solubilization cathode" we mean a cathode which is placed in the vicinity where titanium tetrachloride is introduced into the cell and solubilized by cathodic reduction to a reduced titanium chloride such as $TiCl_2$ or $TiCl_3$. By the term "deposition cathode" is meant a cathode upon the surface of which titanium chlorides, such as $TiCl_4$, $TiCl_3$, or $TiCl_2$, are reduced and deposited as metallic titanium. Titanium tetrachloride is introduced into said electrolyte in proximity to the solubilization cathode. Meanwhile electric current is passed between each of said cathodes and said anode, the amount of current added to said cathodes being from 1 to 2 faradays at the solubilization cathode and from 2 to 3 faradays at the deposition cathode for each mol of titanium tetrachloride introduced. The titanium tetrachloride introduced into said electrolyte in proximity to the solubilization cathode is reduced and solubilized to titanium trichloride and titanium dichloride.

Means are provided in the cell for separating the gaseous product, e. g. chlorine, released at the anode from contact with either of said cathodes and for preventing contact of the titanium dichloride and trichloride with the anode. For convenience a porous diaphragm may be employed in the salt bath, with a non-porous gas barrier extending upward from the bath surface. The so-formed reduced titanium chlorides solubilized in the fused salt electrolyte are transferred through the electrolyte and are reduced to metal and deposited as titanium metal on the deposition cathode. The entire process should be carried out for efficient results so that the titanium salts dissolved in the electrolyte are preferably maintained within the molality limits of no greater than 2.0 for titanium trichloride and no less than 0.05 for titanium dichloride in proximity to the deposition cathode.

In the instant process titanium tetrachloride is preferably bubbled into an electrolytic cell in proximity to the solubilization cathode and it is reduced substantially to titanium dichloride by passing 1.7–2.0 faradays of electricity through the solubilization cathode simultaneously with the addition of each mol of $TiCl_4$. The titanium values solubilized in the fused salt bath according to this preferred procedure are present mostly as titanium dichloride although a small amount of titanium trichloride is also formed. The soluble titanium values formed by the solubilization cathode are then transferred through the electrolyte to the deposition cathode where they are reduced to titanium metal and are deposited as metal on the deposition cathode by simultaneously passing a current of 2.0–2.3 faradays through the deposition cathode.

It has further been discovered according to the process of the instant invention that the character of the metal produced, particularly the purity of the metal, is affected by the concentrations of the titanium dichloride and the titanium trichloride present in proximity to the deposition cathode. In order to produce titanium metal of a type suitable for commercial use it is necessary that the concentrations of both titanium dichloride and titanium trichloride be held within certain limits in the electrolyte during the process of this invention. It has been found that titanium metal of high purity may be obtained if the molality of the titanium trichloride is no greater than 2.0 and the molality of the titanium dichloride is no less than 0.05 in proximity to the deposition cathode. When the electrolytic process is carried out within these limits titanium metal may be produced which has a Brinell hardness of less than 450. For producing metal of extremely high purity it is desirable to maintain the molality of the titanium trichloride no greater than 0.25 times the molality of titanium dichloride and the molality of titanium dichloride no less than 0.1 in proximity to the deposition cathode. It is also usually advantageous to maintain the molality of titanium dichloride no greater than 2.0 adjacent to the deposition cathode. Metal produced by the instant process under conditions which fall within these

preferred concentration ranges will be ductile, coarse-grained metal which possesses a Brinell hardness of less than 200. Such metal is extremely valuable for fabrication into sheets, rods, and the like. It is not necessary to maintain such critical limits of concentrations of both titanium dichloride and titanium trichloride in proximity to the solubilization cathode. It is, however, desirable to maintain the molality of the titanium dichloride no less than 0.1 in proximity to the solubilization cathode, and it is desirable to maintain a current density in amperes per square centimeter on the solubilization cathode no more than the numerical molality of the titanium trichloride.

It has been found that when higher concentrations of titanium values in the salt melt are present in the vicinity of the solubilization cathode, current may be passed through at an increased rate and the capacity of the cell thereby improved. It has been found quite convenient to operate at a titanium dichloride molality of about 10. Besides increasing the capacity of the cell, the higher current densities are advantageous in another way, that is, they have the effect of heating the cell, and if the cell is sufficiently large and the current density sufficiently high, no other means for supplying heat need be used.

It is not difficult to maintain the concentrations of both titanium dichloride and titanium trichloride within the limitations given above. It is, of course, possible to choose and maintain a salt bath composition which meets the limitations both for electrolyte in proximity with the solubilization cathode and for electrolyte in proximity with the deposition cathode. It is often desirable from an operational standpoint, however, to operate in such a manner that the electrolyte in the vicinity of the solubilization cathode is of a different concentration with respect to the reduced titanium values than the electrolyte near the deposition cathode. This may be accomplished in many ways. One such method which has been proven to be satisfactory is to divide the cell into two sections, each section having a cathode. It is convenient to place a porous diaphragm as the boundary between the two sections. In this type of cell construction, the soluble titanium values formed at the solubilization cathode pass through the diaphragm and are reduced to titanium metal and deposited on the deposition cathode in the second chamber. The action of the diaphragm will cause the concentration of the titanium values in the second chamber to be maintained considerably lower than the concentration of titanium values in the first chamber. Another method of obtaining the desirable differential between the titanium concentrations in proximity to the two cathodes is to provide a solid wall between the two cathodes to form two separate chambers and to pump a small portion of the solution from the solubilization cathode chamber into the second chamber containing the deposition cathode. Another type of apparatus which may also be employed provides a single chamber containing both cathodes but having the cathodes spaced at a considerable distance from one another so that the diffusion of titanium values formed at the solubilization cathode is slow enough to provide a low concentration of titanium values at the deposition cathodes.

In order to define more clearly the process of the instant invention the following drawings are presented in which

Fig. 1 shows a vertical cross section of an electrolytic cell in which titanium metal may be produced continuously,

Fig. 2, a horizontal cross section of the cell shown in Fig. 1 cut across line 2—2,

Fig. 3, a perspective view of another type of electrolytic cell partially cut out.

Fig. 4, a front view of the cell shown in Fig. 3 partially cut out, and

Fig. 5, a cross section of the cell shown in Fig. 4 cut along line 5—5.

Referring now to Fig. 1 an electrolytic cell is placed in a suitable furnace which is provided with heating means such as gas burners **11**. Disposed within the heated zone is cell container **12** which is made from corrosion-resistant material such as fused impervious silica and preferably protected externally by a metallic sheath **13**, for instance of stainless steel or other metal resistant to the heat effects involved. The cell container **12** is filled, or partially filled with electrolyte **14** in which are suspended cathodes **16** and **17** which may preferably comprise elongated plates of a noble metal such as tantalum. Cathode **16** is the solubilization cathode while **17** is the deposition cathode. The anode **18** may be formed of graphite rods, and is also submerged in the electrolyte. The cathodes are separated from the anode by a porous diaphragm **19**, which surrounds the immersed portion of the anode **18** to form an anode compartment.

In this particular design an additional porous diaphragm **20** surrounds the deposition cathode **17**. Cover **21** is provided to enclose the top of the cell and contains means **22** for admission of inert gas, such as argon or helium to protect the surface of the molten electrolyte. The space above the anode compartment is provided with means **23** as pipes for carrying off the chlorine released at the anode. Titanium tetrachloride is added preferably through tube **24** which terminates in the cell at a point near solubilization cathode **16**. The upper portion of the diaphragm **19** which extends above the surface of the electrolyte may be constructed of non-porous material, e. g. an impervious sleeve **25** which will act as a non-porous top section on the diaphragm if desired in order to insure complete separation of the chlorine gas evolved during the entire electrolytic process.

Fig. 2 illustrates a horizontal cross section of the cell shown in Fig. 1 cut along line 2—2.

In operating this cell the titanium tetrachloride is substantially completely reduced to titanium dichloride at cathode **16**. The titanium values produced pass through the second mentioned porous diaphragm **20** and are reduced and deposited as titanium metal on deposition cathode **17**.

Another type of cell which may also be used with equal efficiency is the type shown in Fig. 3. In this type of cell the cell container **31** is also placed in a gas furnace. The electrolyte **32** is placed in the container and anode **33** and two cathodes **34** and **35** are submerged in the electrolyte. Cathode **34** is the solubilization cathode while cathode **35** is the deposition cathode. The anode is preferably placed between the two cathodes. In order to separate the anode from the two cathodes, porous diaphragms **36** and **37** are inserted. In operating this cell titanium tetrachloride is introduced through tubes **38** which terminate near the solubilization cathode **34**. The melt containing the titanium values formed by cathode **34** is pumped through passageway **39** by pump **40** from the chamber surrounding cathode **34** into the chamber surrounding deposition cathode **35**. The titanium values arre reduced in the second chamber and deposited as titanium metal on deposition cathode **35**. The solution partly depleted of titanium values in the second chamber is pumped back into the first mentioned cathode chamber.

Fig. 4 is a front view of the same cell shown in Fig. 3, and is given to supplement the description of Fig. 3.

Fig. 5 is a horizontal cross-section of the cell shown in Figs. 3 and 4, taken along the line 5—5 of Fig. 4, and shows in addition to the features illustrated in Figs. 3 and 4, pump **42** and passageway **43** by means of which the solution depleted of titanium values is pumped back from the chamber surrounding deposition cathode **35** into the chamber surrounding solubilization cathode **34**.

The type of electrolyte used in carrying out the process of this invention must be chosen to accomplish certain desired effects. The constituents of the electrolyte should be selected with a view to melting temperature, corrosive effects, compatability and appropriate electrical character-

istics. The electrolyte may comprise metal halides or mixtures thereof; and it is preferred to employ the halides of the alkali metals and alkaline earth metals including magnesium and preferably the chlorides of such metals. Mixtures which form low melting point eutectics are decidedly advantageous. One such mixture of alkali metal and alkaline earth metal chlorides which has been particularly satisfactory in view of the low melting point eutectic is a mixture of strontium chloride and sodium chloride. It is particularly advantageous to employ a mixture of 73 parts of strontium chloride and 27 parts of sodium chloride by weight. Such a mixture has a melting point of about 560° C. and in addition appears to affect beneficially the character of the deposited titanium metal.

The diaphragms used in the cell may be constructed of any porous electrically non-conductive material which will withstand the temperature and corrosiveness of the salt bath and will permit the flow of ions but retard convectional mixing of different portions of the melt. Satisfactory results have been obtained by the use of a sintered alumina porous diaphragm. Diaphragms which are capable of passing particles of a maximum size between one micron and 20 microns in aqueous media have been particularly successfully employed in the electrolytic process.

In order to accomplish the production of titanium metal on a continuous basis, it is desirable to add current of about 2 faradays per mol of titanium tetrachloride introduced to each of the cathodes employed in the cell by distributing the total of 4 faradays per mol of titanium tetrachloride introduced about evenly between the two cathodes, i. e. about 2 faradays to each cathode. To avoid reduction of a portion of the titanium tetrachloride all the way to metallic titanium in the solubilization cathode chamber which is ordinarily undesirable, it is preferred to maintain a small amount of titanium trichloride in the salt mixture in this chamber, i. e. to add slightly less than two faradays on the solubilization cathode per mol of titanium tetrachloride introduced. In actual practice, however, small losses of current efficiency generally result in the retention of a small amount of titanium trichloride in the melt even when exactly 2 faradays are added through the solubilization cathode for each mol of titanium tetrachloride introduced.

In some cases, depending upon the manner in which the cell is operated, minor proportions of the titanium tetrachloride introduced may be reduced to metallic titanium at the solubilization cathode, or else small amounts of titanium trichloride or dichloride may find their way into the anode compartment. Infiltration of traces of air may cause some of the reduced titanium values in the cell to be partially reoxidized. And finally, a small portion of the salt melt containing some titanium dichloride and trichloride values adheres to the deposition cathode as it is withdrawn from the cell. Any of these eventualities will obviously cause the total amount of current fed through the solubilization cathode to exceed that which would otherwise be expected for a given qantity of titanium produced at the deposition cathode. Reduction of titanium tetrachloride through titanium trichloride and titanium dichloride down to titanium metal may be accomplished in a rapid manner by maintaining the concentrations of titanium dichloride and titanium trichloride within the above-mentioned specified limits.

In order to illustrate more fully the instant invention the following examples are presented:

Example I

A mixture of 7300 grams of strontium chloride and 2700 grams of sodium chloride was put into a cell of the general type shown in Fig. 1, except that porous diaphragm **20** surrounded introduction cathode **16** instead of deposition cathode **17**. The mixture was heated externally by gas flame to 750° C. Titanium tetrachloride was introduced at the rate of 177 grams per hour into the cell through a tube which terminates in the cell at a point near the solubilization cathode. Simultaneously during such addition, a current was supplied to this cathode at the rate of 50 amperes. Addition of titanium tetrachloride and passage of current through the solubilization cathode was continued until analysis of the salt melt adjacent to the deposition cathode showed the molality of titanium dichloride to be 0.5, and that of titanium trichloride to be 0.1. The salt melt in the solubilization cathode chamber was also analyzed at the same time and the molality of titanium dichloride in that chamber was found to be 5.0, while the molality of titanium trichloride was 1.0. Current was then passed through the deposition cathode for 12 hours at an average rate of 45 amperes, during which time titanium tetrachloride addition and current supply through the solubilization cathode were continued at the same rate as before. The circuits through both cathodes were completed through the common anode. A total of 2,124 grams of titanium tetrachloride were added at a rate of 177 grams per hour during this 12 hour period. The system was kept under an argon atmosphere by adding a stream of argon over the electrolyte in the solubilization cathode chamber.

Chlorine was evolved from the anode at a rate of 125 grams per hour and a total of 1500 grams of chlorine was collected and condensed. Titanium metal was deposited on the deposition cathode, in the form of coarse adherent crystals. The depositing cathode was removed from the bath at intervals of 1 hour and replaced by a fresh cathode. The cathode removed from the bath was cooled under an atmosphere of argon and the adhering salts were leached out of the deposit with cold dilute hydrochloric acid. The deposit of titanium metal was then scraped off the cathode, water washed, dried and weighed. 425 grams of titanium metal were recovered over a period of 12 hours corresponding to a yield of about 80% of the theoretical quantity based on the amount of titanium tetrachloride added during the 12 hour period. At the end of the 12 hour period the concentration of titanium dichloride and titanium trichloride in both cathode chambers were substantially the same as at the start of the 12 hours. These titanium values were allowed to remain in the cell and were eventually deposited in subsequent operation.

The molality of the titanium dichloride adjacent to the deposition cathode was held between 0.5 and 1.5, while the molality of the titanium trichloride was held between 0.1 and 0.3 during the entire run. The molality of titanium dichloride adjacent to the solubilization cathode was held from 5.0 to 10.0 while the molality of the titanium trichloride adjacent to the solubilization cathode was held form 1.0 to 2.0. The current density on the solubilization cathode was 0.5 ampere per cm.^{2}. The titanium metal recovered was coarse-grained and substantially pure. After melting down to form an ingot it possessed a Brinell hardness of 180. This product possessed sufficient purity and ductility for commercial fabrication into rods, sheets and other fabricated products.

Example II

A mixture of 730 kg. of strontium chloride and 270 kg. of sodium chloride was put into a cell of the type shown in Figure 3 and the mixture was heated to 750° C. by an alternating current voltage applied across auxiliary heating electrodes (not shown in the figure). Titanium tetrachloride was then introduced at the rate of 0.4 kg. per hour into the cell through tubes terminating near the solubilization cathode. While the titanium tetrachloride was being added, current was supplied to the solubilization cathode at the rate of 115 amperes until the concentration of the titanium dichloride in the electrolyte was 0.32 molal, at which time the concentration of titanium trichloride was found to be 0.24 molal. Current was then supplied through the deposition cathode at an average rate of 176 amperes and was continued for 24 hours. During the 24 hour period 9.6 kg. of titanium tetrachloride were added

near the solubilization cathode at the same rate as before, viz. 0.4 kg. per hour, and current was supplied through the solubilization cathode continuously at a rate of 114 amperes. This corresponds to a current density of 0.15 ampere per cm.^{2} at the solubilization cathode, and 0.55 ampere per cm.^{2} at the deposition cathode. Both circuits were completed through the common central anode.

Throughout the addition period electrolyte was pumped from the solubilization cathode chamber to the deposition cathode chamber at a rate of 100 kg. per minute and returned from the deposition cathode chamber to the solubilization cathode chamber at substantially the same rate. The concentration of titanium dichloride in the solubilization cathode chamber was 0.32 molal, and the concentration of titanium trichloride 0.24 molal. The system was protected from the atmosphere throughout the run by maintaining a helium atmosphere over the surface of the salt bath.

Chlorine was evolved from the anode at a rate of 0.30 kg. per hour and was collected. The deposition cathode carrying the titanium metal deposit was removed from the bath at 1 hr. intervals and replaced. The deposit was cooled in an inert atmosphere, leached, scraped off the cathode, water washed and weighed as in Example I.

Over the 24 hour period of operation, 1.9 kg. of titanium metal were recovered, corresponding to about 80% of the theoretical yield based on the amount of titanium tetrachloride added during that period. The concentration of titanium values in the salt melt was substantially the same as at the start of the 24 hour period, and the dissolved titanium values were subsequently deposited in another cycle. The metal produced was substantially pure and sufficiently ductile for commercial fabrication.

As has been shown by the foregoing description and examples the present invention provides a method whereby titanium metal of high purity and ductility may be produced electrolytically. Moreover, it provides an economical method for producing titanium metal directly from titanium tetrachloride. Furthermore, it provides a method whereby titanium metal can be produced continuously on a commercial scale.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

We claim:

1. A method for electrolytically producing titanium metal in an electrolytic cell having a fused salt electrolyte selected from the group consisting of alkali metal halides, alkaline earth metal halides, magnesium halides and mixtures thereof, a non-consumable anode, a solubilization cathode and a deposition cathode, and separating means for separating a product released at the anode from contact with said cathodes, comprising: introducing titanium tetrachloride into said electrolyte in proximity to said solubilization cathode, meanwhile passing electric current between each of said cathodes and said anode, the amount of current added through each cathode being from 1 to 2 faradays at the solubilization cathode and from 2 to 3 faradays at the deposition cathode for each mole of titanium tetrachloride introduced, to produce titanium dichloride and titanium trichloride in proximity to the solubilization cathode, transferring the so-formed titanium dichloride and titanium trichloride to said deposition cathode and depositing titanium metal on said deposition cathode while releasing chlorine at said anode, and maintaining the molality of the titanium trichloride no greater than 2.0 and the molality of titanium dichloride no less than 0.05 in proximity to the deposition cathode.

2. Method according to claim 1 in which the molality of titanium trichloride is no greater than 0.25 times the molality of titanium dichloride and the molality of titanium dichloride is no less than 0.1 in proximity to the deposition cathode.

3. Method according to claim 1 in which the molality of the titanium values is no less than 0.1 in proximity to the solubilization cathode and the current density in amperes per square centimeter on said solubilization cathode is no more than the numerical molality of the titanium trichloride.

4. Method according to claim 3 in which the current density of the solubilization cathode is no greater than 2 amperes per square centimeter.

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