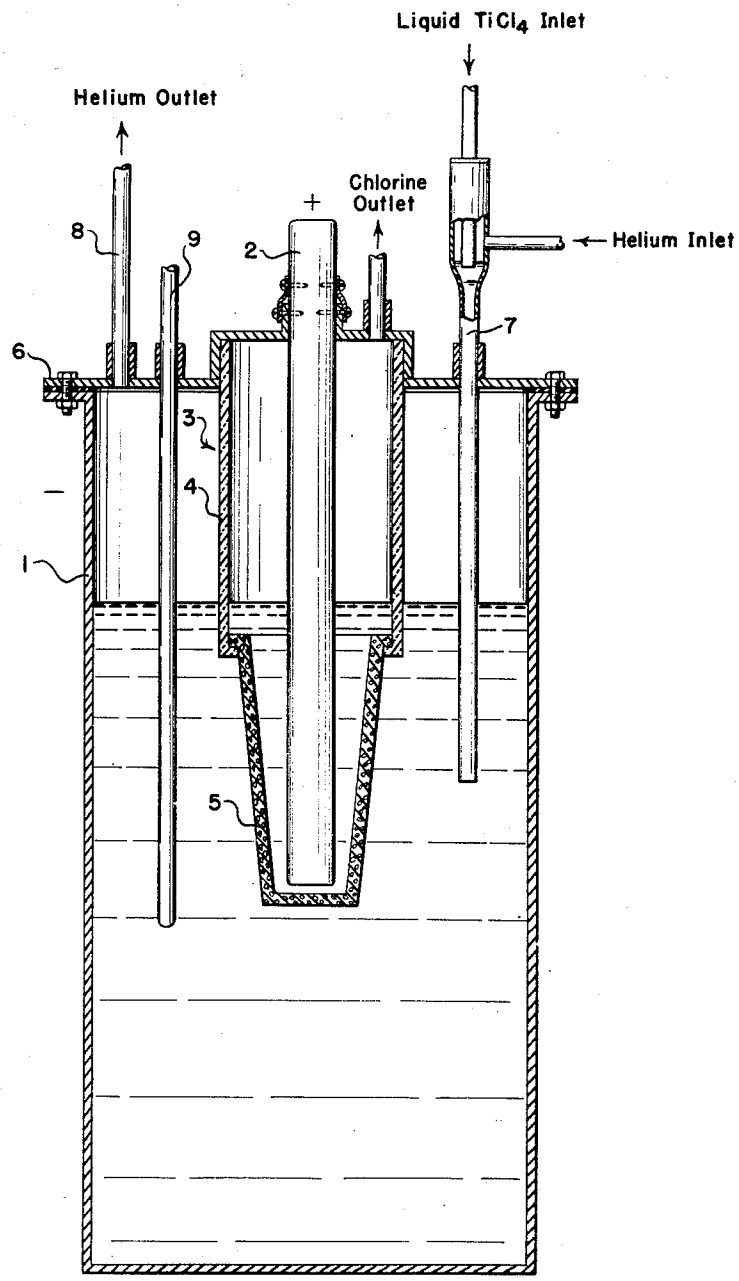
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PRODUCTION OF METALLIC TITANIUM

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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 the production of metallic titanium directly from titanium tetrachloride by electrolysis in a fused salt bath.

Careful study of attempts to produce the metal by introducing a titanium tetrahalide into a fused salt bath have demonstrated that fused baths, and particularly fused alkali metal halides and alkaline earth metal halides, and mixtures thereof, have a low capacity for holding titanium tetrahalides in solution. Thus, it has been repeatedly observed that the introduction of titanium tetrachloride into a fused halide salt bath is accompanied by the prompt emission of the titanium tetrachloride from the salt bath and into the atmosphere thereabove. As a result, it has been considered impossible heretofore to cause the fused salt bath to retain a sufficient quantity of titanium tetrachloride to effectuate the electrolytic decomposition of the titanium halide to form the metal.

It has been established that titanous chlorides, that is, titanium chlorides in which the titanium has a valence of less than four, are appreciably soluble in fused baths of alkali metal halides and alkaline earth metal halides. Moreover, it has been found that when such a lower halide of titanium is dissolved in a fused halide bath, electrolysis of the resulting fused bath leads to the formation of metallic titanium. However, the inconvenience and expense entailed in reducing titanium tetrahalide to the desired lower halides outside the cell has made it clear that such a process leaves much to be desired from the commercial point of view.

In the course of an attempt to ascertain whether prolonged delivery of titanium tetrachloride into a fused halide salt bath would ultimately build up a significant titanium component in the bath, we have discovered that the persistent introduction of titanium tetrachloride into a water-clear fused bath of lithium, sodium and potassium chlorides produced a yellow coloration in the upper portion of the bath which, after continued accumulation, we found to be due to the apparent formation of a potassium chloride-titanium chloride complex. We have further found that when a voltage was applied to the resulting cell bath, while maintaining the introduction of titanium tetrachloride thereinto, a noticeable increase in the electrical conductivity of the bath gradually developed with time. Upon continued introduction of titanium tetrachloride into the bath, along with continued electrolysis, the bath developed a green color apparently associated with titanium in a trivalent state in a fused salt bath (this green color resembling that of an aqueous solution of nickel chloride) and the current flowing between the electrodes in the salt bath gradually increased with the resulting production of metallic titanium at the cathode of the fused bath cell. Subsequent investigations have demonstrated that this phenomenon is not limited to the specific halide bath used in the initial experiments and that other complexes may function in substantially the same way as the potassium chloride-

titanium chloride complex so as to establish a trivalent titanium chloride content in the bath. Further than this, it has subsequently been found that regardless of the source of trivalent titanium in the fused salt bath, that is, whether the trivalent titanium is produced in situ as described hereinbefore or is introduced into the bath from an extraneous source, and regardless of whether trivalent titanium chloride, titanium dichloride, or some other chloride of titanium having a valence of less than four is introduced into the diluent salt bath, the conditioning of the bath by this establishment of a lower valence titanium or "titanous" component therein makes it possible for the bath to assimilate titanium tetrachloride introduced thereinto.

Accordingly, the method of the present invention for producing metallic titanium from titanium tetrachloride by subjecting a titanium chloride to electrolyzing conditions in a fused diluent salt bath consisting essentially of at least one halide of a metal of the group consisting of the alkali metals and alkaline earth metals comprises establishing in the fused diluent salt bath a concentration of titanous chloride at least sufficient to impart a green color to the translucence of the bath during electrolysis thereof, and electrolyzing the resulting fused salt bath while maintaining the titanium chloride content of the bath substantially exclusively by introducing substantially oxygen-free titanium tetrachloride thereinto. Once the bath has been conditioned as aforesaid by the development of the green color attributable to trivalent titanium ions, electrolysis of the bath or the introduction of the titanium tetrachloride thereinto may be stopped and started at will without further conditioning, and the metallic titanium will be obtained in a useful form.

Although emphasis has been placed heretofore on the desirability of obtaining the metallic titanium in the form of a dense adherent deposit on the cell cathode, we have found that the titanium deposit is equally amenable to recovery if it is obtained as a substantially non-adherent loose deposit of metallic particles which will settle readily to the bottom of the cell. Such in fact is the character of the metallic titanium obtained in the practice of the method of our invention. Thus, we have found that when the metallic titanium is deposited from the fused salt bath characterized by the aforementioned green color of trivalent titanium, titanium metal collects on the cathode as discrete and loosely adhering particles which either fall of their own accord to the bottom of the bath or can be made to do so by simple mechanical jolting, tapping or scraping of the cathode.

Although there is no uncertainty with respect to the fact that metallic titanium is produced pursuant to the method of our invention, some of the metal may be produced by a combination of electrochemical and chemical means. For example, titanium dichloride is known to disproportionate into titanium metal and titanium tetrachloride to an extent especially dependent upon temperature. There is a possibility that titanium dichloride, produced by electrochemical means may thus produce some metallic titanium by chemical means. Inasmuch as electrolysis takes place within the cell in a manner consistent with conventional fused salt electrolysis procedure and inasmuch as the metal is deposited directly on the cathode, it appears that metal is deposited by electrolytic reduction directly from a titanous chloride to titanium metal. However, it has sometimes been observed that small amounts of metallic titanium are deposited on surfaces within the cell which are electrically insulated from the anode and cathode. For example, we have observed thin deposits of titanium metal on glass tubes and metal parts inserted into the fused bath. Although production of metallic titanium by direct electrolytic reduction and

production of metallic titanium by disproportionation are wholly different mechanisms, they are compatible mechanisms to the extent that both may function in the same cell at the same time. Careful analysis of all conditions prevailing in the practice of our invention leads us to believe that chemical reactions may play a part in the production of metallic titanium pursuant to the process of our present invention.

It will be appreciated, accordingly, that pursuant to the method of our invention metallic titanium is produced in a form in which it collects in the bottom of the fused bath whence it can be withdrawn without removing the cathode from the cell or in any other way interfering with normal cell operation. The diluent salt or salts entrained in the removed metal may be separated therefrom by any suitable means such as heating, preferably under reduced pressure, to a temperature at which the entrained salts will volatilize and be driven off from the metal. The resulting metal product, which analyses better than 99% titanium, is amenable to melting down to massive form by conventional technique such as an electric arc in an inert atmosphere. The massive metal has been found to be of sufficient purity to have the ductility required for rolling and other forming operations.

The diluent salt bath which is used in practicing the invention comprises, as indicated hereinbefore, one or more of the halides of the alkali metals and alkaline earth metals. Thus, the chlorides, bromides, iodides and fluorides of sodium, potassium and lithium as well as the same halides of calcium, magnesium, barium and strontium may be used with advantage. However, in the interest of simplifying the recovery of the halogen which is liberated at the anode during electrolysis, we presently prefer to use only the chlorides of these metals in making up the diluent salt bath when electrolyzing a titanium chloride. Although an individual halide may be used as a single constituent bath, it is preferred to use a combination of these halides inasmuch as such combinations are characterized by relatively lower melting points than the individual salts. We have found it particularly advantageous, when using a combination of the aforementioned halides, to mix these halides in proportions approximating a eutectic composition. For example, we have used with particularly satisfactory results a eutectic mixture composed of 5 mol percent of sodium chloride, 40 mol percent of potassium chloride and 55 mol percent of lithium chloride, the mixture having a reported melting point of 372° C. but actually melting according to our own observations at a temperature of about 345° C. Another useful eutectic mixture, composed of an alkali metal chloride and an alkaline earth metal chloride, is represented by the eutectic mixture composed of 48.5 mol percent of sodium chloride and 51.5 mol percent of calcium chloride having a melting point of 505° C.

The aforementioned halide salt bath is maintained in a conventional type of fused bath cell wherein means are provided for confining to a limited region adjacent the anode the halogen gas which is liberated at the anode. While this result may be achieved by a baffle surrounding the anode, we have obtained particularly satisfactory results in a compartmented cell in which the anode and cathode compartments are separated by a baffle the lower portion of which is closed by a porous diaphragm of conventional structure and composition.

It will be understood, of course, that after appreciable operation of the cell any water contained in the salt bath will have been removed by electrolysis. However, because of the particularly detrimental effect of oxygen-containing compounds on metallic titanium produced at temperatures even as high as those prevailing in a fused salt bath, we have found it advisable to minify the water-content of the bath before the titanium tetrachloride is introduced thereinto. This dehydration of the bath can be facilitated by numerous techniques including the passage of a dry inert gas such as helium through the fused bath or by passing dry hydrogen chloride through the bath, or by electrolyzing the salt in the cell prior to establishing any significant titanium component therein. We have found, however, that the most effective means of lowering the moisture content of the bath to an unobjectionable value comprises a combination of these techniques, preferably using the electrolysis step last. In practicing the electrolysis step, we have found that by applying voltage across the cell electrodes and by continuing electrolysis of the halide salt bath until the cell current has been decreased to at least about one-tenth of its initial value, the moisture content of the bath will have been reduced to a value at which it has no significant effect upon operation of the cell and little detrimental effect on the quality of the metallic titanium obtained in the practice of the method of the invention.

The absence of moisture, oxygen and nitrogen from the cell bath during operation may be readily assured by maintaining an atmosphere adjacent the surface of the salt bath which, exclusive of any contained titanium tetrachloride, is inert with respect to the cell contents. Helium, argon and other gases which are inert with respect to metallic titanium and its halides at temperatures of the order of those prevailing in the fused salt bath are readily available and are used with advantage in the practice of our invention. The gas may be supplied to provide this inert atmosphere simply by delivering a steady stream of the gas to that portion of the cell immediately above the salt bath. Where the inert gas is further used as a carrier and diluent for the titanium tetrachloride introduced into the bath, the inert gas stream may be directed, as discussed further herein, either into that portion of the cell immediately above the surface of the salt bath or it may be introduced into the cell below the surface of the bath.

The titanium tetrachloride supplied to the cell bath should also be free of oxygen-containing constituents. Such constituents would ordinarily be provided by any moisture contained in the titanium tetrachloride, the halide being hydrolyzed by this moisture to form titanium oxychlorides or hydrous titanium oxide, or both. Purification of the titanium tetrachloride by conventional distillation technique will insure the absence from the titanium tetrachloride not only of moisture itself but of other oxygen-containing contaminants. Of course, when pure titanium metal is desired, the titanium tetrachloride should be free from metallic impurities.

As pointed out hereinbefore, the method of our invention is not limited to any specific means for establishing the desired lower valence titanium content of the bath, it being understood that the expressions "lower valence titanium" and "titanous" chlorides are used herein and in the claims to include any titanium chloride in which the titanium has a valence of less than four. For example, the titanous chloride content of the bath may be established by continuously introducing the titanium tetrachloride in vapor form, and advantageously carried by the aforementioned diluent inert gas, while maintaining an impressed voltage across the cell electrodes of a magnitude either below or above the decomposition voltage of one or more components of the halide salt bath but sufficient to effect the aforementioned reduction of the titanium tetrachloride to titanous chloride. This procedure has been found to be facilitated by the presence in the bath of potassium chloride which appears to form a double chloride with the titanium tetrachloride and thus hold in the bath a sufficient quantity of the tetrachloride to permit its reduction to titanium trichloride and thus build up the concentration of the latter in the salt bath. When the titanous chloride content of the bath is established in this manner, it will be found necessary to continue the introduction of the titanium tetrachloride for a considerable period of time before the characteristic green color of trivalent titanium ions is imparted to light transmitted through the bath or through

a sample of the bath removed from the main body thereof. After normal cell operation has been established, the presence of the desired titanous chloride content in a fresh diluent salt bath will be indicated not only by the development of the aforementioned green color but also by the passage of a much higher current.

The titanous chloride content of the bath may also be established by producing in the bath a sufficient quantity of free alkali metal or alkaline earth metal to reduce the introduced titanium tetrachloride to the trichloride or dichloride form, or both. This result can be achieved by maintaining across the cell electrodes an applied potential in excess of the decomposition voltage of one or more of the alkali metal or alkaline earth metal halides of the salt bath while simultaneously introducing the titanium tetrachloride into the bath. The alkali metal or alkaline earth metal thus liberated electrolytically within the bath is readily available for the desired reduction of titanium tetrachloride introduced into the bath to the desired lower valence state. We have further found that when this expedient is used for initially establishing the titanous chloride content of the diluent salt bath, subsequent normal operation of the cell for the deposition of metallic titanium may be continued while maintaining the same cell voltage above the decomposition voltage of the diluent salt or the cell voltage may be reduced to a value between this decomposition voltage and the decomposition voltage of the titanous chloride dissolved in or held by the bath.

The titanous chloride content of the bath may also be initially established, however, by introducing thereinto a supply of titanium trichloride or titanium dichloride from an extraneous source. This extraneously obtained titanous chloride will establish the requisite concentration of titanous chloride in the diluent salt bath for assimilating titanium tetrachloride in subsequent operation of the cell.

When the titanous chloride content of the cell has thus been established, it will be maintained, in the practice of the method of our invention, substantially exclusively by the introduction of the titanium tetrachloride into the bath. Under steadily applied cell voltage, it has been found that the concentration of trivalent titanium in the bath, as evidenced by the color of the bath, is controllable by variation in the rate of introduction of titanium tetrachloride thereinto. Under such conditions, a rate of introduction of titanium tetrachloride in excess of the rate of electrolysis of the titanium chloride will cause a deepening of the green color of the bath with the ultimate development of a separated phase of finely divided dark particles which impart to the bath such a dark blue to dark purple color as to appear nearly black, and when such a nearly black color is produced it has been found that the titanium metal liberated at the cell cathode is somewhat contaminated by crystals of titanium dichloride. The titanium dichloride occluded by the deposited metal can be effectively separated by subsequent volatilization of the salt from the metal. On the other hand, an inadequate supply of titanium tetrachloride during cell operation results in the progressive development of a paler green color in the cell bath until the bath becomes substantially water-white, and as this depletion of the titanous chloride content of the bath progresses the conductivity of the bath decreases and the rate of production of metallic titanium rapidly diminishes. Accordingly, once the aforementioned titanous chloride content of the bath has been established, it can be maintained by control of the amount of titanium tetrachloride introduced into the bath, a rich green color in the translucence of the bath being generally indicative of satisfactory titanium-deposition conditions.

As pointed out hereinbefore, the establishment of a titanous chloride content in the fused diluent salt bath sufficient to impart thereto a green color further imparts to the bath a distinctive ability to assimilate titanium

tetrachloride. The avidity of the trivalent titanium-containing bath for titanium tetrachloride is evidenced by the fact that it will absorb titanium tetrachloride from a gaseous or vapor atmosphere above but in contact with the bath. This property of the cell bath makes it possible to supply the titanium tetrachloride to the bath simply as a component of the gaseous atmosphere established above the bath. However, it has been found to be practical to supply the titanium tetrachloride in its normally liquid form by dropping the liquid directly into the bath. When the liquid titanium tetrachloride comes into contact with the molten cell bath, it is immediately volatilized. If the resulting tetrachloride vapors are immediately released into the cell atmosphere, they will be effectively absorbed by the cell bath as described hereinbefore. However, it is our presently preferred practice to drop liquid titanium tetrachloride into the line supplying the inert gas such as helium to the cell, the tetrachloride being volatilized by the heat of the bath and being carried into the bath along with the stream of helium which is bubbled thereinto.

The cell voltage required for electrolysis of the titanium chloride-containing salt bath in the practice of our invention is within the conventional range and, other things being the same, varies somewhat with the salt bath composition, the decomposition voltage of the titanium chloride decreasing with increasing bath temperature. For example, with the aforementioned eutectic mixture of sodium, potassium and lithium chlorides maintained at a temperature of about 410° C., the decomposition voltage of the titanium chloride is about 2.3 volts whereas the minimum breakdown voltage of the diluent bath is about 3.7 volts. With the aforementioned calcium chloride-sodium chloride eutectic mixture at a temperature of 540° C., the decomposition voltage of the titanium chloride in solution therein as about 2.15 volts whereas the minimum breakdown voltage of the diluent bath is about 3.4 volts. Of course, the actual voltage across the cell electrodes may exceed these values inasmuch as the conductivity of the titanous chloride-containing bath accounts for a substantial portion of the cell voltage being used for the IR drop through the cell. With proper choice of cell voltage within the foregoing description, appropriate cell design and other optimum conditions made possible current efficiencies considerably in excess of 90% in the practice of the invention.

The cell electrodes should, of course, be so chosen as to not introduce extraneous elements into the fused bath. Thus, a nonmetallic anode such as graphite or carbon should be used, graphite having been found in practice to be wholly suitable for this purpose. Carbon, graphite, titanium, nickel, and corrosion-resistant alloy cathodes have also been used with successful results. At the prevailing cell temperatures, the aforementioned cathode materials have been found not to contaminate the deposited metallic titanium to any significant degree.

Conventional current densities can be used effectively in practicing the invention. Current densities ranging from 5 to about 25 amperes per square decimeter are suitable for producing a suitable deposit of the metal, although it must be understood that this range is merely illustrative and not limitative. Within this range of current densities, we have found that densities of 5 to 15 amperes per square decimeter lead to uniform results in the deposition of titanium from the titanium chloride in solution in a fused eutectic bath of sodium, potassium and lithium chlorides. Successful results have also been obtained with a current density of about 15 amperes per square decimeter where the diluent salt comprised a eutectic mixture of sodium and calcium chlorides. It will be appreciated, of course, that such factors as current density depend, in large scale operation, upon cell design, electrode composition, bath composition, etc., and that the optimum values for these factors can be determined only by actual full scale operation. It must be borne in mind that the operability of the method of the invention

is not predicated upon any critical operating characteristic such as current density or the like. The only requirements are that the diluent bath be of the type described hereinbefore, that the titanous chloride content of the bath be sufficient to establish the aforementioned green color to the bath during electrolysis thereof, and that the cell voltage be sufficient to effect electrolytic decomposition of the titanous chloride in the bath. Under these conditions, metallic titanium will be produced in a form readily recoverable from the bath as previously described.

The practice of the method of the present invention is illustrated by the following example carried out in a cell such as that shown in the accompanying drawing wherein the single figure comprises a vertical cross-section of the cell:

A mixture of 1595 grams of KCl, 1250 grams of LiCl, and 155 grams of NaCl was melted at 500 to 550° C. in a nickel alloy cylindrical tank **1** having an internal diameter of approximately 4½ inches and about 12 inches deep. An initial quantity of moisture was evolved during the melting operation, but a considerable quantity remained in the molten salt bath in the dissolved and combined forms. Accordingly, dry hydrochloric acid gas was forced through the melt to chloridize any basic chlorides and so release combined oxygen. Simultaneously, the hydrochloric acid gas carried moisture from the melt, and this action was supplemented by passing helium gas over the melt.

When the evolution of steam had subsided, helium alone was passed through the melt, a graphite electrode **2** was placed in the melt, and a potential was applied between this graphite rod as anode and the cell wall as cathode. After 24 hours the conductivity of the melt was such that when 2.5 volts were applied, the amperage dropped from an initial 1 ampere to a final current of less than 0.1 ampere.

The graphite electrode was then removed and replaced by another graphite anode enclosed in an anode hood **3**. The anode hood consisted of two parts, a quartz tube **4** above the melt to separate the chlorine gas from the melt and a porous alumina diaphragm **5** below the melt. The porous part of the anode hood had an outside diameter of 2 inches and an inside diameter of 1½ inches and protruded 3 inches into the melt. Approximately 2¾ inches of the length of the anode was wetted by the melt.

The cell was closed with a gas-tight lid **6** which carried the aforementioned anode-anode hood assembly. This lid also contained an inlet tube **7**, an outlet tube **8**, and a thermocouple inlet **9**. Helium was led into the melt through the inlet tube and was permitted to escape through the outlet tube. Liquid titanium tetrachloride was admitted to the helium inlet tube and dropped towards the molten salt where it was converted to a gas by the heat of the surroundings and was forced to bubble through the melt with the helium.

At first most of the titanium tetrachloride appeared to be driven from the melt and was discharged with the helium gas exhaust. Part of the tetrachloride condensed on the cooler upper parts of the cell wall, ran down the wall and was again converted to gas on the hotter lower portion of the cell wall. Slowly the clear colorless melt assumed a yellow tone and a slight increase in conductivity was noted. As the addition of titanium tetrachloride was continued, while maintaining the cell voltage at about 2.5 volts, the conductivity of the melt increased and the color of the melt assumed a green tone. Concurrently, the deposition of titanium metal became apparent.

The voltage across the cell was then slowly increased to 5.2 volts, at which point the cell current was of the order of 19 amperes. During the entire period of electrolysis, titanium tetrachloride was added as above described in proportion to the current flow on the basis that 1 gram molecule (190 grams) of titanium tetrachloride would require four faradays for its complete decomposition to metal and chlorine. Specifically, 190 grams of titanium tetrachloride were added over a period of 5 hours, 38½ minutes, at a substantially uniform current flow of 19 amperes. Periodic inspection of the melt showed that for most of the operation the melt was deep green, and during some periods a blue-black color was present. When this latter condition prevailed, it could be maintained by regular tetrachloride additions; by withholding the addition of the tetrachloride for a short period, the clear green color reappeared.

After 1195 milliliters (2062 grams) of titanium tetrachloride had been added to the cell, the electrolysis was continued without further addition of the tetrachloride until the melt was water-white and its conductivity was considerably reduced. The cell lid was then removed, the liquid melt was poured off, and the deposit of titanium metal crystals with adhering melt was removed and stored in an airtight container. It is noteworthy that only a very small fraction of the deposited titanium metal adhered to the cell wall and that all of the metal product was crystalline in nature. In fact, a considerable portion of the metal consisted of crystals sufficiently large to be easily distinguishable without optical aid. The metal-salt mixture removed from the cell was subsequently subjected to vacuum evaporation to effect removal of the salt. The residual metal sponge was finally arc-melted to metal ingots which, upon chemical analysis, were found to contain 99.5±0.5 percent titanium. Total metallic impurities by spectrographic analysis were 0.22 percent.

Significant operating data for the foregoing specific example are as follows:

$TiCl_4$ used in run: 1195 milliliters
Titanium content of $TiCl_4$ ..... 521 grams
Current used: 1210 ampere-hours
Titanium equivalent of current used ... 541 grams
Actual titanium metal recovered ..... 512.9 grams

$$\text{Utilization of } TiCl_4\text{—per cent} = \frac{512.9}{521} \times 100 = 98.2\%$$

$$\text{Current efficiency} = \frac{512.9}{541} \times 100 = 94.7\%$$

Electrodeposition of metallic titanium pursuant to our invention thus involves no unusual conditions provided the composition of the halide bath is controlled according to the aforementioned prescription. The diluent salt bath is merely maintained in a fused condition in a cell of conventional design for fused salt electrolysis. The cell itself is preferably of the closed type so as to permit withdrawal of the halogen gas liberated at the anode without contamination of the ambient atmosphere and to permit control of the atmosphere in contact with the cell bath. Thus, the method of the invention requires for its practice substantially only those considerations which prevail in most fused bath electrolysis processes and is readily adapted to commercial scale operation.

The foregoing description and discussion of the method of the invention has been directed specifically to the use of titanium tetrachloride in the interest of clarity. It must be understood, however, that although present economic considerations point to titanium tetrachloride as the most desirable source of titanium for the practice of this method, the invention is in no other respect limited to the use of the tetrachloride. Thus, titanium tetraiodide, titanium tetrabromide and titanium tetrafluoride can be substituted for the tetrachloride, in which case the respective iodides, bromides or fluorides of the alkali and alkaline earth metals are preferred for the constitution of the fused bath.

We claim:

1. In the method of producing metallic titanium from titanium tetrachloride by subjecting a titanium chloride to electrolyzing conditions in a fused diluent salt bath consisting essentially of at least one halide of a metal of the group consisting of the alkali and alkaline earth

metals the improvement which comprises imparting to the bath a solubility for titanium tetrachloride by establishing in the fused diluent salt bath a concentration of titanous chloride at least sufficient to impart a green color to the translucence of the bath during electrolysis thereof, and electrolyzing the resulting fused salt bath to effect electrodeposition of metallic titanium while maintaining said titanous chloride content of the bath substantially exclusively by introducing substantially oxygen-free titanium tetrachloride thereinto.

2. In the method of producing metallic titanium from titanium tetrachloride by subjecting a titanium chloride to electrolyzing conditions in a fused diluent salt bath consisting essentially of at least one chloride of a metal of the group consisting of the alkali and alkaline earth metals the improvement which comprises imparting to the bath a solubility for titanium tetrachloride by establishing in the fused diluent salt bath a concentration of titanous chloride at least sufficient to impart a green color to the translucence of the bath during electrolysis thereof, and electrolyzing the resulting fused salt bath to effect electrodeposition of metallic titanium while maintaining said titanous chloride content of the bath substantially exclusively by introducing substantially oxygen-free titanium tetrachloride thereinto.

3. The method of producing metallic titanium from titanium tetrachloride by subjecting a titanium chloride to electrolyzing conditions in a fused diluent salt bath consisting essentially of a potassium halide and at least one other halide of a metal of the group consisting of the alkali and alkaline earth metals which comprises establishing in the fused diluent salt bath a concentration of titanous chloride at least sufficient to impart a green color to the translucence of the bath during electrolysis thereof, and electrolyzing the resulting fused salt bath to effect electrodeposition of metallic titanium while maintaining said titanous chloride content of the bath substantially exclusively by introducing substantially oxygen-free titanium tetrachloride thereinto.

4. The method of producing metallic titanium from titanium tetrachloride by subjecting a titanium chloride to electrolyzing conditions in a fused diluent salt bath consisting essentially of a substantially eutectic mixture of sodium chloride, potassium chloride and lithium chloride which comprises establishing in the fused diluent salt bath a concentration of titanous chloride at least sufficient to impart a green color to the translucence of the bath during electrolysis thereof, and electrolyzing the resulting fused salt bath to effect electrodeposition of metallic titanium while maintaining said titanous chloride content of the bath substantially exclusively by introducing substantially oxygen-free titanium tetrachloride thereinto.

5. In the method of producing metallic titanium from titanium tetrachloride by subjecting a titanium chloride to electrolyzing conditions in a fused diluent salt bath consisting essentially of at least one halide of a metal of the group consisting of the alkali and alkaline earth metals the improvement which comprises imparting to the bath a solubility for titanium tetrachloride by establishing in the fused diluent salt bath a concentration of titanous chloride at least sufficient to impart a green color to the translucence of the bath during electrolysis thereof, and electrolyzing the resulting fused salt bath to effect electrodeposition of metallic titanium while maintaining said titanous chloride content of the bath substantially exclusively by introducing substantially oxygen-free titanium tetrachloride into the atmosphere immediately above and in contact with said bath.

References Cited in the file of this patent

UNITED STATES PATENTS

2,712,523	Alpert et al.	July 5, 1955

FOREIGN PATENTS

263,301	Germany	Aug. 5, 1913
615,951	Germany	July 16, 1935