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(54) PROCESS FOR PRODUCING Ti THROUGH Ca REDUCTION AND APPARATUS THEREFOR

(57) An apparatus for producing Ti by Ca reduction by the invention includes a reaction tank retaining a molten salt in which a molten salt $CaCl_2$ is contained and Ca is dissolved, an electrolytic cell retaining a molten salt containing $CaCl_2$, and a continuum body which is movably constructed while part of the continuum body is immersed in the molten salt either within the reaction tank or electrolytic cell. In the inventive method for producing Ti by Ca reduction, the molten salt in the electrolytic cell is electrolyzed to generate Ca on the cathode side which is transported to the reaction tank while deposited on and adheres to the continuum body, and $TiCl_4$ is supplied to the reaction tank to generate Ti. The invention enables a feed rate of $TiCl_4$ as a raw material to be enhanced, and continuous production to be performed, while allowing Ca consumed in the $TiCl_4$ reduction reaction to be replenished by electrolysis of $CaCl_2$, which proves to have an economical advantage, thus becoming means for efficiently and economically producing high-purity metallic Ti to widely be applied.

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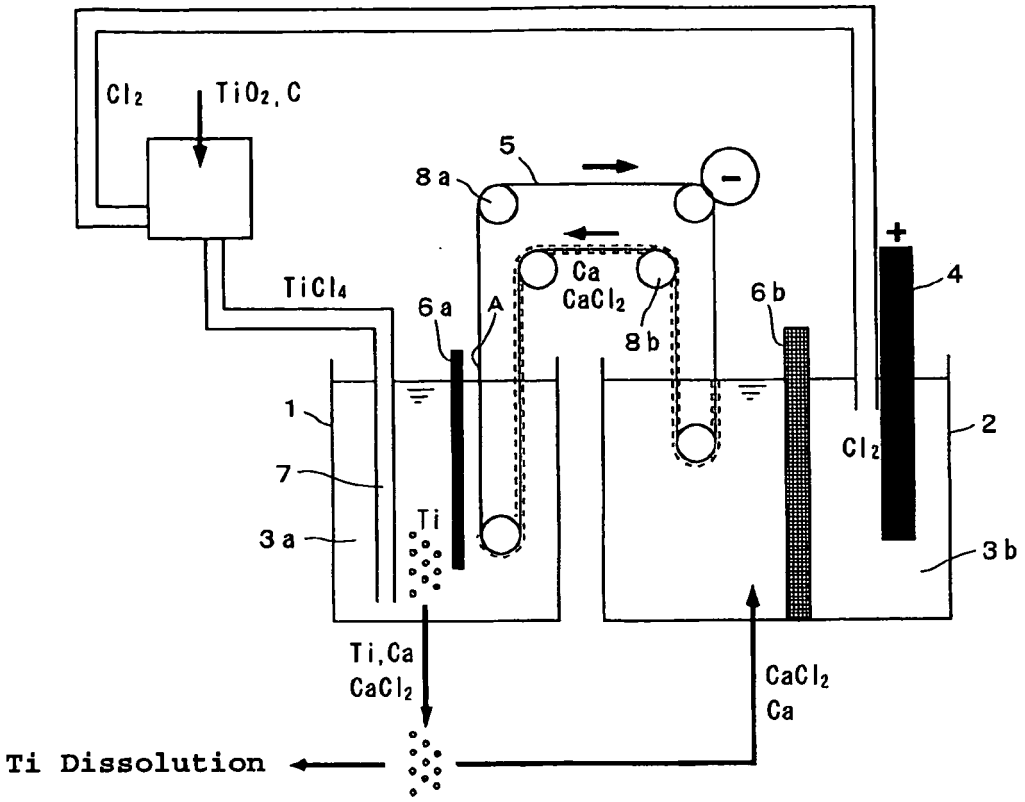
(Cont. next page)

FIG. 1


Cl2
TiO2, C
5
8a
TiCl4
6a
A
Ca
CaCl2
8b
6b
4
1
7
3a
Ti
Cl2
2
3b
Ti,Ca
CaCl2
CaCl2
Ca
Ti Dissolution

Description

TECHNICAL FIELD

[0001] The present invention relates to a method and an apparatus for producing metallic Ti through reduction by Ca, in which titanium tetrachloride ($TiCl_4$) is reduced by Ca to produce the metallic Ti.

BACKGROUND ART

[0002] The Kroll method for reducing $TiCl_4$ by Mg is generally used as a method for industrially producing the metallic Ti. $TiCl_4$ is obtained by chlorinating titanium oxide (TiO_2). In the Kroll method, the metallic Ti is produced through a reduction step and a vacuum separation step. In the reduction step, $TiCl_4$ is reduced by Mg in a reactor vessel. In the vacuum separation step, unreacted Mg and magnesium chloride ($MgCl_2$) formed as a by-product are removed from the sponge metallic Ti produced in the reactor vessel.

[0003] In the reduction step, the reactor vessel is filled with molten Mg, and the $TiCl_4$ liquid is supplied from above to a liquid surface of the molten Mg. This allows $TiCl_4$ to be reduced by Mg near the liquid surface of the molten Mg to generate the granular metallic Ti. At the same time, molten $MgCl_2$ which is of the by-product is generated near the liquid surface. The generated metallic Ti sequentially moves downward. Because a specific gravity of the molten $MgCl_2$ is larger than that of the molten Mg, the molten $MgCl_2$ also moves downward, and the molten Mg comes up to the liquid surface instead. The molten Mg is continuously supplied to the liquid surface by the specific-gravity difference substitution, and the reduction reaction of $TiCl_4$ proceeds continuously.

[0004] In the metallic Ti production by the Kroll method, although a high-purity product is produced, production costs increase and products become remarkably expensive. One of factors of the increased production costs is some difficulty in enhancing a feed rate of $TiCl_4$. The following items (a) to (c) can be cited as the reason why the feed rate of $TiCl_4$ is restricted.

[0005] (a) In order to improve productivity in the Kroll method, it is effective to enhance the feed rate of $TiCl_4$, i.e., to enhance an amount of molten Mg supplied to the liquid surface per unit area or unit time. However, when the feed rate of $TiCl_4$ is excessively enhanced, the rate of the specific-gravity difference substitution cannot respond to the reaction rate, $MgCl_2$ remains on the liquid surface, and $TiCl_4$ is supplied to the $MgCl_2$, which reduces utilization efficiency of $TiCl_4$. That is, the supplied $TiCl_4$ becomes unreacted lower chloride gases (referred to as "unreacted gases") such as an unreacted $TiCl_4$ gas and an unreacted $TiCl_3$ gas, and the unreacted gases are discharged outside the reactor vessel, which reduces utilization efficiency of $TiCl_4$. It is necessary to avoid the generation of such unreacted gases, because a rapid increase in inner pressure of the reactor vessel is associated with the generation of the unreacted gases. Accordingly, there is a limit of the feed rate of $TiCl_4$.

[0006] (b) When the feed rate of $TiCl_4$ is enhanced, Mg vapor generated from the liquid surface of the molten Mg reacts with $TiCl_4$ vapor to increase the amount of deposited Ti in the inner surface of the reactor vessel above the liquid surface of the molten Mg. On the other hand, the liquid surface of the molten Mg rises as the reduction of $TiCl_4$ proceeds. Therefore, the Ti deposited on the inner surface of the upper portion of the reactor vessel is immersed in the molten Mg at a later stage of the reduction step, which causes the effective area of the liquid surface to be reduced to decrease the reaction rate. In order to suppress the decrease in reaction rate, it is necessary that the feed rate of $TiCl_4$ be restricted to prevent the Ti deposition on the inner surface of the upper portion of the reactor vessel as much as possible.

[0007] Japanese Patent Application Publication No. 0H8-295955 proposes a method in which the reaction efficiency is enhanced by supplying the liquid $TiCl_4$ in a dispersive manner to the liquid surface where the molten Mg exists, and thereby the Ti deposition is suppressed on the inner surface of the upper portion of the reactor vessel. However, the method proposed in Japanese Patent Application Publication No. 08-295955 is not enough to suppress the Ti deposition.

[0008] (c) In the Kroll method, because the reaction is performed only near the liquid surface of the molten Mg in the reactor vessel, an exothermic area is narrowed and a temperature rises locally. Therefore, cooling is hardly performed, which causes the feed rate of $TiCl_4$ to be restricted.

[0009] Although the feed rate of $TiCl_4$ is not directly affected, in the Kroll method, Ti generated in the granular form near the liquid surface of the molten Mg is aggregated because of wetting properties (adhesion properties) of the molten Mg, the Ti granules moves downward while aggregated, and the Ti granules are sintered to generate grain growth of the Ti granules by the heat generated from the molten melt during the downward movement. Therefore, it makes difficult to take out the generated Ti as fine particles to the outside of the reactor vessel to recover the generated Ti. In the Kroll method, the continuous production is difficult to perform, and the improvement of the productivity is blocked. This is because that Ti is produced as a sponge titanium in a batch manner in the reactor vessel.

[0010] With reference to the Ti production methods except for the Kroll method, for example, US Patent No. 2205854 describes that, in addition to Mg, Ca can be used as the reducing agent of $TiCl_4$. US Patent No. 4820339 describes a method for producing Ti through the reduction reaction by Ca, wherein the molten salt of calcium chloride ($CaCl_2$) is

held in a reactor vessel, metallic Ca powders are supplied into the molten salt from above, Ca is dissolved in the molten salt, and $TiCl_4$ gas is supplied from below to react the dissolved Ca with $TiCl_4$ in the molten salt of $CaCl_2$.

[0011] In the reduction by Ca, the metallic Ti is generated from $TiCl_4$ by the reaction of the following chemical formula (i), and $CaCl_2$ which is of the by-product is also generated at the same time:

$$TiCl_4 + 2Ca \rightarrow Ti + 2CaCl_2 \qquad (i)$$

[0012] Ca has an affinity for Cl stronger than Mg has, and Ca is suitable for a reducing agent of $TiCl_4$ in principle. Particularly, in the method described in US Patent No. 4820339, Ca is used while dissolved in molten $CaCl_2$. When the reduction reaction by Ca is utilized in the molten $CaCl_2$, compared with the Kroll method in which $TiCl_4$ is supplied to the liquid surface of the reducing agent in the reactor vessel, an area (reaction field) where the reaction is created is enlarged, and the exothermic area is also enlarged, which facilitates the cooling. Accordingly, the feed rate of $TiCl_4$ can be largely enhanced, and the improvement of the productivity can be also expected.

[0013] However, the method described in US Patent No. 4820339 is hardly adopted as the industrial Ti production method. In the method, because highly expensive metallic Ca powders are used as the reducing agent, the production cost becomes higher than that of the Kroll method.

[0014] US Patent No. 2845386 describes another Ti production method (Olsen method) in which TiO_2 is directly reduced by Ca not through $TiCl_4$. The method is a kind of oxide direct-reduction method. Although the method is highly efficient, the oxide direct-reduction method is not suitable to produce a high-purity Ti because it is necessary to use expensive high-purity TiO_2.

DISCLOSURE OF THE INVENTION

[0015] An object of the present invention is to provide a method and an apparatus for economically producing a high-purity metallic Ti with high efficiency without using an expensive reducing agent.

[0016] In order to achieve the above object, the inventors consider that the reduction of $TiCl_4$ by Ca is indispensably required, and the inventors study the method for utilizing Ca dissolved in the molten salt of $CaCl_2$ as described in US Patent No. 4820339.

[0017] In the method described in US Patent No. 4820339, Ca in the molten salt is consumed in the reduction reactor vessel as the reaction expressed by the chemical formula (i) proceeds, and it is necessary to continuously supply the metallic Ca powders to the reduction reactor vessel to replenish the consumed Ca.

[0018] However, in order to industrially establish the method for producing Ti through reduction by Ca, the inventors proposes a method for generating Ca by electrolysis of the molten $CaCl_2$ liquid in an electrolytic cell to supply the $CaCl_2$ liquid containing Ca to the reaction tank in consideration of the fact that it is necessary that Ca consumed by the reduction reaction is economically replenished into the molten salt, i.e., it is necessary that Ca is replenished at low costs.

[0019] That is, when the molten $CaCl_2$ liquid is electrolyzed in the electrolytic cell, electrode reactions expressed by the following chemical formulas (ii) and (iii) proceed to generate a Cl_2 gas near the surface of an anode while Ca is generated near the surface of a cathode, which allows the Ca concentration to be increased in the electrolytic bath salt (molten $CaCl_2$ liquid) near the cathode. Therefore, the molten $CaCl_2$ liquid containing the high-concentration Ca near the cathode is deposited on and adheres to a metal plate, net, or wire having a temperature lower than a bath temperature, and the molten $CaCl_2$ liquid is transported into the reaction tank, which allows Ca consumed for the reduction of $TiCl_4$ to be replenished as needed. Therefore, the replenishment of the metallic Ca from the outside or the extraction of the metallic Ca is not required, which allows the metallic Ti to be economically produced.

$$\text{Anode: } 2Cl^- \rightarrow 2e^- + Cl_2 \qquad (ii)$$

$$\text{Cathode: } Ca^{2+} + 2e^- \rightarrow Ca \qquad (iii)$$

[0020] The present invention is made based on the above consideration, and the summary of the present invention resides in (1) a Ti production method and (2) a production apparatus in which the Ti production method is implemented.

[0021] (1) A first aspect of the present invention provides a method for producing Ti through reduction by Ca, the method including: a Ti generation step wherein $TiCl_4$ is supplied to a reaction tank to generate Ti in a molten salt while the molten salt is retained in the reaction tank, the molten salt containing $CaCl_2$, the Ca being dissolved in the molten salt; an electrolytic step wherein a molten salt is electrolyzed in an electrolytic cell to generate Ca on an cathode side while the molten salt is retained in the electrolytic cell, the molten salt containing $CaCl_2$; and a Ca transportation step wherein the Ca generated in the electrolytic step is transported to the reaction tank while the Ca is deposited on and adheres to a continuum body in the electrolytic cell, the continuum body being movably constructed while part of the continuum body is immersed in the molten salt either within the reaction tank or electrolytic cell, and the transported Ca

is caused to dissolve in the molten salt retained in the reaction tank.

[0022] In the Ti production method of (1), preferably the continuum body is caused to function as a cathode. Therefore, Ca can directly, electrolytically be deposited on the surface of the continuum body.

[0023] In the Ti production method of (1), preferably a cathode is provided near part of the continuum body, the part of the continuum body being immersed in the molten salt.

[0024] In the Ti production method of (1), preferably the molten salt or the cathode in the electrolytic cell is kept at a temperature of a melting point of Ca or less. Therefore, Ca can surely electrolytically be deposited on the surface of the cathode.

[0025] In the Ti production method of (1), preferably Ti generated in the Ti generation step is extracted to the outside of the reaction tank along with the molten salt, Ti is separated, and the molten salt is transported to the electrolytic cell. Therefore, Ti can continuously be produced.

[0026] (2) A second aspect of the present invention provides an apparatus for producing Ti through reduction by Ca, the apparatus comprising: a reaction tank in which $TiCl_4$ supplied to a molten salt is caused to react with Ca to generate Ti while the molten salt is retained, the molten salt containing $CaCl_2$, the Ca being dissolved in the molten salt; an electrolytic cell which retains a molten salt containing $CaCl_2$, the electrolytic cell including an anode and a cathode, the electrolytic cell performing electrolysis in the molten salt to generate Ca on the cathode side; and a continuum body which is movably constructed while part of the continuum body is immersed in the molten salt either in the reaction tank or electrolytic cell, the continuum body transporting the generated Ca to the reaction tank while Ca is deposited on and adheres to the part immersed in the electrolytic cell, the continuums body causing the transported Ca to dissolve in the molten salt retained in the reaction tank.

[0027] In the Ti production apparatus of (2), preferably the continuum body constitutes a cathode. Therefore, Ca can directly electrolytically be deposited on the surface of the continuum body.

[0028] In the Ti production apparatus of (2), preferably a cathode is provided near part of the continuum body, the part of the continuum body being immersed in the molten salt.

[0029] In the Ti production apparatus of (2), preferably the molten salt or the cathode in the electrolytic cell is kept at a temperature of a melting point of Ca or less. Therefore, Ca can surely electrolytically be deposited on the surface of the cathode.

[0030] In the Ti production apparatus of (2), preferably the Ti production apparatus includes means for separating Ti from the molten salt to transport the molten salt to the electrolytic cell after the Ti separation, the Ti being generated in the reaction tank and extracted to the outside of the reaction tank along with the molten salt. Therefore, Ti can continuously be produced.

[0031] The method for producing Ti through reduction by Ca according to the present invention is directed to a method for reducing $TiCl_4$ in which the high purity material is easily obtained, so that the high-purity metallic Ti can be produced. Ca is used as a reducing agent, and $TiCl_4$ is caused to react with Ca in the molten salt containing $CaCl_2$, so that the feed rate of $TiCl_4$ can be enhanced. Ca to be consumed in the reduction reaction can be replenished by the electrolysis of the molten $CaCl_2$ liquid, so that the present invention has the economical advantage.

[0032] In addition, Ca is inferior to Mg in wetting properties (adhesion properties), and the Ti granules are generated in the molten $CaCl_2$ liquid, so that the aggregation in the generated Ti granules and the grain growth by the sintering are significantly lessened. Therefore, the Ti granules can be taken out to the outside of the reactor vessel, and the Ti production can continuously be operated. The Ti production method of the present invention can preferably implemented with the Ti production apparatus of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]

Fig. 1 is a view showing a configuration example of an apparatus in which a Ti production method of the present invention can be implemented; and

Fig. 2 is a view showing another configuration example of the apparatus in which the Ti production method of the present invention can be implemented

BEST MODE FOR CARRYING OUT THE INVENTION

[0034] A method and an apparatus according to the present invention for producing Ti through reduction by Ca will be described below with reference to the drawings.

[0035] Fig. 1 is a view showing a configuration example of an apparatus (Ti production apparatus of the present invention) in which a Ti production method of the present invention can be implemented. As shown in Fig. 1, the apparatus comprises a reaction tank 1, an electrolytic cell 2, and a continuum body 5. In the reaction tank 1, $TiCl_4$ supplied into a

molten salt 3a is caused to react with Ca to generate Ti. The electrolytic cell 2 retains a molten salt 3b containing $CaCl_2$, and the electrolytic cell 2 includes an anode 4 and a cathode (in the example, the continuum body 5 constitutes the cathode). In the electrolytic cell 2, the electrolysis is performed in the molten salt 3b to generate Ca on the cathode side. The continuum body 5 is movably constructed while part of the continuum body 5 is immersed in the molten salt 3a, 3b either within the reaction tank 1 and electrolytic cell 2. The continuum body 5 serves to transport the generated Ca into the reaction tank 1 while Ca is deposited on and adheres to the immersed part of the continuum body 5 in the electrolytic cell 2, and the transported Ca is dissolved in the molten salt 3a retained in the reaction tank 1.

[0036] The continuum body 5 is a so-called endless belt, and the continuum body 5 is moved in an arrow direction of Fig. 1 while part of the continuum body 5 is immersed in the molten salt 3a in the reaction tank 1 as well as another part thereof being immersed in the molten salt 3b in the electrolytic cell 2. The continuum body 5 is rotatably constructed. However, when attention is focused on the movement of a particular portion in the surface of the continuum body 5, the portion can be deemed to be moved (i.e., the portion is moved in the rotating direction of the continuum body), so that the expression of "the continuum body 5 is movably constructed" is adopted here according to the function in which Ca is transported into the reaction tank 1 while Ca generated in the electrolytic cell 2 is deposited and adheres to the continuum body 5 in the electrolytic cell 2.

[0037] In the example of Fig. 1, a barrier membrane 6b is provided in the electrolytic cell 2, and a partition wall 6a is attached in the reaction tank 1. The barrier membrane 6b blocks the movement of Ca generated on the cathode side to the anode side. A lower portion of the partition wall 6a is opened. The apparatus also includes means for transporting only the molten salt 3a into the electrolytic cell 2 after recovering Ti by the extraction of Ti generated in the reaction tank 1 to the outside of the reaction tank 1 along with the molten salt 3a. The apparatus is configured so as to perform an operation in which chlorine (Cl_2) generated by the anode 4 in the electrolytic cell 2 is recovered and caused to react with titanium oxide (TiO_2) to generate $TiCl_4$ supplied into the reaction tank 1.

[0038] In order to implement the Ti production method of the present invention using the apparatus having the above configuration, at first the molten salt 3a in which $CaCl_2$ is includes while Ca is dissolved is retained in the reaction tank 1, and $TiCl_4$ is supplied into the reaction tank 1 to generate Ti in the molten salt 3a. That is, a "Ti generation step" is performed.

[0039] Usually the molten $CaCl_2$ having a melting point of 780 °C is used as the molten salt 3a. However, preferably the temperature of the molten salt 3a is lowered because a lifetime of the reaction tank 1 is extended while the vaporization of Ca or the molten salt from the liquid surface is suppressed, when the temperature of the molten salt 3a is lowered. Therefore, desirably a mixed salt of $CaCl_2$ and another salt is used as the molten salt 3a. For example, when the mixed salt of $CaCl_2$ and NaCl is used as the molten salt 3a, the melting point of the molten salt 3a can be lowered to about 500 °C at the lowest temperature.

[0040] Desirably $TiCl_4$ is supplied in a gas state to the molten salt 3a in the reaction tank 1 in consideration of contact efficiency between $TiCl_4$ and Ca in the molten salt. However, the present invention is not limited to the gaseous $TiCl_4$, but the liquid $TiCl_4$ can be supplied on the liquid surface of the molten salt 3a or into the molten salt 3a. In the example of Figs.1 or 2, the liquid $TiCl_4$ is supplied to the neighborhood of a bottom portion of the reaction tank 1 through a supply pipe 7.

[0041] The supply of $TiCl_4$ into the reaction tank 1 causes the reaction of the chemical formula (i) to proceed to generate the metallic Ti. Although Ca in the molten salt 3a is consumed in association with the generation of Ti, Ca transported from the electrolytic cell 2 to the continuum body 5 is dissolved, and the molten salt whose Ca concentration is increased is supplied to the neighborhood of a front end of the $TiCl_4$ supply pipe 7 through the opening in the lower portion of the partition wall 6a. Therefore, the reaction of the chemical formula (i) proceeds effectively.

[0042] Ti is generated in the form of granule or powder. The Ca is much inferior to Mg in wetting properties (adhesion properties), and Ca adhering to the deposited Ti granule is dissolved in $CaCl_2$. Therefore, the aggregation of the generated Ti granules or the grain growth by sintering is hardly generated compared with the case of Mg.

[0043] Ti generated in the molten salt 3a can be separated from the molten salt 3a either inside the reaction tank 1 or outside the reaction tank 1. However, when Ti is separated from the molten salt 3a inside the reaction tank 1, the operation becomes a batch manner. In order to enhance the productivity, preferably Ti is extracted to the outside of the reaction tank 1 along with the molten salt 3a, and Ti is separated from the molten salt 3a outside the reaction tank 1. Although only the generated Ti can be extracted to the outside of the reaction tank 1, the operation becomes a batch manner because $CaCl_2$ is continuously increased in the reaction tank 1.

[0044] The apparatus of Fig. 1 includes means for extracting the generated Ti to the outside of the reaction tank along with the molten salt 3a. Because the generated Ti takes the granular or powder form, the generated Ti can easily separated from the molten salt by a squeezing operation such as mechanical compression, and the operation can continuously be performed. The separated Ti is conveyed to a melting step.

[0045] On the other hand, the molten salt 3b containing $CaCl_2$ is also retained in the electrolytic cell 2, and the molten salt 3b is electrolyzed to generate Ca on the cathode side. That is, an "electrolytic step" is performed.

[0046] As described above, when the molten $CaCl_2$ liquid is electrolyzed, Ca is generated near the surface of the

cathode by the electrode reactions of the chemical formulas (ii) and (iii). The molten salt in which Ca is consumed by the reaction of the chemical formula (i) in the reaction tank 1 to lower the Ca concentration can also be used as the molten $CaCl_2$ liquid.

[0047] The apparatus of Fig. 1 includes the means for transporting only the molten salt into the electrolytic cell 2 after recovering Ti by the extraction of Ti generated in the reaction tank 1 to the outside of the reaction tank 1 along with the molten salt 3a, which allows the formation of the cycle, in which the molten salt is delivered to the electrolytic cell 2 after Ti is recovered and Ca generated by the electrolysis is deposited on and adheres to the continuum body 5 is returned to the reaction tank 1. Therefore, Ti can continuously be produced.

[0048] During the electrolysis of the molten $CaCl_2$ liquid, there is a risk of generating a back reaction. In the back reaction, Ca generated on the cathode side is returned to $CaCl_2$ by combining Ca and Cl_2 generated on the side of the anode 4. However, in the apparatus of Fig. 1, the continuum body 5 constitutes the cathode, and the generated Ca is immediately deposited on and adheres to the surface of the cathode (i.e., continuum body 5) while Cl_2 generated on the side of the anode 4 is recovered as described later. Therefore, the back reaction is hardly generated. Furthermore, in the example of Fig. 1, because the barrier membrane 6b is provided to block the movement of Ca generated on the cathode side to the side of the anode 4 (however, the barrier membrane 6b cannot block the movements of Ca^{2+} and Cl), there is no risk of generating the back reaction. Like the partition wall 6a, a partition wall whose lower portion is opened can be used in place of the barrier membrane 6b.

[0049] As shown in Fig. 1, in order to supply Ca generated in the electrolytic cell 2 to the reaction tank 1, the continuum body 5 is used in the Ti production method of the present invention. The continuum body 5 is movably constructed while part of the continuum body 5 is immersed in the molten salt either in the reaction tank 1 or electrolytic cell 2. The generated Ca is deposited on and adheres to the continuum body 5 in the electrolytic cell 2, Ca is transported into the reaction tank 1, and Ca is dissolved in the molten salt 3a retained in the reaction tank 1. That is, a "Ca transportation step" is performed. In Fig. 1, a broken line shown in part of the continuum body 5 indicates the deposited and adhered Ca.

[0050] The continuum body 5 is slowly moved in the arrow direction by drive rollers 8a and 8b. Focusing attention on a portion of the continuum body 5 (for example, the portion designated by the letter A in Fig. 1 where the continuum body 5 is pulled up in air from the molten salt 3a), the temperature of the portion A in motion is lowered while moving from the position, where the portion A is currently shown in Fig. 1 (at this point, Ca is completely dissolved without adhering to the continuum body 5), through the drive roller 8a until the portion A is immersed in the molten salt 3b in the electrolytic cell 2. Therefore, the dissolved Ca near the portion A is deposited on and adheres to the portion A (i.e., the surface of the continuum body 5) along with $CaCl_2$ soon after the portion A is immersed in the molten salt 3b in the electrolytic cell 2. In the apparatus of Fig. 1, the continuum body 5 constitutes the cathode, and Ca is directly deposited on the surface of the continuum body 5, so that the deposition and adhesion of Ca are generated more rapidly.

[0051] At this point, for example, when the mixed salt of $CaCl_2$ and NaCl is used as the molten salt, the temperature of the molten salt is lowered to about 500 °C which is much lower than the melting point (839 °C) of Ca. As the result, Ca can be deposited efficiently and securely on the cathode.

[0052] Because the continuum body 5 (portion A) reaches the reaction tank 1 through the drive roller 8b while Ca and $CaCl_2$ are deposited and adhere to the surface of the continuum body 5 (portion A), Ca is transported from the electrolytic cell 2 to the reaction tank 1 in association with the movement of the continuum body 5. When the deposited and adhered Ca comes into contact with the molten salt 3a in the reaction tank 1, Ca is gradually dissolved to increase the Ca concentration of the molten salt 3a in the reaction tank 1.

[0053] The metal plate, and the metal net or wire can be used as the continuum body 5. Molybdenum, tantalum, and titanium are suitable for the continuum body 5 because of excellent durability in the molten salts 3a and 3b. When the continuum body is made of metal, as shown in Fig. 1, the continuum body can function as the cathode to directly electrolytically deposit Ca on the surface of the continuum body. Therefore, desirably the continuum body is made of metal.

[0054] The moving speed of the continuum body 5 can appropriately be adjusted as long as Ca generated in the electrolytic cell 2 is deposited on and adheres to the continuum body 5 without troubles, as long as Ca is transported into the reaction tank 1 without troubles, and as long as the transported Ca is dissolved in the molten salt 3a in the reaction tank 1 without trouble.

[0055] Desirably the molten salt 3a in the reaction tank 1 is kept at the temperature equal to or higher than the temperature of the molten salt 3b in the electrolytic cell 2. Therefore, solubility of Ca is enhanced to increase the Ca concentration of the molten salt 3a, and the $TiCl_4$ reduction reaction of the chemical formula (i) can efficiently be performed. Additionally, Ca which is deposited on and adheres to the continuum body 5 can be dissolved in the molten salt 3a at a higher rate.

[0056] The apparatus of Fig. 1 is configured to perform the operation in which Cl_2 generated by the anode 4 in the electrolytic cell 2 is recovered to cause Cl_2 to react with TiO_2 and carbon (C) and thereby $TiCl_4$ supplied to the reaction tank 1 is generated. That is, the Cl_2 gas generated in the electrolytic step is recovered, the Cl_2 gas is caused to react with TiO_2 at a high temperature to generate $TiCl_4$, and $TiCl_4$ is used as $TiCl_4$ supplied to the reaction tank 1.

[0057] When the operation (step) is incorporated into the Ti production method, $CaCl_2$ which is of the by-product

through the reduction of $TiCl_4$ is introduced into the electrolytic cell 2 and electrolyzed in the electrolytic cell 2, Ca generated by the cathode is cyclically used as the reducing agent, and Cl_2 generated by the anode is utilized in producing $TiCl_4$. This enables the metallic Ti to be continuously produced only by replenishing TiO_2 and C.

[0058] Fig. 2 is a view showing another configuration example of the apparatus (Ti production apparatus of the present invention) in which the Ti production method of the present invention can be implemented. In the apparatus of Fig. 2, a cathode 9 is provided near a portion where the continuum body 5 is immersed in the molten salt 3b, while all other configurations of the apparatus of Fig. 2 are similar to those of Fig. 1.

[0059] The temperature of the continuum body 5 immersed in the molten salt 3b in the electrolytic cell 2 is considerably lowered compared with the temperature of the molten salt 3b. Therefore, in the apparatus of Fig. 2, Ca generated near the surface of the cathode 9 can be transported from the electrolytic cell 2 to the reaction tank 1 while deposited on and adheres to the surface of the continuum body 5.

[0060] An electrode being made of a material and in a shape, which are commonly applied in the molten salt electrolysis such as $CaCl_2$, can be used as the cathode 9. For example, an electrode made of a metal such as Fe and Ti can be used, and particularly a porous electrode is desirably used. Because a surface area per unit mass is increased, the electrolytic current can be enhanced to increase the amount of generated Ca.

[0061] Desirably the porous electrode is made of the metal such as Fe and Ti. The titanium oxide sintered material can also be used because the titanium oxide sintered material exhibits good conductivity at high temperatures.

[0062] When the cathode 9 is arranged near the continuum body 5 (i.e., near the portion where the continuum body 5 is immersed in the molten salt 3b), Ca generated near the surface of the cathode 9 is easily deposited on and adheres to the surface of the continuum body 5, which allows Ca to be transported from the electrolytic cell 2 to the reaction tank 1.

INDUSTRIAL APPLICABILITY

[0063] According to the method for producing Ti through reduction by Ca of the present invention, the feed rate of $TiCl_4$ which is of the raw material can be enhanced, and the continuous production can be performed. Furthermore, the method of the present invention has an economical advantage because Ca consumed in a reduction reaction of $TiCl_4$ can be replenished by the electrolysis of $CaCl_2$. Therefore, the Ti production method of the present invention can efficiently be utilized as means for economically producing the high-purity metallic Ti, and the Ti production apparatus of the present invention can suitably be used for the Ti production method of the present invention.

Claims

1. A method for producing Ti through reduction by Ca, **characterized in that** said method includes:

   a Ti generation step wherein $TiCl_4$ is supplied to a reaction tank to generate Ti in a molten salt while said molten salt is retained in said reaction tank, the molten salt containing $CaCl_2$ and having Ca dissolved therein;
   an electrolytic step wherein a molten salt is electrolyzed in an electrolytic cell to generate Ca on a cathode side while said molten salt is retained in said electrolytic cell, the molten salt containing $CaCl_2$; and
   a Ca transportation step wherein the Ca generated in said electrolytic step is transported to said reaction tank while the Ca is deposited on and adheres to a continuum body in said electrolytic cell, said continuum body being movably constructed while part of said continuum body is immersed in said molten salt either within said reaction tank or electrolytic cell, and said transported Ca is caused to dissolve in said molten salt retained in said reaction tank.

2. The method for producing Ti through reduction by Ca according to claim 1, **characterized in that** said continuum body is caused to function as a cathode.

3. The method for producing Ti through reduction by Ca according to claim 1,**characterized in that** a cathode is provided near part of said continuum body, the part of said continuum body being immersed in said molten salt.

4. The method for producing Ti through reduction by Ca as in any one of claims 1 to 3, **characterized in that** said molten salt or said cathode in said electrolytic cell is kept at a temperature of a melting point of Ca or less.

5. The method for producing Ti through reduction by Ca as in any one of claims 1 to 4, **characterized in that** Ti generated in said Ti generation step is extracted to the outside of said reaction tank along with said molten salt, Ti is separated, and said molten salt is transported to said electrolytic cell.

6. An apparatus for producing Ti through reduction by Ca, **characterized in that** said apparatus comprises:

a reaction tank in which $TiCl_4$ supplied to a molten salt is caused to react with Ca to generate Ti while said molten salt is retained, the molten salt containing $CaCl_2$ and having Ca dissolved therein;
an electrolytic cell which retains a molten salt containing $CaCl_2$, said electrolytic cell including an anode and a cathode, said electrolytic cell performing electrolysis in said molten salt to generate Ca on said cathode side; and
a continuum body which is movably constructed while part of said continuum body is immersed in said molten salt either within said reaction tank or electrolytic cell, the continuum body transporting said generated Ca to said reaction tank while Ca is deposited on and adheres to the part immersed in said electrolytic cell, the continuum body causing said transported Ca to be dissolved in said molten salt retained in said reaction tank.

7. The apparatus for producing Ti through reduction by Ca according to claim 6, **characterized in that** said continuum body constitutes a cathode.

8. The apparatus for producing Ti through reduction by Ca according to claim 6, **characterized in that** a cathode is provided near part of said continuum body, the part of said continuum body being immersed in said molten salt.

9. The apparatus for producing Ti through reduction by Ca as in any one of claims 6 to 8, **characterized in that** said molten salt or said cathode in said electrolytic cell is kept at a temperature of a melting point of Ca or less.

10. The apparatus for producing Ti through reduction by Ca as in any one of claims 6 to 9, **characterized in that** said apparatus comprises means for separating Ti from said molten salt to transport said molten salt to said electrolytic cell after said Ti separation, the Ti being generated in said reaction tank and extracted to the outside of said reaction tank along with said molten salt.

FIG. 1

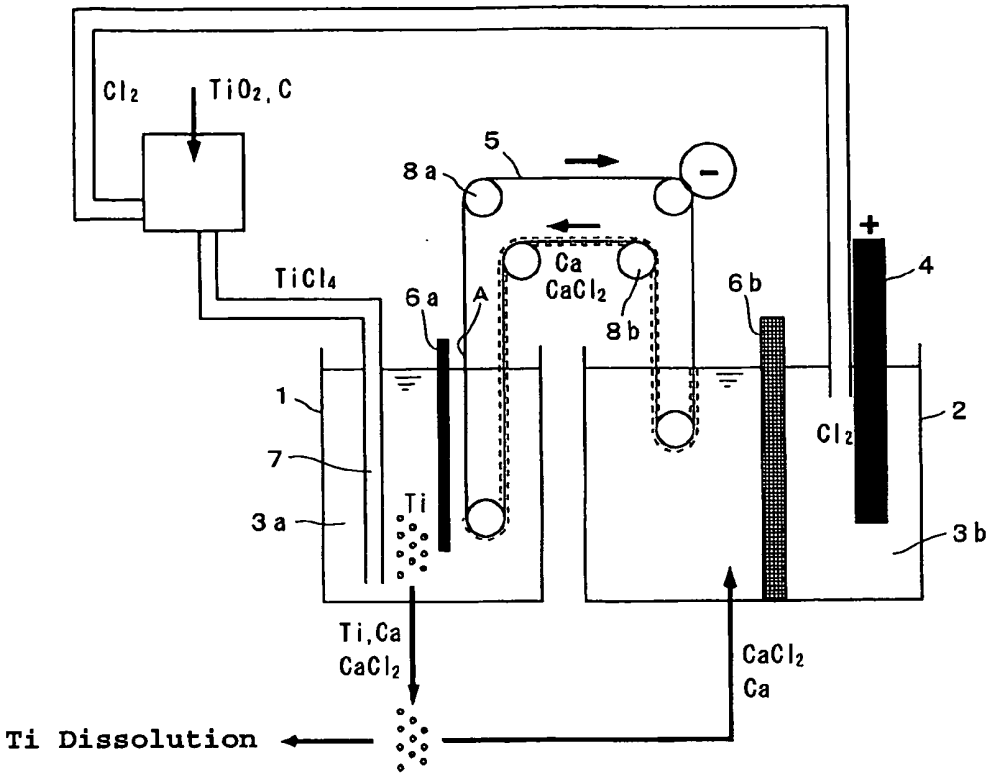
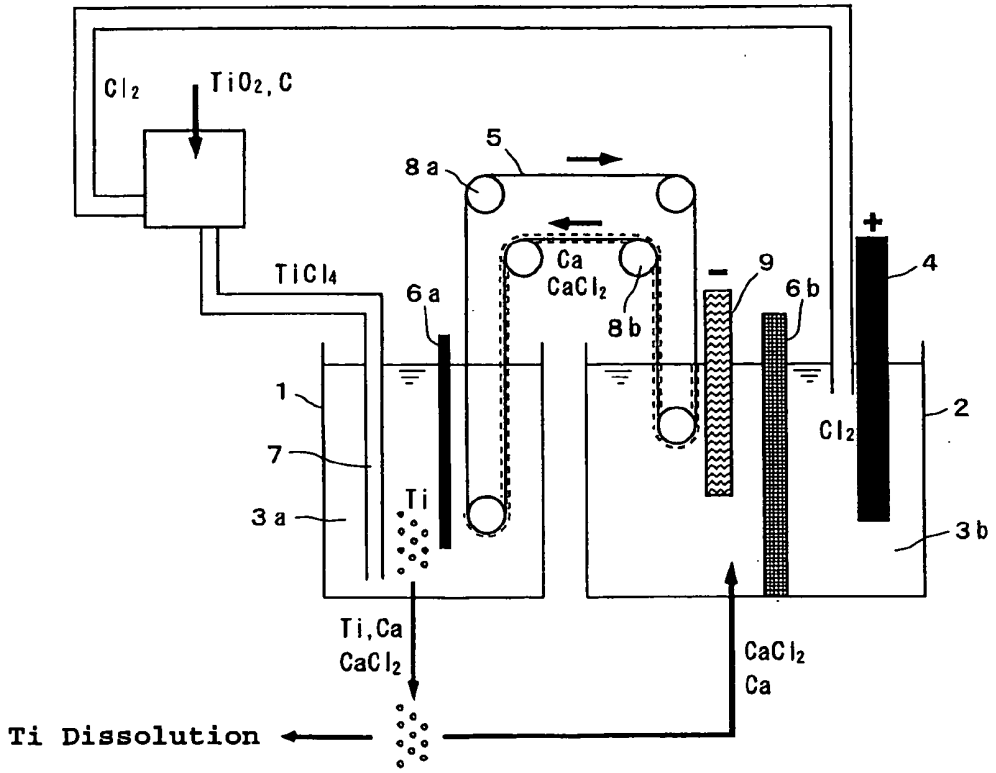

Cl2
TiO2, C
5
8a
−
+
4
Ca
CaCl2
8b
6b
TiCl4
6a
A
1
2
7
Cl2
Ti
3a
3b
Ti, Ca
CaCl2
CaCl2
Ca
Ti Dissolution

FIG. 2


Cl2
TiO2, C
5
8a
+
4
Ca
CaCl2
−
9
6b
8b
TiCl4
6a
1
2
7
Cl2
Ti
3a
3b
Ti, Ca
CaCl2
CaCl2
Ca
Ti Dissolution

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/019655

A. CLASSIFICATION OF SUBJECT MATTER
C22B5/04(2006.01), ***C22B34/12***(2006.01), ***C25C3/28***(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B5/04, C22B34/12, C25C3/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006
Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-306725 A (Zaidan Hojin Seisan Gijutsu Kenkyu Shoreikai), 31 October, 2003 (31.10.03), (Family: none)	1-10
A	JP 2002-129250 A (Katsutoshi ONO), 09 May, 2002 (09.05.02), (Family: none)	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 January, 2006 (19.01.06)	31 January, 2006 (31.01.06)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

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