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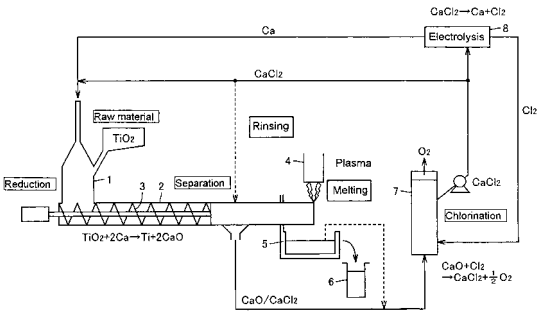
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(54) METHOD AND APPARATUS FOR PRODUCING METAL

(57) The present invention relates to a method for producing a metal by a direct oxide reduction process with Ca. A $CaCl_2$-based molten salt containing Ca is held in a reduction chamber 1, a metal oxide is introduced into the molten salt in the reduction chamber 1, and the metal oxide is reduced with the Ca in the molten salt to form said metal. The metal formed in the molten salt is separated from the molten salt in a separation means 2, and the molten salt deprived of the metal is introduced into a chlorination chamber 7 and subjected to chlorination treatment with chlorine gas to eliminate the byproduct CaO in the molten salt. The molten salt after chlorination treatment is introduced into an electrolysis chamber 8 and electrolyzed for the formation of Ca and chlorine from $CaCl_2$, and the thus-formed Ca or Ca-containing molten salt is transferred from the electrolysis chamber 8 to the reduction chamber 1. The chlorine obtained in the electrolysis chamber 8 is used in the chlorination chamber 7. Thus, the present invention provides a metal production method and an apparatus wherein high levels of productivity are obtained and the product metal can be inhibited from carbon contamination due to CaO, without any generation of CO_2 from the production process, while their being based on the direct oxide reduction process comprising the step of reducing a metal oxide with Ca.

FIG.3



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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing a metal by a direct oxide reduction process wherein a metal oxide is reduced with Ca to form a metal such as titanium, and to an apparatus for use in practicing the method.

BACKGROUND ART

[0002] It is the Kroll process that is a general method for the commercial production of metallic titanium. In this Kroll process, metallic titanium is produced via a reduction step and vacuum separation step. In the reduction step, titanium tetrachloride ($TiCl_4$) in a reaction vessel is reduced with Mg, whereby titanium metal sponge is produced. In the vacuum separation step, the unreacted Mg and the byproduct magnesium chloride ($MgCl_2$) are eliminated from the titanium metal sponge in the reaction vessel, whereby the product titanium is produced.

[0003] In the production of metallic titanium by the Kroll process, high-purity products can be produced but the production cost becomes high, rendering the product price high. Therefore, it is a limitation of the Kroll process that it can produce only high-quality and highly-priced metallic titanium.

[0004] On the other hand, the production of low-priced metallic titanium, though somewhat lower in purity, is demanded for use as structural members, for instance. In response to such a demand, works have been planned to develop a method for continuously producing metallic titanium relatively low in purity at low cost and, in line with above, direct oxide reduction processes consisting in reducing titanium oxide with Ca have been investigated.

[0005] Fig. 1 is an illustration of a direct oxide reduction process known in the prior art. As a typical example of the known direct oxide reduction processes, there is the Olson process described in United States Patent No. 2,845,386. In this process, a TiO_2 powder is charged to a molten salt containing $CaCl_2$ for the formation of Ti as a result of the reduction of TiO_2 with Ca, as shown in Fig. 1. At the same time, CaO is electrolyzed in the molten salt containing $CaCl_2$ using an iron cathode and a graphite anode.

[0006] In the Olson process mentioned above, CaO is formed as a byproduct on the surface of the TiO_2 powder with the progress of the reaction. Since, however, the byproduct CaO is soluble in $CaCl_2$, the CaO formed on the surface of the TiO_2 powder is dissolved in the $CaCl_2$ and the reaction between TiO_2 and Ca progresses continuously on the surface of the TiO_2 powder. Further, upon electrolysis of the CaO-containing molten salt ($CaCl_2$), the CaO is removed from the $CaCl_2$, as shown below by the chemical formulas (1)-(3).

[0007] Thus, according to the Olson process, the byproduct CaO formed on the surface of the TiO_2 powder is dissolved in the $CaCl_2$ and, further, the dissolved CaO is continuously removed from the $CaCl_2$ as a result of electrolysis, hence is never accumulated. The reaction for the formation of Ti from TiO_2 thus continues.

[0008]

$$2CaO + C \rightarrow 2Ca + CO_2 \text{ (on the anode surface)} \quad (1)$$

$$5Ca + 2CO_2 \rightarrow CaC_2 + 4CaO \text{ (in the vicinity of the anode)} \quad (2)$$

$$2Ti + CaC_2 \rightarrow 2TiC + Ca \text{ (on the catode)} \quad (3)$$

[0009] As described above, the Olson process can form Ti from TiO_2 continuously without allowing accumulation of the byproduct CaO. On the other hand, however, CaC_2 is formed in the molten salt as the electrolysis of CaO proceeds. The thus-formed CaC_2 deteriorates the quality of Ti by mixing Ti with TiC, as shown by the chemical formula (3) given above.

[0010] In other words, the Olson process can form Ti continuously and is therefore efficient but Ti is contaminated with TiC resulting from the reaction of CaC_2 formed in the molten salt containing $CaCl_2$ with the progress of electrolysis of CaO. The deterioration in product quality due to contamination with carbon (C) becomes a critical problem in the production of metallic titanium and, therefore, any process based on direct oxide reduction process has not yet been put to practical use.

DISCLOSURE OF THE INVENTION

[0011] It is an object of the present invention to provide a metal production method which is highly productive and free from such quality deterioration as contamination with carbon in spite of its employing the direct oxide reduction process featured by reducing a metal oxide with Ca, and a metal production apparatus for practicing such method.

[0012] To accomplish the above object, the method for producing a metal according to the present invention comprises a reduction step in which a metal oxide is introduced into a $CaCl_2$-based molten salt containing Ca for the formation of the corresponding metal by reduction of the metal oxide with Ca in the molten salt, a separation step in which the metal formed in the molten salt is separated from the molten salt, a chlorination step in which the molten salt after separation of the metal is subjected to chlorination treatment with chlorine gas to chlorinate the byproduct CaO in the molten salt, and an electrolysis step in which a part or the whole of the molten salt after chlorination treatment is electrolyzed to form Ca and chlorine from $CaCl_2$ and the thus-formed Ca or Ca-containing molten salt is recycled to the above-mentioned reduction step.

[0013] The metal production apparatus according to the present invention comprises a reduction chamber in

which a $CaCl_2$-based molten salt containing Ca is held and a metal oxide introduced into the molten salt is reduced with Ca in the molten salt to obtain said metal, means for separating the metal formed in the molten salt from the molten salt, a chlorination chamber in which the molten salt after separation of the metal is held and the molten salt is subjected to chlorination treatment with chlorine gas for the chlorination of the byproduct CaO in the molten salt, an electrolysis chamber in which a part or the whole of the molten salt after chlorination treatment is held and the molten salt is electrolyzed to form Ca and chlorine from $CaCl_2$, and means for transferring the thus-formed Ca or Ca-containing molten salt from the electrolysis chamber to the reduction chamber mentioned above.

[0014] In producing metallic titanium, for instance, by the metal production method of the present invention, the desired product titanium is formed based on the reactions represented below by the chemical equations (4) - (6):

$$TiO2 + 2\,Ca \rightarrow Ti + 2CaO \quad \text{(reduction step)} \quad (4)$$

$$2CaO + 2Cl_2 \rightarrow 2CaCl_2 + O_2 \quad \text{(chlorination step)} \quad (5)$$

$$CaCl_2 \rightarrow Ca + Cl_2 \quad \text{(electrolysis step)} \quad (6)$$

[0015] First, in the reduction step, the titanium oxide introduced is reduced with Ca in the molten salt and, as a result, metallic titanium is continuously formed and CaO is formed as a byproduct. Therefore, the molten salt after reduction is composed of $CaCl_2$, metallic titanium and the byproduct CaO.

[0016] Then, in the separation step, the metallic titanium formed in the molten salt is separated from the molten salt.

[0017] Further, in the chlorination step, the molten salt after separation of the metallic titanium is subjected to chlorination treatment with chlorine gas, whereby $CaCl_2$ is formed from the CaO formed as a byproduct of the reduction reaction. As a result, the molten salt after chlorination treatment is almost free of CaO and substantially comprises $CaCl_2$ alone.

[0018] The molten salt substantially comprising $CaCl_2$ alone after chlorination treatment is partly or as a whole sent to the electrolysis step, in which Ca is formed in the molten salt by the electrolysis treatment. The $CaCl_2$-based molten salt now containing Ca again after the electrolysis step is recycled to the reduction step. In this manner, continuous production of metallic titanium becomes possible.

[0019] The present invention is based on a first and second characteristic feature. The first feature consists in carrying out the electrolysis outside the region of the reduction reaction. The second feature consists in chlorinating CaO in the molten salt prior to electrolysis. By combining these first and second features, it becomes possible to prevent the accumulation of CaO in the reduction step and at the same time prevent the generation of CaC_2 otherwise resulting from electrolysis of CaO and thus avoid the carbon contamination of the product metal. Thus, it is possible to continue the reduction reaction while preventing the product from being contaminated.

[0020] Furthermore, the present invention provides an advantage that no oxygen gas is formed although chlorine gas is formed on the anode in the electrolysis. In ordinary electrolytic processes, graphite is used as the anode material. As is indicated in Fig. 1 referring to the Olson process, the generation of oxygen gas on the anode results in the generation of carbon dioxide.

[0021] In the electrolysis shown in Fig. 1, the Ca generated on the cathode side has a high reducing power and therefore reduces the metal oxide. However, as shown in the above chemical equations (2) and (3), carbon dioxide, when it is present in the molten salt, forms CaC_2, and this CaC_2 mixes the carbonized metal into the product metal and thereby deteriorates the quality of the product metal.

[0022] On the contrary, no oxygen gas is generated on the graphite anode in the electrolysis according to the present invention and, as a result, no carbon dioxide is generated, hence there is no risk of carbon contamination of the product metal. In addition, now that the graphite anode is not consumed, stable electrolysis conditions can be secured.

[0023] In the production process according to the present invention, it is necessary to control the molten salt temperature at the melting point (780°C) or more of $CaCl_2$ in the reduction step, chlorination step and electrolysis step in which the molten salt is circulated. In this connection, the melting point of Ca is 848°C but when Ca is dissolved in the molten salt $CaCl_2$, Ca can be dissolved therein even at 848°C or less. While the exact solubility varies depending on the dissolution temperature, Ca can be dissolved to a level of about 1.5% by weight relative to $CaCl_2$, and CaO can be dissolved to a level of about 8.0% by weight relative to $CaCl_2$.

[0024] In the reduction step, powdery, granular or lumpy titanium oxide is introduced into the molten salt. The metallic titanium separated from the molten salt after reduction is also powdery, granular or lumpy and wet with the molten salt. From the reduction efficiency viewpoint, the use of powdery titanium oxide as the raw material is desirable.

[0025] The separation of metallic titanium in the separation step is effectively carried out in the manner of separation through settling or a physical method such as compacting. The reasonable amounting metallic titanium in bulk once separated and taken out by settling or compacting can be made up into ingots by any of the conventional melting methods, for example by the plasma melting method.

[0026] In the melting step, either of a bottomless cru-

cible or a bottomed crucible may be used as the crucible for melting. The use of the bottomless crucible makes it possible to carry out continuous casting.

[0027] When titanium oxide is introduced in the form of particles with small diameter, the formed metallic titanium also becomes small in diameter and, therefore, the separation through settling in the reduction step may become inefficient in some instances. In such cases, an efficient method to be employed comprises the step of carrying out the reduction step in a bottomed vessel, extracting, from the vessel bottom, the molten salt with the product metallic titanium suspended therein at a high concentration as resulting from still and static separation and, thereafter, separating the product metallic titanium from the molten salt by compacting together, for instance. The remaining molten salt is subjected to chlorination treatment, whereby the efficiency of utilization of the molten salt can be improved.

[0028] In the chlorination step, the chlorination treatment can be carried out continuously and efficiently by bubbling chlorine gas into the molten salt.

[0029] If CaO remains in the metallic titanium formed in the reduction step, the oxygen constituent of the CaO is included in the metallic titanium in the step of melting and the oxygen concentration in the titanium increases. For preventing this, it is desirable to insert the so-called rinsing step, namely the step of injecting CaO-free $CaCl_2$ after chlorination treatment into an appropriate location during the separation step to thereby rinse the metallic titanium separated from the molten salt with the $CaCl_2$ after chlorination treatment.

[0030] Since up to about 8.0% by weight of CaO can be dissolved in $CaCl_2$, as mentioned hereinabove, the CaO remaining in the metallic titanium is dissolved in the CaO-free $CaCl_2$ that has been injected and thus is removed from the metallic titanium.

[0031] In the electrolysis step, Ca is generated on the cathode side, while chlorine gas is generated on the anode side. As the Ca concentration in the Ca-containing $CaCl_2$ extracted from the cathode site in the electrolyzer increases, the reducing capacity in the reduction step can be increased accordingly.

[0032] In case the Ca concentration in the electrolyzer exceeds the solubility thereof in $CaCl_2$, the excess Ca is suspended as a solid or dissociated and floated to the surface. The $CaCl_2$ with Ca suspended therein can be sent to the reduction step. Upon consumption, in the reduction step, of the Ca originally being contained, the suspended portion of Ca is newly dissolved to serve to continue reducing reaction thereof.

[0033] It is not always necessary to transfer the whole of the $CaCl_2$ from the chlorination step to the electrolysis step. Only part thereof may be transferred. In that case, the remaining portion of $CaCl_2$ may be directly sent from the chlorination step to the reduction step without subjecting to the electrolysis step. The reason why part of the $CaCl_2$ is transferred from the chlorination step to the electrolysis step is as follows.

[0034] The solubility of Ca in $CaCl_2$ is low. Therefore, in cases where the $CaCl_2$ containing Ca dissolved therein is sent to the reduction step, it becomes necessary to cycle a large amount of $CaCl_2$ so that the predetermined reducing capacity may be secured. On the contrary, when molten Ca alone is transferred from the electrolysis step to the reduction step, it is unnecessary any more to cycle a large amount of $CaCl_2$.

[0035] When the Ca from the electrolysis step is stored on the melt surface in the reduction step, Ca is dissolved from the Ca layer formed on the liquid surface into the $CaCl_2$ layer, whereby the Ca concentration in the $CaCl_2$ layer can be increased. Thus, that portion of Ca consumed for the reduction of TiO_2 by the dissolved Ca in the $CaCl_2$ layer is supplemented by the dissolution of Ca from the Ca layer into the $CaCl_2$ layer.

[0036] The production apparatus of the present invention is an apparatus for producing a metal utilizing the above-mentioned production method of the present invention. In the production apparatus of the present invention, the electrolysis chamber is desirably configured such that a partition wall is provided for separating the anode side and cathode side from each other. By providing such a partition wall, it becomes possible to prevent the chlorine gas generated on the anode side from travelling into the cathode side and further prevent the Ca generated on the cathode side from returning to the anode side. In case of providing a partition wall, the use of a porous ceramic plate (diaphragm) is recommended.

[0037] On the other hand, by continuously extracting the Ca-containing $CaCl_2$ from the cathode side while continuously introducing the $CaCl_2$ fed from the chlorination step into the anode side, it becomes possible to form a steady flow from the anode side to the cathode side. Once such a flow is formed, the same Ca separation effect as in case of using a porous plate can be expected by using a solid/non-porous plate being disposed below the liquid level and having an opening or hole(s) through which a small amount of the molten salt can pass, for example a slit metal plate, without using a porous plate as the partition wall.

[0038] The chlorine gas generated on the anode side in the electrolysis chamber is used for bubbling in the chlorination step.

[0039] For reducing the size of the apparatus, the chlorination chamber may be integrated with the reduction chamber. For the same purpose, it is also possible to integrate the electrolysis chamber with the reduction chamber together. By using the word "integrate" herein, it is meant that another chamber is arranged next to a specific chamber; the partition wall for separating both chambers from each other may be provided or may not be provided. The case of no partition wall being provided is touted as unification, which will be described later herein.

[0040] The cathode side of the electrolysis chamber integrated with the reduction chamber can be unified with the reduction chamber by removing the partition wall sep-

arating both chambers from each other. This electrolysis chamber can be formed in a ring-like manner around the reduction chamber which has a cylindrical shape. More specifically, the system can comprise an outer cylinder serving as the anode as well and an inner cylinder serving as the cathode as well and allowing the passage of the molten salt, where the inside of the inner cylinder serves as the reduction chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041]

Fig. 1 is a drawing explaining a direct oxide reduction method known in the art.
Fig. 2 is a drawing explaining the configuration of a titanium production apparatus according to a first embodiment of the present invention.
Fig. 3 is a drawing explaining the configuration of a titanium production apparatus according to a second embodiment of the present invention.
Fig. 4 is a drawing explaining the configuration of a titanium production apparatus according to a third embodiment of the present invention.
Fig. 5 is a drawing explaining the configuration of a titanium production apparatus according to a fourth embodiment of the present invention.
Fig. 6 is a drawing explaining the configuration of a titanium production apparatus according to a fifth embodiment of the present invention.
Fig. 7 is a drawing explaining the configuration of a titanium production apparatus according to a sixth embodiment of the present invention.
Fig. 8 is a drawing explaining the cross-sectional configuration, seen from the direction of an arrow X-X, shown in Fig. 7.

BEST MODE FOR CARRYING OUT THE INVENTION

[0042] In the following, the first to sixth embodiments of the present invention are described referring to the drawings.

(First embodiment)

[0043] Fig. 2 is a drawing explaining the configuration of a titanium production apparatus according to the first embodiment of the present invention. In the first embodiment, the apparatus comprises a tower-shaped reduction chamber 1 and a horizontal separation means 2 connected to the lower part of the chamber 1. A $CaCl_2$-based molten salt containing Ca is contained in the reduction chamber 1, and the raw material titanium oxide (TiO_2) in the form of a powder is continuously introduced into the molten salt.

[0044] Thus, in the reduction chamber 1, TiO_2 charged into the molten salt is reduced by Ca in the molten salt and metallic titanium (Ti) is formed and, at the same time, CaO is formed as a byproduct. Both the product Ti and the byproduct CaO settle and are separated from the molten salt and flow into the separation means 2 together with a certain amount of $CaCl_2$.

[0045] A $CaCl_2$-based molten salt containing Ca, together with the raw material titanium oxide, is additionally supplied from the upper part to the reduction chamber 1. On the other hand, the molten salt is extracted sideways from the lower part of the reduction chamber 1 by the separation means 2. As a result, a downward flow or current of the molten salt is formed in the reduction chamber 1. This molten salt flow promotes the above-mentioned settling and separation of the product Ti and byproduct CaO.

[0046] In the separation means 2, the molten salt abundant in product Ti and byproduct CaO, after flowing thereinto, is physically compressed by means of a perforated cylindrical screw 3 in a cylindrical body. This physical separation procedure makes it possible to squeeze out the molten salt from the product Ti and compact together said product Ti. The compacted porous product Ti is successively discharged from the separation means 2 and melted in a melting means 4.

[0047] The product Ti separated from the molten salt by compression in the separation means 2 can be subjected to rinsing with a CaO-free molten salt containing $CaCl_2$ as a main component. This treatment is to prevent CaO from remaining in the product Ti since the retention of CaO therein results in an increased oxygen concentration in the step of melting due to the oxygen constituent in CaO being included in the metallic titanium. More specifically, a CaO-free molten salt after chlorination treatment in a chlorination chamber 7, which is to be mentioned later herein, is used for rinsing to dissolve the CaO remaining in the product Ti in $CaCl_2$, consequently removing the same from the product Ti.

[0048] In the melting means 4, a plasma device is used. The lumpy product Ti is melted in an inert atmosphere and the molten Ti is collected in a water-cooled primary mold 5. In the water-cooled primary mold 5, the molten Ti settles, while the molten salt floats to the surface. The molten Ti separated from the molten salt is allowed to flow into a water-cooled secondary mold 6 and thus is cast to give a Ti ingot.

[0049] In spite of its separation from the molten salt by compression in the separation means 2, the Ti melted in the melting means 4 still contains a certain amount of the molten salt. Therefore, the molten Ti is once collected in the water-cooled primary mold 5, where the molten salt floats to the surface and can be separated. The molten salt separated is sent to a chlorination chamber 7, which is to be described later herein.

[0050] The molten salt separated from the product Ti in the separation means 2 and the molten salt separated by floating in the water-cooled primary mold 5 are sent to the chlorination chamber 7. Since these molten salt portions contain the byproduct CaO in large amounts, chlorine gas is bubbled into the molten salt introduced

into the chlorination chamber 7 to chlorinate the CaO in the molten salt. This chlorination of CaO converts the CaO contained in the molten salt to $CaCl_2$, and a CaO-free molten salt substantially consisted $CaCl_2$ is formed.

[0051] The above CaO-free molten salt is then sent to an electrolysis chamber 8. Part thereof is sent to the separation means 4 for rinsing treatment, as mentioned above. In the electrolysis chamber 8, the molten salt introduced is electrolyzed by using a graphite anode and an iron cathode. Chlorine gas is generated on the anode side in the chamber and Ca is formed on the cathode side. In this way, a $CaCl_2$-based molten salt containing Ca is formed.

[0052] In the chlorination chamber 7, the CaO to be eliminated is chlorinated. On the other hand, the reduction chamber 1 requires a Ca-containing molten salt and, therefore, the Ca-containing molten salt formed in the electrolysis chamber 8 is sent to the reduction chamber 1. Thus, it is substantially unnecessary to supplement $CaCl_2$ and Ca from the outside source. The chlorine gas formed as a byproduct in the electrolysis chamber 8 is sent to the chlorination chamber for reuse.

[0053] In this electrolysis chamber 8, the anode side and cathode side are separated from each other by a porous partition wall 9. The molten salt sent from the chlorination chamber 7 is introduced into the anode side, and the Ca-containing molten salt is drawn out from the cathode side and sent to the reduction chamber 1. In this way, a flow from the anode side toward the cathode side is formed. As a result, the molten salt is inhibited from flowing backward from the cathode side to the anode side. The chlorine gas is also prevented from entering the cathode side from the anode side.

(Second embodiment)

[0054] Fig. 3 is a drawing explaining the configuration of a titanium production apparatus according to the second embodiment of the present invention. The second embodiment differs from the above-mentioned first embodiment as shown in Fig. 2 in that part of the molten salt after completion of the chlorination treatment in the chlorination chamber 7 is sent to the electrolysis chamber 8, while almost whole of the remaining molten salt is returned to the reduction chamber 1 and that the transfer of Ca from the electrolysis chamber 7 to the reduction chamber 1 is carried out in the form of a metal. In the second embodiment, however, the transfer of Ca in the metal form to the reduction chamber 1 may be combined with the method comprising the step of transferring Ca being dissolved in $CaCl_2$.

[0055] Therefore, in the electrolysis chamber 8, the molten salt from the chlorination chamber 7 is introduced into the anode side, and the Ca formed on the liquid surface on the cathode side, either alone or together with a certain amount of $CaCl_2$, is sent to the reduction chamber 1. The Ca transferred to the reduction chamber 1 floats to the surface of the molten salt in the chamber and is dissolved in $CaCl_2$. Therefore, the Ca concentration in the $CaCl_2$ in the reduction chamber 1 is maintained at a high level in spite of the fact that the amount of the molten salt or Ca transferred from the chlorination chamber 7 to the reduction chamber 1 via the electrolysis chamber 8 is small.

[0056] Considering that the solubility of Ca in $CaCl_2$ is low, as mentioned above, part of the molten salt is transferred from the chlorination chamber 7 to the electrolysis chamber 8. In this way, the total production efficiency can be improved while avoiding the cycle involving a large amount of $CaCl_2$.

(Third embodiment)

[0057] Fig. 4 is a drawing explaining the configuration of a titanium production apparatus according to the third embodiment of the present invention. The third embodiment differs from the production apparatus according to the second embodiment as shown in Fig. 3, featured in that the chlorination chamber 7 is integrated with the reduction chamber 1. Otherwise, the configuration is substantially the same as that of the production apparatus according to the second embodiment.

[0058] The chlorination chamber 7 is laterally disposed being annexed to the vertical type reduction chamber 1 via a partition wall 10. In the reduction chamber 7, titanium oxide is introduced into the $CaCl_2$-based molten salt within the chamber through a feeding tube 11 inserted into the $CaCl_2$. The titanium formed from titanium oxide upon reduction with Ca in the $CaCl_2$ settles on the bottom of the reduction chamber 1 and downwardly extracted and sent to the lower separation means 2.

[0059] The $CaCl_2$ containing the byproduct CaO flows from the lower part of the reduction chamber 1 into the chlorination chamber 7 and undergoes chlorination treatment with chlorine gas injected thereinto from a site at the lower part thereof, whereby CaO is chlorinated. The $CaCl_2$ rises through the chlorination chamber 7 together with the chlorine gas flow (gas lift) rising within the chlorination chamber 7. The $CaCl_2$ separated from the metallic titanium in the separation means 2 is also introduced into the lower part of the chlorination chamber. On the other hand, the oxygen gas formed as a byproduct in the chlorination chamber 7 is drawn out upwards.

[0060] Most of the $CaCl_2$ outgoing from the chlorination chamber 7 is returned from the upper part of the chlorination chamber 7 to the reduction chamber 1. The remaining portion of $CaCl_2$ is transferred to the electrolysis chamber 8. In the electrolysis chamber 8, Ca is formed from the $CaCl_2$ thus introduced. The Ca formed in the electrolysis chamber 8 is transferred, either alone or together with a small amount of the Ca-rich $CaCl_2$, to the reduction chamber 1. The byproduct chlorine gas is sent to the chlorination chamber 7 for reuse.

[0061] The Ca introduced into the reduction chamber 1 forms a layer covering over the $CaCl_2$ in the reduction chamber 1. The feeding tube 11 mentioned above serves

for charging titanium oxide into the $CaCl_2$ through the Ca layer over the $CaCl_2$.

[0062] In the titanium production apparatus comprising the chlorination chamber 7 integrated with the reduction chamber 1, the transfer of $CaCl_2$ between both chambers becomes easy. It is also possible to transfer whole of the $CaCl_2$ coming out of the chlorination chamber 7 to the electrolysis chamber 8.

(Fourth embodiment)

[0063] Fig. 5 is a drawing explaining the configuration of a titanium production apparatus according to the fourth embodiment of the present invention. As compared with the production apparatus according to the third embodiment as shown in Fig. 4, the electrolysis chamber 8 is further added to the integrated reduction chamber 1 in the fourth embodiment. Otherwise, the configuration is substantially the same as that of the production apparatus according to the third embodiment.

[0064] The electrolysis chamber 8 is sideways disposed, as opposed to the chlorination chamber 7, having the reduction chamber 1 between them, and there is no partition wall provided between the reduction chamber and electrolysis chamber. The electrolysis chamber 8 is provided with a graphite anode 12 and an iron cathode 13, and the anode side is separated from the cathode side by a partition wall 9. The cathode side is located on the side of the reduction chamber 1 and unified with the reduction chamber 1 without any partition wall. The partition wall 9 is configured so that the molten salt can pass therethrough, like the case of the first embodiment.

[0065] The $CaCl_2$ transferred from the chlorination chamber 7 is introduced into the anode side. The chlorine gas generated as a byproduct on the anode side is sent to the chlorination chamber 7. The $CaCl_2$ introduced into the anode side passes through the partition wall 9 and migrates to the cathode side. Thus, to let the molten salt pass through the partition wall 9, there is formed, in the electrolysis chamber 8, a bath flow from the anode 12 side to the cathode 13 side with the supply of the molten salt to the anode side.

[0066] On the cathode side of the electrolysis chamber 8, Ca is formed on the surface of the iron cathode 13, and the Ca thus formed migrates to the reduction chamber 1 side while floating to the surface being carried by the bath flow. In the vicinity of the bath surface from the cathode 13 to the reduction chamber 1 side, there is provided a Ca reservoir 14. The Ca reservoir 14 is a box-like body whose bottom is open. It catches up the Ca that is formed on the surface of the cathode 13 and migrates toward the reduction chamber 1 side, and thus prevents the same from being cropped out above the bath surface. The Ca collected in the Ca reservoir 14 is dissolved in the $CaCl_2$ in the reduction chamber 1 and used for the reduction reaction within the reduction chamber 1.

[0067] In the fourth embodiment, the Ca reservoir 14 is made of iron, like the cathode 13, and it may be unified with the cathode 13 so that it can have the same potential as the cathode 13. The aim of providing the Ca reservoir 14 is to inhibit the Ca layer from being cropped out above the bath surface. In case that the space above the liquid surface on the reduction chamber side from the cathode 13 can be filled with an inert gas atmosphere, the Ca layer may be cropped out above the bath surface. However, in case the ingress of air is unavoidable for some or other operational reasons, the Ca layer cropping out above the bath surface leads to the formation of CaO by oxidation. In this regard, the Ca reservoir 14 is provided to avoid the formation of CaO as a result of oxidation as such.

[0068] Further, in the fourth embodiment, the upper part of the partition wall 9 is protruded toward the cathode 13 and is in contact with the cathode 13. This structure inhibits the Ca generated on the surface of the cathode 13 from staying between the cathode 13 and the partition wall 9.

[0069] In the titanium production apparatus in which the electrolysis chamber 8 is integrated with the reduction chamber 1, the transfer of Ca from the electrolysis chamber 8 to the reduction chamber 1 becomes easy. In particular, the cathode side where Ca is formed within the electrolysis chamber 8 can be unified with the reduction chamber 1 and therefore the partition wall between both the chambers can be eliminated. Therefore, the structure of the apparatus can be particularly simplified and the apparatus can be rendered small-sized.

(Fifth embodiment)

[0070] Fig. 6 is a drawing explaining the configuration of a titanium production apparatus according to the fifth embodiment of the present invention. In the configuration according to the fifth embodiment, the partition wall 9 in the electrolysis chamber 8 as found in the configuration of the production apparatus according to the fourth embodiment as shown in Fig. 6 has been eliminated. The other structural elements are substantially the same as those in the titanium production apparatus according to the fourth embodiment.

[0071] In the electrolysis chamber 8 unified with the reduction chamber 1, the molten salt is introduced into the anode side, as mentioned above, so that a flow of the molten salt from the anode 12 side to the cathode 13 side is formed. Therefore, even when the partition wall 9 separating the anode side and cathode side from each other is omitted, the efficiency can be prevented from decreasing because of the reflux of the molten salt. However, the cathode 13, like the partition wall 9, has a structure such that the molten salt can pass therethrough.

[0072] Above the cathode 13, however, there is provided a curtain wall type partition wall 15 made of a chlorine gas-resistant material such as a refractory material. It may be conceived that the cathode 13 be lengthened beyond the liquid surface level in lieu of the newly provided partition wall 15. In this case, however, there arises

the problem that the lengthened portion of the cathode 13 may be corroded by the chlorine gas generated on the anode side. Thus, it becomes necessary to provide the partition wall 15 separately from the cathode 13.

[0073] By omitting the partition wall 9 separating the anode side and cathode side from each other in the electrolysis chamber 8 according to the fifth embodiment, the apparatus structure is still more simplified and can be reduced the size more. On the other hand, there is no Ca reservoir on the reduction chamber side of the cathode 13 and, therefore, it is necessary to control the space above the liquid surface level on the reduction chamber side of the cathode 13 with an inert gas atmosphere.

(Sixth embodiment)

[0074] Fig. 7 is a drawing explaining the configuration of a titanium production apparatus according to the sixth embodiment of the present invention. Fig. 8 is a drawing explaining the cross-sectional configuration, seen along the line X-X, of the titanium production apparatus shown in Fig. 7.

Like the fourth and fifth embodiments, the sixth embodiment has a configuration such that the electrolysis chamber 8 is integrated with the reduction chamber 1. However, it has a configuration such that the reduction chamber 1 is formed like a cylinder and the electrolysis chamber 8 is formed like a cylinder surrounding the reduction chamber 1.

[0075] The cylindrical electrolysis chamber 8 provided outside the reduction chamber 1 has a cylindrical anode 12 serving also as the outer wall and a cylindrical cathode 13 serving also as the inner wall. All of the CaO and the Ca-free $CaCl_2$ obtained in the chlorination chamber 7 positioned sideways to the reduction chamber 1 are introduced into the ring-like space between the anode 12 and cathode 13. The inside cathode 13 serves also as part of the cylindrical outer wall of the reduction chamber 1, and the inside thereof is unified with the reduction chamber 1.

[0076] As shown in Fig. 8, the cathode 13 in the sixth embodiment comprises a plurality of cathode segments arranged in a swirling manner in the circumferential direction, and there is provided a slit 13a between every two cathode segments 13. This slit 13a is configured so as to pass the molten salt from the outside to the inside and thus it has a shape such that the space thereof gradually increases from the inside toward the outside. This configuration of each slit 13a causes the formation of an internal swirling flow and external swirling flow on each side of the cathode 13 and, at the same time, it promotes the flow of the molten salt from the outside to the inside.

[0077] Above the cathode 13, as a continuum, there is provided a cylindrical partition wall 15 made of a chlorine gas-resistant material, for example a refractory material. For the same reason as in the fifth embodiment, it becomes necessary to provide the partition wall 15 in addition to the cathode 13.

[0078] In the sixth embodiment, a swirling flow is generated on the external side of the cylindrical cathode 13 and, further, the molten salt flowing into the inside of the cathode 13, while swirling, comes down in the reduction chamber 1 and, thus, the Ca formed on the surface of the cathode 13 is smoothly drawn into the inside thereof. The Ca flowing into the inside of the cathode 13 floats to the surface above the $CaCl_2$ in the reduction chamber 1 and is dissolved in the $CaCl_2$, and the dissolved Ca contributes to the reduction reaction in the reduction chamber 1.

[0079] By configuring the electrolysis chamber 8 integrated with the reduction chamber 1 cylindrically and externally to the reduction chamber 1, it becomes possible to increase the areas of the anode 12 and cathode 13 in the electrolysis chamber 8. This enables more efficient apparatus designing. While, in the case described herein, the whole amount of the $CaCl_2$ obtained in the chlorination chamber 7 is introduced into the electrolysis chamber 8, it is also possible to introduce only a partial amount thereof into that chamber.

[0080] Although the cases of metallic titanium production have been described hereinabove, the metal to be produced in accordance with the present invention includes not only titanium but also tungsten, niobium, tantalum, chromium, zirconium and neodymium.

INDUSTRIAL APPLICABILITY

[0081] In accordance with the metal production method and metal production apparatus of the present invention, the electrolysis in the direct oxide reduction method comprising the step of reducing a metal oxide with Ca is carried out in a region outside the reduction area and the CaO is eliminated from the molten salt to be subjected to electrolysis, so that the problems encountered in the prior art of direct oxide reduction processes, namely the low productivity and the product quality deterioration due to contamination with carbon, can be avoided. The present invention thereby can greatly contribute to the practical use of the oxide reduction method in the field of metal production.

Claims

1. A method for producing a metal which comprises:

a reduction step in which a metal oxide is introduced into a $CaCl_2$-based molten salt containing Ca for the formation of said metal by reduction of the metal oxide with Ca in the molten salt;
a separation step in which said metal formed in the molten salt is separated from the molten salt;
a chlorination step in which the molten salt after separation of said metal is subjected to chlorination treatment with chlorine gas to chlorinate the byproduct CaO in the molten salt; and

an electrolysis step in which the molten salt after chlorination treatment is electrolyzed to form Ca and chlorine from $CaCl_2$, and the thus-formed Ca or Ca-containing molten salt is sent to the above-mentioned reduction step.

2. A method for producing a metal which comprises:

a reduction step in which a metal oxide is introduced into a $CaCl_2$-based molten salt containing Ca for the formation of said metal by reduction of the metal oxide with Ca in the molten salt;
a separation step in which the metal formed in the molten salt is separated from the molten salt;
a chlorination step in which the molten salt after separation of said metal is subjected to chlorination treatment with chlorine gas to chlorinate the byproduct CaO in the molten salt; and
an electrolysis step in which the molten salt after chlorination treatment is electrolyzed to form Ca and chlorine from $CaCl_2$, and the thus-formed Ca or Ca-containing molten salt is sent to the above-mentioned reduction step,

wherein, in said reduction step, the metal formed is allowed to settle and the metal that has settled is drawn out together with the molten salt and transferred to the separation step.

3. A method for producing a metal according to claim 1 or 2, wherein said metal is one of titanium, tungsten, niobium, tantalum, chromium, zirconium and neodymium.

4. A method for producing a metal according to claim 1 or 2, wherein part of the molten salt after chlorination treatment is sent to the electrolysis step and the remaining portion of the molten salt is sent to the reduction step.

5. A method for producing a metal according to claim 1 or 2, wherein the chlorine gas formed in said electrolysis step is used in said chlorination step.

6. A method for producing a metal according to claim 1 or 2, wherein, in said electrolysis step, an electrolysis chamber in which the anode side and cathode side are separated from each other by a partition wall is used.

7. A method for producing a metal according to claim 6, wherein a flow of the molten salt from the anode side toward the cathode side is formed in the electrolysis chamber.

8. A method for producing a metal according to claim 1 or 2, further comprising the step of rinsing the metal separated from the molten salt using part of the $CaCl_2$ after completion of said chlorination step.

9. A method for producing a metal according to claim 1 or 2, wherein, in said separation step, said metal is separated from the molten salt by physical compacting together.

10. A method for producing a metal according to claim 1 or 2, further comprising the step of melting the metal obtained in the separation step in an inert atmosphere to make an ingot.

11. An apparatus for producing a metal comprising:

a reduction chamber in which a $CaCl_2$-based molten salt containing Ca is held and a metal oxide introduced into the molten salt is reduced with Ca in the molten salt to obtain said metal;
means for separating the metal formed in the molten salt from the molten salt;
a chlorination chamber in which the molten salt after separation of the metal is held and the molten salt is subjected to chlorination treatment with chlorine gas for the chlorination of the byproduct CaO in the molten salt;
an electrolysis chamber in which the molten salt after chlorination treatment is held and the molten salt is electrolyzed to form Ca and chlorine from $CaCl_2$; and
means for transferring the thus-formed Ca or Ca-containing molten salt from the electrolysis chamber to said reduction chamber.

12. An apparatus for producing a metal comprising:

a reduction chamber in which a $CaCl_2$-based molten salt containing Ca is held and a metal oxide introduced into the molten salt is reduced with Ca in the molten salt to obtain said metal;
means for separating the metal formed in the molten salt from the molten salt;
a chlorination chamber in which the molten salt after separation of the metal is held and the molten salt is subjected to chlorination treatment with chlorine gas for the chlorination of the byproduct CaO in the molten salt;
an electrolysis chamber in which the molten salt after chlorination treatment is held and the molten salt is electrolyzed to form Ca and chlorine from $CaCl_2$; and
means for transferring the thus-formed Ca or Ca-containing molten salt from the electrolysis chamber to said reduction chamber,

wherein said chlorination chamber is unified with said reduction chamber.

13. An apparatus for producing a metal comprising:

a reduction chamber in which a $CaCl_2$-based molten salt containing Ca is held and a metal oxide introduced into the molten salt is reduced with Ca in the molten salt to obtain said metal;
means for separating the metal formed in the molten salt from the molten salt;
a chlorination chamber in which the molten salt after separation of the metal is held and the molten salt is subjected to chlorination treatment with chlorine gas for the chlorination of the by-product CaO in the molten salt;
an electrolysis chamber in which the molten salt after chlorination treatment is held and the molten salt is electrolyzed to form Ca and chlorine from $CaCl_2$; and
means for transferring the thus-formed Ca or Ca-containing molten salt from the electrolysis chamber to said reduction chamber,

wherein said electrolysis chamber is integrated with said reduction chamber.

14. An apparatus for producing a metal according to any of claims 11-13, wherein said electrolysis chamber has, between the anode side and cathode side, a partition wall through which the molten salt can pass.

15. An apparatus for producing a metal according to claim 13, wherein the cathode side of said electrolysis chamber is unified with said reduction chamber.

16. An apparatus for producing a metal according to claim 15, wherein said electrolysis chamber is configured in such a manner that the molten salt introduced into the anode side can flow through the cathode to the reduction chamber.

17. An apparatus for producing a metal according to claim 16, further comprising a Ca reservoir for retaining Ca in the liquid on the reduction chamber side from the cathode.

18. An apparatus for producing a metal according to claim 15, wherein said electrolysis chamber is formed like a ring surrounding the reduction chamber which has a cylindrical shape.

19. An apparatus for producing a metal according to claim 18, wherein said electrolysis chamber comprises an outer cylinder serving also as the anode and an inner cylinder serving also as the cathode and allowing the molten salt to pass therethrough, the inside of said inner cylinder being the reduction chamber.

FIG.1

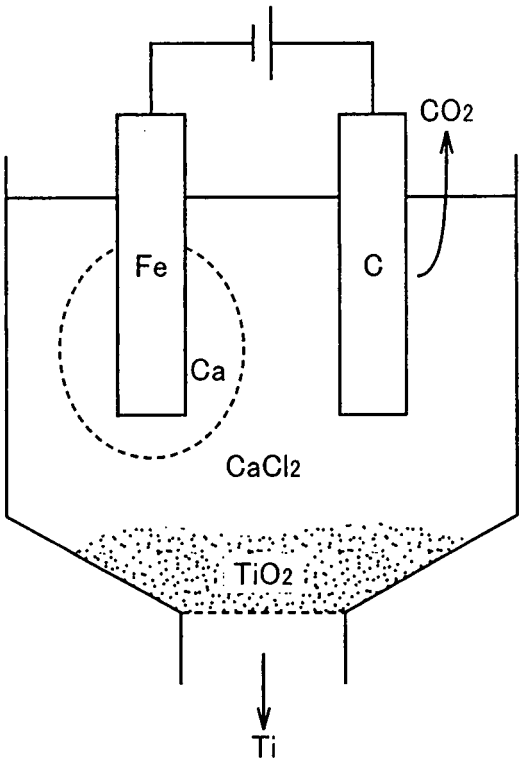


FIG.2

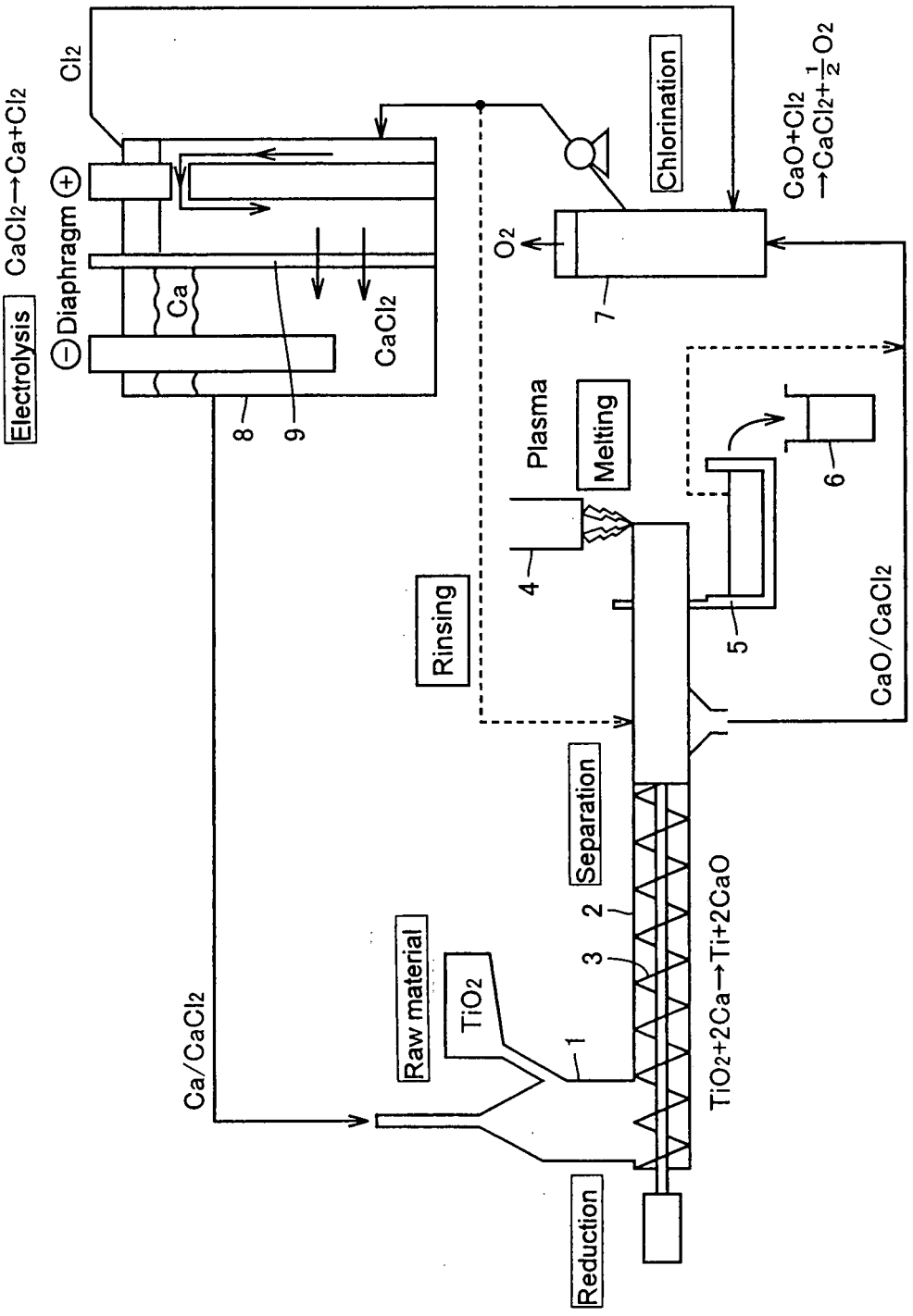

Electrolysis
CaCl2→Ca+Cl2
Cl2
⊖Diaphragm⊕
Ca
CaCl2
8
9
Chlorination
O2
7
CaO+Cl2
→CaCl2+1/2 O2
Plasma
Melting
6
4
Rinsing
5
CaO/CaCl2
Separation
2
3
1
Raw material
TiO2
Ca/CaCl2
TiO2+2Ca→Ti+2CaO
Reduction

FIG.3

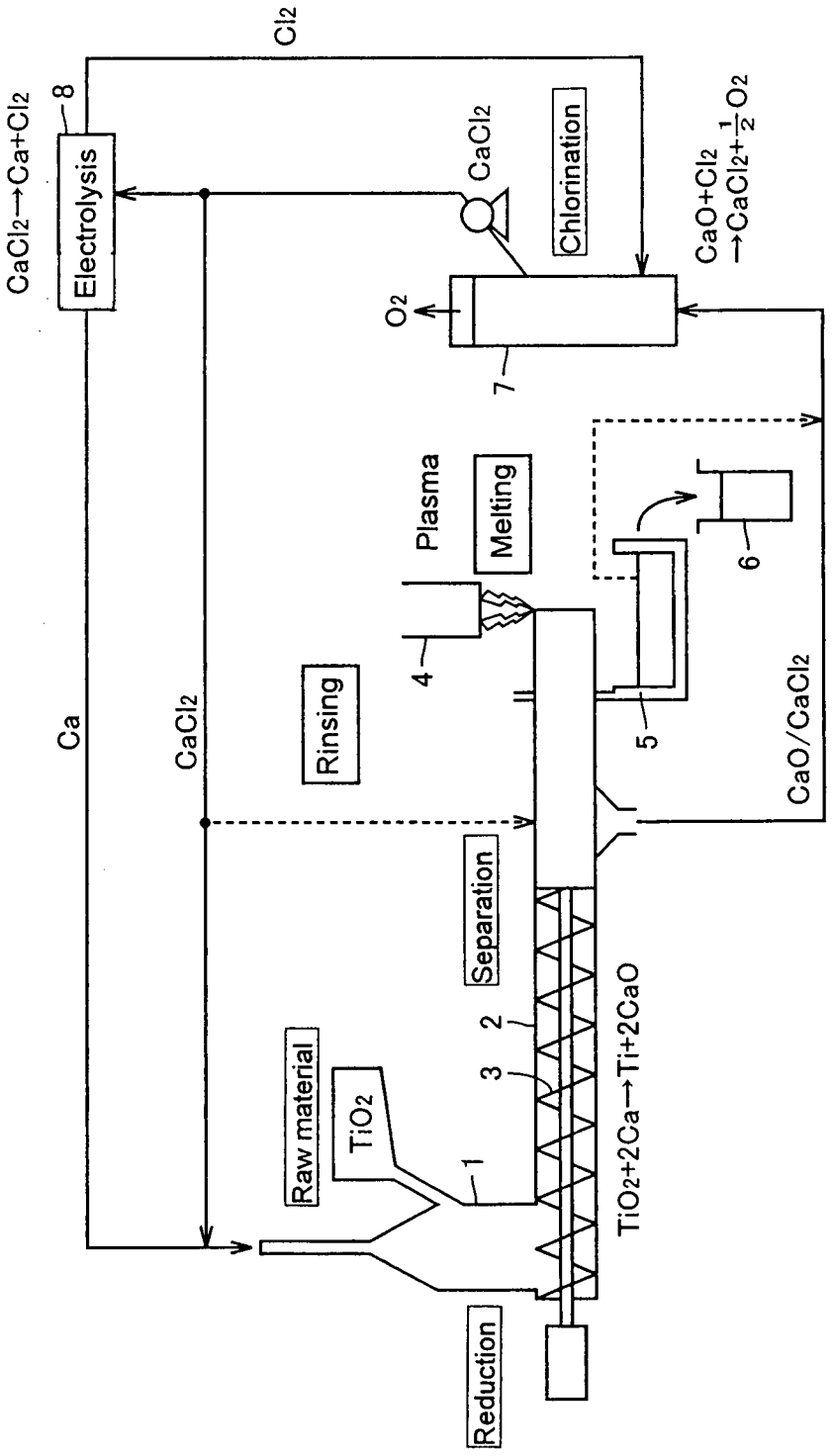

Cl2
CaCl2→Ca+Cl2
8
Electrolysis
CaCl2
Chlorination
CaO+Cl2
→CaCl2+1/2O2
O2
7
Plasma
Melting
6
4
5
Ca
CaCl2
Rinsing
CaO/CaCl2
Separation
2
3
Raw material
TiO2
1
TiO2+2Ca→Ti+2CaO
Reduction

FIG.4

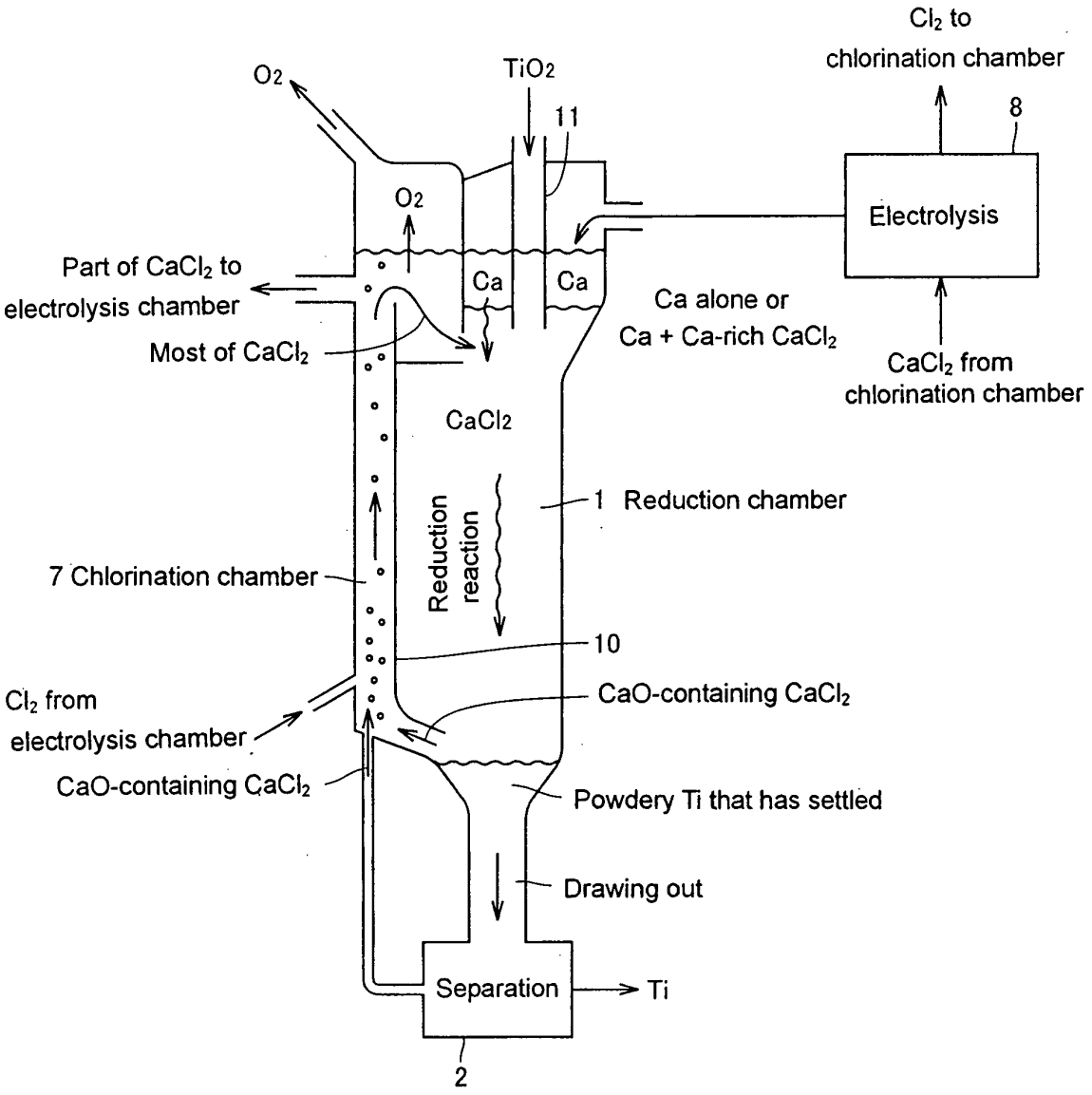

Cl_2 to
chlorination chamber
8
Electrolysis
$CaCl_2$ from
chlorination chamber
O_2
TiO_2
11
O_2
Part of $CaCl_2$ to
electrolysis chamber
Most of $CaCl_2$
Ca
Ca
Ca alone or
Ca + Ca-rich $CaCl_2$
$CaCl_2$
1 Reduction chamber
Reduction
reaction
7 Chlorination chamber
10
Cl_2 from
electrolysis chamber
CaO-containing $CaCl_2$
CaO-containing $CaCl_2$
Powdery Ti that has settled
Drawing out
Separation
Ti
2

FIG.5

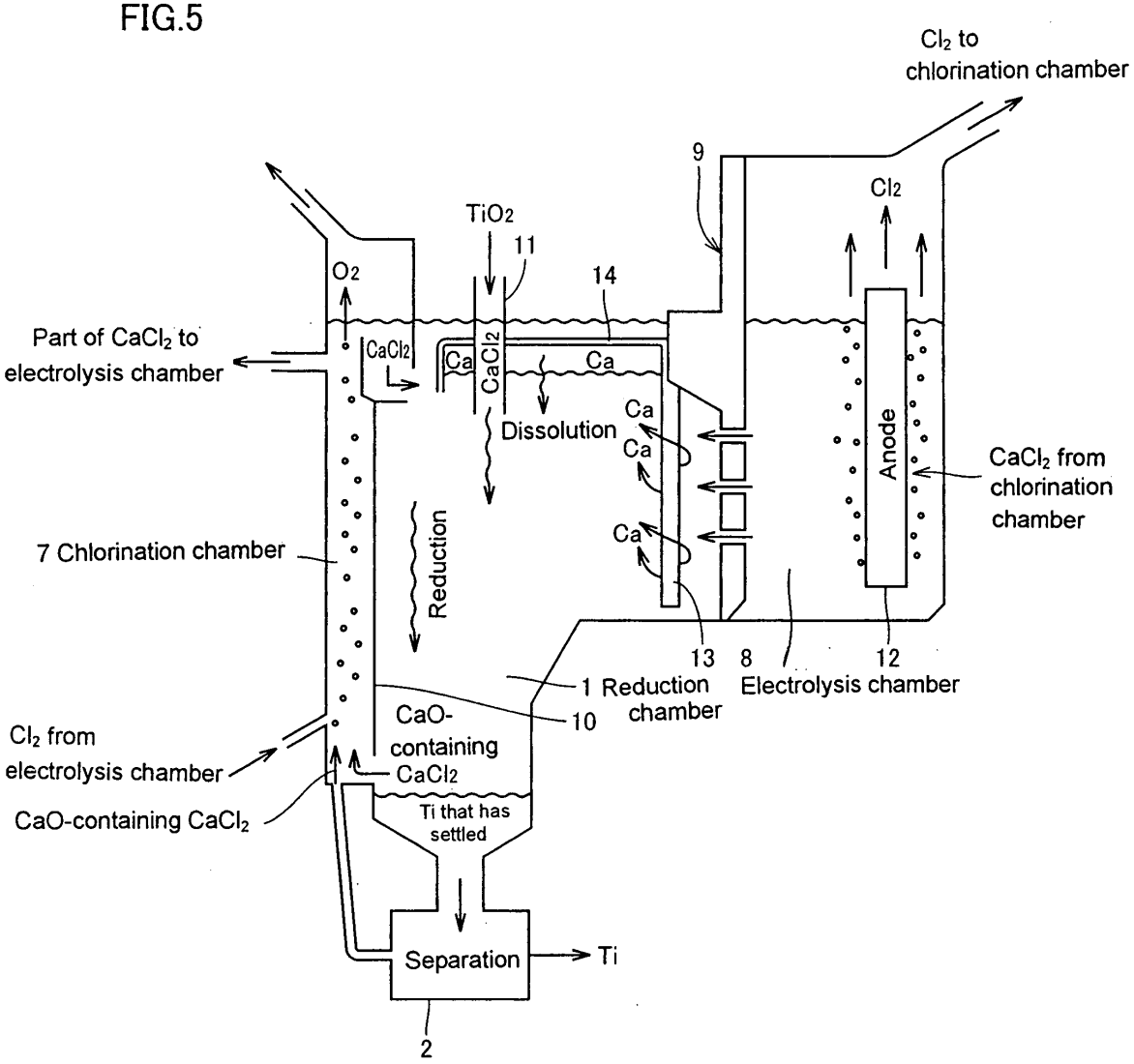

Cl_2 to chlorination chamber
9
Cl_2
TiO_2
11
14
O_2
Part of $CaCl_2$ to electrolysis chamber
$CaCl_2$
Ca
$CaCl_2$
Ca
Dissolution
Ca
Ca
Ca
Anode
$CaCl_2$ from chlorination chamber
7 Chlorination chamber
Reduction
13
8
12
1 Reduction chamber
Electrolysis chamber
10
Cl_2 from electrolysis chamber
CaO-containing $CaCl_2$
CaO-containing $CaCl_2$
Ti that has settled
Separation
Ti
2

FIG.6

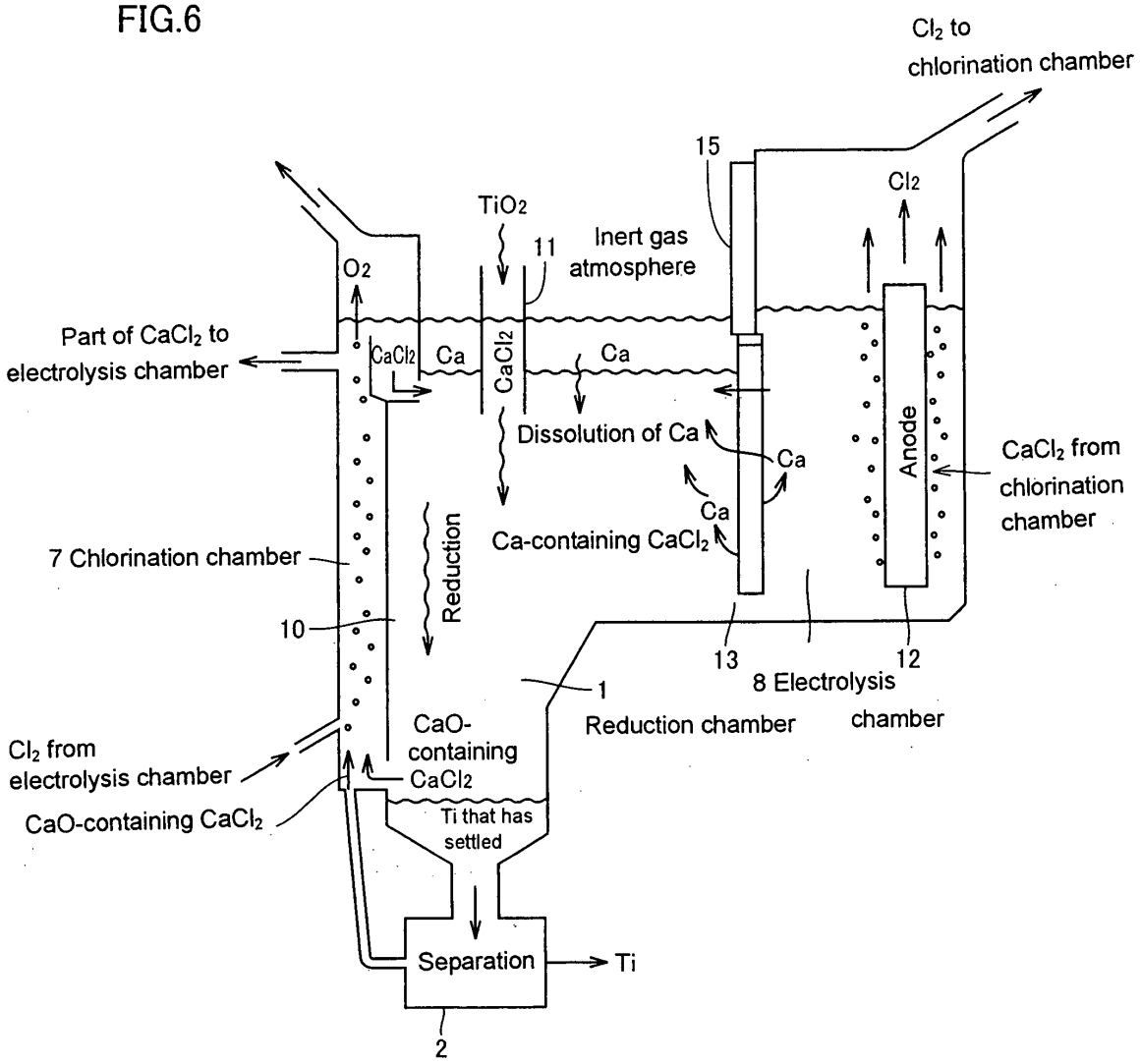

Cl_2 to chlorination chamber
15
Cl_2
TiO_2
11
Inert gas atmosphere
O_2
Part of $CaCl_2$ to electrolysis chamber
$CaCl_2$
Ca
$CaCl_2$
Ca
Dissolution of Ca
Ca
Ca
Anode
$CaCl_2$ from chlorination chamber
Ca-containing $CaCl_2$
7 Chlorination chamber
Reduction
10
13
12
1
8 Electrolysis chamber
Reduction chamber
Cl_2 from electrolysis chamber
CaO-containing $CaCl_2$
CaO-containing $CaCl_2$
Ti that has settled
Separation
Ti
2

FIG.7

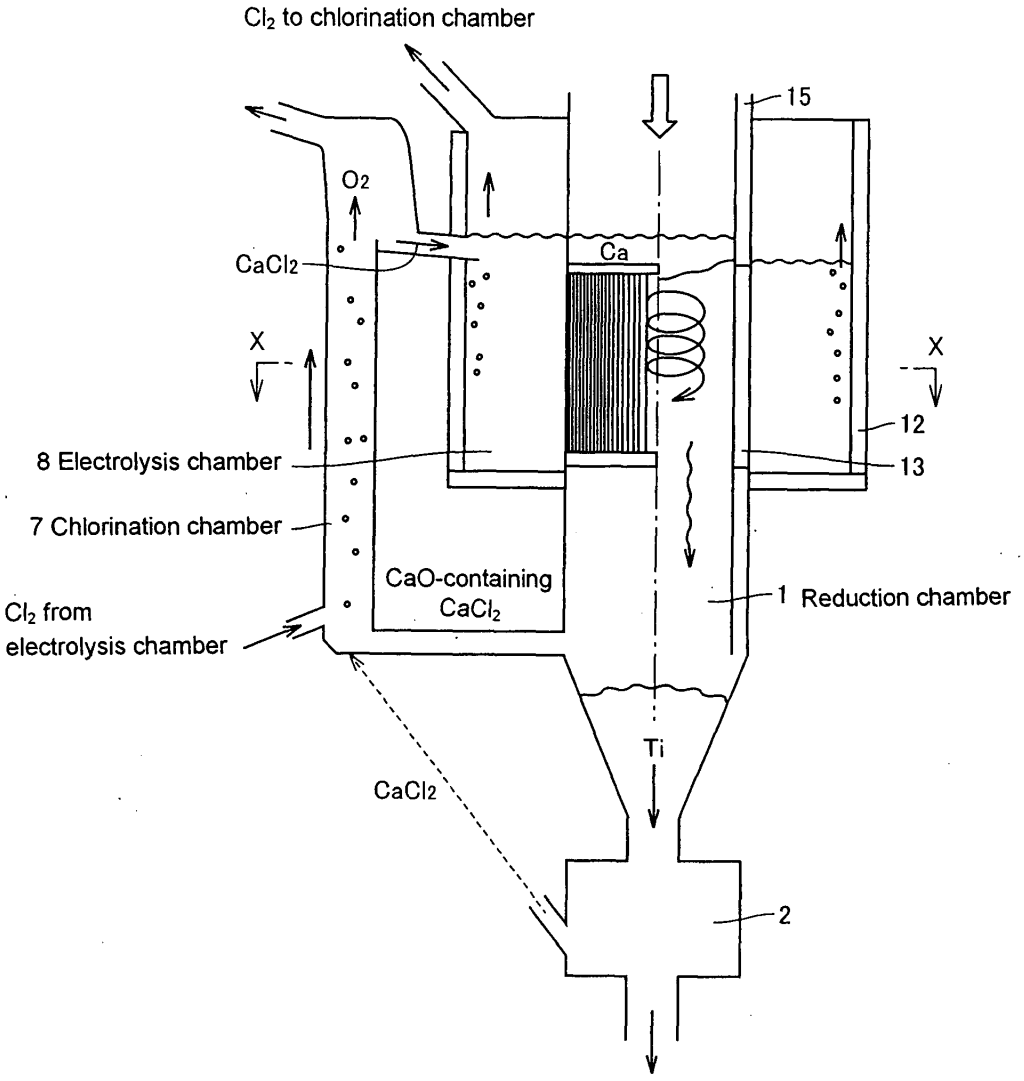
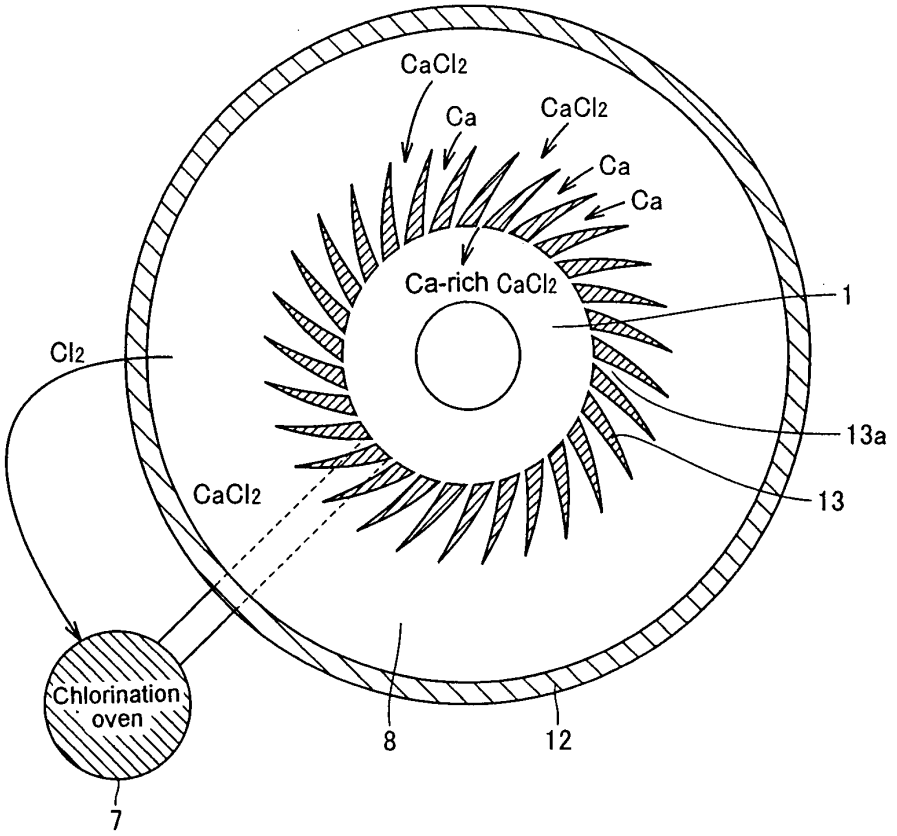

Cl2 to chlorination chamber
15
O2
CaCl2
Ca
X
X
12
8 Electrolysis chamber
13
7 Chlorination chamber
CaO-containing
CaCl2
1 Reduction chamber
Cl2 from
electrolysis chamber
Ti
CaCl2
2

FIG.8


CaCl2
Ca
CaCl2
Ca
Ca
Ca-rich CaCl2
1
Cl2
13a
CaCl2
13
Chlorination oven
8
12
7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/010024

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C22B34/12, C22B5/02, C22B34/14, C22B34/22, C22B34/32, C22B34/36, C22B59/00, C25C3/02

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)
Int.Cl[7] C22B34/12, C22B5/02, C25C3/02

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 1996-2004
Kokai Jitsuyo Shinan Koho 1971-2004 Toroku Jitsuyo Shinan Koho 1994-2004

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	Ryosuke O. SUZUKI et al., Calciothermic Reduction of Titanium Oxide and in-situ Electrolysis in Molten $CaCl_2$, Metallurgical & Materials Transactions B, June 2003, Vol.34B, pages 287 to 295	1-19
A	JP 2002-129250 A (Katsutoshi ONO), 09 May, 2002 (09.05.02), Par. Nos. [0012] to [0018] (Family: none)	1-19
A	Katsutoshi ONO et al., "Kangensei Yoyuen ni yoru Sanka Titanium no Chokusetsu Kangen", Materia, 2002, Vol.41, No.1, pages 28 to 31	1-19

☒ 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
04 October, 2004 (04.10.04)	26 October, 2004 (26.10.04)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/010024

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Ryosuke O. SUZUKI et al., Calciothermic Reduction of Titanium Oxide in Molten $CaCl_2$, Metallurgical & Materials Transactions B, June 2003, Vol.34B, pages 277 to 286	1-19
A	G.Z. Chen et al., Direct Electrochemical Reduction of Titanium Dioxide to Titanium in Molten Calcium Chloride, Nature, 2000, Vol.407, pages 361 to 363	1-19
A	JP 2000-345252 A (Kabushiki Kaisha Sumitomo Sitix Amagasaki), 12 December, 2000 (12.12.00), Claims (Family: none)	1-19
P,A	JP 2004-131784 A (Katsutoshi ONO et al.), 30 April, 2004 (30.04.04), Claims; drawings (Family: none)	1-19
P,A	JP 2004-52073 A (Katsutoshi ONO et al.), 19 February, 2004 (19.02.04), Claims; drawings (Family: none)	1-19

Form PCT/ISA/210 (continuation of second sheet) (January 2004)