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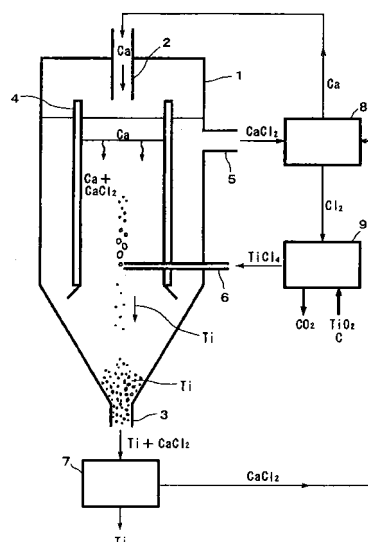
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(54) **METHOD FOR PRODUCING Ti OR Ti ALLOY THROUGH REDUCTION BY Ca**

(57) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction step of holding a molten salt, containing CaCl_2 and having Ca dissolved therein, in a reactor vessel 1, and reacting a metallic chloride containing TiCl_4 with Ca in said salt to generate particles of Ti or Ti alloys in said salt; and a separation step of separating particles of Ti or Ti alloys, generated in said salt, from said salt. An electrolysis step 8, in which CaCl_2 discharged outside the reactor vessel 1 is electrolyzed into Ca and Cl_2 , and the generated Ca is used for the generation reaction of Ti or Ti alloys in the reactor vessel 1, is preferably added. In the electrolysis step 8, an alloy electrode made of a molten Ca alloy, if applied for a cathode, is effective in enhancing the electricity efficiency, and also can be effectively utilized as a carrier medium of Ca for raising a Ca concentration of molten salt. By this method, high-purity Ti metals can be efficiently and economically produced.

FIG. 1



Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing Ti or Ti alloys through reduction by Ca (hereinafter, can be referred to as "by a Ca reduction"), in which a metallic chloride containing TiCl_4 is reduced by Ca to produce Ti metals or Ti alloys.

BACKGROUND ART

[0002] The Kroll method for reducing TiCl_4 by Mg is generally used as an industrial production method of Ti metals. In the Kroll method, Ti metal is produced through a reduction step - vacuum separation step. In a reduction step, TiCl_4 which is of a raw material of Ti is reduced by Mg in a reactor vessel to produce the sponge-like Ti metals. In a vacuum separation step, unreacted Mg and MgCl_2 formed as a by-product are removed from the sponge-like Ti metals produced in the reactor vessel.

[0003] To explain the reduction step in detail, in the reduction step, the reactor vessel is filled with the molten Mg, and TiCl_4 liquid is supplied from above the liquid surface of molten Mg. This allows TiCl_4 to be reduced by Mg in the vicinity of the liquid surface of molten Mg to generate Ti metals in a particulate form. The generated Ti metal sequentially moves downward. At the same time, molten MgCl_2 is generated as a by-product in the vicinity of the liquid surface. A specific gravity of molten MgCl_2 is larger than that of molten Mg. The molten MgCl_2 which is of the by-product moves downward due to the specific-gravity difference, and the molten Mg emerges in the liquid surface instead. The molten Mg is continuously supplied to the liquid surface by the specific-gravity difference substitution, and the reaction is continued.

[0004] In the production of Ti metals by the Kroll method, high-purity products can be produced. However, in the Kroll method, because the products are produced in a batch manner, the production costs are increased and the price of products becomes remarkably expensive. One of factors of the increased production costs is the difficulty of enhancing a feed rate of TiCl_4 . The following three reasons are considered to restrict the feed rate of TiCl_4 .

[0005] In order to improve the productivity in the Kroll method, it is effective to increase the feed rate of TiCl_4 which is of the raw material of Ti, i.e., to enhance a supply amount of molten Mg to the liquid surface per unit area and/or per unit time. However, when the feed rate is excessively increased, the rate of the specific-gravity difference substitution cannot keep up with the reaction rate, so that MgCl_2 remains in the liquid surface, and TiCl_4 is supplied to MgCl_2 , thus resulting in decreasing the utilization efficiency of TiCl_4 . As a result, the supplied raw material becomes an unreacted generated gas (referred to as an unreacted gas) such as an unreacted TiCl_4 gas and an unreacted TiCl_3 gas, and the unreacted gas is discharged outside the reactor vessel. It is necessary to avoid the generation of unreacted gas, because a rapid increase in the inner pressure within the reactor vessel is associated with the generation of unreacted gas. There is a limit of the feed rate of TiCl_4 which is of the raw material of Ti by reason of the above.

[0006] When the feed rate of TiCl_4 is enhanced, a precipitation amount of Ti is increased in the inner surface of reactor vessel above the liquid surface. As the reducing reaction proceeds, the liquid surface of molten Mg rises intermittently. Therefore, the precipitated Ti in the inner surface of the upper portion of the reactor vessel is immersed in the molten Mg in the later stage of the reducing reaction, which causes the effective area of the Mg liquid surface to be decreased to thereby reduce the reaction rate. In order to suppress the decrease of reaction rate, it is necessary that the feed rate of TiCl_4 be restricted to prevent the Ti precipitation in the inner surface of the upper portion of reactor vessel. Japanese Patent Application Publication No. 8-295955 proposes a different countermeasure for suppressing the Ti precipitation in the inner surface of the upper portion of reactor vessel. However, the countermeasure proposed in Japanese Patent Application Publication No. 8-295955 is not sufficient.

[0007] In the Kroll method, since the reaction is performed only in the vicinity of the liquid surface of molten Mg liquid in the reactor vessel, an exothermic area is narrowed. Therefore, when TiCl_4 is supplied at a high rate, cooling cannot keep up with the supply of TiCl_4 in the reaction area. This also causes the feed rate of TiCl_4 to be restricted.

[0008] Although the feed rate of TiCl_4 is not directly affected, in the Kroll method, Ti is generated in a particulate form in the vicinity of the liquid surface of molten Mg liquid, and Ti moves downward. However, because of wetting properties (adhesion properties) of molten Mg, the generated Ti particles moves downward and sinks to accumulate as sediment while aggregated, and the Ti particles are sintered to grow in particulate size to be the lump-like Ti at melting-temperature conditions during moving downward, which makes it difficult to discharge the Ti particles outside the reactor vessel. Therefore, in the Kroll method, the continuous production is difficult to be performed, and the improvement of productivity is blocked. This is why Ti is produced in the batch manner as well as in the form of sponge titanium by the Kroll method.

[0009] With reference to Ti production methods except the Kroll method, for example, US Patent No. 2,205,854 describes that, besides Mg, Ca can be used as the reducing agent of TiCl_4 . US Patent No. 4,820,339 describes a method for producing Ti through the reducing reaction by Ca, in which the molten salt of CaCl_2 is held in the reactor vessel, the metallic Ca powder is supplied into the molten salt from above, Ca is dissolved in the molten salt, and a TiCl_4 gas is

supplied from below to react the dissolved Ca with TiCl_4 in the molten salt of CaCl_2 .

[0010] In the reduction by Ca, Ti metals are generated from TiCl_4 by the reaction of the following chemical formula (i), and CaCl_2 is also generated as the by-product at the same time. Ca has a stronger affinity to Cl than Mg has, and Ca is suitable for the reducing agent of TiCl_4 in principle. Particularly, in the method described in US Patent No. 4,820,339, Ca is used while dissolved in the molten CaCl_2 . When the reducing reaction by Ca is utilized in the molten CaCl_2 , like the Kroll method, TiCl_4 is supplied to the liquid surface of reducing agent in the reactor vessel, which enlarges the reaction area compared with the case that the reaction area is restricted in the vicinity of liquid surface. Accordingly, since the exothermic area is also enlarged to facilitate cooling, the feed rate of TiCl_4 which is of the raw material of Ti can be largely enhanced, and the remarkable improvement of productivity can be also expected.

[0011] $\text{TiCl}_4 + 2\text{Ca} \rightarrow \text{Ti} + 2\text{CaCl}_2$ --- (i)

[0012] However, it is difficult for the method described in US Patent No. 4,820,339 to be adopted as the industrial Ti production method. It is because the metallic Ca powder is used as the reducing agent. Namely, since the metallic Ca powder is highly expensive, the purchase and use of metallic Ca powder leads to increase the production costs to be higher than that of the Kroll method in which the feed rate of TiCl_4 is restricted. In addition, highly reactive Ca is extremely difficult to handle, which also becomes the factor of blocking the industrial application of the method for producing Ti by the Ca reduction.

[0013] US Patent No. 2,845,386 describes the Olsen method as another Ti production method. This method is a kind of oxide direct-reduction method for directly reducing TiO_2 by Ca. Although the oxide direct-reduction method is highly efficient, it is not suitable for producing high-purity Ti. The reason is that this method entails to use expensive high-purity TiO_2 .

DESCLOSURE OF THE INVENTION

[0014] It is an object of the present invention to provide a method for economically producing high-purity Ti metals or high-purity Ti alloys with high efficiency without using an expensive reducing agent.

[0015] In order to achieve the above object, the present inventors consider that reducing TiCl_4 by Ca is indispensable and made an attempt to utilize Ca that dissolves in the molten salt of CaCl_2 as described in US Patent No. 4,820,339. Since Ca dissolves in CaCl_2 by about 1.5%, by utilizing the reducing reaction that Ca reduces TiCl_4 in this molten CaCl_2 , there is a possibility that the feed rate of TiCl_4 can be increased to thereby enhance the production efficiency dramatically, as afore-mentioned.

[0016] In the method for producing Ti by such a Ca reduction, Ca in the molten salt is consumed as the reaction expressed by the above equation (i) progresses. In replenishing the consumed amount, the metallic Ca powder needs to be continuously supplied into the reducing reaction vessel according to the method described in US Patent No. 4,820,339.

[0017] The present inventors consider that Ca in the molten salt, decreased by consumption during the reducing reaction, needs to be economically replenished in order to industrially establish the method for producing Ti by a Ca reduction, and came up with, as the replenishing means, the method of utilizing Ca being produced by an electrolysis of molten salt, as well as with the method of using this Ca in circulation. Namely, although Ca in the molten salt should be consumed in association with the reducing reaction, when electrolyzing this molten salt, Ca is generated in the molten salt. So by reusing Ca thus obtained for the reducing reaction, it becomes unnecessary to replenish Ca by outside source. Moreover, in this method, there is no need to strictly take out Ca only, which should be one factor to enhance the economic efficiency. If Ca should be independently extracted as a solid matter, a lot of difficulties are accompanied, while merely generating Ca in the molten salt is relatively easy to be done.

[0018] The present invention is completed based on such conception and pertains to a method for producing Ti or Ti alloys by a Ca reduction as described in the following (1), (2) or (3).

[0019] (1) A method for producing Ti or Ti alloys by a Ca reduction, includes: a reduction step in which a molten salt, containing CaCl_2 and having Ca dissolved therein, is held in a reactor vessel, and a metallic chloride containing TiCl_4 is reacted with Ca in the molten salt to generate Ti particles or Ti alloy particles in the molten salt; and a separation step in which Ti particles or Ti alloy particles, generated in the molten salt, are separated from the molten salt (hereinafter, referred to as a first production method).

[0020] (2) A method for producing Ti or Ti alloys by a Ca reduction, the method comprising a combined process of a reduction step and a circulation-type electrolysis step, wherein said reduction step includes the steps of: holding a molten salt, containing CaCl_2 and having Ca dissolved therein, in a reactor vessel; and, reacting a metallic chloride containing TiCl_4 with Ca in the molten salt to generate Ti particles or Ti alloy particles in the molten salt, and wherein said circulation-type electrolysis is configured such that the molten salt, being used for producing said Ti or Ti alloys and discharged outside said reactor vessel, is electrolyzed to generate and replenish Ca in said molten salt which is returned to said reactor vessel, and wherein, in electrolyzing as above, an alloy electrode made of molten Ca alloy is employed for a cathode (hereinafter, referred to as a second production method).

[0021] (3) A method for producing Ti or Ti alloys by a Ca reduction, includes the steps of: generating Ca by an electrolysis in which a molten salt containing CaCl_2 is electrolyzed by employing a molten Ca alloy as a cathode to increase a Ca content ratio in said molten Ca alloy; replenishing Ca by dissolving Ca in relevant molten salt in which the molten Ca alloy, having Ca increased by the Ca generation step, get contacted with the molten salt containing CaCl_2 ; and, generating Ti by a reducing reaction such that a metallic chloride containing TiCl_4 is supplied into the molten salt having the dissolved Ca by the Ca replenishing step to thereby generate Ti or Ti alloys in the molten salt (hereinafter, referred to as a third production method).

[0022] A first production method as above is the method including: a reduction step in which Ti particles or Ti alloy particles are generated in the molten salt; and, a separation step in which Ti particles or Ti alloy particles thus generated are separated from the molten salt, but can adopt the embodiment mode, as described hereinbelow, such that CaCl_2 generated as a by-product in association with the generation of Ti or Ti alloys is discharged outside the reactor vessel to be electrolyzed for generating Ca that is to be utilized in the generation reaction (namely, the reducing reaction of TiCl_4) of Ti or Ti alloys. A second production method has a feature in respect of using an alloy electrode made of molten Ca alloy for a cathode. Besides, in these methods i.e., a first and a second production method, in order to use Ca in circulation, the molten CaCl_2 salt with the enhanced Ca concentration is circulated between the reducing step and the electrolysis step.

[0023] Also, a third production method appears to be similar to a second production method in respect of using an alloy Ca alloy electrode in the electrolysis step, but has a feature of making use of molten Ca alloy with the increased Ca content ratio as a carrier medium for transferring Ca, in using Ca circularly.

[0024] The method for producing Ti or the Ti alloys by a Ca reduction is named the "OYIK method" after initials of four persons of Ogasawara, Yamaguchi, Ichihashi, and Kanazawa who deeply engages in conception, development, and completion.

[0025] In a first through a third production method, as Ti particles are generated by the Ca reduction in the molten salt containing CaCl_2 , the region where the reducing reaction takes place expands and simultaneously the exothermic region is also enlarged. Further, the vapor pressure of Mg at 850 °C is 6.7 kPa (50 mmHg), whereas the vapor pressure of Ca is as extremely small as 0.3 kPa (2 mmHg). By this difference in the vapor pressure, Ti precipitated on the inner surface at the upper portion of reactor vessel, when Ca is used, is much less than that when Mg is used. Consequently, in a first through a third production method, it becomes possible to greatly increase the feed rate of TiCl_4 .

[0026] Further, Ca is inferior in wetting properties (adhesion properties) to Mg, and the Ca adhering to precipitated Ti particles is dissolved in CaCl_2 , so that the aggregation of particles becomes less in the generated titanium particles and sintering is significantly lessened. Therefore, generated Ti can be discharged outside the reactor vessel in a particle state, and the Ti production can continuously be operated.

[0027] In a first through a third production method, a metallic chloride containing TiCl_4 (hereinafter, may referred to as TiCl_4 simply) reacts with Ca dissolved in the molten salt containing CaCl_2 (hereinafter, may be referred to as a molten salt or molten CaCl_2 simply). Further, in a first production method, it is not prohibited to hold the molten Ca liquid on the molten CaCl_2 liquid surface within the reactor vessel. Rather, by holding the molten Ca liquid on the molten CaCl_2 liquid surface, Ca can be supplied from the Ca liquid layer to the CaCl_2 liquid layer located below to thereby enable the reaction efficiency to be raised. Also, the reducing reaction even in the molten Ca liquid becomes possible, thus enabling the reaction efficiency to be raised too.

[0028] In a first through a third production method, as a supply mode of TiCl_4 to the molten CaCl_2 liquid, although it is preferable for TiCl_4 in a gas state to be directly supplied into the molten CaCl_2 liquid since the contact efficiency of TiCl_4 with Ca in the molten CaCl_2 liquid is high, it is also possible for TiCl_4 in a liquid state or in a gas state to be supplied on the liquid surface of molten CaCl_2 liquid, or it is also possible for TiCl_4 in a liquid state or in a gas state to be supplied on the liquid surface of molten Ca liquid or deep into the liquid which is held on the liquid surface of molten CaCl_2 liquid.

[0029] And further, when the method for reducing TiCl_4 by Ca is applied to the supply of TiCl_4 , there are various advantages compared with the Kroll method in which the reduction is performed by Mg.

[0030] In the Kroll method in which the reduction is performed by Mg, the TiCl_4 liquid is supplied to the liquid surface of molten Mg liquid. Conventionally it is tried that TiCl_4 gas is supplied into the molten Mg liquid in aiming the expansion of the reaction region. However, as described above, since Mg has the large vapor pressure, Mg vapor intrudes in a supply nozzle to react with TiCl_4 , and a supply pipe is clogged.

The problem of nozzle clogging still remains even if TiCl_4 gas is supplied into the molten MgCl_2 liquid. This is attributed to the fact that the melt is agitated by bubbling of TiCl_4 and sometimes molten Mg reaches the supply nozzle, although a clogging frequency of the supply pipe is decreased. As much as anything, even if TiCl_4 is supplied to the molten MgCl_2 liquid, because Mg is not dissolved in the melt, the Ti precipitation reaction is unlikely to occur.

[0031] On the contrary, in the method of reducing TiCl_4 by Ca, the nozzle clogging is hardly generated when the TiCl_4 gas is supplied into the molten CaCl_2 liquid. Therefore, TiCl_4 gas can be supplied into the molten CaCl_2 liquid, and TiCl_4 gas can also be supplied into the molten Ca liquid. That the molten Ca has the small vapor pressure is cited as the reason why the nozzle clogging is hardly generated.

[0032] Namely, in a first through a third production method in which TiCl_4 is reduced by Ca, it is particularly desirable that TiCl_4 be directly supplied in a gas state into the molten salt, and this supply mode can be applied with no problem in the actual operation. It is also possible that TiCl_4 is supplied on the liquid surface of molten salt, or it is also possible that liquid or gaseous TiCl_4 is supplied on the liquid surface or into the liquid of the molten Ca liquid held on the molten CaCl_2 liquid. These supply modes can also be applied with no problem in the actual operation.

[0033] In a first through a third production method, the reduction step (Ti generation step by the reducing reaction in a third production method as above corresponds to the reduction step) is meant to undergo the reducing reaction by Ca dissolved in the molten salt to generate Ti or Ti alloys in a particulate form and/or powder form (hereinafter, may referred to as Ti particles or Ti alloy particles) within the reactor vessel.

[0034] In handling Ti particles or Ti alloy particles generated in the molten salt, it is also possible for these to be separated from the molten salt in the reactor vessel. However, in this case, the production mode becomes the batch manner. In order to improve the productivity in the Ti production, Ti particles and the molten CaCl_2 liquid may be separated from each other outside the reactor vessel by utilizing the Ti generated in a particulate form to discharge the Ti particles outside the reactor vessel together with the molten CaCl_2 liquid. The Ti particles can simply be separated from the molten CaCl_2 liquid by a squeezing operation such as a mechanical compression. In a first production method as above, this separation step is included, and a second and a third production method can also employ such an embodiment mode.

[0035] CaCl_2 is generated as the by-product at the same time when Ti is generated in the molten salt. Namely, the dissolved Ca concentration decreases, while CaCl_2 increases. Therefore, it is preferable for CaCl_2 within the vessel to be discharged toward the outside of the vessel according to the extent of the generation of CaCl_2 , and particularly preferable to discharge it at the later stage after Ca is used for generating Ti, i.e., at the stage in which Ca dissolved in CaCl_2 is consumed. In a second production method, this discharging operation is included, and a first production method can employ the embodiment mode to apply this discharging operation. However, in a third production method, the molten Ca alloy is utilized as a carrier medium for transferring Ca as afore-mentioned, so the molten salt is not discharged to the outside.

[0036] It is preferable that CaCl_2 discharged as above is electrolyzed into Ca and Cl_2 and the Ca thus produced replenishes the depleted Ca in the molten salt in which Ca concentration is lowered in association with the reducing reaction. Also, it is preferable that Ti particles or Ti alloy particles generated in the molten salt is extracted together with the molten salt outside the reactor vessel, and further, the remaining molten salt after Ti particles or Ti alloy particles are separated is similarly treated. A second production method as above comprises this circulation-type electrolysis step, and a first production method can be operated with the embodiment mode including this step.

[0037] The molten salt in which the Ca concentration recovers like this is returned to the reduction step, and by repeating this operation over and over again, Ti or Ti alloys are produced. The phenomenon that takes place here regarding Ca is basically an increase or decrease only in the dissolved Ca concentration in the molten salt in circulation process, and the operation such as discharging Ca independently and replenishing Ca is not required. Therefore, high-purity Ti metals or Ti alloys can be produced with high efficiency plus economically without using an expensive reducing agent.

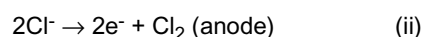
[0038] Further, a third production method also comprises a Ca generation step in which the molten salt containing CaCl_2 is electrolyzed, and a Ca replenishment step in which Ca in the molten salt whose Ca concentration is lowered is replenished, but differs from a first or a second production method in terms of utilizing the molten Ca alloy as a carrier medium for Ca.

[0039] In a first through a third production method, an electric current efficiency in an electrolysis step should affect the economic efficiency, which influences on the success and failure of establishing a commercially viable production technology. One of grave causes that lower the electric current efficiency in this electrolysis step is the presence of unreacted dissolved Ca in the molten salt being transferred from the reduction step to the electrolysis step.

Namely, in the reduction step, while the reducing reaction proceeds in the molten salt within the reactor vessel, the dissolved Ca, i.e., a reducing agent, in the molten salt is consumed, but not necessarily consumed entirely, so that it cannot be avoided for the unreacted dissolved Ca to be retained more or less in the molten salt being transferred from the reduction step to the electrolysis step.

[0040] In the electrolysis step, the reactions expressed by chemical formulas (ii) and (iii) proceed, Ca is generated at a cathode and Cl_2 gas is generated at an anode. The prevention of Ca generated at the cathode from moving to the anode can be achieved by using a separating membrane etc., for instance. However, when the dissolved Ca is retained in the molten salt transferred to the electrolysis step, it is difficult to remove Ca from the neighborhood of the anode, so that, due to the back reaction in which the above Ca reacts with the released Cl_2 to turn back to CaCl_2 , the electric current efficiency during electrolyzing is lowered.

[0041]





[0042] Although it is necessary in the reduction step that Ca exists in the molten salt, on the contrary, in the electrolysis step of replenishing Ca, the existence of Ca provides harm.

[0043] In a second production method, an alloy electrode made of molten Ca alloy (hereinafter, referred to as the molten Ca alloy electrode, or the alloy electrode simply) is employed for the cathode in the electrolysis step. By this, it becomes possible to rigorously preclude the adverse effect by the unreacted dissolved Ca in the molten salt transferred to the electrolysis step. In this case, it is preferable that the molten salt within the electrolytic cell, together with the interface between the molten Ca alloy constituting the above alloy electrode and the molten salt is divided into an anode side and a counter-anode side by installing a partition wall to thereby introduce the molten salt being supplied from the reactor vessel into the above counter-anode side.

[0044] Like this, when the molten salt on the anode side is electrolyzed while supposing that the dissolved Ca is essentially not contained, not only Cl_2 gas emerges on the surface of the anode but also Ca is generated at the interface between the molten Ca alloy constituting the cathode and the molten salt on the anode side, and the generated Ca is absorbed by the above molten Ca alloy electrode. The molten salt on the anode side usually does not contain the dissolved Ca, and, if any, the amount is extremely small, so that neither the back reaction nor its accompanying effect like the drop of the electric current efficiency takes place.

[0045] Meanwhile, the molten salt on the counter-anode side is the one transferred from the reduction step, which contains the unreacted dissolved Ca though the amount is not so much. At the interface between the alloy electrode (cathode) and the molten salt on the counter-anode side, Ca is released from the alloy electrode (cathode) to the molten salt on the counter-anode side. Namely, only the anode side within the electrolytic cell becomes an electrolysis processing region, and, on this anode side, Ca is efficiently generated by the electrolysis of molten salt in the state where the dissolved Ca does not exist, so that, by the generated Ca, Ca is replenished to the molten salt on the counter-anode side (namely, the used molten salt which being transferred from the reduction step) via the above alloy electrode (cathode).

[0046] Thus, while the drop of the electric current efficiency in the electrolysis step due to that the unreacted and dissolved Ca remains is avoided, the dissolved Ca is replenished to the molten salt. The reason why the absorption of Ca takes place on the anode side of alloy electrode and Ca is released on the counter-anode side thereof is considered as below.

[0047] Ca is generated at the alloy electrode and at the interface on the anode side of the molten salt, but, as the anode side has an electric potential (the electric potential difference is generated), the generated Ca metals are taken into the alloy electrode in the cathode. Consequently, the Ca concentration in the alloy electrode rises. Meanwhile, as there is no electric potential at the alloy electrode and at the interface on the counter-anode side of the molten salt, Ca is driven to dissolve in the molten salt from the alloy electrode owing to the difference of Ca concentration between the alloy electrode and the molten salt. Since the Ca concentration in the molten salt on the counter-anode side becomes low due to the reducing reaction, Ca can readily dissolve in the molten salt. The above reason is applicable to the molten Ca alloy electrode to be employed in a third production method as described hereinbelow.

[0048] On the anode side, the amount of molten salt decreases as the electrolysis proceeds. To replenish it, it can be done by either way: the molten salt that does not contain the dissolved Ca is newly replenished; or part of the molten salt transferred from the reduction step is circularly used. In the event that part of the molten salt transferred from the reduction step is used only, the amount of dissolved Ca to be brought in as the mixture is limitedly small, so that the back reaction can be controlled so as not to pose any harm.

[0049] As regards the Ca alloy constituting a molten Ca alloy electrode, Mg - Ca alloy, Al - Ca alloy, Zn - Ca alloy and the like are preferable. It is because the melting point of these Ca alloys is relatively low such that it is 500°C or above in case of Mg - Ca alloy, 600°C or above in case of Al - Ca alloy, and 420°C or above in case of Zn - Ca alloy respectively. In order to ensure such a low melting point, it is preferable for the Ca concentration in Mg - Ca alloy to be 45% or less, more preferably 15% or less. In case of Al

- Ca alloy, it is preferable to be 20% or less. Also, in case of Zn - Ca alloy, it is preferable to be 40% or less, more preferably 20% or less. Meanwhile, the lower limit of Ca concentration is preferably set to 0.5%. The reason is that the more the difference between the Ca concentration of molten salt on the counter-anode and the Ca concentration of molten Ca alloy is, the faster the dissolving rate of Ca into the molten salt becomes.

[0050] It is not impossible to use Pb - Ca alloy or Sn - Ca alloy, but either one has a drawback that the melting point is too low.

[0051] By the way, the usage of molten alloy electrode as a cathode for the electrolysis of CaCl_2 , is described in the specification of US Patent No. 4,992,096. However, the electrolysis of CaCl_2 in it is applied for producing Fe/Nd by a Ca reduction, and moreover, the circulation of CaCl_2 is not applied, thus the above two aspects distinguish over the usage of molten alloy electrode in a first through a third production method.

[0052] In a first or a second production method as above, as the means for the replenishment of Ca in the molten salt that is consumed in the reducing reaction, the molten salt whose Ca concentration is raised by the electrolysis of molten salt is circularly used. However, this method entails circulating a large amount of molten salt between the reactor vessel and the electrolytic cell, thereby requiring a large scale of equipment.

[0053] Eventually, in a third production method, the molten Ca alloy electrode is used for a cathode in the electrolysis step, and is utilized as a carrier medium for transferring Ca. Namely, in a second production method, the generated Ca on the side of cathode gets dissolved in the molten Ca alloy constituting the electrode and this Ca elutes off from the above molten Ca alloy to the used molten salt, that is introduced from the reactor vessel, to thereby raise the Ca concentration of molten salt, which is circularly operated to end up in using Ca in circulation. By contrast, in a third production method, the molten Ca alloy with the increased Ca content ratio is transferred to the reactor vessel to get contacted with the molten salt containing CaCl_2 , and Ca gets dissolved into this molten salt, thus enabling Ca to be used circularly.

[0054] In a third production method as above, the electrolytic cell is necessary for proceeding the Ca generation step by the electrolysis (namely, to carry out the operation of the Ca generation step), and the reactor vessel is necessary for proceeding the Ti generation step by the reducing reaction. But the electrolytic cell and the reactor vessel can be one cell (or vessel) to be used in share.

[0055] In case the electrolytic cell and the reactor vessel are independently provided, for example, the molten salt containing CaCl_2 is held in the electrolytic cell and in the reactor vessel, wherein the operation of Ca generation step by the electrolysis in the electrolytic cell is proceeded and, in parallel, the molten Ca alloy is transferred from the electrolytic cell to the reactor vessel to thereby proceed the Ca replenishment step along with the Ti generation step within the reactor vessel and transfer the molten Ca alloy salt whose Ca is consumed within the cell to the electrolytic cell reversely.

[0056] In this case, it is possible to give the temperature difference of molten salt between in the electrolytic cell and in the reactor vessel. In this regard, there is a merit as below. For example, it is the case that the temperature of molten salt in the electrolytic cell is set lower than that in the reactor vessel. Namely, it comes as a combination of a high-temperature reduction and a low-temperature electrolysis. In this respect, owing to the high-temperature reduction, the Ca reactivity rises to enhance the efficiency of generating Ti or Ti alloys, and, owing to the low-temperature electrolysis, the Ca solubility in the molten salt is reduced, thus resulting in promoting the transfer of Ca from the molten salt to the molten Ca alloy.

[0057] In case the electrolytic cell and the reactor vessel becomes one cell (or vessel) to be used in share, for example, the molten salt containing CaCl_2 is held in the reactor vessel that serves as the electrolytic cell also, and the molten salt within the reactor vessel, together with the interface between this molten salt and the molten Ca alloy that constitutes the cathode is divided into an anode side and a counter-anode side by incorporating a partition wall, and thus, electrolyzing is proceeded. In the vicinity of the anode, Cl_2 gas is generated, and Ca is generated at the cathode (the molten Ca alloy) or in the neighboring region to the cathode, that is divided by the partition wall and disposed toward the anode side (Ca generation step). The generated Ca is taken in the molten Ca alloy. Meanwhile, on the counter-anode side, the replenishment step that Ca elutes off from the molten Ca alloy to the molten salt proceeds.

[0058] In this case, although the operation to incorporate the temperature difference of molten salt between in the electrolytic cell and in the reactor vessel becomes difficult, the structure of the cell (or vessel) becomes simple, and neither the facility nor the costs for transporting the molten salt are needed.

[0059] As regards handling of Ti particles or Ti alloy particles generated in the molten salt, as afore-mentioned, a third production method also can adopt an embodiment mode that includes the Ti separation step in which the generated Ti or Ti alloys is separated from the molten salt.

[0060] As regards handling of the molten salt that is separated from Ti or Ti alloys, it is rational and economical to introduce it to the Ca generation step by the electrolysis and/or to the Ti generation step by the reducing reaction.

[0061] Also, it can be arranged such that the molten salt separated from Ti or Ti alloys in the Ti separation step gets reacted with the molten Ca alloy whose Ca is consumed in the Ti generation step to increase Ca in the molten Ca alloy by the unreacted Ca in the molten salt and then this molten Ca alloy can be used in the Ca replenishment step. By doing so, Ca can be replenished into the molten Ca alloy without relying on the electrolysis.

[0062] And, by subjecting it to react with the molten Ca alloy whose Ca is consumed as above, the unreacted Ca can be removed from the molten salt that is separated from Ti or Ti alloys. Owing to this, when the molten salt separated from Ti or Ti alloys is introduced into the Ca generation step by the electrolysis, the back reaction can be prevented, which proves to be advantageous.

[0063] It is better for this replenishment of Ca without relying on the electrolysis to be proceeded at the low temperature. In case of the low temperature operation, the Ca solubility in the molten salt decreases, the removal efficiency of the unreacted is enhanced, and also, the transfer of Ca into the molten Ca alloy is promoted, so that Ca in the molten Ca alloy readily gets increased.

[0064] In a first through a third production method, although CaCl_2 with the melting point of 780°C as the molten salt is used, a mixed molten salt with NaCl, KCl or CaF_2 can be used also. If the mixed molten salt should be used, the

melting point decreases to enable the temperature of molten salt to be lowered, thus increasing the durability of the vessel material to extend the service life thereof and suppressing the vaporization of Ca and salt from the liquid surface. For example, if it were the mixed salt with NaCl, the melting point of molten salt can be lowered down to about 500°C.

[0065] The merit for the vessel material by lowering the temperature of molten salt can be appreciated in all steps including the reduction step and the electrolysis step. In addition, in the electrolysis step, by lowering the temperature of molten salt, the Ca solubility decreases, and the convection and the diffusion of molten salt are also suppressed, thereby resulting in suppressing the back reaction of Ca as described above. If the extent of reaction in the reduction step should be regarded as important, only the temperature of molten salt in the reduction step can be elevated.

[0066] Further, in a first production method as above, the embodiment mode that the molten Ca liquid can be held on the molten salt in the reactor vessel could be employed, but in this case, it becomes impossible to lower the temperature of molten salt to the melting point of Ca (838°C) or less. That said, by mixing Ca with other alkaline-earth metal or alkali metal, the melting point thereof can be lowered. For example, by mixing Ca with Mg, the melting point can be lowered down to 516°C. What is more, since only Ca from the mixture of Ca and Mg dissolves in the molten salt of CaCl₂ and Mg hardly does, it is possible to proceed the reducing reaction of TiCl₄ by Ca dissolved in CaCl₂ even if the molten metal of Ca with addition of Mg should be used.

[0067] In a first through a third production method, as for the raw material of Ti, basically TiCl₄ is adopted, but by using TiCl₄ as the mixture of other metallic chloride, Ti alloys can be produced also. Since TiCl₄ and other metallic chloride are reduced by Ca simultaneously, Ti alloy particles can be produced by this method. Meanwhile, the metallic chloride here in can be either gaseous state or liquid state.

[0068] Now, as regards the size of the generated Ti or Ti alloys, the average particle diameter thereof is preferably set to 0.5 - 50 μm. The reason is as below. Namely, after these particles are generated in the molten salt, these particles should be discharged from the molten salt. But, if it were not small size enough so as to flow together with the molten salt, it becomes difficult to discharge it. Therefore, the proper size is preferably 50 μm or less. Here, why the minimum proper size is set to 0.5 μm is that, when being lower than this, although possible to discharge it, it becomes difficult to separate from the molten salt.

[0069] With regard to handling of CaCl₂ that is discharged outside the reactor vessel, as afore-mentioned, this is electrolyzed into Ca and Cl₂ and the generated Ca by the electrolysis is used for the generation reaction of Ti in the reactor vessel. Meanwhile, it is preferable that the generated Cl₂ by the electrolysis gets reacted with TiO₂ to yield TiCl₄ that is to be utilized for the generation reaction of Ti in the reactor vessel.

[0070] By configuring such a cycle, Ca which is very expensive to buy can be repeatedly used as the reducing agent, and the costs for generating TiCl₄ can be maintained lower, thus enabling the production costs of Ti or Ti alloys to be decreased.

[0071] Here, what should be particularly noted is that the costs for producing Ca is lowered by requiring no strict separation of Ca, that is generated by the electrolysis step, from CaCl₂. One of the reasons why Ca has not been utilized thus far for the commercial production of Ti metals, is that the separation of Ca from CaCl₂ is difficult. Namely, while Mg can be produced by electrolyzing MgCl₂, Mg hardly dissolve in MgCl₂, thus enabling the generated Mg to be recovered efficiently. Also, Na can be efficiently produced by electrolyzing NaCl in similar manner with Mg. On the other hand, Ca can be produced by electrolyzing CaCl₂, but the generated Ca dissolves in CaCl₂, thus making it difficult to efficiently produce Ca only, which is additionally compounded by the phenomenon that the generated Ca turns back to CaCl₂ due to the back reaction. Such being the case, the productivity is poor, although the technique to enhance the recovery rate of Ca by the application of cooling the electrode in producing Ca by the electrolysis should be attempted, still leaving the production costs of Ca to be significantly high.

[0072] In a first through a third production method, the molten salt with the dissolved Ca is proactively utilized, so that, even if Ca is mixed with the molten salt in the electrolysis step, it is not an issue at all by simply taking care of the back reaction, and there is no need to strictly separate Ca only. Namely, it is sufficient enough that the whole molten salt with Ca, or Ca that gets contained in the molten Ca alloy is charged from the electrolytic cell to the reactor vessel. Thus, the production costs of Ca by the electrolysis can be dramatically cut.

BRIEF DESCRIPTION OF THE DRAWINGS

[0073] Fig. 1 is a view explaining a configuration of an apparatus for producing Ti metals that represents a first embodiment mode in a first production method;

Fig. 2 is a view explaining a configuration of an apparatus for producing Ti metals that represents a second embodiment mode in a first production method;

Fig. 3 is a view explaining a configuration of an apparatus for producing Ti metals that represents a third embodiment mode in a first production method;

Fig. 4 is a view explaining a configuration of an apparatus for producing Ti metals that represents a first embodiment

mode in a second production method;

Fig. 5 is a view explaining a configuration of an apparatus for producing Ti metals that represents a second embodiment mode in a second production method;

Fig. 6 is a view explaining a configuration of an apparatus for producing Ti metals that represents a third embodiment mode in a second production method;

Fig. 7 is a view explaining a configuration of an apparatus for producing Ti metals that represents a first embodiment mode in a third production method;

Fig. 8 is a view explaining a configuration of an apparatus for producing Ti metals that represents a second embodiment mode in a third production method; and,

Fig. 9 is a view explaining a configuration of an apparatus for producing Ti metals that represents a third embodiment mode in a third production method.

BEST MODE FOR CARRYING OUT THE INVENTION

[0074] Hereinbelow, each embodiment mode for a first production method through a third production method is recited with reference to the drawings.

1. A First Production Method

Fig. 1 is a view explaining a configuration of an apparatus for producing Ti metals that represents a first embodiment mode in a first production method.

[0075] In a first embodiment mode for a first production method, a cylindrical reactor vessel 1 is employed. The reactor vessel 1 is a closed vessel made of iron. A reducing agent supply pipe 2 for supplying Ca which is a reducing agent is disposed at the ceiling portion of the reactor vessel 1. The bottom portion of reactor vessel 1 is made to have a tapered

figuration with the opening diameter that gradually getting smaller downward so as to facilitate the discharge of the generated Ti particles, and, at the center part of the lower end part thereof, a Ti discharge pipe 3 for discharging the generated Ti is provided.

Meanwhile, at the inside of the reactor vessel 1, a cylindrical separating wall 4 with the embedded heat exchanger is disposed at the position with a predetermined space off from the inside surface of straight cylindrical vessel body. At the upper area of reactor vessel 1, a molten salt discharge pipe 5 for discharging sideways CaCl_2 in the reactor vessel is provided, and, at the lower area thereof, a raw material supply pipe 6 for supplying TiCl_4 that is a raw material of Ti is provided to penetrate the separating wall 4 to reach the central part of the plenum in the vessel.

[0077] During the operation, the molten CaCl_2 liquid, as the molten salt, where Ca dissolves is held in the reactor vessel 1. The liquid surface thereof is set to the height level that is lower than the upper end of the separating wall 4 but higher than the molten salt discharge pipe 5. At the inside of separating wall 4, the molten Ca liquid as the molten metal containing Ca is held on the molten CaCl_2 liquid surface.

[0078] Then, as being set as above, TiCl_4 gas as a metallic chloride containing TiCl_4 is supplied to the molten CaCl_2 at the inner side from the separating wall 4 by means of the raw material supply pipe 6. By this, at the inner side from the separating wall 4, TiCl_4 is reduced by Ca in the molten CaCl_2 liquid to thereby generate Ti metals in a particulate form within the molten CaCl_2 liquid.

[0079] TiCl_4 gas that is supplied into the molten CaCl_2 liquid turns to numerous bubbles which buoy and move upward in the molten CaCl_2 liquid and promote stirring the molten CaCl_2 liquid, thus enhancing the reaction efficiency.

[0080] Thus generated Ti particles in the molten CaCl_2 liquid on the inner side from the separating wall 4 within the reactor vessel 1 moves downward in the above liquid to accumulate as sediment at the bottom area within the vessel. The accumulated Ti particles are discharged downward together with the molten CaCl_2 liquid through the Ti discharge pipe 3 and transferred to a separation step 7.

[0081] The molten CaCl_2 liquid in which Ca is consumed by the reducing reaction on the inner side from the separating wall 4 within the reactor vessel 1 moves, via the lower part of separating wall 4, upward on the outer side of separating wall 4, and gets discharged through the molten salt discharge pipe 5. The discharged molten CaCl_2 liquid is to be transferred to an electrolysis step 8.

[0082] On the inner side from the separating wall 4, Ca elutes in the molten CaCl_2 liquid from the molten Ca liquid held on the liquid surface of molten CaCl_2 liquid to thereby get replenished. Along with this, on the molten CaCl_2 liquid at the inner side from the separating wall 4, Ca is replenished through the reducing agent supply pipe 2.

[0083] The way things are, the Ti metals can be continuously produced within the reactor vessel 1. On the inner side from the separating wall 4, by utilizing the molten CaCl_2 liquid in which Ca dissolves, as the reducing reaction is carried out by Ca within said molten CaCl_2 liquid, the reaction region expands to the almost all area on the inner side from the separating wall 4, thus enabling the feed rate of TiCl_4 to be increased. By reason of various aspects including the above, high-purity Ti particles are produced with the high efficiency, being exactly what is afore mentioned.

[0084] Here, the separating wall 4 blocks the molten CaCl_2 liquid containing Ca abundantly prior to be used in reducing TiCl_4 to mix with the molten CaCl_2 liquid with few Ca after use to thereby enhance the reaction efficiency.

[0085] Meanwhile, in the separation step 7, the Ti particles discharged together with the molten CaCl_2 liquid from the reactor vessel 1 are separated from the molten CaCl_2 liquid. To be concrete, said Ti particles are compressed to squeeze out the molten CaCl_2 liquid. Then, Ti particles are cleaned. The molten CaCl_2 liquid that is obtained in the separation step 7 is transferred together with the molten CaCl_2 liquid discharged from the reactor vessel 1 to the electrolysis step 8.

[0086] In the electrolysis step 8, the molten CaCl_2 liquid from the reactor vessel 1 as well as the separation step 7 is electrolyzed into Ca and Cl_2 gas. Ca returns to the inside of reactor vessel 1. Here, Ca does not need to be separated strictly from CaCl_2 , and can return to the inside of reactor vessel 1 together with CaCl_2 without causing any problem. It is because CaCl_2 with the dissolved Ca is used in the reactor vessel 1. Owing to this ease in the separation operation, the production costs of Ca by the electrolysis is lowered.

[0087] Cl_2 gas generated in the electrolysis step 8 is transferred to a chlorination step 9. Here, TiO_2 is subjected to a chlorination process to yield TiCl_4 . Further, by using a carbon powder, oxygen generated as a by-product is discharged in the form of CO_2 . TiCl_4 thus made is introduced into the inside of reactor vessel 1 through the raw material supply pipe 6. The way things are, by circulating CaCl_2 , Ca as the reducing agent and Cl_2 gas are cycled. That is, essentially by only supplementing TiO_2 and C, Ti metals are continuously produced.

[0088] Fig. 2 is a view explaining a configuration of an apparatus for producing the Ti metals that represents a second embodiment mode in a first production method. A second embodiment mode in a first production method here differs from a first embodiment mode with respect to that the reducing agent supply pipe 2a is provided at the lower part of reactor vessel 1 and from its lower part, Ca is supplied on the inner side of separating wall 4.

[0089] In this second embodiment mode, the molten Ca liquid as the reducing agent comes up from below to float on the inner side of separating wall 4 due to the specific gravity difference from the molten CaCl_2 liquid. In this flotation process, Ca gets dissolved in CaCl_2 to enhance the efficiency of Ca dissolution. The molten Ca thus floated remains to lie on the surface of molten CaCl_2 liquid to get Ca dissolved in the molten CaCl_2 located below.

[0090] Fig. 3 is a view explaining a configuration of an apparatus for producing Ti metals that represents a third embodiment mode in a first production method;

This third embodiment mode differs in terms of the location of the raw material supply pipe 6a. Namely, in a first embodiment mode or in a second embodiment mode, the raw material supply pipe 6a is configured to supply TiCl_4 into the central part of the inside of vessel, while in a third embodiment mode, it is configured to supply TiCl_4 into the off-set position from the centerline, being located on the inner side from the separating wall 4. By applying this configuration, the convection due to the gas lift of TiCl_4 gas takes place within the molten CaCl_2 liquid on the inner side of separating wall 4. Owing to this convection in CaCl_2 , the dissolution of Ca into CaCl_2 is promoted to thereby enhance the dissolution efficiency.

[0091] 2. A Second Production Method

Fig. 4 is a view explaining a configuration of an apparatus for producing Ti metals that represents a first embodiment mode in a second production method.

[0092] In the first embodiment mode in a second production method, the reactor vessel 1 in which the reduction step is carried out and the electrolytic cell 10 in which the electrolysis step is carried out are employed. The reactor vessel 1 holds the Ca-rich molten CaCl_2 , as the molten salt, in which comparatively abundant Ca dissolves. The melting point of CaCl_2 is about 780°C , and this molten salt is heated to the melting point or above.

[0093] As regards the reactor vessel 1, the gaseous TiCl_4 is injected into the molten salt within the reactor vessel 1 in a randomly-dispersed manner, and is reduced by the dissolved Ca in the molten salt to generate Ti metals in a particulate form. The generated Ti particles incrementally accumulate at the bottom of reactor vessel 1 due to the specific gravity difference.

[0094] Ti particles accumulated at the bottom of reactor vessel 1 are discharged, together with the molten salt lying at the said bottom, from the reactor vessel 1 and transferred to the separation step 7. In the separation step 7, Ti particles that are discharged together with the molten salt from the reactor vessel 1 are separated from the molten salt. To be concrete, said Ti particles are compressed to squeeze out the molten salt. Ti particles obtained in the Ti separation step 7 are to be melted to yield Ti ingots.

[0095] Meanwhile, the molten salt separated from Ti particles in the Ti separation step 7 is the used molten salt where Ca is consumed and the Ca concentration is lowered. This molten salt is transferred from the reactor vessel 1 to the electrolytic cell 10.

[0096] In the electrolytic cell 10, the molten CaCl_2 as the molten salt is electrolyzed between an anode 11 and a cathode 12 to generate Cl_2 gas on the side of anode 11 and to generate Ca on the side of cathode 12. Here, the cathode 12 denotes a molten Ca alloy electrode 14, comprising: a heat resistant vessel 13 with an open bottom part to be inserted into the molten salt in the electrolytic cell 10; a molten Ca alloy 14 contained within the heat resistant vessel 13; an electrode rod 15 penetrating the ceiling part of heat resistant vessel 13 to be inserted into said molten Ca alloy 14; and a partition wall 16 dividing the molten salt within the electrolytic cell 10 into an anode side and a counter-anode side.

[0097] The molten Ca alloy 14 here is represented by, for example, Mg

- Ca liquid whose specific gravity is smaller than that of the molten salt. The partition wall 16 which is heat resistant and has an insulation capability is provided just beneath the cathode 12, wherein the upper end part of said wall is inserted into the molten Ca alloy 14 and the lower end part is closely attached to the bottom plate part of electrolytic cell 10 so as to bisect the molten salt within the electrolytic cell 10 together with the interface between the molten Ca alloy 14 and the molten salt located below into the anode side and the counter-anode side.

[0098] The molten salt transferred to the electrolytic cell 10 directly from the reactor vessel 1 or via the Ti separation step 7 is introduced on the counter-anode side within the electrolytic cell 10. The molten salt on the anode side essentially consists of the molten CaCl_2 without containing the dissolved Ca. This molten salt on the anode side is electrolyzed between the anode 11 and the cathode 12 to generate Cl_2 gas on the side of anode 11 and Ca on the side of cathode 12. The generated Ca on the side of cathode 12 elutes into the molten Ca alloy.

[0099] Meanwhile, the molten salt on the counter-anode side is the used molten salt which is introduced from the reactor vessel 1, and contains unreacted and dissolved Ca, while dissolved Ca therein is consumed. Ca elutes into this molten salt from the molten Ca alloy 14. Thus, dissolved Ca is replenished to the used molten salt which is introduced from the reactor vessel 1, and the molten salt that became Ca-rich is introduced to the reactor vessel 1 through the reducing agent supply pipe 2, thus being circularly used in generating Ti particles by the Ca reduction.

[0100] On the other hand, the Cl_2 gas generated in the vicinity of the surface of anode 11 is transferred to a chlorination step 9. In the chlorination step 9, TiO_2 is chlorinated to yield TiCl_4 as a raw material of Ti. TiCl_4 thus made is introduced into the reactor vessel 1 through the raw material supply pipe 6 to be used circularly for producing Ti particles by the Ca reduction.

[0101] As shown as above, in a first embodiment mode in a second production method, the molten salt (the molten CaCl_2 in which Ca dissolved) circulates among the reduction step (reactor vessel 1), the separation step 7 and the electrolysis step (electrolytic cell 10), and by repeating the operation that the Ca consumed in the reduction step (reactor vessel 1) is replenished in the electrolysis step (electrolytic cell 10), the production of Ti continues in the reduction step (reactor vessel 1). Namely, without replenishing nor discharging the solid Ca, by simply controlling the Ca concentration in the molten salt, high-quality Ti particles are continuously produced by the Ca reduction.

[0102] Moreover, in the process where, to replenish Ca, the used molten salt that contains unreacted and dissolved Ca is introduced to the electrolysis step, the unreacted dissolved Ca is introduced to the counter-anode side that is a non-electrolyzing region within the electrolytic cell 10 and is kept indifferent with the electrolysis to thereby block the back reaction by said dissolved Ca. Therefore, the electric current efficiency in the electrolysis step is enhanced. On the anode side that is an electrolyzing region within the electrolytic cell 10, as electrolyzing proceeds, the molten CaCl_2 is consumed. To replenish it, the molten CaCl_2 that does not contain the dissolved Ca essentially is supplemented from the outside source. Or, a small amount of used molten salt is introduced on the anode side, independently from or in combination with the above supplementing (route shown by the broken line in Fig. 4).

[0103] By the way, the temperature of molten salt in either step is controlled to be higher than the melting point of CaCl_2 (about 780°C).

[0104] Fig. 5 is a view explaining a configuration of an apparatus for producing Ti metals that represents a second embodiment mode in a second production method.

[0105] In this second embodiment mode, the structure of reactor vessel 1 is concretely defined. The reactor vessel 1 that is employed here is a closed vessel with a cylindrical form that is made of iron. A reducing agent supply pipe 2 for supplying Ca which is a reducing agent is disposed at the ceiling portion of the reactor vessel 1. The bottom portion of reactor vessel 1 is made to have a tapered figuration with the opening diameter that gradually getting smaller downward so as to facilitate the discharge of the generated Ti particles, and, at the center part of the lower end part thereof, a Ti discharge pipe 3 for discharging the generated Ti is provided.

[0106] Meanwhile, at the inside of the reactor vessel 1, a cylindrical separating wall 4 with the embedded heat exchanger is disposed at the position with a predetermined space off from the inside surface of straight cylindrical vessel body. At the upper area of reactor vessel 1, a molten salt discharge pipe 5 for discharging sideways CaCl_2 in the reactor vessel is provided, and, at the lower area thereof, a raw material supply pipe 6 for supplying TiCl_4 that is a raw material of Ti is provided to penetrate the separating wall 4 to reach the central part of the plenum in the vessel.

[0107] During the operation, the molten CaCl_2 liquid, for example as the molten salt, where Ca dissolves is held in the reactor vessel 1. The liquid surface thereof is set to the height level that is lower than the upper end of the separating wall 4 but higher than the molten salt discharge pipe 5.

[0108] Then, as being set as above, TiCl_4 gas as a metallic chloride containing TiCl_4 is supplied to the molten CaCl_2 at the inner side from the separating wall 4 by means of the raw material supply pipe 6. By this, at the inner side from the separating wall 4, TiCl_4 is reduced by Ca in the molten CaCl_2 liquid to thereby generate Ti metals in a particulate form within the molten CaCl_2 liquid.

[0109] TiCl_4 gas that is supplied into the molten CaCl_2 liquid turns to numerous bubbles which buoy and move upward in the molten CaCl_2 liquid and promote stirring the molten CaCl_2 liquid, thus enhancing the reaction efficiency.

[0110] The generated Ti particles in the molten CaCl_2 liquid on the inner side from the separating wall 4 within the reactor vessel 1 move downward in this liquid to accumulate as sediment at the bottom area within the vessel. The accumulated Ti particles are discharged downward together with the molten CaCl_2 liquid through the Ti discharge pipe 3 and transferred to a separation step 7.

[0111] The molten CaCl_2 liquid in which Ca is consumed by the reducing reaction on the inner side from the separating wall 4 within the reactor vessel 1 moves, via the lower part of separating wall 4, upward on the outer side of separating wall 4, and gets discharged through the molten salt discharge pipe 5. The discharged molten CaCl_2 liquid is to be transferred to an electrolysis step 8.

[0112] The way things are, the Ti metals can be continuously produced within the reactor vessel 1. On the inner side from the separating wall 4, by utilizing the molten CaCl_2 liquid in which Ca dissolves, as the reducing reaction is carried out by Ca within said molten CaCl_2 liquid, the reaction region expands to the almost all area on the inner side from the separating wall 4, thus enabling the feed rate of TiCl_4 to be increased. By reason of various aspects including the above, high-purity Ti particles are produced with the high efficiency, being exactly what is afore-mentioned.

[0113] Here, the separating wall 4 blocks the molten CaCl_2 liquid containing Ca abundantly prior to be used in reducing TiCl_4 to mix with the molten CaCl_2 liquid with few Ca after use to thereby enhance the reaction efficiency.

[0114] Meanwhile, in the separation step 7, the Ti particles discharged together with the molten CaCl_2 liquid from the reactor vessel 1 are separated from the molten CaCl_2 liquid. To be concrete, said Ti particles are compressed to squeeze out the molten CaCl_2 . Then, Ti particles are cleaned. The molten CaCl_2 liquid that is obtained in the separation step 7 is transferred together with the molten CaCl_2 liquid discharged from the reactor vessel 1 to the electrolysis step 8.

[0115] In the electrolysis step 8, the molten CaCl_2 liquid from the reactor vessel 1 as well as the separation step 7 is electrolyzed into Ca and Cl_2 gas. Ca returns to the inside of reactor vessel 1. Here, Ca does not need to be separated strictly from CaCl_2 , and can return to the inside of reactor vessel 1 together with CaCl_2 without causing any problem. It is because CaCl_2 with the dissolved Ca is used in the reactor vessel 1. Owing to this ease in the separation operation, the production costs of Ca by the electrolysis is lowered.

[0116] Cl_2 gas generated in the electrolysis step 8 is transferred to a chlorination step 9. Here, TiO_2 is subjected to a chlorination process to yield TiCl_4 . Further, by using a carbon powder, oxygen generated as a by-product is discharged in the form of CO_2 . TiCl_4 thus made is introduced into the inside of reactor vessel 1 through the raw material supply pipe 6. The way things are, by circulating CaCl_2 , Ca as the reducing agent and Cl_2 gas are cycled. That is, essentially by only supplementing TiO_2 and C, Ti metals are continuously produced.

[0117] Fig. 6 is a view explaining a configuration of an apparatus for producing Ti metals that represents a third embodiment mode in a second production method.

[0118] In a third embodiment mode, the position of the raw material supply pipe 6a is different in comparison with a second embodiment mode. Namely, in a second embodiment mode, the raw material supply pipe 6a is configured to supply TiCl_4 into the central part of the inside of vessel, while in a third embodiment mode, it is configured to supply TiCl_4 into the off-set position from the centerline, being located on the inner side from the separating wall 4.

[0119] By applying this configuration, the convection due to the gas lift of TiCl_4 gas takes place within the molten CaCl_2 liquid on the inner side of separating wall 4. Owing to this convection in CaCl_2 , the reduction efficiency is enhanced.

[0120] In either embodiment mode, that the temperature of molten salt can be lowered by using the mixed molten salt is as afore-mentioned.

[0121] 3. A Third Production Method

Fig. 7 is a view explaining a configuration of an apparatus for producing Ti metals that represents a first embodiment mode in a third production method.

[0122] In a first embodiment mode in a third production method, the reactor vessel 1 in which the Ti generation step by the reducing reaction is carried out and the electrolytic cell 10 in which the Ca replenishment step by electrolyzing is carried out are employed. The reactor vessel 1 holds the Ca-rich molten CaCl_2 , as the molten salt, in which comparatively abundant Ca dissolves. The melting point of CaCl_2 is about 780°C , and this molten salt is heated to the melting point or above.

[0123] The inside cavity except the bottom part in the reactor vessel 1 is bisected by the heat resistant partition wall 17, wherein one is a reduction compartment 18 and the other is a Ca replenishment compartment 19 in which the molten Ca alloy gets in contact with the molten salt so as to make Ca in the molten Ca alloy to dissolve in the molten salt. Both compartments are in flow communication at the under part of reactor vessel 1 where to allow the molten salt to freely flow back and forth.

[0124] As regards the reduction compartment 18, the gaseous TiCl_4 is injected into the molten salt within the reactor vessel 1 in a randomly-dispersed manner, and is reduced by the dissolved Ca in the molten salt to generate Ti metals in a particulate form. The generated Ti particles incrementally accumulate at the bottom of reactor vessel 1 due to the specific gravity difference.

[0125] Ti particles accumulated at the bottom of reduction compartment 18 are discharged, together with the molten salt lying at the said bottom, from the reduction compartment 18 and transferred to the Ti separation step 7. In the Ti separation step 7, Ti particles that are discharged together with the molten salt from the reduction compartment 18 are separated from the molten salt. To be concrete, said Ti particles are compressed to squeeze out the molten salt. Ti particles obtained in the Ti separation step 7 are to be melted to yield Ti ingots.

[0126] Meanwhile, the molten salt separated from Ti particles in the Ti separation step 7 is the used molten salt where Ca is consumed and the Ca concentration is lowered. This molten salt is transferred to said electrolytic cell 10.

[0127] In the electrolytic cell 10, molten CaCl_2 as the molten salt is held and the electrolysis of said molten CaCl_2 is carried out by means of an anode 11 and a cathode 12. By this, Cl_2 gas is generated on the side of anode 11 and Ca is generated on the side of cathode 12.

[0128] Here, the cathode 12 denotes a molten Ca alloy electrode, to be concrete, comprising: a heat resistant vessel 13 having insulation capability and an open bottom part to be inserted into the molten salt in the electrolytic cell 10; a molten Ca alloy 14 contained within the heat resistant vessel 13; and, an electrode rod 15 penetrating the ceiling part of heat resistant vessel 13 to be inserted into said molten Ca alloy 14. The generated Ca on the side of cathode 12 is taken into the molten Ca alloy 14 within the heat resistant vessel 13 as an alloy or in the liquid state. Thus, the Ca concentration in the molten Ca alloy 14 within the heat resistant vessel 13 rises.

[0129] When the Ca concentration in the molten Ca alloy 14 within the heat resistant vessel 13 reaches the predetermined concentration (for example, 15%), this molten Ca alloy 14 with the high Ca concentration is charged to the Ca replenishment compartment 19 within the reactor vessel 1 from above through a first transport pipe 20.

[0130] At this occasion, on the molten salt within the Ca replenishment compartment 19, the molten Ca alloy 14' that was charged previously floats. This molten Ca alloy 14' has the high Ca concentration when charged, but, by releasing Ca toward the molten salt located below to have it dissolved, it becomes to have a low Ca concentration (for example, a few %). In this regard, in parallel with the transport of molten Ca alloy having the high Ca concentration from the heat resistant vessel 13 to the Ca replenishment compartment 19, the used molten Ca alloy 14' with the low Ca content that floats above the molten salt in the Ca replenishment compartment 19 is transported to the inside of heat resistant vessel 13 through a second transport pipe 21.

[0131] Thus, the Ca replenishment by dissolving from the molten Ca alloy 14 to the below molten salt can be continued in the Ca replenishment compartment 19. As a result, Ca that is consumed in association with the generation of Ti particles in the reduction compartment 18 can be replenished to thereby sustain said generation reaction.

[0132] On the other hand, the Cl_2 gas generated in the vicinity of the surface of anode 11 is transferred to a chlorination step 9. In the chlorination step 9, TiO_2 and C are chlorinated to yield TiCl_4 as a raw material of Ti and to release CO_2 gas also. TiCl_4 thus made is introduced into the reactor vessel 1 through the raw material supply pipe 6 to be used circularly for producing Ti particles by the Ca reduction.

[0133] The way things are, in a first embodiment mode in a third production method, Ca in the molten salt is consumed by the Ca reducing reaction in the reactor vessel 1, and then, this Ca is generated by the electrolysis of molten salt in the electrolytic cell 10 to be used circularly for generating Ti particles by the reducing reaction. Moreover, there is no need to circulate the molten salt between the reactor vessel 1 and the electrolytic cell 10 for using Ca in circulation. The molten Ca alloy 14 is used for the cathode in the electrolytic cell 10, and by utilizing it as a carrier medium for transferring Ca to merely reciprocate between the reactor vessel 1 and the electrolytic cell 10, it becomes possible to keep supplying Ca to the molten salt in the reactor vessel 1 to sustain the Ti production.

[0134] Hence, without replenishing nor discharging the solid Ca, as well as without circulating a huge amount of molten salt, in quite a simple manner, high-quality Ti particles can be continuously produced by the Ca reduction. By the way, the temperature of molten salt in either step is controlled to be higher (for example, 800 - 850°C) than the melting point of CaCl_2 (about 780°C).

[0135] Fig. 8 is a view explaining a configuration of an apparatus for producing Ti metals that represents a second embodiment mode in a third production method.

[0136] As the molten salt, a multi-element system molten salt having the low melting point where CaCl_2 is mixed with other chloride is employed. Before introducing the molten salt, being separated from Ti particles in the Ti separation step 7, to the electrolytic cell 10, said molten salt is introduced to the Ca removal cell 22. Let the melting point of molten salt be set to, for example, 650°C, the high-temperature operation such that the temperature of molten salt is heightened to 850°C or so is applied in the reactor vessel 1. Meanwhile, the low-temperature operation such that the temperature of molten salt is lowered down to 700°C or so is applied in the electrolytic cell 10 and in the Ca removal cell 22.

[0137] By carrying out the high-temperature operation (high-temperature reduction) in the reactor vessel 1, the reactivity of Ca rises, thus making it possible to offset the decrease of reactivity due to the drop of Ca content ratio in the relevant molten salt. Meanwhile, by carrying out the low-temperature operation in the electrolytic cell 10 and in the Ca removal cell 22, the unreacted Ca in the molten salt to be introduced to the electrolytic cell 10 can be eliminated beforehand, thus suppressing the back reaction and its resultant effect on decreasing the electric current efficiency.

[0138] Namely, the molten salt transferred from the reactor vessel 1 to the electrolytic cell 10 via the Ti separation

step 7 is the used one which still retains the unreacted dissolved Ca, while the majority of the dissolved Ca is consumed. When the unreacted Ca happens to be brought in to the electrolytic cell 10, it reacts with Cl_2 gas generated on the side of anode 11 to turn back to CaCl_2 , i.e., the so-called back reaction takes place, where the electrolytic current is consumed, thus lowering the electric current efficiency.

[0139] In the Ca removal cell 22, the molten salt introduced from the Ti separation step 7 (retains the unreacted Ca) is mixed with part of the used molten Ca alloy 14' (designated by Mg in Fig. 8) having the low Ca concentration and being transferred from the Ca replenishment compartment 19 to the heat resistant vessel 13 in the electrolytic cell 10. Hence, the unreacted Ca in the molten salt is taken into the molten Ca alloy 14' with the low Ca concentration, so that the unreacted Ca is removed and the molten Ca alloy 14 with the high Ca concentration is generated.

[0140] By introducing the molten salt without the unreacted Ca to the electrolytic cell 10 in this way, the molten salt can be circularly used without any waste, and the back reaction, attributable to the unreacted Ca in the molten salt, as well as the resultant drop of electric current efficiency can be suppressed. The molten Ca alloy 14 (designated by Mg - Ca in Fig. 8) with the high Ca concentration, being regenerated in the Ca removal cell 22, is introduced to the Ca replenishment compartment 19 in the reactor vessel 1.

[0141] By carrying out the low-temperature operation in the electrolytic cell 10, the Ca solubility in the molten salt decreases, and also, the convection and diffusion of molten salt are suppressed. From this aspect also, the back reaction can be suppressed. Besides, by carrying out the low-temperature operation in the Ca removal cell 22, the Ca solubility decreases to precipitate Ca, and then, the precipitated Ca is absorbed by the alloy.

[0142] As above, in a second embodiment mode in a third production method, by incorporating the temperature difference in molten salt between the reactor vessel 1 and the electrolytic cell 10, the electric current efficiency in the Ca generation step by the electrolysis can be enhanced.

[0143] Fig. 9 is a view explaining a configuration of an apparatus for producing Ti metals that represents a third embodiment mode in a third production method. This third embodiment mode differs from a first embodiment mode and a second embodiment mode over the following aspects.

[0144] The reactor vessel 1 doubles as the electrolytic cell, comprising a reduction compartment 24 with a deep bottom and an electrolysis compartment 24 with a shallow bottom. An anode 11 is disposed within the electrolysis compartment 24 but on the counter side as opposed to the reduction compartment side, whereas the heat resistant vessel 13 constituting a cathode 12 is disposed so as to ride over the interface between the reduction compartment 23 and the electrolysis compartment 24. And, the molten salt in the reactor vessel 1, together with the interface between the molten Ca alloy 14 and the molten salt within the heat resistant vessel 13, is divided into an anode side and a counter-anode side by a partition wall 16 that is disposed at the interface between the reduction compartment 23 and the electrolysis compartment 24. In other words, the anode side corresponds to the electrolysis compartment 24 with the shallow bottom, while the counter-anode side corresponds to the reduction compartment 23 with the deep bottom.

[0145] As regards the operation, on the counter-anode side within the reactor vessel 1, i.e., in the reduction compartment 23, TiCl_4 as a raw material of Ti is introduced in the molten salt therein to be reduced by Ca in the molten salt to thereby generate Ti particles. Meanwhile, on the anode side, i.e., in the electrolysis compartment 24, the electrolysis of molten salt by means of the anode 11 and cathode 12 proceeds to generate Ca. The generated Ca is taken in the molten Ca alloy 14 within the heat resistant vessel 13. The Ca taken in the molten Ca alloy 14 is released and dissolves in the molten salt on the counter-anode side, i.e., in the reduction compartment 23 within the reactor vessel 1. Hence, the Ca consumed in association with the generation of Ti particles is replenished.

[0146] With regard to a feature in a third embodiment mode, firstly, it should be noted that, since the reactor vessel doubles as the electrolytic cell, the structure of vessel is simple. Secondly, since there is no transport of molten Ca alloy 14 between the electrolytic cell and the reactor vessel, the operational efficiency rises. Moreover, the equipment for the transport between the electrolytic cell and the reactor vessel becomes unnecessary, so that the equipment is simplified from this aspect. However, it is difficult to incorporate the temperature difference in the molten salt between the reducing region and the electrolyzing region.

[0147] By the way, although not shown in the diagram, also in a third embodiment mode in a third production method, Ca in the molten salt to be introduced to the electrolysis compartment 24 can be removed beforehand like the case in a second embodiment mode.

INDUSTRIAL APPLICABILITY

[0148] Since either method for producing Ti or Ti alloys by the Ca reduction shown in a first through a third production method as above is the method of reducing TiCl_4 , high-purity Ti metals or Ti alloys can be produced. Ca is used as the reducing agent for it, particularly the molten salt containing CaCl_2 and having Ca dissolved therein is held in the reactor vessel, and the metallic chloride containing TiCl_4 is reacted with Ca in the molten salt to generate Ti particles or Ti alloy particles in the molten CaCl_2 liquid, which allows the enhancement of the feed rate of TiCl_4 which is of the raw material of Ti, and also allows the continuous operation. Further, there is neither the need to replenish expensive Ca metals nor

the need to apply the operation for independently handling Ca which is highly reactive and difficult to handle.

Also, according to a second production method, in addition to the above, the drop of electric current efficiency due to the mixture of unreacted Ca, being of an issue in the electrolysis step, can be effectively suppressed by employing the molten Ca alloy electrode. Further, according to a third production method, the molten Ca alloy electrode employed in the electrolysis step is utilized as a carrier medium for transferring Ca, so that the circulation of molten salt in a large scale becomes unnecessary.

Accordingly, the method for producing Ti or Ti alloys by the present invention can be widely applied as means for producing high-purity Ti metals with high efficiency and economically.

Claims

1. A method for producing Ti or Ti alloys through reduction by Ca, **characterized by** comprising:

a reduction step in which a molten salt, containing CaCl_2 and having Ca dissolved therein, is held in a reactor vessel, and a metallic chloride containing TiCl_4 reacts with said Ca in the molten salt to generate Ti particles or Ti alloy particles in said molten salt; and
a separation step in which the Ti particles or Ti alloy particles, generated in said molten salt, is separated from said molten salt.

2. A method for producing Ti or Ti alloys through reduction by Ca according to claim 1, **characterized in that** said molten salt containing CaCl_2 is a molten salt containing CaCl_2 and NaCl.

3. A method for producing Ti or Ti alloys through reduction by Ca according to claim 1, **characterized in that** said metallic chloride containing TiCl_4 is a mixed gas containing TiCl_4 and other metallic chloride.

4. A method for producing Ti or Ti alloys through reduction by Ca according to claim 1, **characterized in that**, by holding a molten metal containing Ca on a molten salt, Ca is supplied from the molten metal to the molten salt located below.

5. A method for producing Ti or Ti alloys through reduction by Ca according to claim 4, **characterized in that** said molten metal containing Ca is a molten metal containing Ca and Mg.

6. A method for producing Ti or Ti alloys through reduction by Ca according to claim 1, **characterized in that** CaCl_2 being a by-product associated with the generation of Ti or Ti alloys is discharged outside the reactor vessel.

7. A method for producing Ti or Ti alloys through reduction by Ca according to claim 6, **characterized by** including an electrolysis step of electrolyzing CaCl_2 , being discharged outside the reactor vessel, into Ca and Cl_2 , wherein Ca generated by the electrolysis step is used for the generation reaction of Ti or Ti alloys in the reactor vessel.

8. A method for producing Ti or Ti alloys through reduction by Ca, **characterized by** comprising a combined system of a reduction step and a circulation-type electrolysis step, wherein said reduction step includes the steps of: holding a molten salt, containing CaCl_2 and having Ca dissolved therein, in a reactor vessel; and reacting a metallic chloride containing TiCl_4 with Ca in the molten salt to generate Ti particles or Ti alloy particles in the molten salt, and wherein said circulation-type electrolysis is configured that a molten salt, being used for producing said Ti or Ti alloys and discharged from said reactor vessel, is electrolyzed to generate and replenish Ca in said molten salt which is returned to said reactor vessel, and wherein, in electrolyzing as above, an alloy electrode made of a molten Ca alloy is employed for a cathode.

9. A method for producing Ti or Ti alloys through reduction by Ca according to claim 8, **characterized in that**, in said electrolysis step, a molten salt within an electrolytic cell, together with the interface between a molten Ca alloy, constituting said alloy electrode, and said molten salt, is divided into an anode side and a counter-anode side by installing a partition wall, and wherein a molten salt to be supplied from said reactor vessel is introduced on said counter-anode side.

10. A method for producing Ti or Ti alloys through reduction by Ca according to claim 8, **characterized by** including a Ti separation step in which the generated Ti particles or Ti alloy particles are separated from a molten salt within or outside said reactor vessel, wherein, in a discharging step in which a molten salt being used for generating Ti

particles or Ti alloy particles is discharged outside said reactor vessel, Ti particles or Ti alloy particles generated in a molten salt are discharged, together with said molten salt, outside the reactor vessel, and wherein, in said Ti separation step, said Ti particles or Ti alloy particles are separated from a molten salt discharged outside the reactor vessel, and wherein, in said electrolysis step, the molten salt from which said Ti particles or Ti alloy particles are separated and removed is electrolyzed.

11. A method for producing Ti or Ti alloys through reduction by Ca according to claim 1 or claim 8, **characterized in that**, in said electrolysis step, a metallic chloride containing TiCl_4 is supplied in a molten salt.

12. A method for producing Ti or Ti alloys through reduction by Ca, **characterized by** comprising:

a Ca generation step by electrolyzing, wherein a molten salt containing CaCl_2 is electrolyzed by employing a molten Ca alloy as a cathode to increase a Ca content ratio in said molten Ca alloy;

a Ca replenishment step, wherein the molten Ca alloy in which Ca has increased by the Ca generation step gets contacted with the molten salt containing CaCl_2 to have Ca dissolved in said molten salt; and,

a Ti generation step by a reducing reaction, wherein a metallic chloride containing TiCl_4 is supplied into the molten salt in which Ca gets dissolved in the Ca replenishment step to thereby generate Ti particles or Ti alloy particles in the molten salt.

13. A method for producing Ti or Ti alloys through reduction by Ca according to claim 12, **characterized by** including a Ti separation step in which Ti particles or Ti alloy particles generated in a molten salt are separated from the molten salt.

14. A method for producing Ti or Ti alloys through reduction by Ca according to claim 12, **characterized in that** a molten salt containing CaCl_2 is held in an electrolytic cell as well as a reactor vessel, and wherein a Ca generation step by electrolyzing proceeds within the electrolytic cell, while transferring a molten Ca alloy from the electrolytic cell to the reactor vessel, to undergo a Ca replenishment step as well as a Ti generation step, and wherein the molten Ca alloy in which Ca is consumed within the reactor vessel returns to the electrolytic cell.

15. A method for producing Ti or Ti alloys through reduction by Ca according to claim 14, **characterized in that** the temperature of molten salt in said electrolytic cell is set to be lower than that of molten salt in said reactor vessel.

16. A method for producing Ti or Ti alloys through reduction by Ca according to claim 12, **characterized in that**, as holding a molten salt containing CaCl_2 within a reactor vessel doubling as an electrolytic cell, an electrolysis by employing a molten Ca alloy as a cathode is carried out, while a molten salt within the reactor vessel, together with the interface between said molten salt and the molten Ca alloy, is divided into an anode side and a counter-anode side by installing a partition wall, in which a Ca generation step is carried out on the anode side and a Ca replenishment step as well as a Ti generation step are carried out on the counter-anode side.

17. A method for producing Ti or Ti alloys through reduction by Ca according to any of claims 7, 8 and 12, **characterized by** including a chlorination step in which Cl_2 generated in said electrolysis step is reacted with TiO_2 to thereby generate TiCl_4 , wherein TiCl_4 generated in the chlorination step is utilized in the generation reaction for Ti or Ti alloys within a reactor vessel.

18. A method for producing Ti or Ti alloys through reduction by Ca according to claim 1 or claim 13, **characterized in that** generated Ti or Ti alloys, together with a molten salt, is discharged outside said reactor vessel, and wherein said Ti or Ti alloys are separated from the molten salt outside the vessel.

19. A method for producing Ti or Ti alloys through reduction by Ca according to claims 13, **characterized in that** a molten salt being separated from Ti or Ti alloys in a Ti separation step is introduced to a Ca generation step by electrolyzing and/or a Ti generation step by a reducing reaction.

20. A method for producing Ti or Ti alloys through reduction by Ca according to claims 13, **characterized in that** a molten salt being separated from Ti or Ti alloys in a Ti separation step is utilized in a Ti generation step to be reacted with a molten Ca alloy in which Ca is consumed to increase Ca in the molten Ca alloy by unreacted Ca in the molten salt, and then, the molten Ca alloy is used in a Ca replenishment step.

21. A method for producing Ti or Ti alloys through reduction by Ca according to claims 12, **characterized in that** said

molten salt containing CaCl_2 is a multi-element-system molten salt which contains at least one of NaCl, KCl, LiCl and CaF_2 other than CaCl_2 .

5 **22.** A method for producing Ti or Ti alloys through reduction by Ca according to claims 12, **characterized in that** said metallic chloride containing TiCl_4 is a mixture of TiCl_4 and other metallic chloride.

23. A method for producing Ti or Ti alloys through reduction by Ca according to claims 12, **characterized in that** Ti or Ti alloys to be generated are particles with an average particle size of 0.5 - 50 μm .

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FIG. 1

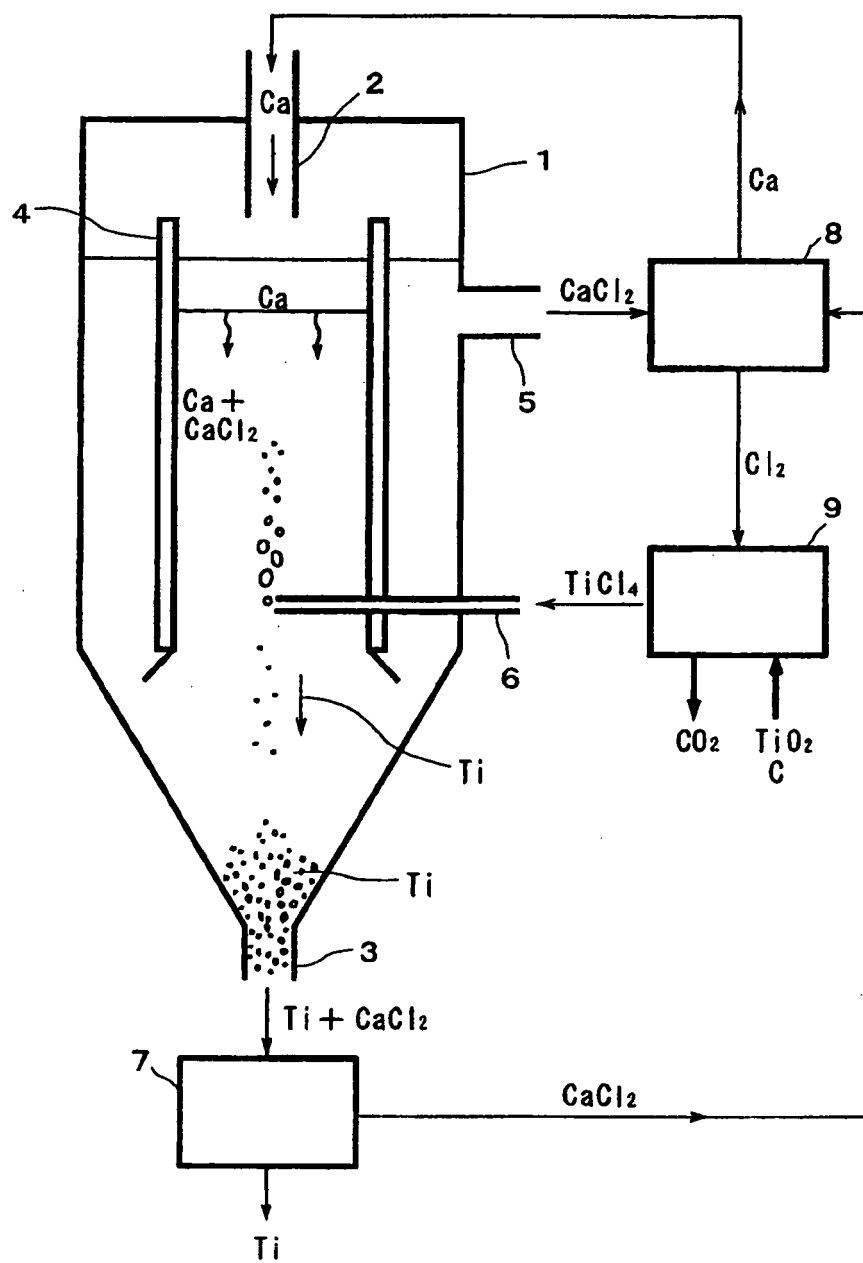


FIG. 2

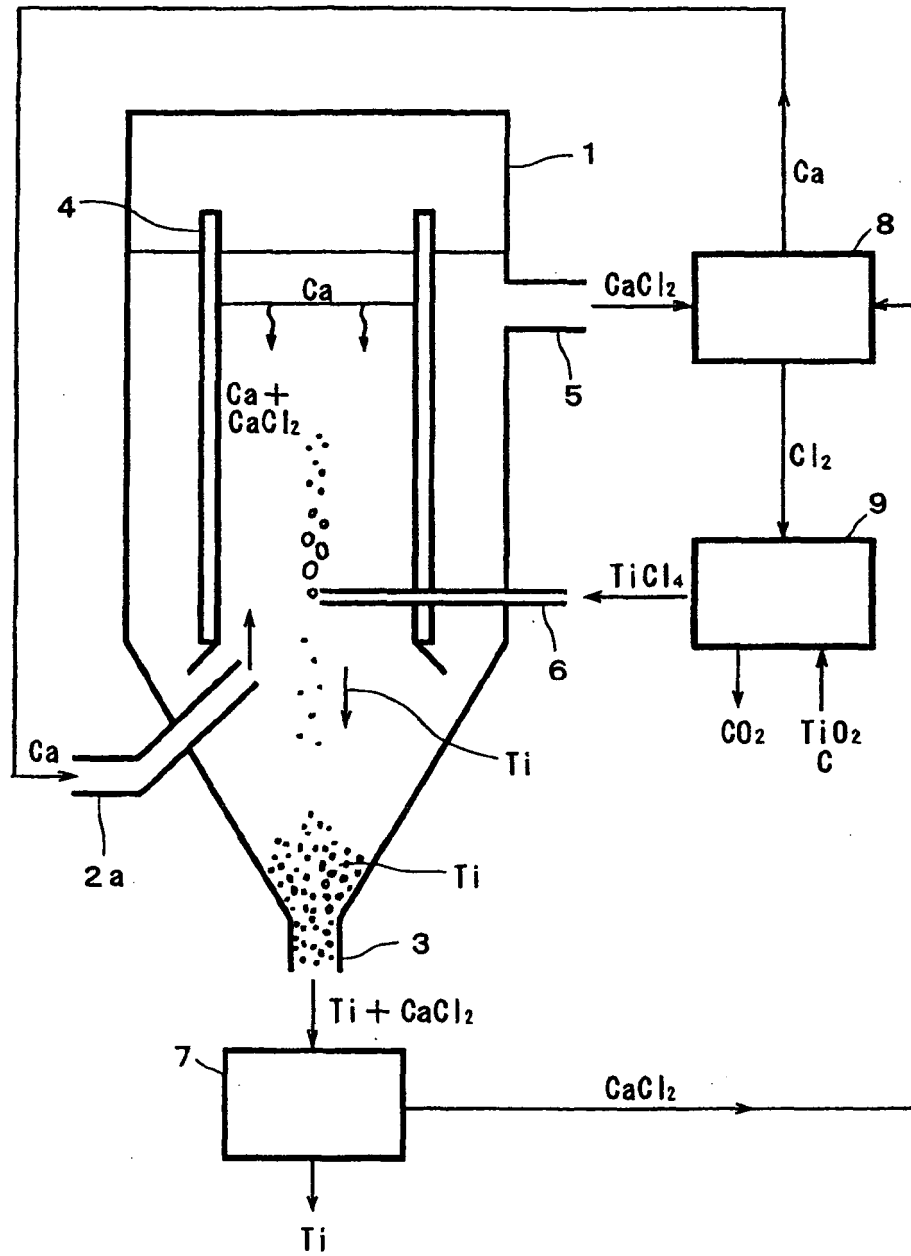


FIG. 3

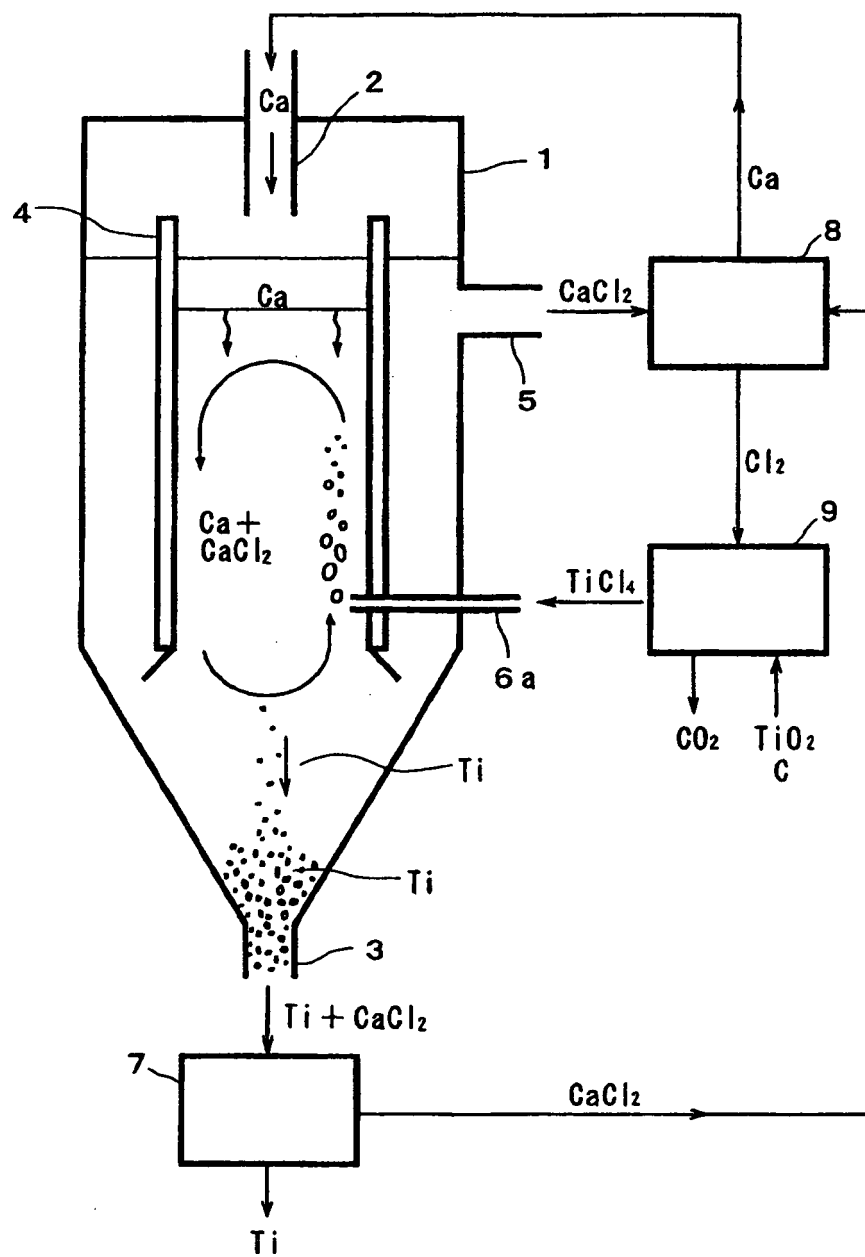


FIG. 4

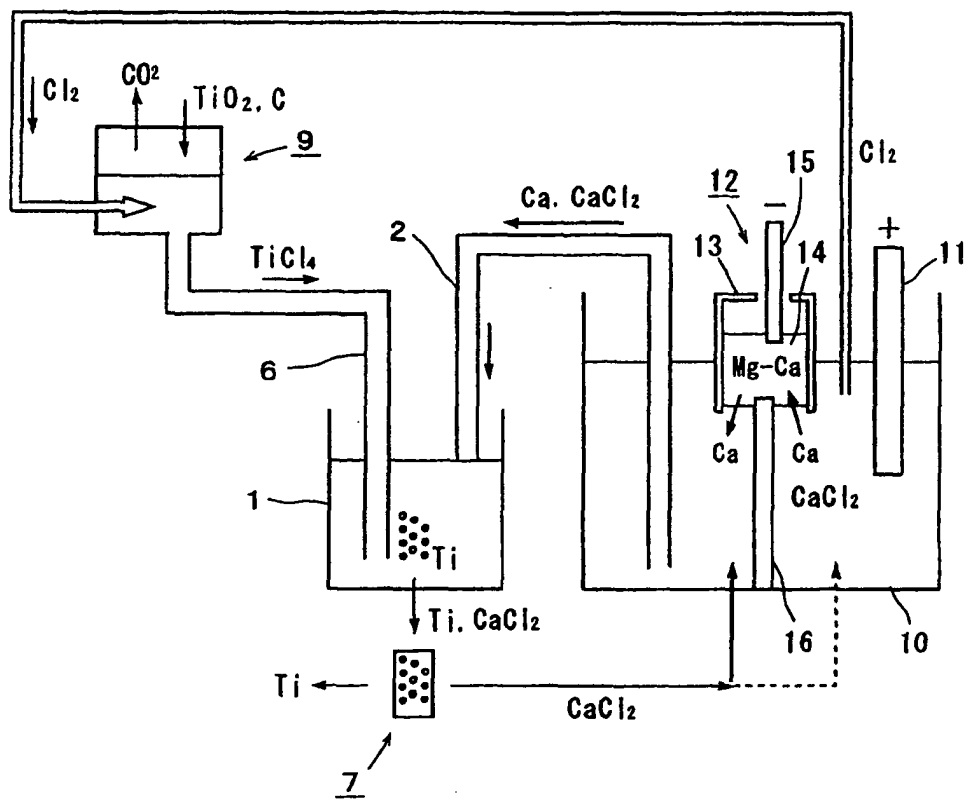


FIG. 5

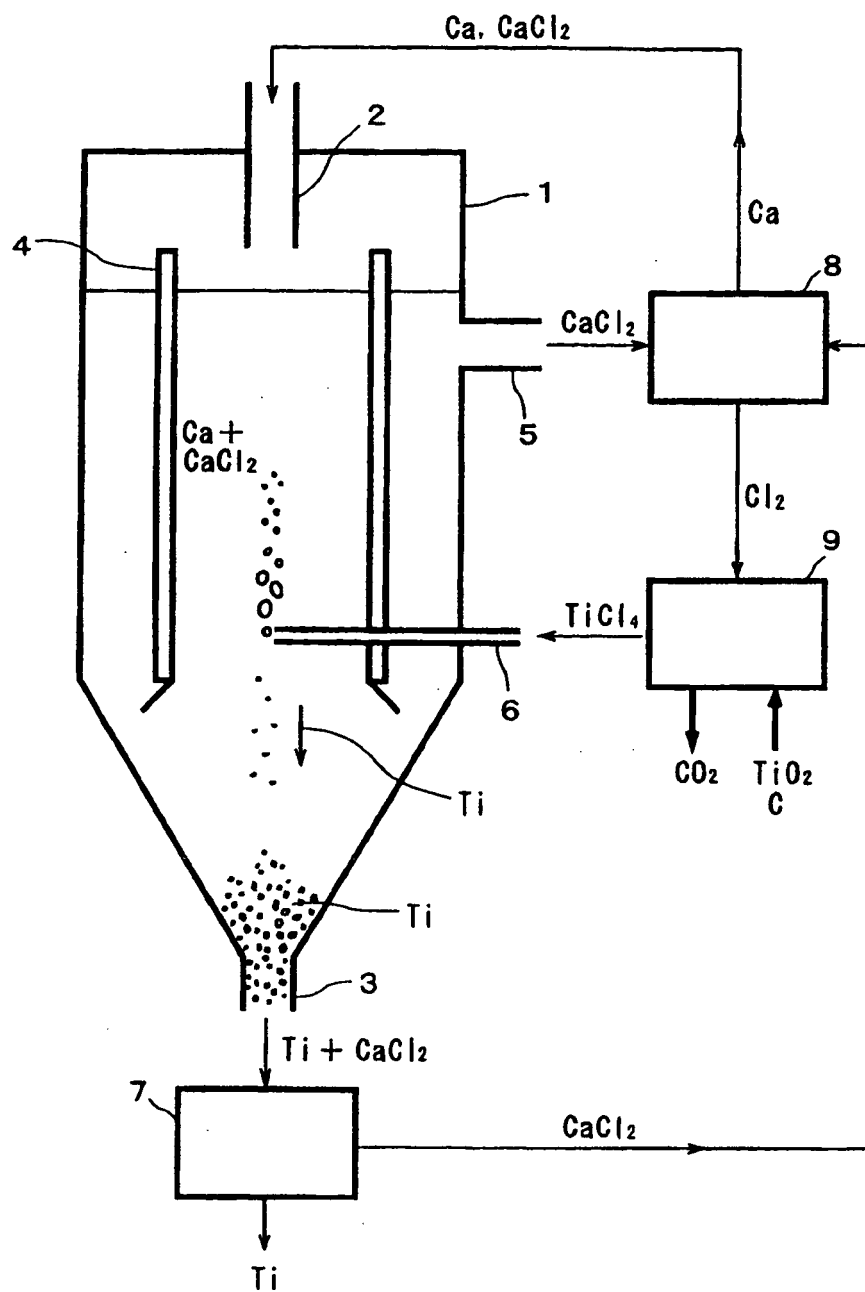


FIG. 6

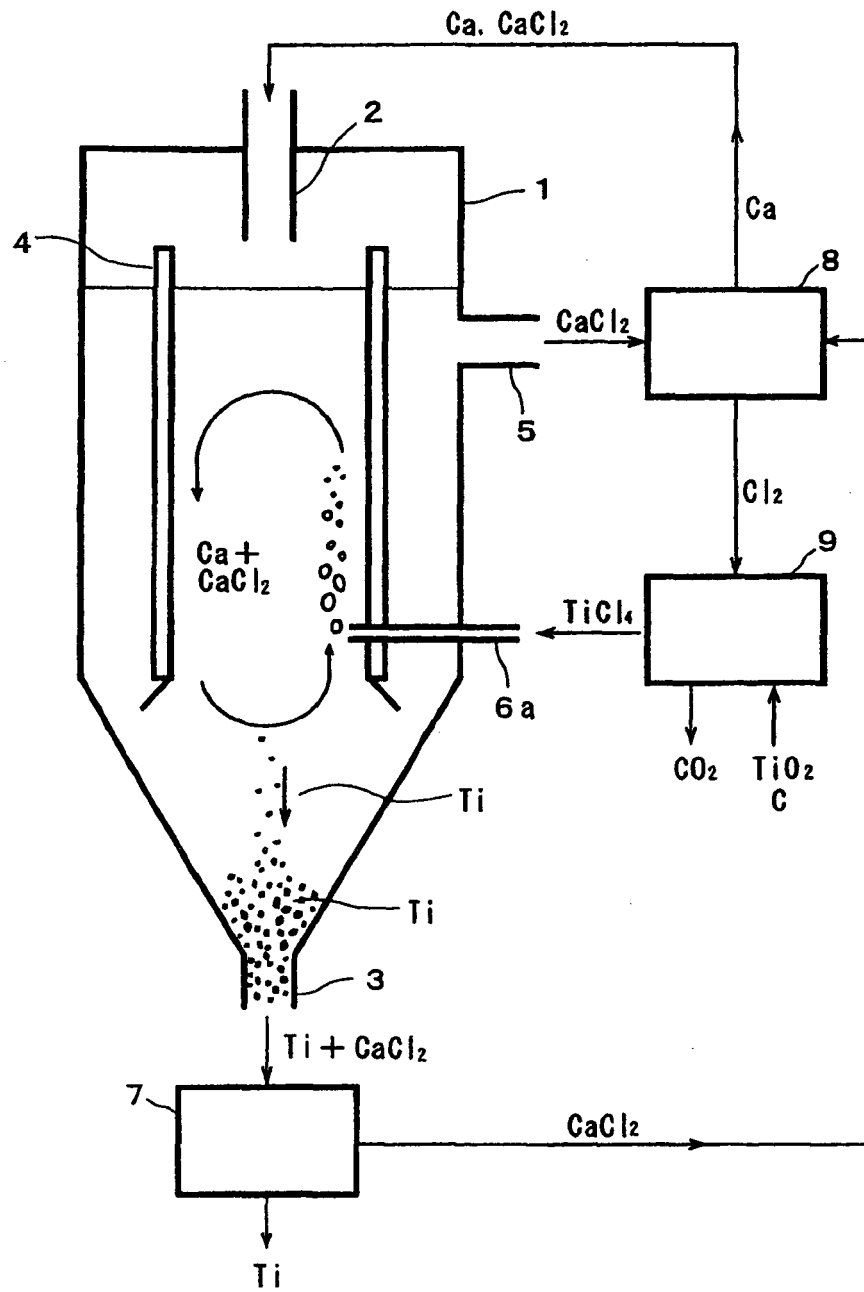


FIG. 7

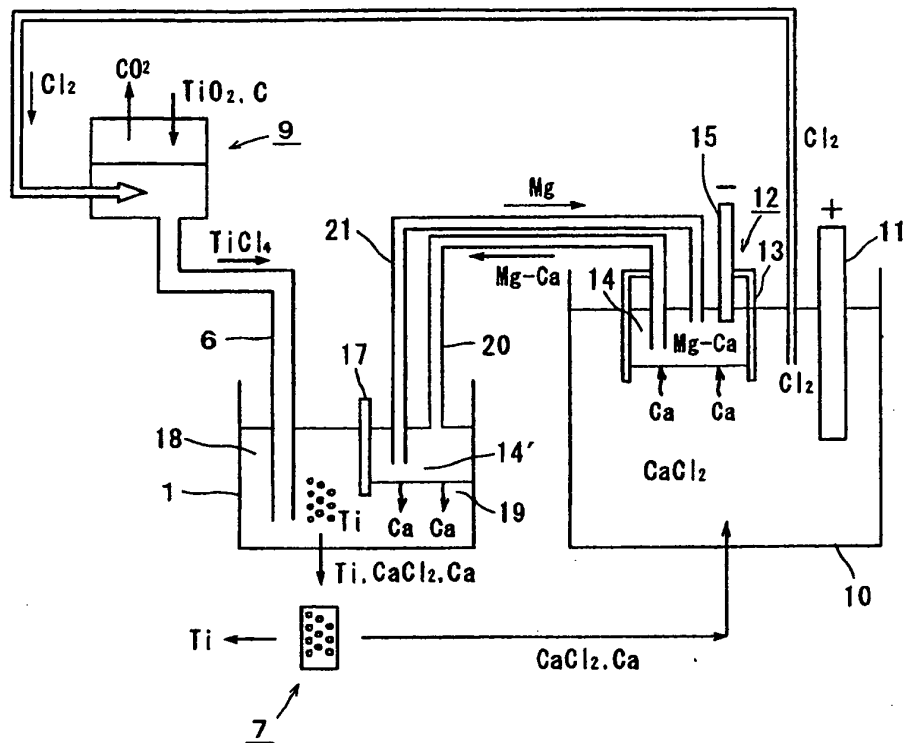


FIG. 8

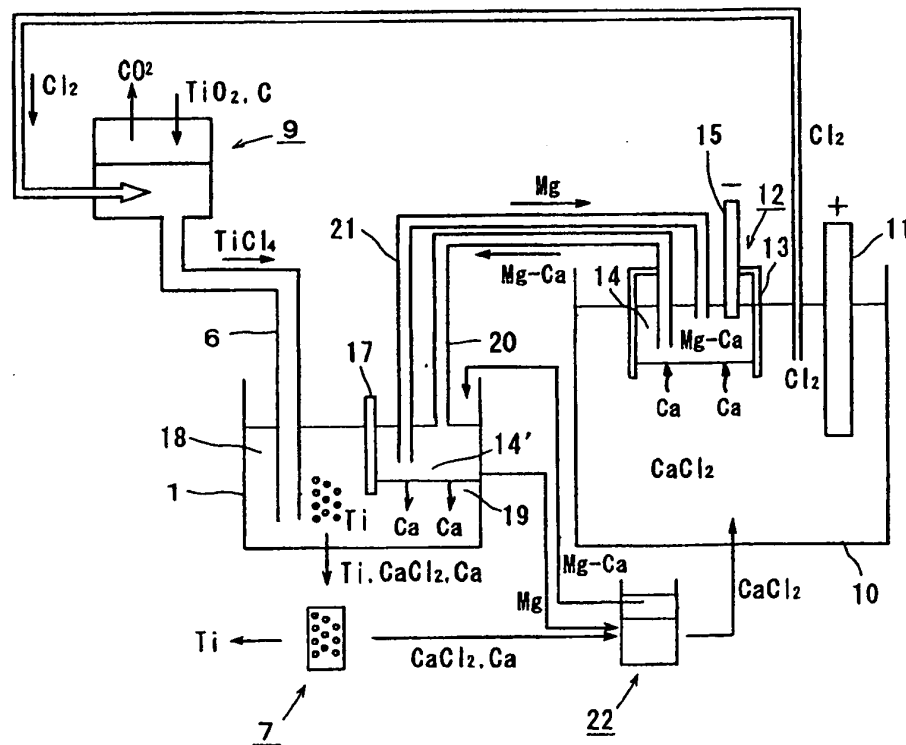
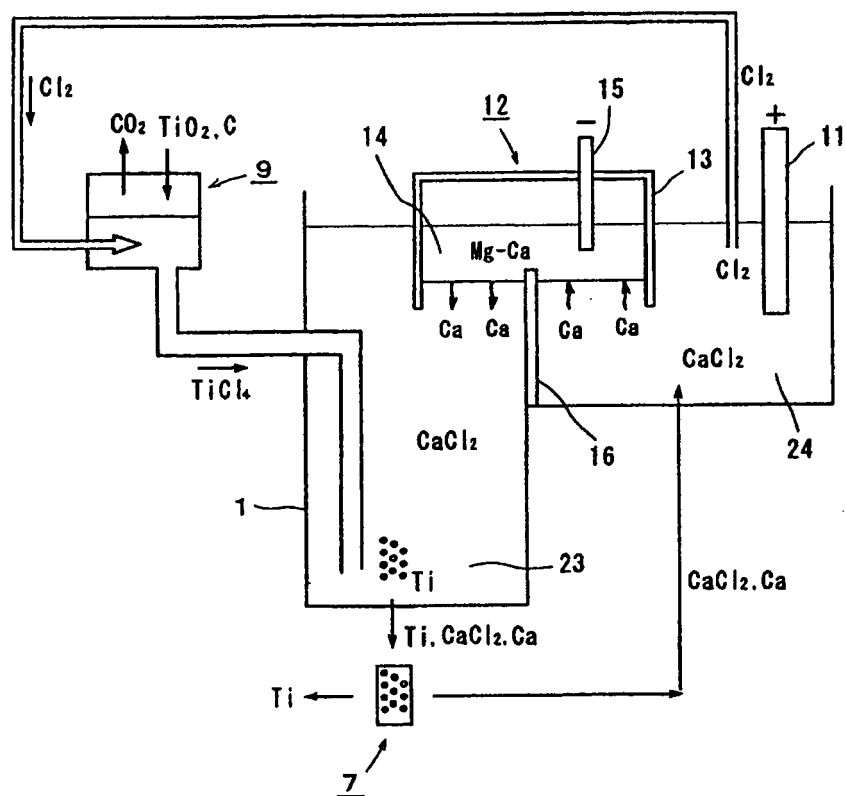


FIG. 9



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/014734

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C22B34/12		
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		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JOIS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2001-192748 A (NKK Corp.), 17 July, 2001 (17.07.01), Claims; Par. Nos. [0043] to [0049], [0055] to [0057]; drawings (Family: none)	1-23
Y	JP 64-047823 A (Toho Titanium Co., Ltd.), 22 February, 1989 (22.02.89), Claims; page 3, upper right column; page 4, lower left column; drawings (Family: none)	1-23
Y	US 4487677 A (METALS PRODUCTION RESEARCH, INC.), 11 December, 1984 (11.12.84), Claims; drawings & JP 60-238429 A	1-23
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 04 November, 2004 (04.11.04)		Date of mailing of the international search report 22 November, 2004 (22.11.04)
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/JP2004/014734

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2003/038156 A1 (Katsutoshi ONO et al.), 08 May, 2003 (08.05.03), Claims; drawings & JP 2003-129268 A	1-23
A	WO 1986/007097 A1 (THE UNIVERSITY OF MELBOURNE), 04 December, 1986 (04.12.86), Claims; drawings & JP 63-500389 A	1-23
A	WO 1996/004407 A1 (KROFTT-BRAKSTON INTERNATIONAL, INC.), 15 February, 1996 (15.02.96), Claims; drawings & JP 10-502418 A	1-23
A	MARTINEZ A.M. et al., A Chemical and Electro chemical Study of Titanium Ions in the Molten Equimolar CaCl ₂ + NaCl Mixture at 550°C, Journal of Electroanalytical Chemistry, Vol.449, 1998, pages 67 to 80	1-23

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