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# Design, Test and Theoretical Assessments for Reduction of Titanium Oxide to Produce Titanium in Molten Salt

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We have investigated the details of the calciothermic reduction of  $\text{TiO}_2$  in  $\text{CaCl}_2$ - $\text{CaO}$ - $\text{Ca}$  molten salt electrolyte and developed a process for Ti production that is proceeding toward commercialization. In this process, when a potential of 3 V is applied between the carbon anode and the stainless steel cathode, the electrolytic decomposition of  $\text{CaO}$  occurs such that Ca deposits at the cathode and immediately dissolves into the molten salt. This Ca attacks the  $\text{TiO}_2$  powders fed into the bath and reduce them to metallic titanium. The engineering aspects of the new reactor have been considered according to the following items; (1) the simplest possible cell structure, (2) permanent inside wall lining, (3) open cell and (4) surface protection layer. The 10 days campaign using a reactor with 2 tons of molten salt and current of 4000 A has been conducted. As a result of the test, we came to propose a definitive model of open reactor body. We have theoretically examined the possibility of prebaked soluble titanium dioxide anode. Application of the oxygen-ion deficient titanium dioxide anode to this process will contribute to achieving the high productivity of titanium as well as the commercial level of oxygen in titanium. [doi:10.2320/matertrans.MK201604]

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## 1. Introduction

Of the various potential routes to produce titanium, the direct reduction of pure titanium oxide in a single reactor may offer the highest possible productivity. The approach presented in this paper is based on the OS process for the production of ductile titanium from rutile in molten salt, and includes both the fundamental and engineering aspects of this process. The process to produce ductile metal via the direct reduction of titanium oxide consists of calciothermic reduction of titanium oxide and *in-situ* molten salt electrolysis of calcium oxide present as a solute in the molten calcium chloride solvent.

This type of high-temperature reactor has not been contemplated thus far, and questions related to the permanent inner wall lining and the operation of the cell, when exposed to atmospheric conditions are of primary interests. The corrosion durability of the materials immersed in the bath has also been examined, and suitable materials to meet the severe corrosion resistance requirements are suggested based on the practical tests carried out in this study. The analysis and experimental data presented in this paper serve as a preliminary guide to the design of a practical reactor.

The definitive anode design is still open for further discussion. In this paper, the use of oxygen-ion deficient titanium dioxide anode has been examined on the theoretical base, and it was thought that prebaked consumable titanium dioxide may provide optimum performance for mutual compatibility with the original OS process.

## 2. Design and Test of Reactor Cell

### 2.1 Process description

The essential features of this process have been reported in previous investigations<sup>1–12</sup>. The process to produce titanium

in a molten salt is based on the characteristics of the phase diagram for the  $\text{CaCl}_2$ - $\text{CaO}$ - $\text{Ca}$  system as shown in Fig. 1<sup>5</sup>. Both  $\text{CaO}$  and  $\text{Ca}$  exhibit solubility in molten  $\text{CaCl}_2$ . The reducing agent is calcium dissolved in the bath as a result of the *in situ* electrolytic decomposition of reduction product  $\text{CaO}$ , which produces a homogeneous liquid phase consisting of the  $\text{CaCl}_2$ - $\text{CaO}$ - $\text{Ca}$  system. When fine  $\text{TiO}_2$  particles are fed into the bath, they are suspended in it, and are reduced by the solute Ca while slowly sinking downwards. The separation of the suspended particles into a dense slurry, containing a higher concentration of solid can occur as sedimentation, resulting in agglomeration into metal powders at the base of the reactor cell. If this electrically conductive deposit is connected to the negative terminal of a power supply, it causes  $\text{CaO}$ -decomposition reactions to occur on the surface of metal particles, and anodic reactions to emit  $\text{O}_2$  gas, but only if an inert anode material is used. In addition, because the solubility of  $\text{TiO}_2$  in liquid  $\text{CaCl}_2$  is 3.2 mass% at 1173 K, electrolytic deposition may occur at the cathode. Both the calciothermic

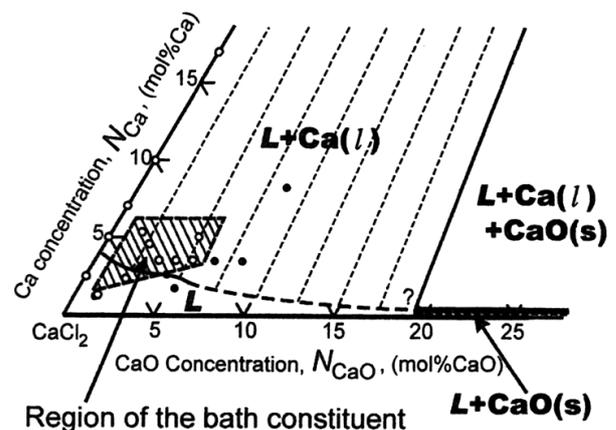


Fig. 1 Isothermal section of the  $\text{CaCl}_2$ - $\text{CaO}$ - $\text{Ca(L)}$  system showing the region of bath composition.

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and electrolytic reductions may therefore occur in parallel. The thermochemical behavior of this molten salt is comparable to that observed in the Hall-Héroult process to produce aluminum in which the oxide,  $\text{Al}_2\text{O}_3$ , is dissolved in molten  $\text{NaF-AlF}$  salt. The liquid aluminum obtained at the cathode by electrolysis is also soluble in the salt at 4 mass% as so-called *metal fog*. In the same way, the Ca that deposits at the cathode immediately leaves that point to enter the  $\text{CaCl}_2$  electrolyte as a stable solute.

One of the authors has investigated the calciothermic reduction of  $\text{TiO}_2$  in molten  $\text{CaCl}_2$  to obtain ductile titanium using the experimental system shown in Fig. 2(a). The  $\text{TiO}_2$  powder to be reduced was placed at the bottom of a container and covered with liquid  $\text{CaCl}_2$ , over which liquid Ca was floating. Under isothermal conditions at 1173 K, the calcium reducing agent diffused into the  $\text{CaCl}_2$  reaching saturation and reacting with the titanium powder, while the reduction product, CaO, was absorbed into the liquid  $\text{CaCl}_2$ . A typical deoxidation curve is shown in Fig. 2(b). Figure 3 shows micrographs of the titanium powders obtained by calciothermic reduction of  $\text{TiO}_2$ .

It has been reported that if the complex oxide  $\text{TiCaO}_3$  is taken as a starting oxide for reduction instead of pure  $\text{TiO}_2$ , then the rate of titanium reduction is higher than that of the

single oxide  $\text{TiO}_2$ <sup>6)</sup>.  $\text{CaTiO}_3$  has merit as a raw material for reduction, it retains the Ca source within its crystal structure during electrolysis. It has also been demonstrated that as the starting material for the reduction, the rate of reduction is much more advantageous to  $\text{CaTi}_x\text{O}_y$  than pure  $\text{TiO}_2$  as the  $\text{CaTi}_x\text{O}_y$  phase is directly convertible to the metallic phase. If  $\text{TiO}_2$  dissolved in the bath exists in a free state, then its reduction proceeds via the stable titanium mono-oxide phase which is difficult to decompose.

## 2.2 Thermodynamic background

In order to definitively establish the process, it must be proven that the process is thermodynamically favorable. Firstly, the conditions for equilibrium, by which the final oxygen concentration is reached in Ti-O binary alloys, must be clarified. For this purpose, Gibbs phase rule is used to determine the thermodynamic factors required to equilibrate the molten salt system containing the solid Ti phase, i.e.,  $\text{CaCl}_2\text{-CaO-Ca-Ti}$ . The number of phases is then  $p = 3$  including argon gas over the condensed phase. Next, the total number of the constituents is counted as  $c = 4$  (Ca, Cl, O, Ti). The degree of freedom is expressed by equation  $f = c + 2 - p$ , which gives  $f = 3$ . The three intensive factors selected for the present system to reach an equilibrated state are temperature  $T$ , pressure  $P$  and activity ratio,  $r = a_{\text{CaO}}/a_{\text{Ca}}$ . Accordingly, the oxygen concentration in Ti, i.e.,  $[\text{O}]_{\text{Ti}}$ , can be calculated as a function of  $T$ ,  $P$  and  $r$  by applying the law of mass action to the following equilibrium reaction,



Figure 4 shows the result of calculations previously reported

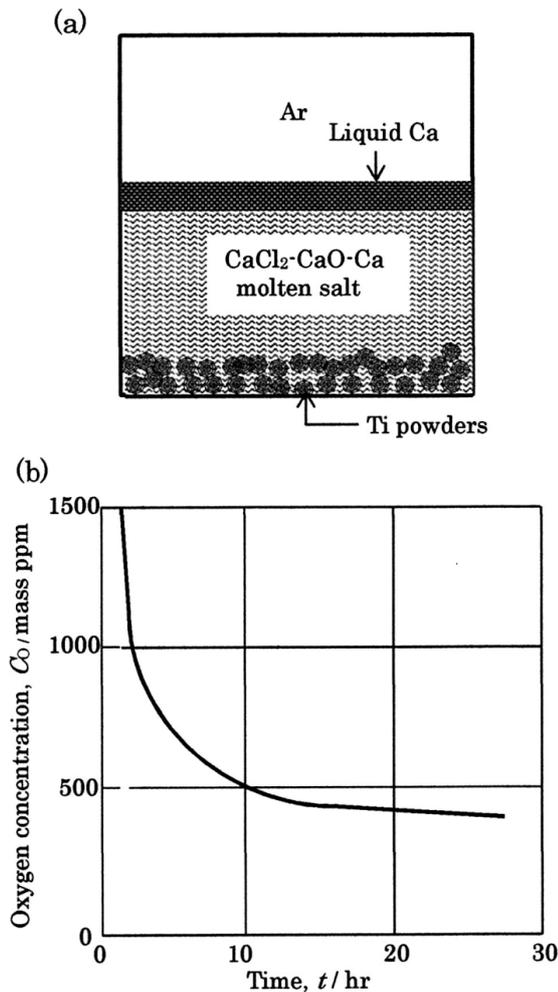


Fig. 2 Calciothermic reduction of  $\text{TiO}_2$  in molten salt. (a) Experimental system. Temperature: 1173 K; Bath composition: 0–3.4 mol%CaO. (b) Variation in oxygen concentration during final stage of reduction.

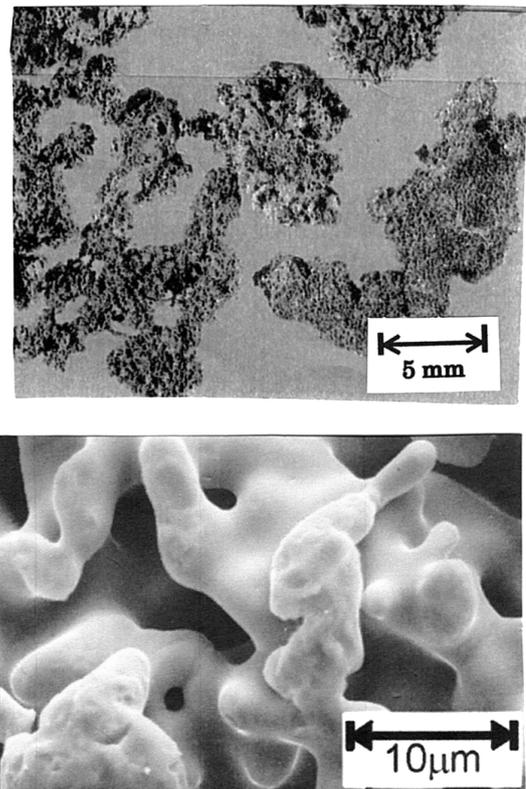


Fig. 3 SEM images of titanium powders reduced from  $\text{TiO}_2$  at 1173 K for 3.6 ks.

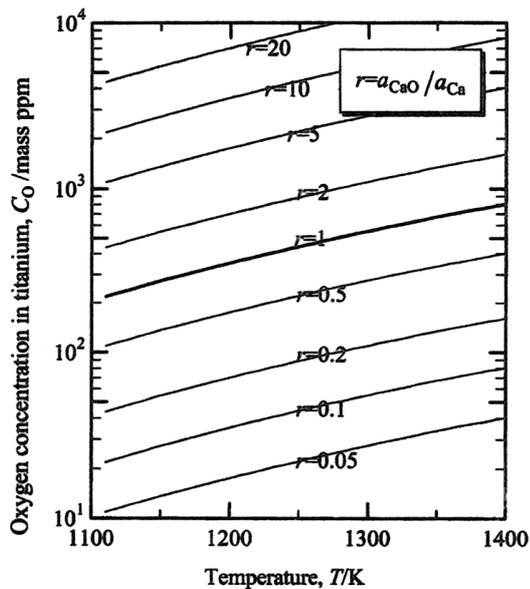


Fig. 4 Equilibrium oxygen concentration in titanium.

by one of the authors<sup>5</sup>). Okabe *et al.* carried out the removal of oxygen from titanium using the halide flux electrochemical deoxidation method and obtained titanium with extra-low oxygen content, i.e., less than 10 mass ppm, hence the thermodynamic capability of the  $\text{CaCl}_2\text{-CaO-Ca}$  system has essentially been proved to be useful<sup>2,3</sup>).

### 2.3 Reactor design considerations

The fundamental design concept for the reactor body was simplicity. The key requirements of a reactor cell for use in practical titanium production have been considered based on the following items that are required to maximize productivity; (1) open-type reactor; (2) simplest possible body structure; (3) permanently self-sustaining inner-wall lining; (4) surface-protection layer. For the open-reactor, it was necessary to examine problems associated with burning of Ca during reactor operation. To evaluate the new titanium production process, it was essential to obtain experimental verification in a commercial scale. Figure 5 is a view of the reactor that was constructed for the present test, and a cross-sectional image is schematically shown in Fig. 6. This equipment was of sufficient size that the optimal operational conditions could be studied in detail. A high-frequency induction furnace (maximum capacity 2 tons) was used to melt  $\text{CaCl}_2\text{+CaO}$  mixture to charge into the reactor. If the reactor could be of permanent use, then self-coated layer or freeze is required to form, when the molten salt is charged into the reactor cell. The molten  $\text{CaCl}_2$  was also used to prepare  $\text{CaCl}_2$  bricks by casting them into a mold. These were piled up to form an inner wall lining. The bricks had to be maintained at  $60^\circ\text{C}$  in a warm room to protect them from melting to atmospheric humidity. The calcium ions inside the bath are transferred towards the cathode riding on the lines of force created by the electrostatic field. As a result, elemental Ca can arise not only from the cathode surface facing the anode plate but also from the surface behind. When undergoing electrolysis, the Ca ion in the salt is converted to elemental Ca at the cathode surface, and then dissolves into the molten salt before the bath be-

comes fully saturated with calcium.

The experimental conditions in the reactor tests were as follows: temperature: 1143–1173 K; operational voltage: 2.7–2.9 V; current: 4000 A (max.); anode current density:  $6.0 \times 10^4\text{--}1.0 \times 10^4$  A/m<sup>2</sup>; campaign duration: 10 days; electrolyte:  $\text{CaCl}_2\text{-4.5 mole\%CaO-3.5 mole\%Ca}$ ; atmosphere: air; anode: carbon; cathode: lattice-type stainless steel rod; refractory lining:  $\text{CaCl}_2$ . No severe problems were experienced in bringing the cell up to normal operating conditions, or in maintaining stable conditions throughout the 10 days campaign. The temperature of the bath was controlled by means of the current provided by the power supply. The analysis of the gas from the anode was made two times a day. Its composition widely changed depending on the anode current density;  $\text{CO}_2$  varied between 65 and 98% and the remaining was the mixture of  $\text{O}_2$  and  $\text{CO}$ .

### 2.4 Test results

#### (1) Bath composition

The first requirement for steady state operation of the new reactor test was the control and stabilization of optimum bath composition, i.e.,  $\text{CaCl}_2\text{-4.5 mole\%CaO-3.5 mole\%Ca}$ . Three factors, the current efficiency, the total current monitored on the line in the vicinity of the power supply and the  $\text{TiO}_2$  powder feeding rate were selected to control; the degradation of current efficiency is caused by the back reaction of Ca with  $\text{CO}_2$  emitted from the carbon anode. For the case where only two factors, the current and  $\text{TiO}_2$  feeding rate, were taken as key factors, it was difficult to keep the optimum bath composition. However, the effect of slowly stirring all over the bath had a favorable effect to settle the bath to the desired composition.

#### (2) Carbon anode

Two kinds of reactions occur at the anode surface: the oxygen ion,  $\text{O}^{2-}$ , donates electrons to the carbon anode to form  $\text{O}_2$ , and part of the  $\text{O}_2$  reacts with the carbon to form  $\text{CO}_2$ : The reactions are  $2\text{O}^{2-} = \text{O}_2 + 4\text{e}$ , and  $\text{C} + \text{O}_2 = \text{CO}_2$ . In the course of ascending the anode surface, the  $\text{O}_2$  bubbles react with the solute Ca in the bath to form  $\text{CaO}$ :  $\text{O}_2 + 2\text{Ca} = 2\text{CaO}$ , and the  $\text{CaO}$  reacts with  $\text{CO}_2$  to form solid  $\text{CaCO}_3$  by the reaction,  $\text{CO}_2 + \text{CaO} = \text{CaCO}_3$ . The oxidation product,  $\text{CO}_2$  is then reduced by the solute Ca to generate fine carbon particles:  $\text{CO}_2 + 2\text{Ca} = \text{C} + 2\text{CaO}$ . Eventually, the solid mixture of  $\text{CaCO}_3$  and C reaches the surface of the bath, evident as a dark grey layer floating on the entire surface of the bath. The presence of this layer proved indispensable, as it protected the dissolved calcium beneath the layer from oxidation. A proportion of the fine carbon particles were also dispersed widely in suspension throughout the molten bath due to the flux in the bath. These particles caused undesirable carbon contamination of the reduced titanium powders.

A new carbon anode, which is particularly applicable to this process, is currently under development by one of the authors<sup>13</sup>). This type of anode system takes advantage of an oxygen-ion conductor, i.e., solid  $\text{ZrO}_2\text{CaO}$  electrolyte, in which the carbon anode emitting  $\text{CO}_2$  is separated from the molten salt by means of a diaphragm made of the solid electrolyte. The oxygen ion enters the solid electrolyte through the interface, being driven by a voltage applied across the carbon anode and the metal cathode. At the opposite interface

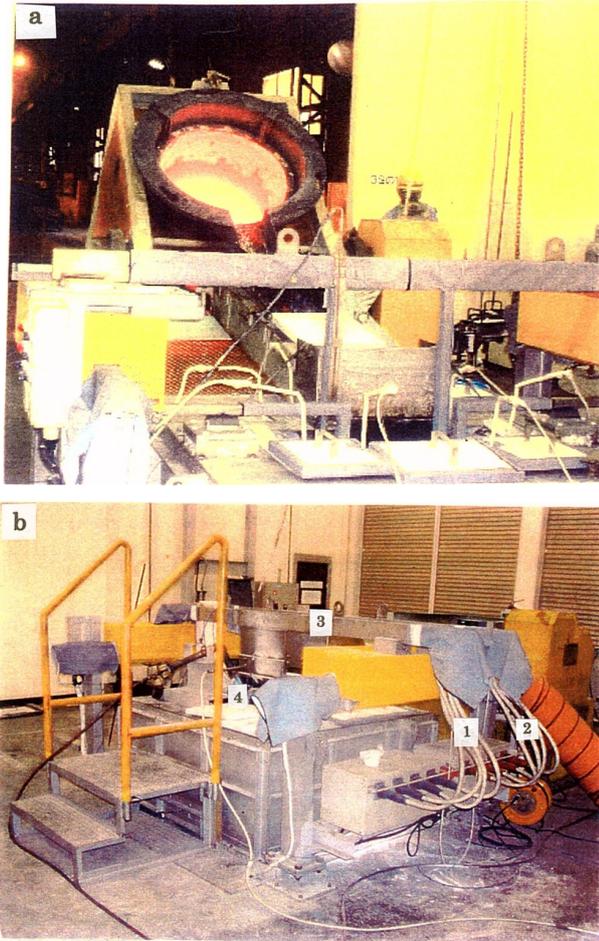


Fig. 5 Test reactor in operation. (a), Charge of the molten salt into the reactor cell. (b), The reactor during electrolysis; 1: Lead wires for the cathode; 2: Lead wires for the anode; 3: Bus bar; 4: View frame.

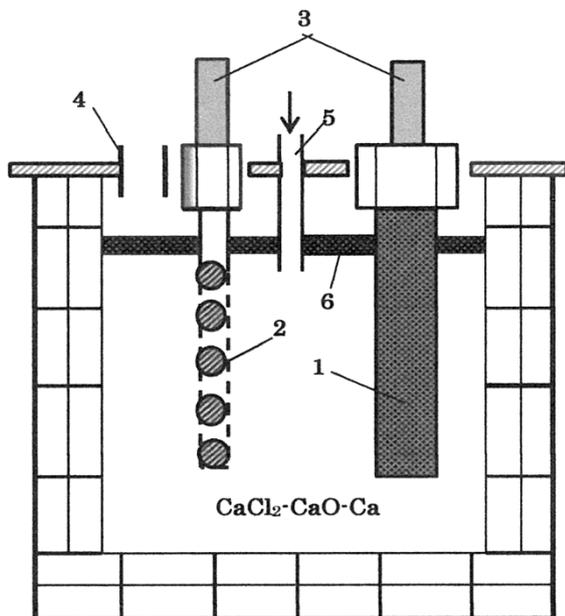


Fig. 6 Schematic illustrating the vertical-section of the test reactor. 1: Carbon anode; 2: Stainless steel lattice-type cathode; 3: Bus bar; 4: View frame; 5:  $\text{TiO}_2$  powder feeding pipe; 6: Surface protection layer.

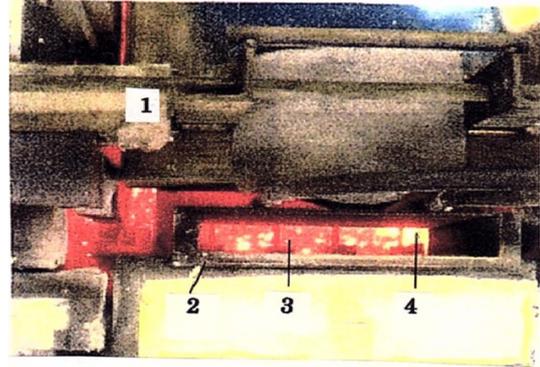


Fig. 7 Photo overlooking the bath surface through the view frame. 1: Bus bar; 2: View frame; 3:  $\text{CaCO}_3\text{-CaO-CaCl}_2$  protection layer; 4 Ca-bearing bath surface.

between the carbon anode and the solid electrolyte, an electrolytic reaction,  $2\text{O}^{2-} + \text{C} = \text{CO}_2 + 4\text{e}$ , occurs, and thus the solid electrolyte permits the effective isolation of  $\text{CO}_2$  from the molten salt containing the calcium reducing agent.

### (3) Self-sustaining surface protection layer

The surface of the bath is covered with a sticky layer consisting of a mixture of  $\text{CaCl}_2$ ,  $\text{CaCO}_3$  and  $\text{CaO}$ . This surface layer can cut off from the air so that the solute calcium beneath the layer remains stable, without being oxidized. It can also prevent the evaporation of  $\text{CaCl}_2$  from the bath. Figure 7 shows how the bath is covered with the protection layer. This photo was taken through the view frame which allows observe the surface of the bath in the reactor undergoing electrolysis. The surface is normally covered almost completely with the red colored protection layer. When we intentionally removed this layer to make several spots in a number of places, we could observe bright yellow radiation emitted from the Ca-bearing molten salt. We did not see any fire and any sparks, because the concentration of Ca is small, below 4 mole%.

### (4) Grounding problem

One area of considerable interest has been the question of grounding the materials, which are immersed in the molten salt bath. Titanium is particularly reactive metal at high temperatures, so the titanium reduced in the bath tends to react easily with impurity ions, even if they are only present at low concentrations. The  $\text{CaCl}_2$  lining, which acts as a kind of insulator wall, is free from stray current corrosion associated with the local battery effect. If a conducting metal rod is dipped in an electrolyte solution where ionic current flows due to an electrostatic field, then it evolves a floating potential which results in the dissolution of the metal. One way of minimizing floating potentials in the materials immersed in the bath (thus resisting corrosion) is to ensure that the buildup of titanium deposits settling at the bottom must be the cathode and connected to ground. The rod to be immersed in the bath must be made of titanium and also connected to ground.

### (5) Suggested reactor body

One outcome of the test is a definitive proposal for the design of the open reactor body. The key points of the design are:

1) The inner lining brick must be made of  $\text{CaO}$  with  $\text{CaCl}_2$  binder.

2) Graphite blocks may be used for the outermost lining due to their strong corrosion resistance in salty environments.  
 3) If the graphite anode emitting  $\text{CO}_2$  is replaced by an inert anode, then the mixed layer of  $\text{CaO}+2\text{CaO}+\text{CaCl}_2+\text{CaCl}_2$  can provide a self-sustaining surface protection layer against burning Ca beneath the layer. All these compounds in the layer are soluble in the bath beneath the layer, hence, the growth of the layer comes to a stop at equilibrium, and the thickness of the layer remains constant. This layer also becomes sticky and can almost completely isolate the air from the bath.

A schematic of the vertical section of the suggested reactor cell structure is shown in Fig. 8. The rectangular form is proposed as the simplest model for the reactor body. The reactor is equipped with a system to recover granular titanium settled in the slurry at the bottom of the molten salt. The slurry is conveyed by a rake towards an ingot making system. This slurry, rich in titanium powder, forms a cooled and solidified ingot whilst passing through a water-cooled crucible equipped with a pinch roll system for ingot withdrawal. The ingot is solid and sound, due to the effect of the  $\text{CaCl}_2$  binder.

### (6) Separation

The titanium grains were settled by sedimentation.  $\text{CaCl}_2$  was completely dissolved in water. Ca and CaO reacted with  $\text{H}_2\text{O}$  to form  $\text{Ca}(\text{OH})_2$  which exhibited a very low solubility in water. Ti ions in the  $\text{CaCl}_2$  phase reacted with water to precipitate insoluble titanate,  $\text{TiO} \cdot x\text{H}_2\text{O}$ ; which is soluble in a strong alkaline solution. Separation of these precipitates from the titanium sponge may be possible by means of the difference in sedimentation rate. If this separation is not sufficient, dilute hydrochloric acid could be used to dissolve these precipitates.

### (7) Electron-beam melting of titanium powders

The titanium powder is highly flammable. Once the powder catches fire, catastrophic combustion immediately ensues, hence, significant stockpiling of titanium powders must be avoided. It is proposed that stockpiling can be avoided by transferring the separated powders directly to the preparation area of an electron-beam (EB) melting furnace, for ingot making. From the investigations carried out for direct melting of powders in the 1 MW EB melting furnace, it was found

that trough (cold-hearth) melting enabled sound ingots to be manufactured. The oxygen concentration increased by an average 2 mass% after melting.

### 3. Prebaked Soluble Titanium Dioxide Anode

Perfectly stoichiometric  $\text{TiO}_2$  is an insulator at room temperature; however at elevated temperatures oxygen-ion deficient  $\text{TiO}_2$  becomes highly conducting, because oxygen ion vacancies introduce excess electrons, which create electronic conduction throughout  $\text{TiO}_2$  anode.  $\text{TiO}_2$  can also dissolve in the  $\text{CaCl}_2$ -CaO molten salt, so the majority of the  $\text{TiO}_2$  present in the molten salt can directly be reduced to metallic titanium. The remainder is deposited at the cathode by electrolysis.

Watanabe<sup>14)</sup> carried out molten salt electrolysis using a  $\text{CaCl}_2$ -CaO electrolyte and a  $\text{TiO}_2$  anode to produce titanium at temperatures between 1223 and 1373 K. He applied the cell voltage ranging from 1.6 to 2.5 V. These values were adopted for the reason of the decomposition voltage of  $\text{TiO}_2$ , so that the anode gas must be pure oxygen. Because these cell voltages are lower than the theoretical decomposition voltage of CaO, 2.7 V, the CaO in the molten salt could not be reduced to generate dissolved Ca, and the oxygen in titanium could not be eliminated to a sufficient degree. The current density is an indication of conductivity necessary to achieve a reasonable productivity of titanium. The anode current density was reported to be high enough as  $2.5 \times 10^4 \text{ A/m}^2$ . Chen *et al.*<sup>12)</sup> used the  $\text{TiO}_2$  cathode in the  $\text{CaCl}_2$ -CaO molten salt electrolysis at 1173 K and showed the current density value on the order of  $10^4 \text{ A/m}^2$ . The current density value, adjusted due to the anode structure and the current efficiency, is somewhat lower than that for the Hall-Héroult process, at  $1.0 \times 10^4 \text{ A/m}^2$ . There appears to be no significant difference in current density between these two different processes. The prebaked soluble  $\text{TiO}_2$  anode may serve as both an electrically conductive electrode and a source of  $\text{TiO}_2$  to be reduced for winning of titanium. To increase the productivity, the soluble  $\text{TiO}_2$  anode can be used together with feeding the  $\text{TiO}_2$  powders directly into the bath. Although this is a preliminary estimate, this may imply that the oxygen-ion deficient  $\text{TiO}_{2-x}$  anode could successfully be used in a practical reactor. Figure 9 represents a concept for the reactor using a soluble  $\text{TiO}_2$  anode and a granular titanium cathode. The  $\text{TiO}_2$  anode can be used in the form of rotating cylinders.

### 4. Conclusion

To achieve a breakthrough in the practical capabilities of this new titanium production process, we have investigated the OS process to produce titanium in molten salt. As a guide to the future we have pursued the simplest possible reactor body. It was our basic concept, and we believe that such a simple reactor construction may eventually offer a high production rate of titanium. The oxygen-ion deficient titanium dioxide anode will contribute to the mutual consistency between the anode and cathode with respect to the high productivity as well as the commercial level of oxygen.

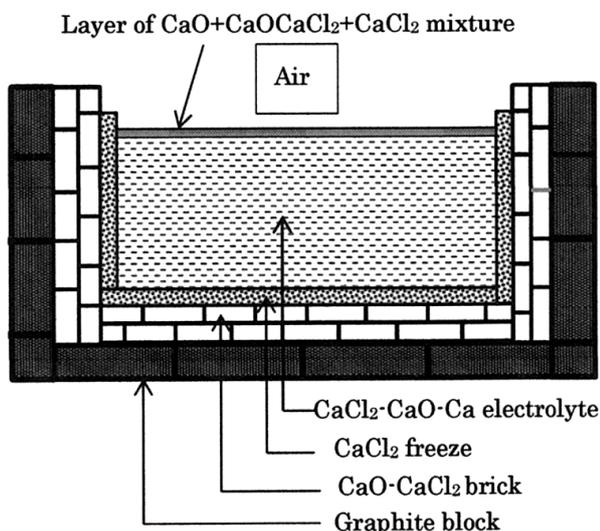


Fig. 8 Vertical-section of reactor body.

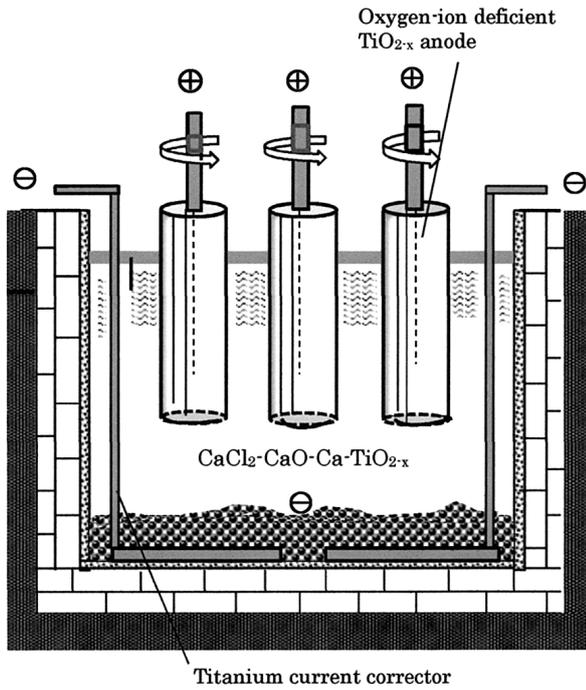


Fig. 9 Conceptual illustration of titanium production by molten salt electrolysis using oxygen-deficient  $TiO_2$  anode.

## Acknowledgement

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