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## Technical review

### Direct Reduction Processes for Titanium Oxide in Molten Salt

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#### SUMMARY

Molten salt electrolysis using  $\text{CaCl}_2$  is employed to produce pure Ti and its alloys directly from  $\text{TiO}_2$  and a mixture of elemental oxides, respectively, as the alternative of Kroll process. This is because CaO, which is a reduction by-product, is highly soluble in  $\text{CaCl}_2$ . Good-quality Ti containing only a small amount of residual oxygen has been successfully produced and scaled to industrial levels. Thermochemical and electrochemical bases are reviewed to optimize the process conditions. Several processes using molten salt are being examined for future progress in Ti processing.

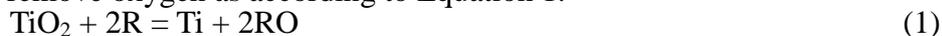
#### 1. Introduction

Titanium (Ti) is currently produced by the Kroll process that consists of the chlorination of  $\text{TiO}_2$ , magnesium reduction of  $\text{TiCl}_4$  and the independent electrolysis of the by-product,  $\text{MgCl}_2$ . Although the apparatuses and procedures have improved over the past 50 years, it is still difficult to recover the waste heat from these individual steps, and the total efficiency of Ti production is worse than that in continuous steel making. The demand for Ti metal is so strong that an increase in its production is necessary; however, the efficiency and resultant cost of the process are obstacles owing to the slow batch operation of the magnesium reduction process. Therefore, alternative processes have been developed to produce low-cost Ti.

Synthetic rutile, which is obtained by extruding iron from ilmenite, provided as the raw material instead of natural rutile, whose supplies are becoming exhausted. The goal of the new process is the conversion of the  $\text{TiO}_2$  particles into ductile Ti without contamination by oxygen and carbon, which have an extremely strong affinity to Ti. Physical and chemical contacts with oxygen and carbon must be completely avoided during refining processes, and the conversion to  $\text{TiCl}_4$  from  $\text{TiO}_2$  is performed during the Kroll process. The new alternative method should possess the same requisites as the Kroll process as well as continuous operation and good energy efficiency. New processes conforming to these requirements have been recently proposed.

#### 2. Direct reduction by calcium

A shortcut method to produce metallic Ti from its oxide involves seeking a qualified reductant R to remove oxygen as according to Equation 1.



Thermodynamically, oxygen should have a stronger affinity to R than to Ti, but reductants such as Al and C pollute the Ti produced. Only Ca and rare earth metals can reduce the residual oxygen to less than 1000 mass ppm. Direct reduction using Ca was proposed before the development of the Kroll process<sup>(1)</sup>, but its industrial application was difficult<sup>(2)</sup>. As illustrated in Fig.1(a)<sup>(3)</sup>, Ca forms a CaO film on the surface of the Ti particles, and this layer physically hinders the successive reduction and deoxidation by Ca. For example, the intergranular CaO surrounded by Ti particles cannot be leached even by an acid solution, and the oxygen produced from CaO migrates to the molten Ti during arc-melting; as a result, a brittle Ti ingot is produced. The lack of an efficient method to remove the CaO film was one of the reasons why the direct reduction method using Ca could not be considered as a realistic process<sup>(2)</sup>.

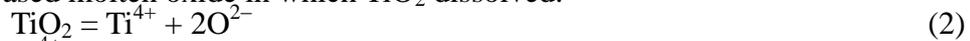
Generally, oxides do not dissolve into the chloride melt. Curiously, however, only  $\text{CaCl}_2$  can dissolve an amount as large as 20 mol% of CaO and a few mol% of Ca. As a

consequence, the CaO film will be eliminated as shown in Fig.1(b), and in practice, the dissolved Ca could reduce TiO<sub>2</sub> to result in an oxygen content of 1500 ppm even within an hour<sup>(3)</sup>. CaCl<sub>2</sub> is commonly available in natural resources and therefore it is cheap (for example, it is used for snow melting). The addition of only a small amount of CaCl<sub>2</sub> can enhance the reduction of TiO<sub>2</sub> when Ca vapor is used<sup>(4)</sup>. Ca liquid or vapor reduction with CaCl<sub>2</sub> will be practical if good quality Ca can be obtained at a reasonable cost.

### 3. Electroslag refining

William J. Kroll predicted that the molten salt electrolysis could replace the Kroll process in the future. Many methods have been proposed, but the electrodeposition of Ti ions could not be realized. This was because of the low current efficiency, low solubility of titanium chlorides, and difficulty in fluorine removal during molten fluoride electrolysis.

Takenaka et al.<sup>(5)</sup> and Quebec Iron and Titanium corporation<sup>(6)</sup> showed the applicability of electroslag refining (ESR) using an electron-conductive CaF<sub>2</sub>-CaO-based molten oxide in which TiO<sub>2</sub> dissolved.



As shown in Fig.2, ohmic heat can melt the product Ti as well as the oxide. TiC or Ti-Fe alloys were reported to be formed because of a crucible problem<sup>(5)</sup>. However, it is interesting to note that molten Ti is possibly extracted continuously, which is similar to the pig-iron making process. The reaction rate is very high because of the high temperature although it is difficult to control the heat balance and CO gas evolution.

### 4. Electrolysis using molten CaCl<sub>2</sub>

#### 4.1 OS process

K. Ono and R.O. Suzuki<sup>(7)</sup> proposed the electrolysis of CaO to produce Ca in molten CaCl<sub>2</sub> in order to use Ca for the reduction of TiO<sub>2</sub> in CaCl<sub>2</sub> and to supply the by-product CaO for further electrolysis. The theoretical decomposition voltage for CaO is approximately 2.6 V, as shown in Fig.3, and it can be decreased to 1.6 V if the carbon anode can be used to decompose CaO to CO and/or CO<sub>2</sub>. The voltage is expected to be as high as 1.8 V even if the thermochemical activity is as low as 0.01, considering the dissolution of CaO in the CaCl<sub>2</sub> melt. These values are sufficiently lower than 3.2 V for CaCl<sub>2</sub> = Ca + Cl<sub>2</sub>, and we may expect that CaO will be reduced to Ca by applying approximately 3.0 V, for example. It was expected that the light Ca liquid could flow upward along the cathode and be recovered to be supplied as a reductant for TiO<sub>2</sub><sup>(7)</sup>. However, pure Ca could not be obtained because of the solubility of Ca (a few mol%), and the deposited Ca dissolved again into the molten CaCl<sub>2</sub>. Previous attempts had also failed to produce pure Ca; this was despite a voltage greater than 3.2 V being applied at which the solvent CaCl<sub>2</sub> was dissociated. A solid carrot-shaped Ca bar can be obtained if the Ca deposited on the cathode is cooled above the electrolyte, similar to the unidirectional solidification of Si ingots.

For the reduction of TiO<sub>2</sub> by Ca, pure Ca is required but not essential. Even the Ca dissolved in molten CaCl<sub>2</sub> (hereafter referred to as Ca) can react with TiO<sub>2</sub> to form metallic Ti<sup>(3)</sup>. In other words, Ca formed in the vicinity of the cathode can be used for the reduction of the molten salt with a strong reducing agent. We may directly introduce TiO<sub>2</sub> into the Ca near the cathode<sup>(7,8)</sup> instead of extracting Ca from the electrolysis bath and feeding it into the reduction bath.

The electrochemical reaction for the CaO decomposition are as shown in Equations 5-7.





This reaction is endothermic, while the reaction with  $\underline{\text{Ca}}$  and  $\text{TiO}_2$  is exothermic. Therefore, the two baths may physically combine the two baths to use the related heat efficiently, as shown in Fig.4(a).

Due to the decomposition of  $\text{CaO}$ , the  $\text{Ca}$  deposited near the basket-like cathode dissolves as  $\underline{\text{Ca}}$  and reacts with the  $\text{TiO}_2$  powder at the cathode.



The by-product  $\text{CaO}$  dissolves in the molten  $\text{CaCl}_2$  as  $\underline{\text{CaO}}$ . This  $\underline{\text{CaO}}$  may be written as  $\text{O}^{2-}$  because of its ionic nature, and it escapes as a gas after reacting with the anodic carbon (Eqs.(5) and (6)).

In the lab-scale test, 1.0 g  $\text{TiO}_2$  powder was successfully reduced and deoxidized to produce 2000 ppm of oxygen for 3 h at 1173 K <sup>(8)</sup>. This method—the so-called OS process—can be applied to the entire oxide reduction process, except for rare-earth oxides (such as  $\text{Y}_2\text{O}_3$ ) that are thermodynamically more stable than  $\text{CaO}$ . In case the reduced metal reacts with  $\underline{\text{Ca}}$  to form an intermetallic compound (e.g., Al forms  $\text{CaAl}_2$ ), it is necessary to remove  $\underline{\text{Ca}}$  after reduction from the products.

A considerable level of basic knowledge has now been accumulated on industrial instruments and processes. such as the carbon anode, the control of convection due to gas evolution, and the temperature distribution. The freeze of  $\text{CaCl}_2$  is the best crucible to hold the molten  $\text{CaCl}_2$  when the reactor can be internally heated <sup>(9)</sup>. If a nonconsumable and oxygen-absorbing anode can be realized instead of the carbon anode, the production of  $\text{Ti}$  without carbon contamination could be realized.

One of the demerits of the OS process is the existence of free carbon that may react with the metal formed <sup>(8,10)</sup> because the gases at the anode react with  $\underline{\text{Ca}}$  if they cannot be rapidly removed. For example, this carbon contamination causes no problems in the case of  $\text{MgO}$  reduction; however, we require some safeguards during  $\text{Ti}$  production because of the low allowance limit against carbon. Ono reviewed the fundamental principles of the OS process as well as its countermeasures <sup>(9)</sup>.

#### 4.2 FFC process

D.J. Fray and his co-workers <sup>(11)</sup> demonstrated a simple mechanism (Fray-Farthing-Chen [FFC] process) as shown in Fig.4(b).  $\text{TiO}_2$  decomposed to  $\text{Ti}$  and  $\text{O}^{2-}$  when a  $\text{TiO}_2$  pellet in the conductive  $\text{CaCl}_2$  melt containing oxygen ion was used as the cathode.  $\text{O}^{2-}$  was extracted from the molten salt and released as  $\text{O}_2$  gas at the carbon anode. This extraction also utilizes the feature that the  $\text{CaCl}_2$  melt can dissolve a large amount of  $\text{CaO}$ , particularly  $\text{O}^{2-}$ . They were able to recover the bulky product  $\text{Ti}$  after the electrolysis, and a good current efficiency was noted. However, the reaction rate was slow because the current was low when the voltage was below 1.8 V. When the thermochemical activity of  $\text{O}^{2-}$  is higher, (i.e., the activity of  $\underline{\text{Ca}}$  is lower at a lower electrochemical potential), commercially pure titanium with low oxygen content cannot be produced <sup>(12)</sup>.

Some questions with regard to the oxygen-ion transfer still exist. It is noted that  $\text{CaTiO}_3$  is often precipitated as an intermediate compound during the electrolysis <sup>(13)</sup>. For the formation of  $\text{CaTiO}_3$ , physical contact between  $\text{CaO}$  and  $\text{TiO}_2$  is required. Even when  $\text{TiO}_2$  was electrically insulated from the cathode,  $\text{TiO}_2$  was reduced to  $\text{TiO}_x$  <sup>(10)</sup>. When the cathode was rotated, the release of  $\text{O}^{2-}$  appears to have been accelerated; however, the residual oxygen content increased <sup>(10)</sup> as shown in Fig.5. This phenomenon was caused by the disappearance of the  $\underline{\text{Ca}}$ -enriched region. The strong contribution of  $\text{O}^{2-}$  cannot be denied, but the existence of  $\underline{\text{Ca}}$  is required to explain these observations, particularly for those involving a voltage greater than 2.5 V.

T. Nohira et al. <sup>(14)</sup> reported that  $\text{CaSi}/\text{CaSi}_2$  and pure  $\text{Si}$  were obtained above 2.8 V and below 2.45 V, respectively, when the  $\text{SiO}_2$  plate was reduced. This indicates the contribution of  $\underline{\text{Ca}}$  in the formation of  $\text{Ca}$ -based alloys, but a less active  $\underline{\text{Ca}}$  does not form these alloys although it can reduce  $\text{SiO}_2$ . The detailed mechanism was not clarified

because Ti forms neither an alloy nor a compound with Ca.

The mechanism to rapidly remove  $O^{2-}$  or CaO from  $TiO_2$  is illustrated in Figure 6.

The region enriched with  $O^{2-}$  or CaO in the vicinity of the cathode should be shifted to the  $CaCl_2$  bulk. When the concentration of CaO in the  $CaCl_2$  melt is locally higher, the solubility of Ca is lower and the effective amount of Ca for reduction is lower near the cathode. Otherwise, an intermediate compound such as  $CaTiO_3$  is formed.

The reduction begins at the surface of  $TiO_2$  and the Ti layer covers the entire surface of the oxide particles. Electrons can be efficiently supplied through this metallic Ti layer to the individual particles to form  $O^{2-}$  or Ca, while oxygen is transferred to this surface by diffusion in the Ti layer. In the case of a dense  $TiO_2$  pellet, complete reduction takes some time even when the temperature is above the melting point of  $CaCl_2$ .

A Ca-enriched zone should attach on the  $TiO_2$  surface, particularly in the case of the OS process. A high current density causes a significant gas evolution and a subsequent convection, and the convection of the melt disturbs the high-Ca region near the cathode, as shown in Fig.5.

The FFC process is fairly simple with regard to its operation. However, it requires additional energy and labor for sintering the  $TiO_2$  pellets, external heat for maintaining the reaction temperature, and longer time for leaching because of the increased sintering for the long reaction time.

#### 4.3 Industrial applicability

Both the OS and FFC processes have the potential to produce an alloy directly from the oxide mixture. In practice, many Ti alloys and compounds were successfully produced in addition to pure Nb, Cr, Ta, and V<sup>(15)</sup>. Currently, TIMET collaborates with a US national project to expand the scope of the FFC process for industrial applications. The Japan Titanium Society is surveying another process using  $CaCl_2$ . Recently, BHP Billiton in Australia announced its success in a pilot plant-level operation for the direct reduction of  $TiO_2$  in  $CaCl_2$ .

Direct reduction from  $TiO_2$  cannot separate Fe in molten  $CaCl_2$  because Fe deposited preferentially on the cathode. It should be completely removed in industrial applications. Therefore, pretreatment for the removal of Fe from synthetic rutile is critical for obtaining low-cost titanium. In an interesting approach, titanium monoxide was used as the anode to deposit metallic Ti on the cathode in a molten salt without oxygen<sup>(16)</sup>; in this approach, Fe may preferentially dissolve from the anode. A new series of high-strength Ti-Fe-C-O alloys may be developed from the low-quality Ti obtained from direct reduction processes.

Direct oxide reduction from  $TiO_2$  is useful for the removal of the oxide film on the surface of Ti scraps<sup>(11)</sup>. Commercially available Ti scrap could not be returned to the virgin material because of the oxidized surface or higher oxygen content in the Ti-O solid solution. However, if these scraps are immersed into molten  $CaCl_2$  with the current lead, it is possible to reuse them. T.H. Okabe et al.<sup>(12)</sup> earlier reported that the solute oxygen in Ti could be electrochemically removed to a level of less than 100 ppm, and the oxide layer on the Ti will also be removed in the molten  $CaCl_2$ .

#### 5. Conclusion

When refining titanium from  $TiO_2$  using oxide electrolysis processes, the melting process can be skipped because molten Ti can be obtained continuously.  $CaCl_2$  is a powerful medium at lower temperatures and is a boon for low-cost titanium production, although the details should be completely elucidated before its industrial application.

This paper reviewed the current research that is mainly on molten salt technology; however, some useful ideas such as those relating to hydrogen or sodium reduction of  $TiCl_4$  appear to be close to practical industrial applicability. These new proposals will not be able to replace the established Kroll process immediately, and for this purpose, long-term studies are required.

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## Figure captions

Fig.1 A schematic illustration for calcium reduction <sup>(3)</sup>.

Fig.2 Electrolysis using electroslag refining by (a) Takenaka et al. <sup>(5)</sup> and (b) Quebec Iron and Titanium Corporation <sup>(6)</sup>.

Fig.3 The electrochemical potential for CaO electrolysis in molten CaCl<sub>2</sub>.

Fig.4 Electrolysis in CaCl<sub>2</sub>: (a) FFC process and (b) OS process.

Fig.5 Reduction in molten CaCl<sub>2</sub> at 1173 K for 7.2 ks. Voltage of 3.0–3.4 V was applied between the electrodes.

Fig.6 Reduction mechanisms near the cathode in molten CaCl<sub>2</sub>.

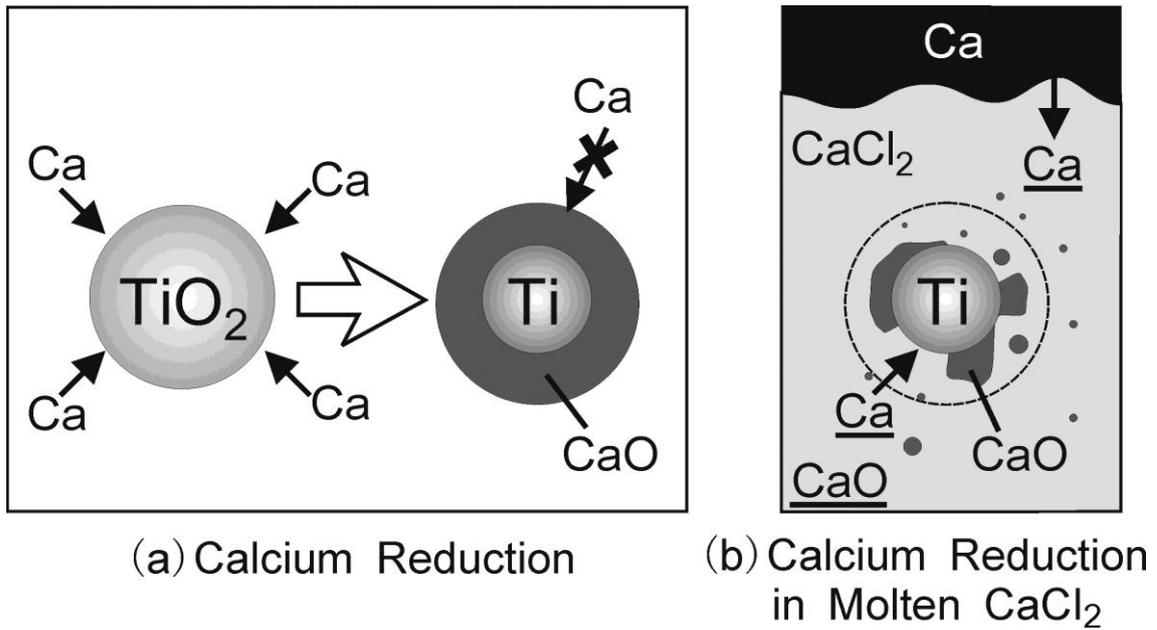


Fig.1 Schematic reduction for calcium reduction <sup>(3)</sup>

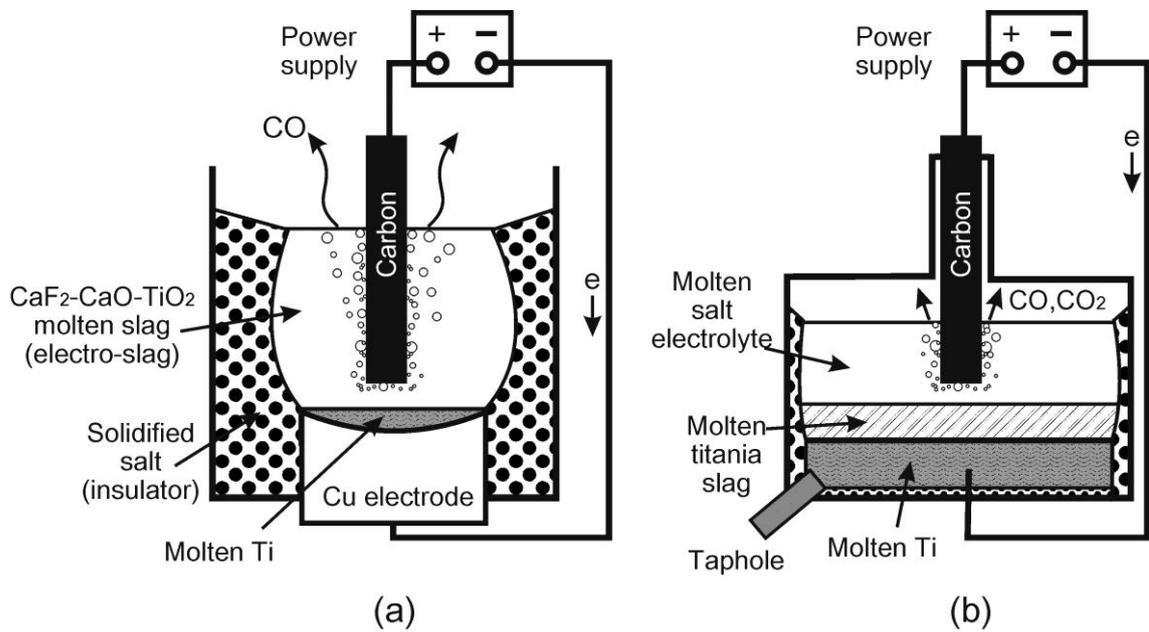


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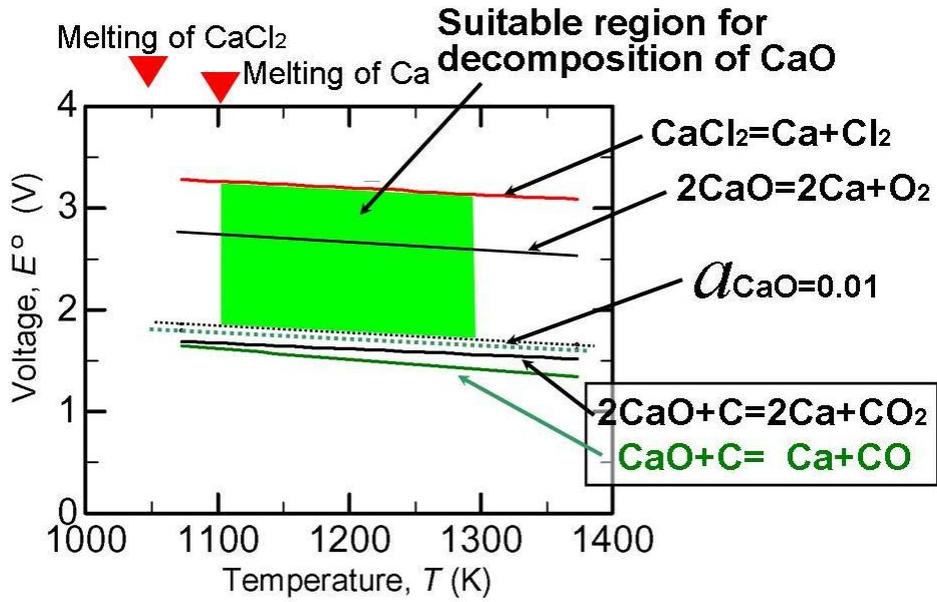


Fig.3 Electrochemical potential for  $\text{CaO}$  electrolysis in molten  $\text{CaCl}_2$ .

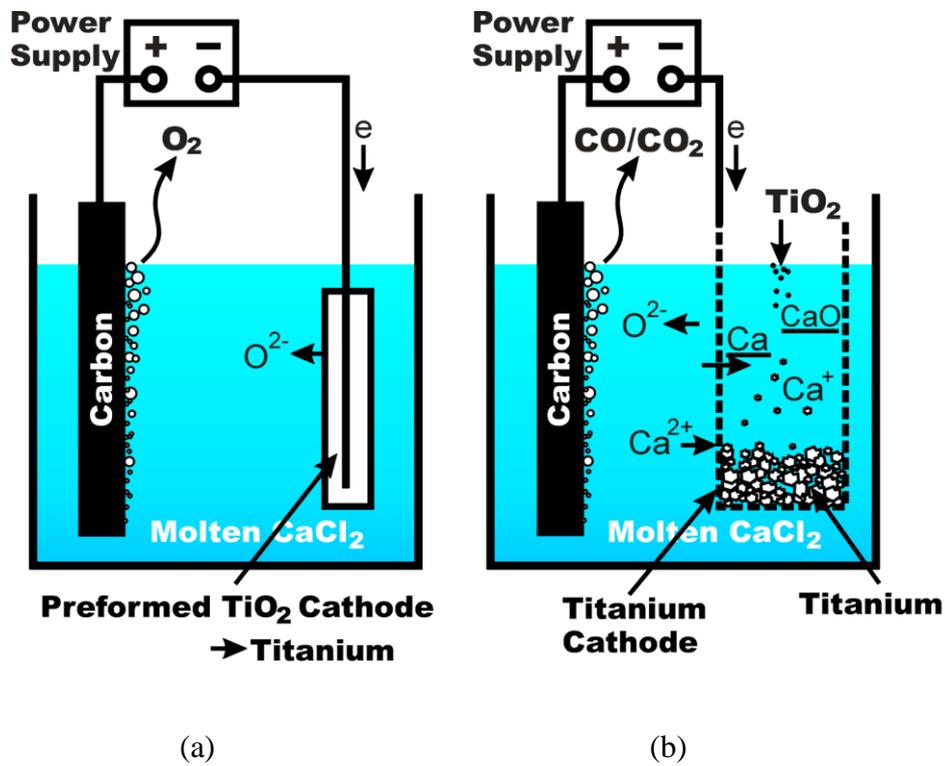


Fig.4 Electrolysis in  $\text{CaCl}_2$ : (a) FFC process and (b) OS process.

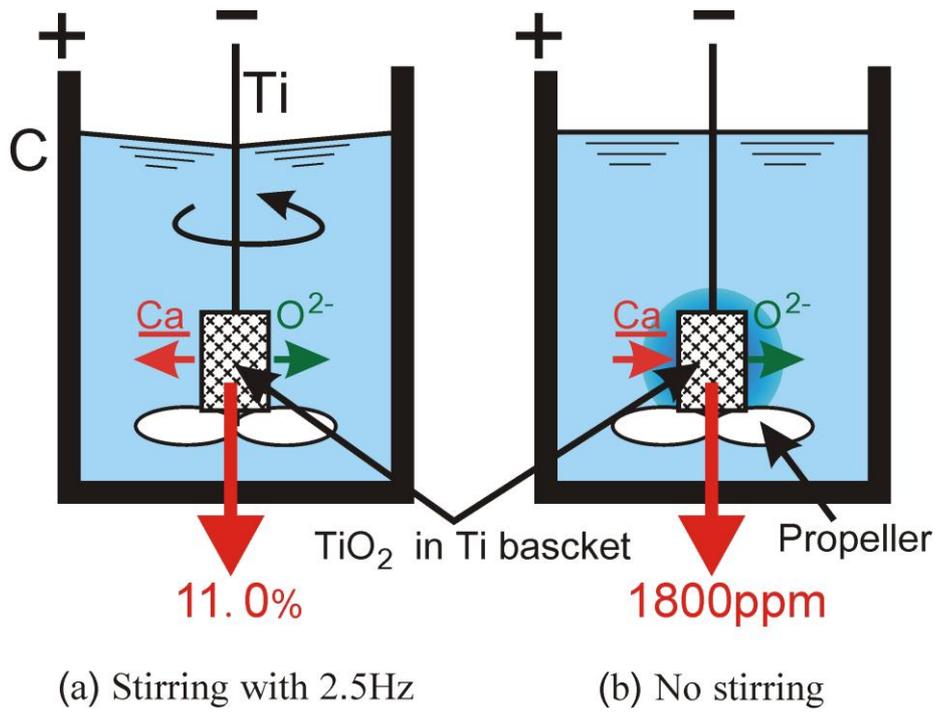


Fig.5 Reduction in molten  $\text{CaCl}_2$  at 1173 K for 7.2 ks. Voltage of 3.0–3.4 V was applied between the electrodes.

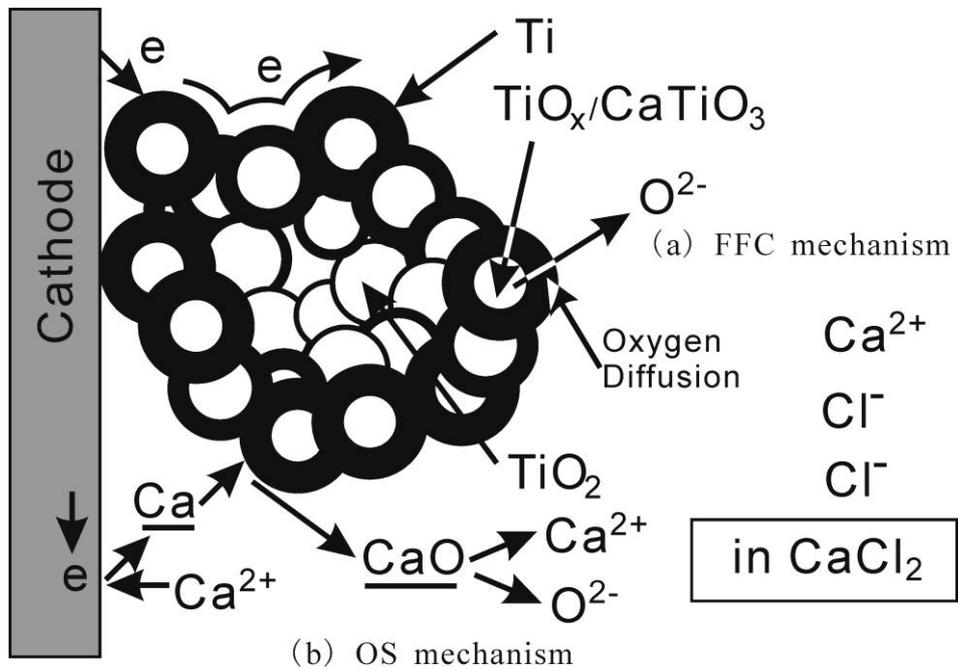


Fig.6 Reduction mechanisms near the cathode in molten  $\text{CaCl}_2$ .