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# Reduction of TiO<sub>2</sub> in Molten CaCl<sub>2</sub> by Ca Deposited during CaO Electrolysis

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Fundamental experiments are conducted to confirm the calcium reactivity with titanium oxide in the molten calcium chloride. The TiO<sub>2</sub> samples placed in the molten salt could be reduced without any electron supply to TiO<sub>2</sub>. In the close vicinity of cathode, TiO<sub>2</sub> could be successfully reduced to α-Ti with 1600 mass ppm oxygen. However, the strong stirring of the melt disturbed the calcium distribution near the cathode and the reduction was incomplete. These findings supported the proposed mechanism that Ca deposited on the cathode and it dissolved immediately into the molten salt. The parasite reactions consumed the dissolved Ca quickly, and they suppressed the effective reduction and subsequent deoxidation.

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**Keywords:** calcium reduction, electrolysis of molten salt, titanium oxide, titanium production

## 1. Introduction

A new refining process of titanium called as “OS process” was proposed as illustrated in Fig. 1 by Ono and Suzuki.<sup>1-9)</sup> Its process has several possible setups but it is generally characterized by the following three points: (1) calcium is selected as the reductant to reduce TiO<sub>2</sub> directly to metallic titanium, (2) the byproduct CaO is electrolyzed into Ca in the molten salt of CaCl<sub>2</sub>, and (3) all the reactions can be operated in the single molten salt. OS process does not use the chemical conversion of TiO<sub>2</sub> into TiCl<sub>4</sub> and the batch type reduction of TiCl<sub>4</sub> by molten Mg, which are the characteristics of the conventional Kroll process. OS process holds the future potential of the simple and continuous operation that TiO<sub>2</sub>, carbon and electricity are served and that titanium is recovered.

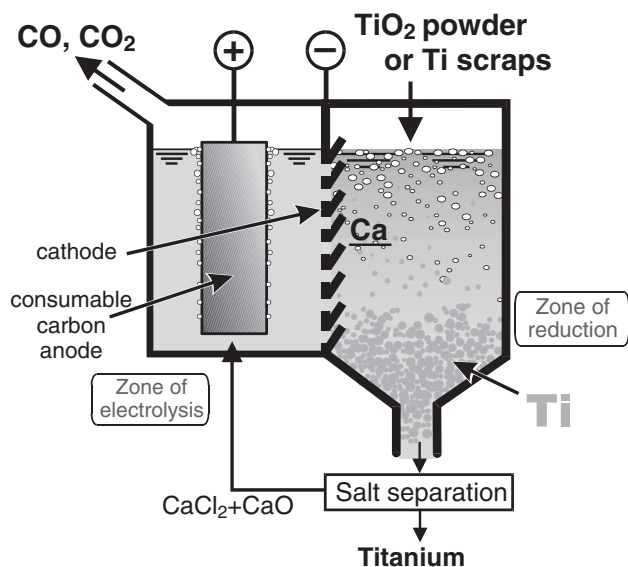


Fig. 1 Schematic illustration of the OS process.

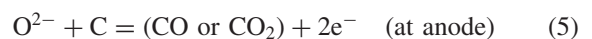
In order to enhance the reduction efficiency of OS process, this work studied fundamentally the concentration profile of Ca that deposits during the electrolysis in the molten CaCl<sub>2</sub>. This is one of the experimental confirmations to support the concept of OS process.

A brief outline of OS process will be described below, because the details were reported separately.<sup>1-9)</sup> When TiO<sub>2</sub> is selected as the raw material for reduction, the single reduction to the metallic state is favorable, and simultaneously the metallic Ti should be deoxidized to the level of 0.2 mass% oxygen, which is required for ductile metal. Only Ca can be chosen from the requisites of thermodynamics and mutual solubility. The reduction and subsequent deoxidation are written as,



respectively. Ca, CaO and O(inTi) are metallic Ca and CaO dissolved in the molten CaCl<sub>2</sub>, and oxygen in solid Ti, respectively. The byproduct CaO covers the surface of Ti and suppresses the complete reduction and deoxidation. Because the melt of CaCl<sub>2</sub> can dissolve about 20 mol% CaO above 1100 K,<sup>10,11)</sup> it can remove solid CaO from the product Ti. The thermochemical activity of CaO is lowered by dissolution, and promotes these reactions.<sup>12-14)</sup> When pure Ca coexisted with CaCl<sub>2</sub>, TiO<sub>2</sub> was successfully reduced to α-Ti with <1000 mass ppm oxygen only for 3.6 ks at 1173 K.<sup>1)</sup>

OS process uses the molten salt electrolysis to recycle CaO into Ca. Because of small solubility of Ca in CaCl<sub>2</sub> (about 4 mol%Ca at 1173 K<sup>15-18)</sup>, Ca formed near the cathode holds the high reducing ability. When TiO<sub>2</sub> is inserted in this region, it is reduced and recovered as metallic Ti. The electrolysis of CaO is written as,



Suzuki *et al.* reported that the Ti powder with 0.20 mass%O was successfully produced at 2.6-2.9 V for 10.8 ks using 0.5 mol%CaO-CaCl<sub>2</sub>.<sup>2)</sup> On the other hands, the current efficiency of OS process was still low and only a small amount of Ti was formed. The reasons of these problems

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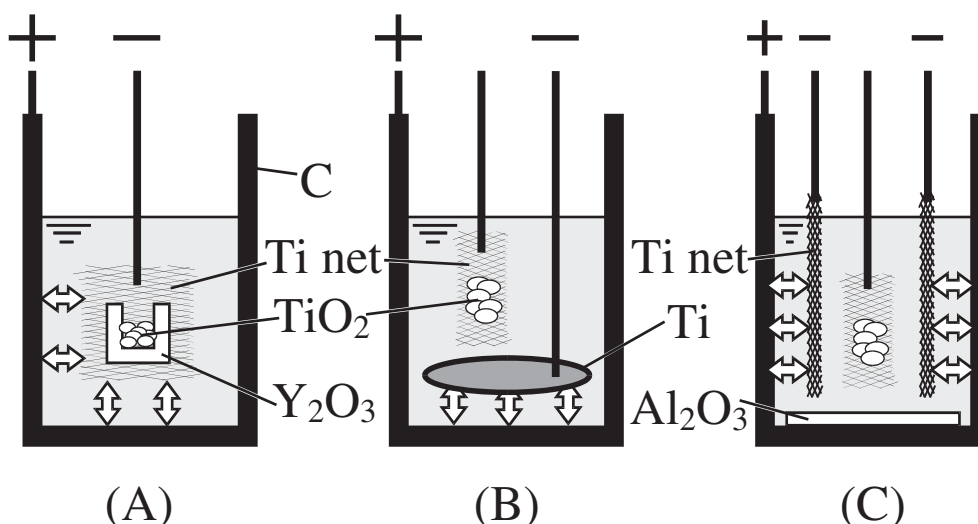


Fig. 2 Schematic illustration of the experimental setup for Exp. A, B and C.

were probably due to the parasite reactions with CO or CO<sub>2</sub> gas, and also due to the inhomogeneous distribution of Ca deposit. The localization of  $\underline{\text{Ca}}$  probably near the cathode is not suitable when TiO<sub>2</sub> powder was injected in a large-scale plant, because a part of TiO<sub>2</sub> powder may expand apart from the cathode and it does not react with  $\underline{\text{Ca}}$  effectively. The details of  $\underline{\text{Ca}}$  distribution near the cathode were not yet studied, although they are required for the further industrial application.

The purpose of this work is to prove the contribution of electrochemically deposited  $\underline{\text{Ca}}$  to the reduction of TiO<sub>2</sub>, and to know the profile of  $\underline{\text{Ca}}$  distribution in the molten salt bath during electrolysis. Here four kinds of experiment are conducted, as reported separately in the following sections.

## 2. Reduction of TiO<sub>2</sub> by Electrolyzed $\underline{\text{Ca}}$

One of the principles in OS process is that  $\underline{\text{Ca}}$ , which is formed on the cathode surface and dissolves into the bulk, reduces TiO<sub>2</sub>. This means that the electrolysis is needed to generate  $\underline{\text{Ca}}$  from  $\underline{\text{CaO}}$  or CaCl<sub>2</sub> in the molten salt, but that the electrolysis does not relate directly with TiO<sub>2</sub> reduction. TiO<sub>2</sub> does not need to attach to the cathode. However, Fray *et al.* proposed another principle that oxygen ions evolved from TiO<sub>2</sub> cathode migrate toward the anode in the molten CaCl<sub>2</sub>.<sup>19–21)</sup> In their FFC process, TiO<sub>2</sub> on the cathode loses oxygen and turns to metallic Ti. Therefore, the negative electrochemical potential should be supplied to TiO<sub>2</sub>, *i.e.*, TiO<sub>2</sub> should contact with the cathode electrically and accept the electron from the cathode. Okabe *et al.*<sup>22–24)</sup> and Nohira *et al.*<sup>25)</sup> pointed the importance of electron transfer from the cathode to TiO<sub>2</sub>.

In this section, therefore, TiO<sub>2</sub> was placed in the electrically neutral position, or at the position apart from the cathode, to check the workability of  $\underline{\text{Ca}}$ . TiO<sub>2</sub> does not receive any electron from the cathode of the setups in this section. Electric insulator Y<sub>2</sub>O<sub>3</sub> was partially used as the crucible for TiO<sub>2</sub>, because it is thermodynamically more stable than TiO<sub>2</sub> and it is not reduced by Ca when existing with pure CaO.<sup>3,26)</sup>

## 2.1 Experimental

All the experiments in this study were commonly done at 1173 K in the Ar gas atmosphere. The graphite crucible (I.D. 140 mm, O.D. 160 mm, 320 mm in depth) was commonly used as anode, except for Exp. F and G. The dimension of the molten salt was scaled up larger than the previous studies.<sup>2,6–8)</sup>

Figure 2 illustrates the experimental layout of electrodes. Table 1 lists the experimental conditions. The cathode of Exp. A was Ti net (100 mesh) wrapping the Y<sub>2</sub>O<sub>3</sub> crucible (I.D. 20 mm, 20 mm in depth) in which the rutile-type TiO<sub>2</sub> was filled. 0.5 mol% CaO-CaCl<sub>2</sub> was taken as the bath by referring to the previous report.<sup>2)</sup> After the pre-electrolysis using Ti cathode bar at 1173 K to remove water and the other impurities, the Y<sub>2</sub>O<sub>3</sub> crucible with TiO<sub>2</sub> was immersed into the molten salt and held at 35 mm high above the bottom of carbon crucible. The constant voltage (3.2 V) from the power supply dropped to 2.2 V when measured at the electrode terminals. This voltage between the electrode terminals decreased during the electrolysis, and correspondingly the current decreased. Note that 3.2 V and 1.6 V are the theoretical decomposition voltages of CaCl<sub>2</sub> and CaO at 1173 K, respectively. The applied voltage in Exp. A was enough to decompose  $\underline{\text{CaO}}$ , but insufficient for the decomposition of CaCl<sub>2</sub>.

The cathode of Exp. B was Ti plate (80 mm in diameter, 1 mm thick), located at 30 mm above the bottom. TiO<sub>2</sub> was also wrapped by Ti net, and located at 30 mm above the cathode, separately from both electrodes.

The cathode of Exp. C was cylindrical Ti net (60 mm in diameter, 80 mm high). Al<sub>2</sub>O<sub>3</sub> plate for electrical isolator was set on the bottom surface of carbon crucible, expecting that the electrolysis would be done mainly between the cylindrical cathode and cylindrical wall of carbon crucible. TiO<sub>2</sub> was wrapped by Ti net and placed in the center of cathodic cylinder.

Commonly after the experiments in this study, all the samples were picked up from the molten salt, and cooled in Ar atmosphere or in vacuum. The solidified salt was removed by flowing water, dilute HCl aqueous solution, distilled water

Table 1 Experimental conditions and results for Exp.A–C.

Exp. No.	Run No.	Molten salt	Amount of TiO <sub>2</sub> (rutile) (g)	Voltage between electrode terminals (V)	Current (A)	Time (ks)	Phases identified by XRD
A	#A	0.5 mol%CaO, 2.6 kg	1.8	1.6~2.2	2.5~5.8	43.2	Ti <sub>2</sub> O, CaTiO <sub>3</sub>
B	#B	0.5 mol%CaO, 3.6 kg	3.0	2.4~2.8	3.7~10.9	17.4	Ti <sub>2</sub> O <sub>3</sub>
	#C-1	0.5 mol%CaO, 3.6 kg	1.5	3.1~3.2	9.2~11.1	5.4	Ti <sub>2</sub> O
C	#C-2	Pure CaCl <sub>2</sub> , 3.6 kg	1.5	4.0~4.3	13.3~15	5.4	Ti <sub>2</sub> O <sub>3</sub> , TiO CaTiO <sub>3</sub>
	#C-3	Pure CaCl <sub>2</sub> , 3.6 kg	1.5	5.1~5.2	20.1~24.5	43.2	Ti <sub>2</sub> O <sub>3</sub> , TiO CaTiO <sub>3</sub>

and alcohol, and dried in vacuum. The oxygen content in the samples was analyzed using LECO-TC336, and the existing phases were identified by X-ray diffraction (XRD) measurements.

## 2.2 Results

Table 1 shows the phase identification in the obtained samples. Neither TiO<sub>2</sub> nor  $\alpha$ -Ti could be detected, and only the lower oxides such as Ti<sub>2</sub>O<sub>3</sub>, TiO or Ti<sub>2</sub>O were found. CaTiO<sub>3</sub>, a compound by the reaction between TiO<sub>2</sub> and CaO, was detected even when CaO was not added in the molten salt. Generally the byproduct CaO cannot be identified by XRD measurements because CaO is removed during handling in aqueous solutions. Therefore, the existence of CaTiO<sub>3</sub> is an index of existence of byproduct CaO, and it can not be explained by FFC mechanism.

When the solidified salt was dissolved in water, the fine bubbles were generated. It is because the dissolved  $\underline{\text{Ca}}$  in the salt reacted with water and formed hydrogen gas.

We may conclude that TiO<sub>2</sub> decomposed and reduced into the lower oxides by dissolved  $\underline{\text{Ca}}$ , and that CaO was formed during the electrolysis, although the reduction was not completed. Because the electric charge did not moved from TiO<sub>2</sub> in these experiments, the reason of TiO<sub>2</sub> reduction is explained only by  $\underline{\text{Ca}}$  formation during the electrolysis. The position of concentrated  $\underline{\text{Ca}}$  will be discussed in the later sections.

## 2.3 Embrittlement of Ti material and parasitic reactions

Suzuki *et al.*<sup>2)</sup> reported that the reaction between the gases evolved at the anode and calcium precipitated at the cathode formed carbon as,



The black powdery layer about 5 mm thick was found on the top surface of the solidified white salt after the experiments #A, #B and #C-1. The black powder consisted of carbon and CaCl<sub>2</sub>. The net, plate and bars made of Ti were embrittled probably due to carbon absorption, because Ti reacts easily with carbon at high temperatures and forms TiC or Ti-C solid solution. These carbon contaminations are not

suitable for industrial material and some improvements are required.

On the other hand, the samples #C-2 and #C-3 were not contaminated. Only a small amount of the black powder covered the top surface of solidified salt, and the Ti net wrapping TiO<sub>2</sub> was as ductile as before usage. In these experiments, Cl<sub>2</sub> gas evolution due to decomposition of CaCl<sub>2</sub> might occur more preferentially than that of CaO, as reported in the small-scale experiments.<sup>2)</sup> Even in this case, the parasite reaction of



can occur as reduction of Cl<sub>2</sub> gas and consume  $\underline{\text{Ca}}$ . In this paper, we refer three reactions (6)–(8) to the parasite reactions. They decrease the reduction efficiency because of  $\underline{\text{Ca}}$  consumption. To suppress these parasite reactions, for example, the shielding between two electrodes by the partition such as membrane is useful, as we will report separately. Another effort to exhaust quickly the evolved gases at the anode is also effective.

## 3. Consumption of $\underline{\text{Ca}}$ by Parasitic Reactions

Here the electrolysis and reduction were separated<sup>1–6)</sup> to check the reducing ability of  $\underline{\text{Ca}}$  containing molten salt. Assuming that the deposited and dissolved  $\underline{\text{Ca}}$  localize only near the cathode and does not spread out in the whole molten salt during the electrolysis, the major part of  $\underline{\text{Ca}}$  can react with TiO<sub>2</sub> even after the electrolysis. A part of  $\underline{\text{Ca}}$  may react with CO, CO<sub>2</sub> and/or Cl<sub>2</sub> gases. The degree of  $\underline{\text{Ca}}$  consumption by the parasite reactions during the electrolysis was studied using the degree of TiO<sub>2</sub> reduction as an index.

### 3.1 Experimental

Experimental setups and conditions are shown in Fig. 3 and Table 2. The voltage above the theoretical decomposition voltage of CaCl<sub>2</sub> (3.2 V) was here applied using pure CaCl<sub>2</sub>.

Exp.D used the carbon crucible and Ti round plate as the anode and the cathode, respectively, as in Fig. 3(a). Once the electrolysis was conducted without TiO<sub>2</sub>, and then cooled to room temperature. The solidified salt was again heated to 1173 K after removal of electrodes and addition of the setting for TiO<sub>2</sub>. TiO<sub>2</sub> wrapped by Ti net was immersed in the

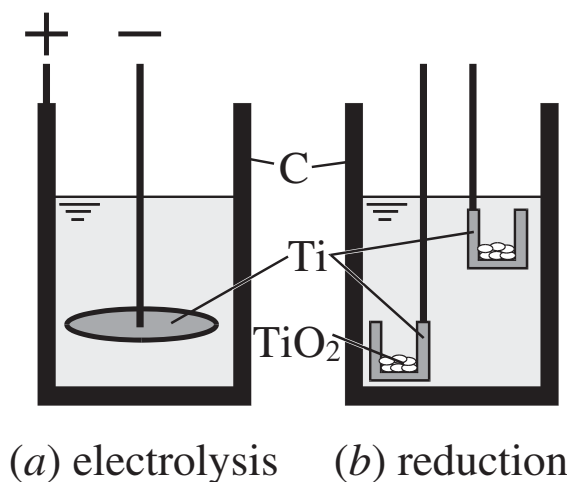


Fig. 3 Schematic illustrations of the experimental setup for Exp.E.

molten salt without electrolysis. The reaction time, 3.6 ks, was selected based on the previous study that the pure Ca liquid had enough reacted with  $\text{TiO}_2$  in  $\text{CaCl}_2$ .<sup>1)</sup>

In Exp.E,  $\text{TiO}_2$  was immediately immersed just after the electrolysis.  $\text{TiO}_2$  was filled in two Ti cups (I.D. 23 mm, 24 mm in depth). One was placed at 5 mm under the melt surface, and the other on the bottom of carbon crucible, as shown in Fig. 3(b). The molten salt was about 65 mm in depth.

### 3.2 Results and discussion

The Ca concentration was analyzed by the combined method of  $\text{H}_2$  gas evolution and wet chemical analysis. However, no reliable data was obtained from the solidified salt in Exp.D. The sampling from the molten salt during electrolysis was not successful because of high reactivity with the atmospheric oxygen during cooling.

The phases identified by XRD were listed in Table 2. The applied electric charge during the electrolysis corresponded to formation of about 15 g Ca for Exp.E1, where the charges were the smallest. This amount of Ca can reduce theoretically

about 15 g  $\text{TiO}_2$ . Although the supplied amount of  $\text{TiO}_2$  was only 1 or 2 g, all the samples were not completely reduced to  $\alpha$ -Ti. Even in Exp.E that  $\text{TiO}_2$  was injected immediately after electrolysis, the reduction was not completed. The formed Ca by electrolysis was consumed so rapidly by the parasite reactions.

The oxygen contents were similar in the samples in Exp.E. Note that the oxygen concentration of  $\text{TiO}_2$  is 40 mass%. This shows that the Ca concentration in the bath did not increase by the longer electrolysis time, comparing the result of Exp.E1 with that of Exp.E2, and it might be steadily constant. Namely, the production rate of Ca by electrolysis and its consumption rate by the parasite reactions are nearly equal at least after 3.6 ks.

The deposited pure Ca should flow upward because of density difference, and the Ca concentration at the top surface would be higher than that at the bottom region. The possible evaporation of Ca was not found. However, the oxygen contents in the samples were not different by the positions. This shows that the pure liquid Ca was not formed because of quick Ca dissolution into  $\text{CaCl}_2$ . The difficulty of liquid Ca deposition has often been reported.<sup>28)</sup>

These results showed that the parasite reactions occurred rapidly, and they affected the reduction rate of  $\text{TiO}_2$ . The efficiency of Ti production was heavily lowered in addition to the carbon contamination in the product Ti.

The efficiency may depend on the experimental setups. Exp.A, B and E used the layout that the carbon anode located below the cathode, where the evolved gas bubbles from the anode might react preferentially with Ca located above. The layouts of electrodes were modified in the experiments below to minimize the carbon contamination.

### 4. Positions with High Ca Concentration

The Ca concentration profile might be dependent on the distance from the formed position, *i.e.*, from the cathode, even during the electrolysis. The Ca concentration in the close vicinity of cathode should be higher because Ca is formed on the cathode and dissolves into the molten salt. The

Table 2 Experimental conditions and results, where the electrolysis and reduction were separated.  $\text{TiO}_2$  was immersed for 3.6 ks in the molten salt after the electrolysis.

Exp. No.	Sample No.	Electrolysis		Electric current (A)	Time (ks)	Reduction		Analysis	
		Used $\text{CaCl}_2$ (g)	Voltage between electrode terminals (V)			Position of $\text{TiO}_2$	amount of $\text{TiO}_2$ (g)	Phases identified by XRD	Oxygen concentration (mass%)
D	#D	800	5.8	15.5–18.3	32.4	—	2.0	$\text{Ti}_3\text{O}_5$ , $\text{Ti}_4\text{O}_7$ , $\text{CaTiO}_3$	—
E1	#E1-1	2000	4.4–4.9	20	3.6	5 mm below surface	1.0	$\text{Ti}_2\text{O}_3$ , $\text{CaTiO}_3$	27
	bottom					1.0	$\text{Ti}_2\text{O}_3$ , $\text{CaTiO}_3$	25	
E2	#E2-1	2000	5.0–5.1	20	7.2	5 mm below surface	1.0	$\text{Ti}_2\text{O}_3$ , $\text{TiO}$ , $\text{CaTiO}_3$	27
	#E2-2					bottom	1.0	$\text{CaTiO}_3$ , $\text{TiO}$	25

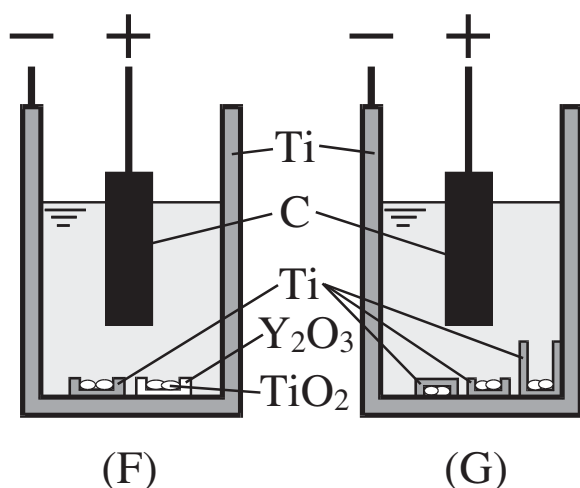


Fig. 4 Schematic illustration of the experimental setup for Exp.F and G.

reducing ability of the salt would be lowered as a function of distance from the cathode.

Here the degree of reduction of TiO<sub>2</sub> in the melt was considered as a good index to expect  $\underline{\text{Ca}}$  concentration. Some fundamental surveys were conducted to know the region where the higher concentration of  $\underline{\text{Ca}}$  exists.

#### 4.1 Experimental

Titanium crucible (I.D. 150 mm, 350 mm in depth) was used as cathode as shown in Fig. 4. graphite bar (50 mm in diameter, 150 mm long) was used as anode. Here 2.0 kg of pure CaCl<sub>2</sub> was used.

In Exp.F, TiO<sub>2</sub> was filled both in Ti dish (I.D. 30 mm, 15 mm in depth) and in Y<sub>2</sub>O<sub>3</sub> dish (I.D. 25 mm, 15 mm in depth). They were set on the bottom of Ti crucible.

In Exp.G, TiO<sub>2</sub> was filled full in the same Ti dish-#1, in Ti cap (I.D. 30 mm, 15 mm in depth), and in another Ti dish-#2 (I.D. 23 mm, 25 mm in depth). The latter Ti dish was placed at the corner of Ti crucible. The C anode was set at 20 mm above the edge of Ti dish-#1, apart 13 mm from the edge of Ti dish-#2.

#### 4.2 Results and discussion

The experimental conditions and results are listed in Table 3. The top surface of the solidified salt was white and no clear carbon layer was found after cooling. This means that the control of upward movement of gas bubbles is a key to prohibit from contamination.

$\alpha$ -Ti with 1600 mass ppmO was successfully obtained in

the sample #F-1. Ti dish-#1 held the same electric potential as the cathode, because it contacted with the cathode. The calcium deposited preferentially at the dish edge, crept along the Ti wall and reduced TiO<sub>2</sub> inside the dish-#2.

The Y<sub>2</sub>O<sub>3</sub> crucible was broken when it was recovered, and it was difficult to identify the obtained phases because some portions of Y<sub>2</sub>O<sub>3</sub> were mixed with the black sample. Because Y<sub>2</sub>O<sub>3</sub> is electrical insulator, the TiO<sub>2</sub> in the Y<sub>2</sub>O<sub>3</sub> crucible was reduced by  $\underline{\text{Ca}}$  which was formed by the electrolysis at the other portions. The path to TiO<sub>2</sub> in the Y<sub>2</sub>O<sub>3</sub> crucible was longer than those for Ti dishes.

These findings show that reactive calcium exists only in the close vicinity of cathode. In comparison with samples #G-1 and #G-3, the oxygen concentrations in Ti (#G-1) were low although the electrodes distance and the morphology of the TiO<sub>2</sub> holders were different. This means that Ca does not exist preferentially at a particular position, but it distributes homogeneously and widely just near the cathodic portions. Namely, the cathodic surface holds homogeneously and equally strong reducing ability.

#### 4.3 Electron transport through metal

The sample #G-2 was surrounded by Ti cap and Ti crucible, and not exposed directly to the molten salt. It was reduced to Ti<sub>3</sub>O, although there were no reaction trace between TiO<sub>2</sub> and the surrounding metallic Ti. The deposited Ca might invade into the inside through the small gaps because Ca gets wet with the metallic surface.

On the other hand, the reduction mechanism was explained also by the "electron mediated reaction"<sup>22-24,26</sup> that the electron was exchanged between TiO<sub>2</sub> and Ca *via* Ti metals such as,



It was explained that these half reactions do not need to occur at the same position, but that they can proceed at the separated places if they are connected with the electron conductive media such as metals.

This reaction resultantly needs the migration of oxygen ions to the anode, but it was difficult by the isolation due to Ti walls. The higher oxygen ion content in the shielded salt might make the reduction incomplete. Namely, the higher CaO concentration in the capped area hindered the decomposition of TiO<sub>2</sub>.

This finding reminds us of the situation that the product Ti formed in advance acts such as Ti cap and that it surrounds the unreacted TiO<sub>2</sub> powder. Although this work used the

Table 3 Experimental conditions and results for Exp.F and G.

Run No.	Voltage between electrode terminals (V)	Supplied current (A)	Time (ks)	Sample No.	Charged amount of TiO <sub>2</sub> (g)	Holder	Phases identified by XRD	Oxygen concentration (mass%)
#F	2.9-2.6	2.1-3.2	24	#F-1	1.0	Ti dish-#1	$\alpha$ -Ti	0.16
				#F-2	0.5	Y <sub>2</sub> O <sub>3</sub> cup	Y <sub>2</sub> O <sub>3</sub> , Ti <sub>2</sub> O <sub>3</sub> ?	—
				#G-1	1.0	Ti dish-#2	$\alpha$ -Ti	0.19
#G	2.9-2.7	2.2-3.3	24	#G-2	0.5	Ti cap	Ti <sub>3</sub> O	12.0
				#G-3	1.0	Ti dish-#1	$\alpha$ -Ti	0.27

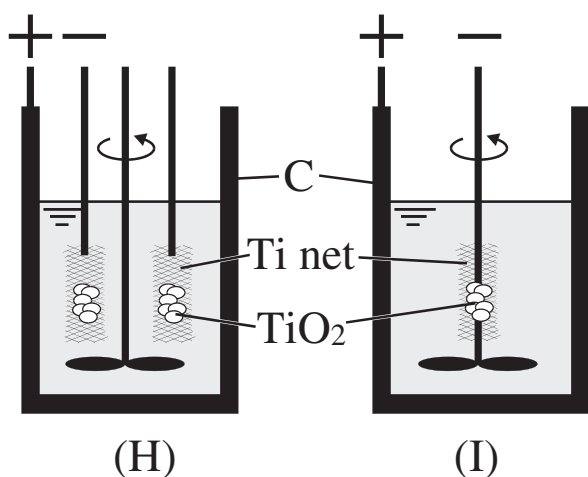


Fig. 5 Schematic illustration of the experimental setup for Exp.H and I.

TiO<sub>2</sub> powder under 200 mesh, the apparent grain size of TiO<sub>2</sub> seems important to avoid this “Ti cap” effect.

## 5. Electrolysis under Stirring

It has been considered that  $\underline{\text{Ca}}$  is localized at the close vicinity of cathode. The stirring may disperse  $\underline{\text{Ca}}$  to the area where TiO<sub>2</sub> is set isolating from the cathode. Here the stirring during the electrolysis was conducted. Note that the steady convection exists in the molten salt during electrolysis because of gas evolution.

### 5.1 Experimental

The experimental setup was shown in Fig. 5. The carbon crucible and 2.0 kg 0.1 mol%CaO-CaCl<sub>2</sub> was used as the anode and the bath, respectively.

Two sets of TiO<sub>2</sub> wrapped by Ti net were placed in Exp.H. One was used for cathode, and the another was electrically isolated. The propeller (40 mm in diameter) was rotated at 2.5 Hz during electrolysis, where the mild eddy was generated. As we will report separately, this stirring condition enhanced the reduction of TiO<sub>2</sub> when pure Ca was used as reductant. In Exp.I, TiO<sub>2</sub> wrapped by Ti net was fixed to the stirring Ti shaft and simultaneously used as the cathode.

### 5.2 Results and discussion

In Exp.H, the samples were not completely reduced to  $\alpha$ -Ti, as shown in Table 4. The result of sample #H-2 was identical with the samples #A, #B and #C, where they were

electrically isolated from the cathode. However, the result of sample #H-1 was different from the results mentioned above. Even the sample attached to the cathode, it was not reduced completely. The oxygen concentration of stirred sample #H-1 was 11.0%, while that of sample #I-2 without stirring was only 0.18%. Therefore, the stirring significantly weakened the reducing ability because  $\underline{\text{Ca}}$  on the cathode surface was dispersed and the  $\underline{\text{Ca}}$  concentration was lowered.

The black carbon layer was found on the top surface of solidified salt in Exp.#H-1, while it was rarely observed when the salt was not stirred. This means that the strong stirring enhanced the parasite reactions, and more amount of Ca was consumed. The dispersed  $\underline{\text{Ca}}$  into the molten salt did not enhance the reduction of TiO<sub>2</sub>, but it was mainly consumed by the parasite reactions.

This phenomenon can be hardly explained by the mechanisms relating with electron transport. In their mechanisms, oxygen ions evolved from TiO<sub>2</sub> do not depend directly on the status of molten salt, but on the charges supplied from the cathode. Stirring would enhance the dispersion of oxygen ions from the cathodic area, and the decrease of oxygen ion concentration would promote TiO<sub>2</sub> decomposition. Therefore, the change of reducing ability by stirring shows that  $\underline{\text{Ca}}$  should exist stably in the salt and react with TiO<sub>2</sub>.

## 6. Conclusion

Summarizing the 4 kinds of experiments, the positions of TiO<sub>2</sub> samples are illustrated in Fig. 6. The experimental results proved that the deposited and dissolved  $\underline{\text{Ca}}$  could reduce TiO<sub>2</sub> in the molten CaCl<sub>2</sub>. Because  $\underline{\text{Ca}}$  with a strong reducing ability localized in the close vicinity of cathode, the TiO<sub>2</sub> samples were preferentially reduced to  $\alpha$ -Ti when they were placed on the cathode surface, such as samples #F-1, #G-1 and #G-3. When the TiO<sub>2</sub> samples were separated from the cathode (samples #A, #B, #C and #F-2), the reduction was delayed. This is because  $\underline{\text{Ca}}$  was not effectively supplied to the samples. For example, the stirring disturbed the  $\underline{\text{Ca}}$  supply to the TiO<sub>2</sub> samples.

Subsequent deoxidation after reduction is driven by the electrochemical deoxidation mechanism that  $\underline{\text{Ca}}$  absorbs the oxygen in  $\alpha$ -Ti.<sup>26,27)</sup> The by-product CaO should be removed by dissolution to the molten salt. When the sample was surrounded by the dense Ti walls (see #G-2), however, the deoxidation was suppressed.

It was found that a fairly large amount of  $\underline{\text{Ca}}$  was consumed by the parasite reactions. Its carbon formation was more significant when the carbon crucible was used. It is natural that the gases evolved from the bottom of anodic crucible go

Table 4 Experimental conditions and results, where the molten salt was stirred.

Exp. No.	Run No.	Amount of TiO <sub>2</sub> (g)	Voltage between electrode terminals (V)	Electric current (A)	Time (ks)	Rotation speed (Hz)	Electric potential	Phases identified by XRD	Oxygen concentration (mass%)
H	#H-1	1.0	2.1–2.4	5.0	14.4	2.5	cathodic	Ti <sub>3</sub> O	11.2
	#H-2	1.0					isolated	Ti <sub>2</sub> O, Ti <sub>2</sub> O <sub>3</sub>	13.7
I	#I-1	1.0	2.9–4.2	10	7.2	2.5	cathodic	Ti <sub>2</sub> O, TiC	11.0
	#I-2	1.0	3.4–4.6	10	7.2	0	cathodic	$\alpha$ -Ti	0.18

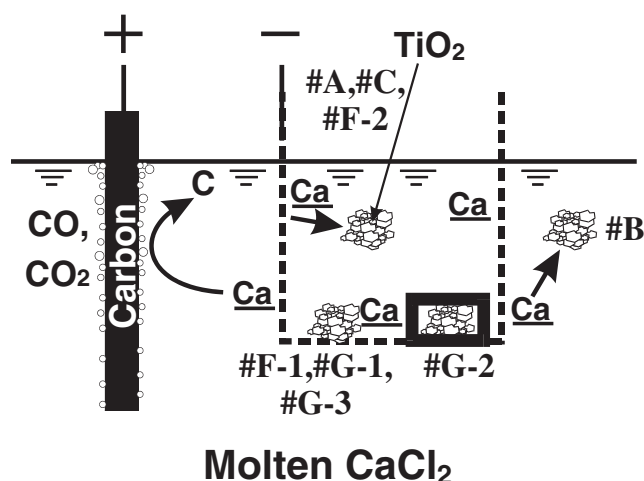


Fig. 6 Reactions between TiO<sub>2</sub> and the dissolved Ca, where 4 sample positions reflect the obtained results corresponding to Exp. Number.

upwards and that they react with Ca at the cathode that was placed upwards. Therefore, the geometric arrangement of electrodes and samples is a key to suppress the parasite reactions and to improve the efficiency of OS process.

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#### REFERENCES

- 1) R. O. Suzuki and S. Inoue: *Metall. Mater. Trans. B* **34B** (2003) 277–285.
- 2) R. O. Suzuki, K. Teranuma and K. Ono: *Metall. Mater. Trans. B* **34B** (2003) 287–295.
- 3) K. Ono and R. O. Suzuki: *Materia Japan* **41** (2002) 28–31.
- 4) K. Ono and R. O. Suzuki: *JOM Mem. J. Min. Met. Mater. Soc.* **54** [2] (2002) 59–61.
- 5) K. Ono and R. O. Suzuki: *Titanium Japan* **50** [2] (2002) 105–108.
- 6) R. O. Suzuki and K. Ono: *Proc. 13th Int. Symp. on Molten Salt*, (The Electrochem. Soc. Pennington, NJ, 2002) pp. 810–21.
- 7) R. O. Suzuki and K. Ono: *Metallurgical and Materials Processing: Principles and Technologies, Vol. III, Aqueous and Electrochemical Processing*, ed. by F. Kongoli, K. Itagaki, C. Yamauchi and H. Y. Sohn, (The Minerals, Metals & Materials Soc., OH, 2003) pp. 187–199.
- 8) R. O. Suzuki: *J. Phys. Chem. Solids*, (2004) accepted.
- 9) R. O. Suzuki: *Proc. 10th World Conference on Titanium*, (Deutsche Geselsch. Metalk. Germany, 2003) in press.
- 10) D. A. Wenz, I. Johnson and R. D. Wolson: *J. Chem. Eng. Data* **14** (1969) 250–252.
- 11) G. S. Pery and L. G. MacDonald: *J. Nucl. Mater.* **130** (1985) 234–241.
- 12) T. H. Okabe, R. O. Suzuki, T. Oishi and K. Ono: *Tetsu-to-Hagané* **77** (1991) 93–99.
- 13) T. H. Okabe, T. Oishi and K. Ono: *J. Alloys Comp.* **184** (1992) 43–56.
- 14) T. H. Okabe, M. Nakamura, T. Ueki, T. Oishi and K. Ono: *Bull. Jpn. Inst. Met.* **31** (1992) 315–317.
- 15) V. Dosaj, C. Aksaranan and D. R. Morris: *J. Chem. Soc. Faraday Trans.* **71** (1975) 1083–1098.
- 16) H. Fischbach: *steel research* **56** (1985) 365–368.
- 17) L.-I. Staffansson and D. Sichen: *Scand. J. Metall.* **21** (1992) 165–171.
- 18) K. M. Axler and G. L. DePoorter: *Mater. Sci. Forum* **73–75** (1991) 19–24.
- 19) G. Z. Chen, D. J. Fray and T. W. Farthing: *Nature* **407**, 21 Sept., 2000, pp. 361–364.
- 20) D. J. Fray: *J. Minerals, Metals & Materials Society (JOM)*, **53** [10] (2001) 26–31.
- 21) G. Z. Chen, D. J. Fray and T. W. Farthing: *Metall. Mater. Trans. B* **32B** (2001) 1041–1052.
- 22) T. H. Okabe and D. R. Sadoway: *J. Mater. Res.* **13** (1998) 3372–3377.
- 23) T. Uda, T. H. Okabe, E. Kasai and Y. Waseda: *J. Japan Inst. Metals* **61** (1997) 602–609.
- 24) T. H. Okabe, I. Park, K. T. Jacob and Y. Waseda: *J. Alloys Comp.* **288** (1999) 200–210.
- 25) T. Nohira, K. Yasuda and Y. Ito: *Nature Materials* **2** (2003) 397–401.
- 26) T. H. Okabe, T.N. Deura, T. Oishi, K. Ono and D. R. Sadoway: *J. Alloys Comp.* **237** (1996) 150–54.
- 27) T. H. Okabe, M. Nakamura, T. Oishi and K. Ono: *Metall. Trans. B* **24B** (1993) 449–56.
- 28) P. D. Ferro, B. Mishra, D. L. Olson and W. A. Averill: *Trans. Ind. Inst. Met.*, **51** (1998) 69–77.