A NEW CONCEPT OF SPONGE TITANIUM PRODUCTION
BY CALCIOTHERMIC REDUCTION OF TITANIUM OXIDE
IN THE MOLTEN CaCl₂

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ABSTRACT

A new cell concept for calciothermic reduction of titanium dioxide and an ongoing test program for its experimental verification are presented. The thermo-chemical background of this concept and new cell designs are described. The reduction system consists in a single cell, where both the thermochemical reaction and the electrochemical reaction for recovery of reducing agent coexist in the same molten CaCl₂ bath. A few mol%Ca dissolves in the melt, which constitutes the media with a strong reducing power. Separated experiments on calciothermic reduction showed that 3.6 ks were enough to reduce TiO₂ powder at 1173 K, where the oxygen content was lowered below 1000 mass ppm. The optimum concentration of CaO in the molten CaCl₂ was lower than 5 mol%. Combining carbon anode and titanium net cathode, titanium sponge containing 2000 ppm oxygen was produced from anatase-type TiO₂ powder.

INTRODUCTION

Kroll process produces metallic titanium commercially in industry. It consists of a two-step operation; the conversion from TiO₂ to TiCl₄, and the subsequent reduction of TiCl₄ to sponge Ti by Mg liquid (1). It takes 2-5 days in this reduction route via TiCl₄. A simpler and more compact process in a single step directly from TiO₂ is desired to get higher productivity and energy saving.

CONCEPT OF CALCIOTHERMIC REDUCTION

Figure 1 shows the oxygen potential of several oxides. Alkaline earth metals, such as Ca and Mg, and some rare earth elements can be selected as the candidates for direct reductant of TiO₂, both because they do not dissolve into Ti and because their oxides are thermodynamically more stable than the titanium mono-oxide, TiO (2). However, the rare earth elements are expensive and not suitable as economic reductants. Mg equilibrates thermodynamically with Ti containing about 2-3 mass% oxygen (3,4), and the acid leaching of MgO was too slow for practical mass production (5).

Residual oxygen in Ti has been measured at 300 - 730 mass ppm O when Ca and CaO coexisted in equilibrium at 1173 - 1373 K (3,4,6-10). This low oxygen level is
applicable for industrial standards. The solubility of Ca in β-Ti is also as low as 50 – 200 ppm Ca at 1155 – 1600 K (11). Alexander proposed the reduction of TiO₂ using Ca first in 1936 (12). The reaction starting from Ca and TiO₂ can be nominally written as,

$$\text{TiO}_2 + 2 \text{Ca} = \text{Ti} + 2 \text{CaO} \quad [1]$$

However, Kroll reported that the ductile titanium could not be produced in eq.[1] (5). At least a few thousand ppm O remain in Ti mainly as CaO (4,6-8). The by-product, CaO, attaches to the surface of Ti particles because the reaction proceeds at the surface of TiO₂, as shown in Figure 2(a) and (b). The slow mass transfer through the attached CaO hinders the further deoxidation (4,6-8). The formed Ti particles tend to sinter tightly, because the reaction [1] is exothermic (13). The CaO phase is easily captured in Ti grain boundaries during this sintering, and it is hardly removed by acid leaching (4,6-8).

Molten CaCl₂ can dissolve about 20 mol% CaO (14-16). In the halide flux deoxidation of Ti, the residual oxygen in Ti could be extracted as CaO into CaCl₂ (17-19). When we apply this dissolution mechanism to Ca reduction from titanium oxide, not from metallic bulk, it is expected that the by-product CaO can be removed in situ from the reaction place, and that this dissolution enhances the reduction and subsequent deoxidation more effectively, as illustrated in Figure 2(c). Note that the solidified CaCl₂ attaching to Ti powder is more easily soluble into water than CaO.
CONCEPT OF ELECTROLYSIS OF CaO IN CaCl$_2$

Considering the recycling of the by-product CaO to the reductant Ca, the process was proposed that the dissolved CaO decomposes into Ca and CO$_2$ gas by the molten salt electrolysis (20-25), and that this Ca returns to the reduction, as shown in Figure 3. However, many previous attempts of CaCl$_2$ electrolysis failed to deposit Ca as the pure liquid state with a good yield, because the precipitated Ca dissolved immediately in the salt to 3.9 mol% Ca-CaCl$_2$ (26-28).

**Figure 3.** Proposal of calciothermic reduction using CaC$_2$.

CaO dissolved in the bath is here converted to "Ca$^+$", (or liquid Ca dissolved in the salt, "Ca", plus electron) and CO$_2$ gas by our electrolysis at temperatures over the melting point of Ca. Between the consumable carbon anode and the cathode, a voltage of 3.0V is applied, which is higher than the decomposition voltage of CaO (1.66V), but below that of CaCl$_2$ (3.2V) (13). Under these conditions, both CO$_2$ and CO gas evolve from the carbon anode but no chlorine gas is formed. The electrolytic reaction is described by,
At the anode:
\[ C + 2 O^{2-} = CO_2 + 4 e', \quad C + O^{2-} = CO + 2 e' \] [2]

At the cathode:
\[ Ca^{2+} + e' = Ca^+ \] [3]

where \( Ca^{2+}, \ Ca^+, \ O^{2-} \) and \( e' \) represent the calcium ions, oxygen ion and electron in the salt, respectively. The \( Ca^+ \) ion leaves the cathode and migrates in the molten \( CaCl_2 \) bath. When the melt is saturated, liquid Ca should deposit on the cathode,

At the cathode:
\[ Ca^{2+} + 2 e' = Ca \] [4]
\[ Ca^+ + e' = Ca \] [5]

The liquid calcium detaches from the cathode surface as small droplets. As mentioned above, it was not easy to recover pure Ca perfectly because of dissolution of Ca.

**COMBINATION OF REDUCTION AND ELECTROLYSIS**

Both the electrolysis and reduction can be combined together as illustrated in Figure 4, or they can be done simultaneously in the same reaction bath as shown in Figure 5 (2,29,30). This single unit operation (Figure 5) can compensate the heat evolution of Ca reduction and the heat absorption of electrolysis.

![Figure 4. Separate model (OS-II3).](image1)

![Figure 5. Combined model (OS-I3).](image2)

\( TiO_2 \) powder is reduced in molten \( CaCl_2 \) containing \( Ca^+ \) and free electrons, and the reduction by-product \( CaO \) dissolves in the bath according to the electrochemical reaction, eq.[6]. If \( TiO_2 \) particles meet liquid Ca droplets, they are also immediately reduced to metal by the thermochemical reaction, eq.[7].
The possibility of eq. [7], was reported considering the application to the rare earth metals and radioactive elements (21-25).

Oxygen in the reduced Ti particles, \([\text{O}]_{\text{Ti}}\), (max. 14 mass\%) is removed by eqs. [8] and [9]. Okabe et al. succeeded in the electrochemical deoxidation using eq. [9] to <100 ppm oxygen level from bulk Ti samples (19, 31).

\[
\text{TiO}_2 + 2 \text{Ca}^+ + 2 \text{e}^- = \text{Ti} + 2 \text{Ca}^{2+} + 2 \text{O}^{2-} \quad [6]
\]

\[
\text{TiO}_2 + 2 \text{Ca} = \text{Ti} + 2 \text{Ca}^{2+} + 2 \text{O}^{2-} \quad [7]
\]

Our proposal will use mainly eqs. [2], [3], [6] and [8] in the unsaturated Ca-CaCl\(_2\) molten salt (2, 29, 30), considering the fast reaction between \(\text{Ca}^{+}\) and TiO\(_2\) in the salt and the relatively slow electrolysis, as reporting below. Summarizing all the reactions working in one bath, we can write simply that TiO\(_2\) is reduced by carbon as,

\[
\text{TiO}_2 + 2 \text{C} = \text{Ti} + 2 \text{CO} \quad [10]
\]

This overall reaction is the same as that in Kroll process where the reductant Mg is circulated. The analogy with aluminum smelting using the consumable carbon anode is noteworthy.

**THERMODYNAMICS OF DESIRED SALT CONSTITUTION**

The thermochemical activity of \(\text{CaO}\), \(a_{\text{CaO}}\), becomes lower by dissolution into CaCl\(_2\), and the attainable oxygen level can be lowered. Using the thermodynamic data of Ti obtained by the equilibrium of pure Ca - pure CaO - pure Ti (9), and defining the activity ratio as \(r = a_{\text{CaO}} / a_{\text{Ca}}\), we can evaluate the residual oxygen level in equilibrium, \([\text{O}]_{\text{Ti}}^{\text{eq}}\).

\[
\ln ([\text{O}]_{\text{Ti}}^{\text{eq}}, \text{mass}\%) = \ln r -7020/T (K) + 2.49 \quad [11]
\]

Figure 6 shows the relationship shown in eq. [11]. The oxygen level in \(\beta\)-Ti attainable with this process can be lowered by decreasing \(r\). Halide flux deoxidation uses this principle setting \(a_{\text{CaO}} = 1\) and \(a_{\text{Ca}} < 1\) (17-19).

Figure 7 shows the isothermal cross-section of salt constitution expected at 1173 K (14-16, 26-28, 32). In the compositional regions (C) and (D) shown in Figure 7, \(a_{\text{CaO}} < 1\) and \([\text{O}]_{\text{Ti}}^{\text{eq}}\) becomes lower. However, the reduction from TiO\(_2\) forms a large amount of CaO during the operation, and the reductant Ca is consumed. Depending on the delicate mass balance of the initial materials, \(a_{\text{CaO}}\) and \(a_{\text{Ca}}\) may happen to become near 1 and
much lower than 1, respectively. This raises \( r \) to \( >1 \) and \([O]_{\text{eq}}\) becomes higher. We should control the final composition within the desired compositions.

\( a_{\text{Ca}} \) in regions (B) and (C) are estimated as 0.995 (33). Therefore, the region (C) is recommended thermodynamically, if we consider both \( a_{\text{Ca}} \) and \( a_{\text{CaO}} \). It is more favorable to adapt a \( \text{CaCl}_2 \)-richer composition in region (C) as the initial point for reduction in

Figure 6. Equilibrium oxygen concentration in Ti evaluated in eq.[11].

Figure 7. Isothermal cross-sectional view of the ternary system of Ca-CaO-CaCl\(_2\) at 1173 K (14-16,26-28,32).
order to enhance the dissolution of CaO. However, the amount of TiO₂ is restricted here because the applicable amount of Ca is limited. In addition, it is difficult to obtain pure Ca with molten salt electrolysis. The alternative choice of the suitable region (B) or (C) was made by the experiments both for reduction and electrolysis.

**SALT COMPOSITION SUITABLE FOR REDUCTION**

The densities of liquid Ca and CaCl₂ at 1173 K are 1.357 and 2.01x10³ kg/m³, respectively (34). At the region (C), this large difference separates into two layers; the lighter Ca and the heavier CaCl₂ layers. Rutile-type TiO₂ particles (density = 4.23x10³ kg/m³) settle down on the bottom of the vessel. As illustrated in Figure 8, TiO₂ does not contact with Ca. We expect that the reduction, eq.(1), proceeds by the dissolved Ca in CaCl₂ (eq.[6]), not by the pure liquid Ca (eq.[7]).

![Figure 8](image.png)

**Figure 8.** Oxygen concentration in Ti when rutile-type TiO₂ powder was reduced using Ca+CaO+CaCl₂ at 1173 K for 3.6 ks.

After cooling the reaction vessel, the solidified CaCl₂ and residual Ca, about 25 mm in depth, was dissolved in the flow of normal drinking water, with cooling below 283 K to avoid the surface oxidation during leaching. The black Ti powder was subsequently rinsed with dilute acetic acid, distilled water and alcohol, in that order, and then dried in vacuum for analysis. When the charge of Ca was just stoichiometric according to eq. [1], the reaction was not complete because some portion of the floating Ca layer was lost due to evaporation. Here twice stoichiometric amount of Ca was used.

Axler and DePoorter reported the Ca and CaO solubility in the ternary Ca-CaCl₂-CaO system at 1173 K, and showed that Ca solubility decreased significantly by addition of CaO (32). Figure 8 shows their solubility and the final salt compositions of our samples, where the increment of CaO due to reduction was considered.

Ti powder obtained was slightly sintered sponge, and contained approximately 1500 ppm Ca. The oxygen concentration in Ti was lowered to the level of < 1000 mass.
ppm oxygen at the CaCl₂ richer region. The better results were obtained at 5 – 7 mol% Ca, as shown in Figure 8. This is mainly because the residual amount of Ca metal was smaller. When a large amount of residual Ca was dissolved in water with the samples, the large exothermal heat due to dissolution of Ca and CaO oxidized the Ti samples even in water.

A significant increase of oxygen concentration was recorded at > 3 mol% CaO, although the saturation of CaO is 19.4 mol% CaO in the binary CaCl₂-CaO system. Because it took a long time to achieve the equilibrium when a large amount of CaO was added into the molten CaCl₂ (26,32), the dissolution speed of CaO might be slowed at the higher concentration region of CaO. Additionally, in order to keep low oxygen content, the activity ratio, r, should be low. Therefore, the desired composition for reduction is hatched in Figure 8. Although the usage of a large amount of Ca reductant generally allows a better yield, the recommendable region was far from pure Ca.

It was proved that the dissolved Ca in CaCl₂ could reduce the titanium oxide as an active reductant. Ti powder was successfully produced with the oxygen content less than 1000 ppm in a short time such as 3.6 ks. In the earlier study of Ca reduction at 1273 K without CaCl₂, it took at least 6 hours to reduce TiO₂ into the lower oxides such as TiO (7), and that the analytical values < 1000 ppm were seldom achieved even in the prolonged treatment (4,6-8). In case of our reduction for 86.4 ks, the oxygen content decreased to 420 ppm, which is well acceptable for industrial material. In situ CaO removal into CaCl₂ was effective to enhance the reaction, and the coexistence of water-soluble CaCl₂ made it easy to remove the solidified salt in water.

**REDUCTION AND IN SITU ELECTROLYSIS**

Figure 9 shows an experimental arrangement for the simultaneous reactions, reduction and in situ electrolysis. A carbon crucible was used for anode, and Ti net shaped like cylinder was used for cathode, in which about 1 g granular anatase-type TiO₂ was filled. After the reaction, Ti cathode was picked up from the melt and the solidified salt was removed in water.

**Figure 9.** Experimental arrangement of Ti net cathode model (OS-III3).
Table 1 shows that CO₂ gas evolved during electrolysis at 1173 K. By applying a constant voltage over that of theoretical decomposition of CaCl₂, Cl₂ gas evolved in addition to CO₂ gas. The evolution of O₂ and CO was not measured. The lower Ti oxides as powder form were often detected with α-Ti in case of the short time operations. This is because the forming rate of “Ca⁺” was not enough fast in our experimental cell.

Table 1. Experimental conditions and results using Ti net cathode.

| Run | Molten salt (mol%) | Voltage (V) | Detected gas | Time (ks) | Total charge (C) | Phases identified by XRD | Oxygen concentration (mass ppm) |
|-----|--------------------|-------------|--------------|----------|-----------------|-------------------------|--------------------------------|
| c-1 | CaCl₂              | 3.5~3.8     | CO₂, Cl₂     | 10.8     | 53 598          | α-Ti                    | 6 860                          |
| c-2 | CaCl₂              | 3.4~3.7     | CO₂, Cl₂     | 3.6      | 17 688          | α-Ti                    | 38 000                         |
| c-3 | CaCl₂              | 3.5~3.7     | CO₂, Cl₂     | 10.8     | 10 443          | α-Ti, TiO₀.₃₂₅          |                                |
| d-1 | 15%CaO             | 2.6~2.8     | CO₂          | 10.8     | 54 126          | α-Ti, TiO₀.₃₂₅          |                                |
| d-2 | 15%CaO             | 2.6~2.8     | CO₂          | 3.6      | 23 055          | TiO₀.₃₂₅, TiO            |                                |
| d-3 | 15%CaO             | 2.6~2.8     | CO₂          | 1.8      | 10 800          | TiO₀.₃₂₅, TiO            |                                |
| e-1 | 1%CaO              | 2.5~2.8     | CO₂          | 10.8     | 40 194          | α-Ti                    | 6 200                          |
| e-2 | 1%CaO              | 2.6~2.8     | CO₂          | 3.6      | 14 931          | α-Ti, TiO₀.₃₂₅          |                                |
| f-1 | 0.5%CaO            | 2.6~2.9     | CO₂          | 10.8     | 36 978          | α-Ti                    | 2 000                          |
| f-2 | 0.5%CaO            | 2.7~2.9     | CO₂          | 3.6      | 10 704          | α-Ti, TiO₀.₃₂₅          |                                |
| g-1 | CaCl₂              | 2.6~2.8     | CO₂          | 10.8     | 25 374          | TiO₀.₃₂₅                |                                |
| g-2 | CaCl₂              | 2.6~2.9     | CO₂          | 3.6      | 5 439           | TiO₀.₃₂₅                |                                |

α-Ti single phase was obtained as slightly sintered lamp, and its oxygen concentration was analyzed to be relatively high. When we define the current efficiency as the ratio, (the necessary charge to attain the analytical oxygen level) / (the applied charge during electrolysis), it was evaluated as 11.8% and 12.9% for Runs #e-1 and #f-1, respectively.

When the salt with the higher concentration of CaO was used, the larger current could be supplied under the same experimental geometry and the same applied voltage. This means that Ca⁺ or Ca could be formed more efficiently by the electrochemical reaction at the higher concentration of CaO. However, the dissolution of CaO from the reducing reaction, eqs.[6] and [8], was delayed due to the higher concentration of CaO. The better oxygen concentration was obtained at the lower concentration of CaO. In case of pure CaCl₂, the current under a constant voltage was limited and α-Ti was not obtained within 3 hours. Therefore, it is essential to keep a good balance among the thermochemical reduction of TiO₂, the physical dissolution of CaO and the electrochemical decomposition of CaO.

In the case of Cl₂ gas evolution, the applied charge may be preferentially consumed for electrolysis of CaCl₂. It is considered, therefore, that the CaO concentration in the salt remained higher than in the case of CO₂ gas evolution, and that the deoxidation from the reduced Ti powder were retarded.
COMPARISON WITH FFC PROCESS

Recently Fray et al. proposed the electrolysis of TiO$_2$ in the CaCl$_2$ bath, which is called as FFC process (35-37). As compared in Figure 10, the carbon plate and the pellet of TiO$_2$ are used as the anode and the cathode, respectively, in their process. They claimed that their process based on the oxygen extraction from TiO$_2$ at the cathode, written as,

\[
\begin{align*}
\text{At the anode:} & \quad 2 \text{O}^{2-} = \text{O}_2 + 4 \text{e}^- \quad [12] \\
\text{At the cathode:} & \quad \text{TiO}_2 + 4 \text{e}^- = \text{Ti} + 2 \text{O}^{2-} \quad [13]
\end{align*}
\]

Two differences between FFC process and our proposal are the workability of Ca or Ca$^+$ near the cathode, and the evolved gas at the anode, as shown in Figure 10. The detailed analysis and merits for the both processes were described in Ref. 30.

CARBON CONTAMINATION

The problems encountered were back reaction due to the solubility of metallic calcium in the melt and parasitic reactions due to CO$_2$ gas bubbles. The most likely reactions are as following,

\[
\begin{align*}
2 \text{Ca} + \text{CO}_2 &= \text{C} + 2 \text{CaO} \quad [14] \\
\text{Ca} + \text{CO} &= \text{C} + \text{CaO} \quad [15]
\end{align*}
\]

Carbon dust was observed in the upper part of the bath and froze as a crust layer. Carbon is one of the harmful element for Ti production and the carbon contamination in Ti should be minimized. By analyzing the cell behavior, we believe that the cathode design is the key to solve the matter.
CONCLUSIONS

Titanium dioxide powder is available from many worldwide sources, and directly top-charged into the molten CaCl₂. Combining the reduction and the electrolysis in the same bath, sufficiently deoxidized titanium metal deposited as the granular sponge. The lower concentration of CaO gave the better oxygen concentration in Ti. Considering the usage of consumable carbon anode and “Ca⁺” dissolved in the CaCl₂ melt, a simple model for industrial application is illustrated in Figure 11.

Figure 11. A model using replaceable carbon anode (OS-III1).

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