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CALCIOTHERMIC REDUCTION AND SIMULTANEOUS ELECTROLYSIS OF CaO IN THE MOLTEN CaCl_2 - SOME MODIFICATIONS OF OS PROCESS

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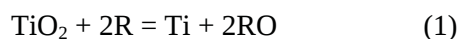
Keywords: *calciothermic reduction, molten calcium chloride, titanium oxide, oxygen concentration, carbon contamination*

1 Introduction

The goal of the new process is the conversion of the TiO_2 particles into ductile Ti without contamination by oxygen and carbon, which have an extremely strong affinity to Ti. Therefore, Kroll took a route via TiCl_4 , where the physical and chemical contacts with oxygen and carbon can be industrially avoided during the refining process. The new alternative method should possess the same requisites as the Kroll process, in addition to new merits such as continuous operation and good energy efficiency that the Kroll process can not realize.

2 Calciothermic Reduction in Molten CaCl_2

A shortcut method to produce metallic Ti from its oxide involves seeking a qualified reductant R to remove oxygen as,



Oxygen should have a thermodynamically stronger affinity to R than to Ti, but the residual reductants such as Al and C pollute the Ti produced. Only Ca and rare earth metals can reduce the residual oxygen content to less than 1000 mass ppm. Direct reduction using Ca was proposed before the development of the Kroll process [1], but its industrial application was not realized [2-4]. As illustrated in Fig.1(a) [5-7], 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 TiO_2 particles forms CaTiO_3 at the late stage of calciothermic reduction. If CaO/ CaTiO_3 is generated at the narrow spaces among Ti particles, it cannot be leached even by an acid solution. The oxygen produced from these residual calcium oxides migrates to the molten Ti during

arc-melting; as a result, a brittle Ti ingot will be 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 [2-4].

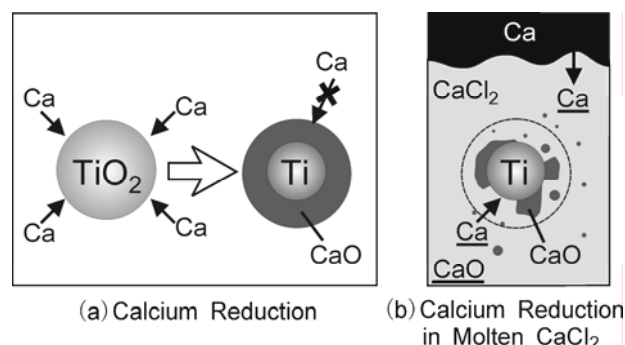


Fig.1. Schematic mechanism for calcium reduction and CaO removal in the molten CaCl_2 [5-7].

Generally, oxides do not dissolve into the chloride melt. Curiously, however, only CaCl_2 can dissolve an amount as large as 20 mol% of CaO and a few mol% of Ca. This mechanism was firstly applied as halid-flux deoxidation of Ti [8,9]. In the calciothermic reduction of TiO_2 , the thicker CaO film will be eliminated as shown in Fig.1(b), and in practice, the dissolved Ca could reduce TiO_2 more efficiently to result in an oxygen content of 1500 ppm even within an hour [5]. CaCl_2 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_2 can enhance the reduction of TiO_2 even when Ca vapor is used [10]. Ca liquid or vapor reduction with CaCl_2 will be practical if good quality Ca can be obtained at a reasonable cost.

3 Electrolysis of CaO in molten CaCl₂

The author's group proposed the electrolysis of CaO to produce Ca in molten CaCl₂ in order to use Ca for the reduction of TiO₂ in CaCl₂ and to supply the by-product CaO for further electrolysis [11-13].

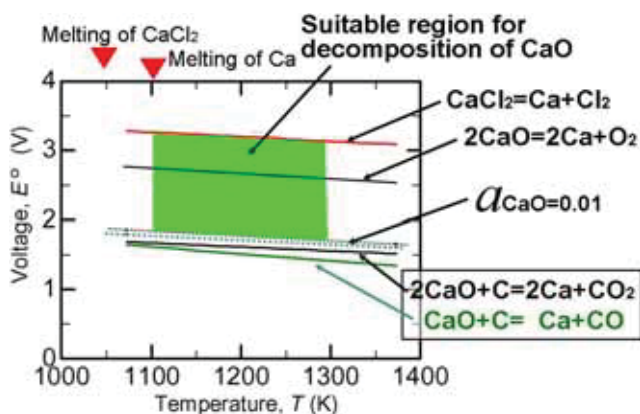
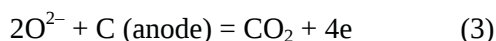


Fig. 2. Electrochemical potential for CaO electrolysis in molten CaCl₂ [11-13].

The theoretical decomposition voltage for CaO to the gaseous oxygen is approximately 2.6 V, as shown in Fig. 2, and it can be decreased to 1.6 V if the carbon anode is used to decompose CaO to CO and/or CO₂, as written as,



This is because the metallic anode is not endurable and because the carbon anode does not dissolve in the molten CaCl₂. The voltage for Eqs.(2)-(4) is expected to be as high as 1.8 V even if the thermochemical activity of CaO is as low as 0.01, considering the dissolution of CaO in the CaCl₂ melt. These values are sufficiently lower than 3.2 V for CaCl₂ = Ca + Cl₂, and we may expect that CaO will be reduced to Ca without Cl₂ gas evolution by applying approximately 3.0 V, for example.

It was originally expected that the light Ca liquid could flow upward along the cathode and be recovered to be supplied as a reductant for TiO₂ [11]. 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 CaCl₂ [12,13]. Previous attempts had also failed to produce pure liquid Ca; this was despite a voltage

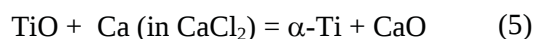
greater than 3.2 V being applied at which the solvent CaCl₂ was dissociated. A solid carrot-shaped Ca bar can be obtained if the Ca deposited on the cathode is cooled above the electrolyte, similar to the unidirectional solidification of Si ingots.

For the reduction of TiO₂ by Ca, pure Ca is desired for the enhancement of reaction but not essential. Even the Ca dissolved in molten CaCl₂ (hereafter referred to as Ca) can react with TiO₂ to form metallic Ti [5]. In other words, Ca formed in the vicinity of the cathode holds a lower thermochemical activity than that of pure Ca, but it can be used for the reduction of the molten salt with a strong reducing agent.

4 Combination of Electrolysis and Reduction

4.1 Concept

For example, the activity of Ca in CaCl₂ is evaluated as 1.48×10^{-4} [14] to form α -Ti by



when we assume the equilibrium with TiO and pure CaO at 1123 K. TiO is the lowest oxide in the binary Ti-O system at the operating temperature range. We may evaluate the minimum concentration of Ca in the melt as low as 6 mol ppm. If CaO dissolves in the melt, a little lower concentration is allowed to be applied to form the metallic Ti. It is noted that α -Ti can be produced even by such a low concentration of Ca, but that the deoxidation from α -Ti requires much higher concentration [8,9].

As illustrated in Fig. 3, Ca is extracted at the cathodic area from the electrolysis bath and fed into the reduction vessel, where the injected TiO₂ powder will be reduced by Ca and the metallic Ti particles are settled downwards. When we can pull the frozen salt with Ti particles continuously from the bottom of the vessel, a continuous reduction for Ti production will be realized.

The electrochemical decomposition of CaO is endothermic, while the reaction with Ca and TiO₂ is exothermic. Therefore, we may physically combine the two baths to use the related heat efficiently, as shown in Fig.4(a). We may directly introduce TiO₂ into the Ca near the cathode [12,13].

Due to the decomposition of CaO, the Ca deposited near the basket-like cathode dissolves as Ca and the overall reaction near the cathode is written thermochemically as,

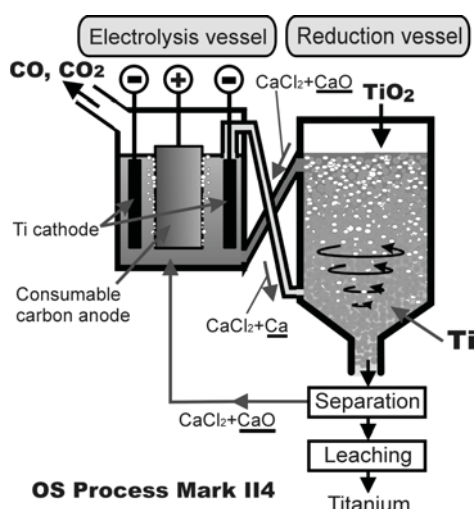


Fig. 3. Separated model (OS Mark II4) [5,12].

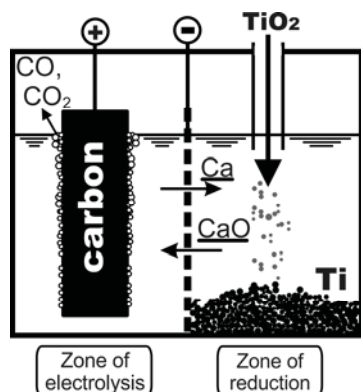


Fig. 4 Fundamental model for OS Mark I [12,13].

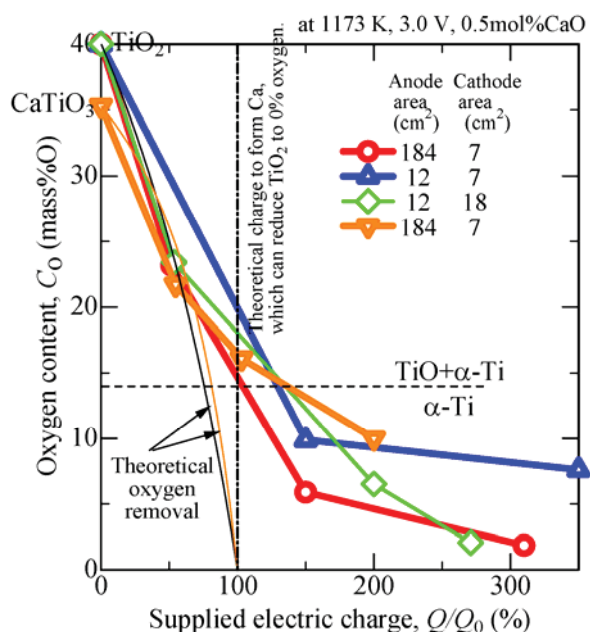
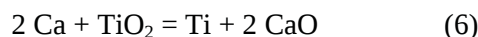


Fig. 5. Oxygen concentration in the obtained samples after the electrolysis of CaO at 1173K [17].



The by-product CaO dissolves in the molten CaCl_2 as CaO . This CaO may be written as Ca^{2+} and O^{2-} because of its ionic nature, and O^{2-} escapes as a gas after reacting with the anodic carbon (Eqs.(3) and (4)).

4.2 Laboratory Scale

In the lab-scale test, 1.0 g TiO_2 powder was successfully reduced and deoxidized to produce 2000 ppm of oxygen for 3 h at 1173 K [5].

Fig. 5 showed some examples for the effects of current density and the starting materials [15]. At the early stage of reduction, when the supplied electric charge was less than the amount of theoretical supply, Q_0 , the current efficiency approached to 100%, but the decrease of oxygen concentration delays in the range of α -Ti solid solution (<14 mass%O). The electrochemical deoxidation from the obtained α -Ti [16,17] becomes important at the late stage of electrolysis. After the reduction to metallic state, a large amount of oxygen diffuses out to the CaCl_2 bulk, which delays the successive diffusion of oxygen from α -Ti surface.

This method—the so-called OS process—can be applied to the entire oxide reduction process, except for rare-earth oxides (such as Y_2O_3) that are thermodynamically more stable than CaO. In case the reduced metal reacts with Ca to form an intermetallic compound (e.g., Al forms CaAl_2), it is necessary to remove Ca after reduction from the products.

4.3 Industrial Model

A considerable level of basic knowledge on OS process has now been accumulated in the industrial instruments and operational parameters, such as the morphology of carbon anode, the control of fluid convection due to gas evolution, and the temperature distribution to form the freeze. The freeze of CaCl_2 seems to be the best crucible to hold the molten CaCl_2 when the reactor can be internally heated.

Fig. 6 shows one example of the industrial models using the frozen salt as the wall material of the bath [18]. Joule heat between the electrodes maintains the salt as the molten state. The cathode and the control panel immersed in the melt regulate the flow behavior of Ca -rich salt and the electrochemical potential of Ca . They also separate the CO/ CO_2 gas bubbles from Ca near the cathode.

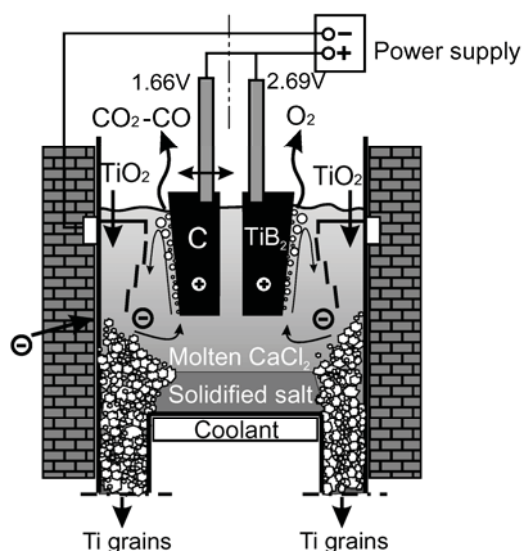


Fig. 6. Conceptual image of an industrial model [18].

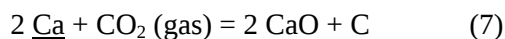
The precipitated Ti particles are recovered from the bottom of vessel.

The usage of inert anode is fruitful against oxidation, as shown in the right half of Fig. 6. In the aluminum industry, this kind of material is developing instead of conventional consumable carbon anode. It can be applied also for OS process, although the decomposition voltage of CaO becomes higher due to O₂ evolution (2.69 V at 1173 K, see Fig. 2).

5 Carbon contaminations

5.1 Why carbon ?

One of the demerits of the OS process is the co-production of free carbon that may react with the produced metals and reduce their qualities [12,13]. Because the bubbles of CO/CO₂ gas are formed at the anode surface, when the Ca concentration in the melt is enough high and when the removal of the gas bubbles from the CaCl₂ surface is slow, the bubbles react with Ca to form CaO and C.



The carbon deposition depends on the cell arrangement and the reaction rate. Fig. 6 showed an example considering the efficient gas bubble removal. However, at the worst cases, the total

surface of the melt was covered by the black carbon powder whose parts were C₆₀. The volume ratio of CO and CO₂ gases changes by the supplied electric charge, the rate of reduction, temperature and the inert gas flow rate to the outlet. The gas mixing ratio may depend in principle on the equilibrium of C-CO-CO₂ under the atmospheric pressure of Ar, when the gas bubbles are generated on the carbon anode. About 86% of the evolved gas was, for example, well exhausted from the furnace, but the residual CO and CO₂ gas consumed Ca, which should be served to reduction of TiO₂ [19].

5.2 Membrane

The usage of ceramic membrane was effective to separate the gas bubbles from the cathodic area. The porous MgO cylinder surrounding the anode was effective, but not perfect because of gas penetration above the melt level [20]. The Y₂O₃-stabilized ZrO₂ (YSZ) was excellent because its oxygen ionic conductivity cut off the Ca ion movement through the membrane although the current become 1/5 - 1/10 [20].

Fig. 7 shows the top surface view of the electrolyte. The carbon precipitates covers around the anode when YSZ membrane was not used, while the metallic liquid Ca floated near the cathode when YSZ was used at the voltage as high as about 10 V.

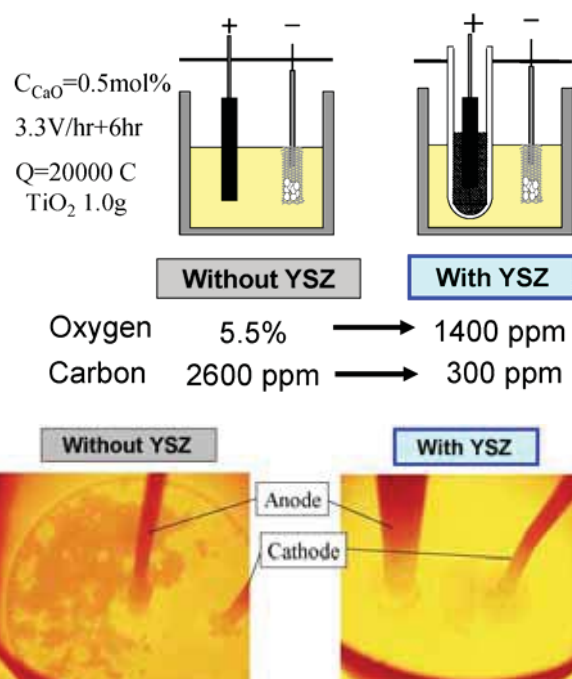


Fig. 7. Comparison of oxygen and carbon content, and the overview of the electrolyte, when the YSZ tube was used as the membrane (a part of anode).

This carbon contamination causes no serious problems, for example, in the case of MgO reduction because the product Mg does not react with carbon. However, we require some safeguards during Ti production because of the low allowance limit in Ti against carbon.

5.3 Solubility of CO₂

As a fundamental of CO₂ gas dissolution into the molten CaCl₂, the equilibrium solubility of CO₂ gas was studied as shown in Fig. 8 [21]. The dissolution rate was fairly fast, and the equilibrium solubility after 3.6 ks increased at the higher pressure, $P(\text{CO}_2)=1$ atm, comparing with the previous report [22].

The difference may cause from the difference of the saturated solid. As shown in Fig. 9, the precipitate under $P(\text{CO}_2)=1$ should be CaCO₃ thermodynamically. Below the equilibrium $P(\text{CO}_2)$ -CaO-CaCO₃, CaO is saturated in the CaCl₂ melt.

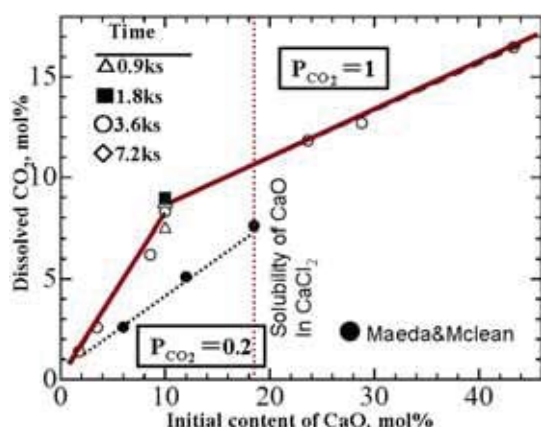


Fig. 8. Solubility of CO₂ gas in the CaO-CaCl₂ melt at 1123 K [21].

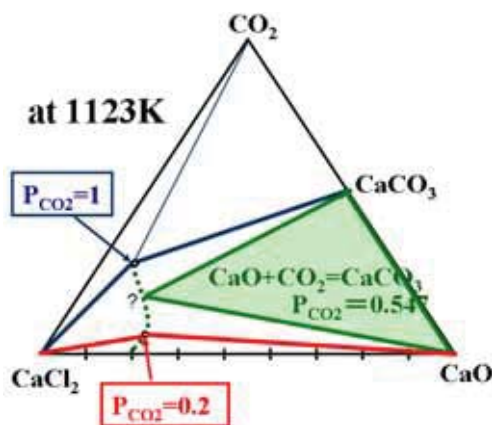


Fig. 9. Isothermal section of the quasi-ternary system of CO₂-CaCl₂-CaO at 1123 K [21].

Although CO gas does not dissolve [22], the dissolution of CO₂ gas bubbles may occur during a short time of electrolysis, if the adhesion of gas bubbles to the carbon anode is kept for a long time. The kinetics of CO₂ dissolution will be studied further.

6 Reduction of TiCl₄

Instead of TiO₂ powder as the starting material such as in Fig. 3, recently Yamaguchi and Yamaguchi, the researchers at Toho titanium and Osaka titanium technologies, propose to blow the high quality of TiCl₄ gas, as reported as JTS method [23,24]. This proposal has the merits to be able to form a high purity Ti, and to get a high reaction rate because of the higher current density due to the decomposition of CaCl₂ to Ca and Cl₂ gas.

An attempt to feed TiCl₄ gas into the cathode was conducted using the arrangement of Fig. 4 [25,26]. Some parts of the obtained powder at the bottom of the MgO crucible was α -Ti, by reacting as

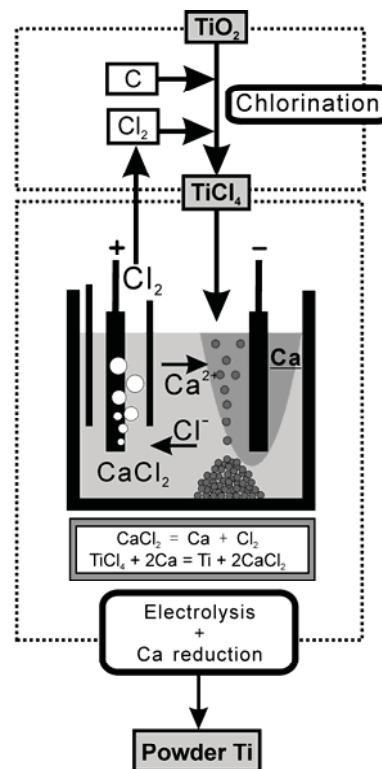
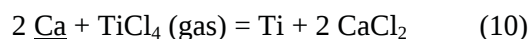


Fig. 10. Flowsheet of reduction of TiCl₄ by Ca. [25,26]

The mass balance between the electrolysis and TiCl_4 gas feed was critical, and the Ca concentration should be kept higher than 2 mol%Ca. The residual amount of TiCl_4 was partially reduced to TiCl_2 and/or TiCl_3 . These lower chlorides reacted easily with the oxide crucible to become the Ti lower oxides. The oxygen source in the reactor should be minimized to enhance the reaction of Eq.(10). The combination of the CaO electrolysis should be taken.

7 Conclusion

TiO_2 was successfully reduced to the metallic titanium in the molten CaCl_2 . For the future application to the industrial scale, carbon contamination should be avoided based on the detailed basic researches. If a nonconsumable and oxygen-absorbing anode can be realized instead of the carbon anode, the production of Ti without carbon contamination could be practically realized.

8 Acknowledgements

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