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Author(s)
Ono, K.; Suzuki, R. O.

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A PROCESS FOR CONTINUOUS TITANIUM PRODUCTION FROM TITANIUM OXIDE

K. Ono and R. O. Suzuki

Department of Energy Science and Technology
Kyoto University
Yoshida, Sakyo, 606-8501, Kyoto, Japan

Abstract

A new process for extraction of titanium metal from its oxide is demonstrated. In this process, raw material to be reduced is titanium oxide synthesized from ilmenite. The reducing agent is the Ca+CaCl₂ two-phase mixture. Titanium is elaborated in the medium consisted of liquid Ca, CaCl₂ and solid TiO₂ at the temperature range 1200 to 1300K by means of mixing mechanically the ingredients in the reactor into a smooth paste. Fluidity of the feed which enables continuous scheme depends on the CaCl₂ content. The oxygen level of the reduced titanium is the range 500 to 1000 mass ppm varying with the operational conditions. The Ca+CaCl₂ reducing agent is taken out from the electrolysis of CaCl₂ at 1140K, and this CaCl₂ is produced by aqueous chemistry conversion using Cl₂ gas recycled from the electrolysis.
Introduction

The mineral primarily used currently in the manufacture of titanium is rutile, but it has been indicated that reserves are becoming increasingly more expensive to mine as they are becoming scarcer. So, this particular source would only partly answer the expanding titanium production in the future. On the other hand, ilmenite would supply the titanium requirements of increasing capacity metal production because of its abundance in the world, and many techniques have been used for upgrading its TiO₂ content to make high-grade synthetic rutile.

For titanium metal production route, the direct reduction of TiO₂ may be attractive, because its long distance transportation is feasible compared to the transportation of titanium tetrachloride or chlorine, both being highly volatile hazardous liquids.

Historically, Dr. Kroll tried to reduce TiO₂ by calcium to elaborate useful metallic titanium in 1923 – 1940, but he could not achieve low oxygen content. Therefore, he switched to the reduction of TiCl₄ by Mg. Production of commercial titanium metal by direct reduction does not require so high purity TiO₂ as that for pigments. Furthermore, the actual titanium content of TiO₂ is 57% vis-à-vis 25% in TiCl₄. So, the production of synthetic TiO₂ from ilmenite using either the sulfate or chloride technology and subsequent direct-reduction may be a short route for titanium metal production.

In this study, the direct reduction of TiO₂ by Ca has been examined especially by focusing both on product quality and its continuous processing.

Closed-loop continuous titanium production from titanium oxide

Figure 1 demonstrates a closed-loop continuous titanium winning process using raw material TiO₂. The main route from TiO₂ to Ti ingot is fast and continuous. Continuity in reduction stage is the key to productivity. Note that in this closed-loop production, the environmental situation is ideal, generating (theoretically) only primary product, recycle materials and O₂ gas. Titanium oxide is reduced by the Ca+CaCl₂ two-phase mixture. This reducing agent is prepared by the fused CaCl₂ electrolysis basing on the multi-polar cell similar to the electrowinning of magnesium metal. The reduction products are Ti granules and CaO partially dissolved in the flux CaCl₂. The Ti granules are settled by continuous water-sedimentation with the overflow containing CaCl₂ in solution and suspended Ca(OH)₂.

Ca(OH)₂ is chemically converted to CaCl₂ using Cl₂ gas recycled from the electrolysis: Ca(OH)₂ suspended in the water reacts with Cl₂ to form calcium hypochlorite, which decomposes to CaCl₂ and O₂ gas by heating.

All the reactions in whole process can be summarized into a simple formula,

\[ \text{TiO}_2 = \text{Ti} + \text{O}_2 \]
Figure 1: Closed-loop titanium production from titanium oxide.

**Thermochemistry of reduction reaction**

The principle of the process has been reported previously\(^1\). The chemical reaction to produce titanium from its oxide can be given by,

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

Subsequently, titanium metal is deoxidized by Ca to lower oxygen content by the following reaction:

\[
\text{O(in Ti)} + \text{Ca} = \text{CaO} \quad (2)
\]

Coexistence of Ca and by-product CaO fixes the equilibrium oxygen potential, by which the residual oxygen in Ti is thermodynamically determined. This equilibrium oxygen concentration corresponds to the limit of deoxidation by pure Ca, and the experimental data are summarized in Figure 2. As shown in this figure, theoretical limit of deoxidation by pure Ca is below 500 mass ppm in the temperature range 1173 to 1273K, and the equilibrium data gives the relationship among oxygen partial pressure, temperature and oxygen content in the beta Ti field,

\[
\frac{1}{2}\ln(p_{O_2}/101325\ P\alpha) = \ln(\%O) + 10.5 - \frac{70050}{T} \quad (1173 - 1373K) \quad (3)
\]
In the case of reduction of TiO₂ powders by pure calcium metal at 1273K, it is difficult to obtain titanium with such low levels of oxygen within short reduction time. This may be due to the fact that the by-product CaO layers cover the surface of Ti particles and prevent penetration of Ca to attack the face of newly born titanium metal. Figure 3 shows the morphology of the starting material TiO₂ and Ti metal particles made by the reduction with pure Ca only. The oxygen contents are 1000 – 3000 mass ppm widely dispersing.

Next step is to measure further removal of oxygen and the basic approach is as follows. The equilibrium oxygen mole fraction in titanium under fixed Ca and CaO activities is expressed as follows.
where \( a_\text{Ca} \) and \( a_\text{CaO} \) are activities of Ca and CaO, \( \gamma_\text{O} \) activity coefficient of oxygen in Ti and \( \Delta G^\circ_\text{CaO} \) standard free energy of formation of CaO. To attain lower equilibrium oxygen concentration under Ca existence, that is to attain lower theoretical deoxidation limit by Ca, one of the ways is to decrease the activity of CaO in the equilibrium system by coexistence of a flux into which CaO can dissolve. Such a flux is CaCl₂ as indicates the solubility of CaO in the liquid CaCl₂, around 20mol\% (12mass\%) at 1100 - 1300K (Figure 4). For example, Figure 5 illustrates that when the activity of CaO in the flux is decreased to a level of 0.01 under existence of Ca, the theoretical deoxidation limit is lowered to 5 mass ppm at 1273K.

On the above thermochemical basis, the molten Ca+CaCl₂ two-phase mixture in the region of the two liquids on the phase diagram of Figure 6 was adopted as reducer for titanium reduction from its oxide. The titanium granules produced using such a reducer at 1273K are shown in Figure 7 and the oxygen content is the range 500 to 1000 mass ppm depending on the reduction conditions such as Ca/CaCl₂ ratio, holding time and temperature. Further removal of oxygen was carried out by repeating the treatment with the Ca+CaCl₂ two-phase flux. Elaboration of extra-low-oxygen titanium are summarized in Table 1.
Figure 5: Equilibrium oxygen concentration in β-Ti under Ca existence.

Figure 6: Phase diagram of the CaCl₂-Ca system. 
### Table I. Elaboration of extra-low-oxygen titanium

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Conditions</th>
<th>Oxygen content (mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flux</td>
<td>Initial</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Holding time</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Ca-CaCl₂, 1173K</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ca: Liquid)</td>
</tr>
<tr>
<td>2</td>
<td>Ca-CaCl₂, 1273K</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ca: Liquid)</td>
</tr>
<tr>
<td>3</td>
<td>Ca-CaCl₂, 1273K</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ca: Liquid)</td>
</tr>
<tr>
<td>4</td>
<td>Ca-CaCl₂, 1273K</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ca: Vapor)</td>
</tr>
<tr>
<td>5</td>
<td>Ca-CaCl₂, 1273K</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ca: Vapor)</td>
</tr>
<tr>
<td>6</td>
<td>Ca-CaCl₂, 1273K</td>
<td>200</td>
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<td>88ks</td>
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<tr>
<td></td>
<td></td>
<td>(Ca: Vapor)</td>
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<tr>
<td>7</td>
<td>Ca-CaCl₂, 1273K</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88ks</td>
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<tr>
<td></td>
<td></td>
<td>(Ca: Vapor) [vacuum dried flux]</td>
</tr>
<tr>
<td>8</td>
<td>Ca-CaCl₂, 1273K</td>
<td>200</td>
</tr>
<tr>
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<td></td>
<td>88ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ca: Vapor) [double deoxidation]</td>
</tr>
</tbody>
</table>
Fluidization of reduction medium

The reaction of TiO$_2$ with Ca is exothermic as the reaction of MgCl$_2$ with Mg:

\[
\begin{align*}
\text{TiO}_2 + 2\text{Ca} &= \text{Ti} + 2\text{CaO} ; \quad \Delta H_{\text{1200K}}^o = -340.3 \text{ kJ} \\
\text{TiCl}_4 + 2\text{Mg} &= \text{Ti} + 2\text{MgCl}_2 ; \quad \Delta H_{\text{1200K}}^o = -420.0 \text{ kJ}
\end{align*}
\]

Still more, calcium has very strong affinity with oxygen. So, in principle, fast reaction rate is expected. However, since the substances concerning with the reaction (5) are solid and liquid, forming the heterogeneous condensed-phase system at around 1200K, the possibility of direct contact of TiO$_2$ particles with the reductant Ca must be enhanced by taking some measure in order to make profit of such a potentially excellent reductant. Figure 8 is the micrograph showing the products of the reduction reaction (5). In this case, the reaction was interrupted at the stage where the reductant Ca was almost consumed. As seen from this figure, the Ti particles to be deoxidized by Ca are surrounded by the byproduct CaO, the direct contact being obstructed.

![Figure 8: Micrographs showing the products of TiO$_2$ reduction by pure calcium. A: As-reduced image. B: Secondary electron image of CaO and Ti particles.](image)

Use of the Ca+CaCl$_2$ two-phase reducer is the consequence of such a consideration. At the reduction stage, Ca and CaCl$_2$ are both liquid and even after the deoxidation stage where the reductant Ca is almost consumed, CaCl$_2$ holds liquid state. Therefore, liquid substance exists throughout the run. As shown in the phase diagram for CaCl$_2$-CaO (Figure 4), liquid CaCl$_2$ can dissolve CaO to a large extent, and it can clear away the CaO layers surrounding the Ti particles, giving newly revealed reaction surface to the reducing agent Ca. Consequently, CaCl$_2$ in the two-phase reducer has multiple role: It acts as a Ca-bearing media, as a flux for removing CaO in the vicinity of Ti particles and as a solvent for lowering the activity of CaO.

To induce above effects, it is necessary to mix mechanically the ingredients into a smooth paste.
Fluidity depends on the CaCl₂ content, but addition of large amount of CaCl₂ causes slurry. In practice, adequate blending of charge must be taken into account according to the operational conditions of the reactor. Suppose a vertical cylindrical vessel filled with the feed moving downward by gravity, solid titanium oxide and metal particles are dispersed in the feed solvent during the reduction and deoxidation periods. It is important that the TiO₂ charge is enough to remain in suspension in the solvent. The feed descending the column becomes progressively richer in metallic Ti than its oxide. The Ti particles grow as they collide each other. In general, the mean free path of particles between collisions with each other increases with increasing fluid velocities.

This fast reactor must operate automatically continuous feeding, discharging and continuous transportation of the feedstock in uni-direction from inlet to outlet with controlled velocity. It must contain a series of horizontal circular blades for mixing of the feed and scrapers fixed to a central shaft which is slowly rotated by a motor.

**Conclusion**

Manufacturing of titanium has been considered according to the following items: elaboration of titanium from its oxide, continuous manner of reduction and attainable level of oxygen in reduced titanium.

Deoxidation limit by pure Ca is around 500 mass ppm in the temperature range 1173 to 1273K. Use of CaCl₂ as a flux is useful for the diminution of deoxidation limit by the reason that CaCl₂ acts as a solvent and lowers the activity of the reduction product, CaO. Titanium granules with oxygen varying between 500 to 1000 mass ppm have been elaborated by the reduction of TiO₂ using the Ca+CaCl₂ two-phase reducer.

Fluidization of the feed in the reactor is key to the continuous operation. For this purpose, the existence of liquid Ca and CaCl₂ in the feed and its mechanical mixing can realize fluidity.
References


