A PROCESS FOR CONTINUOUS TITANIUM PRODUCTION FROM TITANIUM OXIDE

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Abstract

A new process for extraction of titanium metal from its oxide is demonstrated. In this process, row material to be reduced is titanium oxide synthesized from ilmenite. The reducing agent is the $Ca+CaCl_2$ two-phase mixture. Titanium is elaborated in the medium consisted of liquid Ca, $CaCl_2$ and solid TiO_2 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 $CaCl_2$ content. The oxygen level of the reduced titanium is the range 500 to 1000 mass ppm varying with the operational conditions. The $Ca+CaCl_2$ reducing agent is taken out from the electrolysis of $CaCl_2$ at 1140K, and this $CaCl_2$ is produced by aqueous chemistry conversion using Cl_2 gas recycled from the electrolysis.

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Intoduction

The mineral primarily used currently in the manufacture of titanium is rutil, 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 TiO_2 content to make high-grade synthetic rutile.

For titanium metal production route, the direct reduction of TiO_2 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 TiO_2 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 $TiCl_4$ by Mg. Production of commercial titanium metal by direct reduction does not require so high purity TiO_2 as that for pigments. Furthermore, the actual titanium content of TiO_2 is 57% vis-à-vis 25% in $TiCl_4$. So, the production of synthetic TiO_2 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 TiO_2 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 row material TiO_2. The main route from TiO_2 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 O_2 gas.

Titanium oxide is reduced by the $Ca+CaCl_2$ two-phase mixture. This reducing agent is prepared by the fused $CaCl_2$ 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 $CaCl_2$. The Ti granules are settled by continuous water-sedimentation with the overflow containing $CaCl_2$ in solution and suspended $Ca(OH)_2$.

$Ca(OH)_2$ is chemically converted to $CaCl_2$ using Cl_2 gas recycled from the electrolysis: $Ca(OH)_2$ suspended in the water reacts with Cl_2 to form calcium hypochlorite, which decomposes to $CaCl_2$ and O_2 gas by heating.

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

$$TiO_2 = Ti + O_2$$

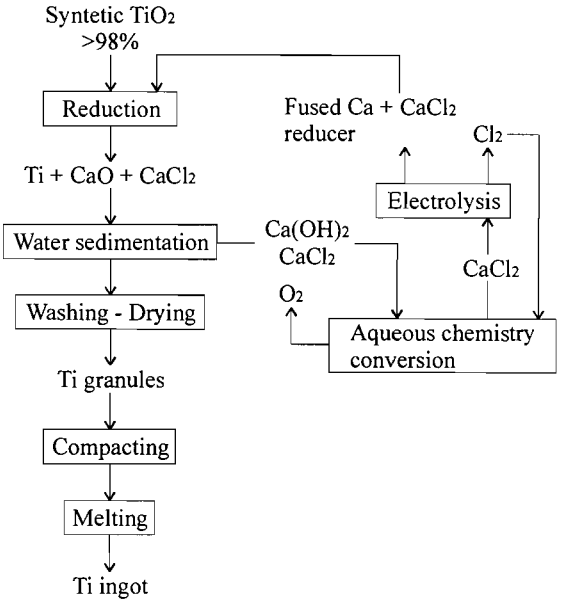

Figure 1: Closed-loop titanium production from titanium oxide.

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,

$$TiO_2 + 2Ca = Ti + 2CaO \tag{1}$$

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

$$O(\text{in Ti}) + Ca = CaO \tag{2}$$

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 tmperature range 1173 to 1273K, and the equilibrium data gives the relationship among oxygen partial pressure, tempeature and oxygen content in the beta Ti field,

$$\frac{1}{2}\ln(p_{O2}/101325Pa) = \ln(\%O) + 10.5 - \frac{70050}{T} \quad (1173\text{-}1373K) \tag{3}$$

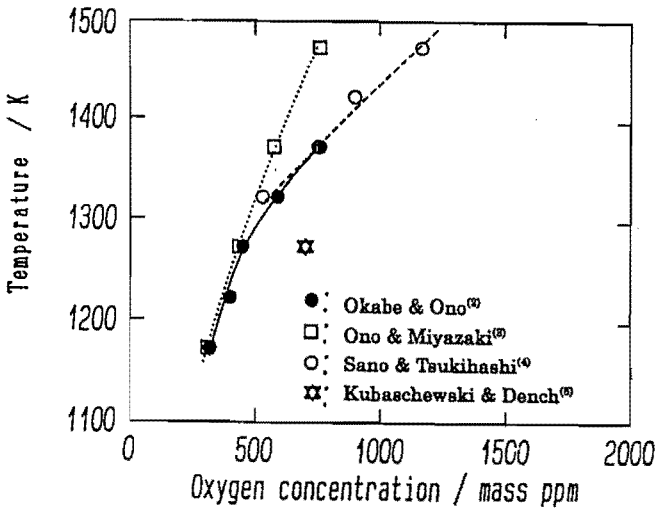

Figure 2: Equilibrium oxygen concentration in Ti under the Ca-CaO coexistence.

In the case of reduction of TiO_2 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 TiO_2 and Ti metal particles made by the reduction with pure Ca only. The oxygen contents are 1000 – 3000 mass ppm widely dispersing.

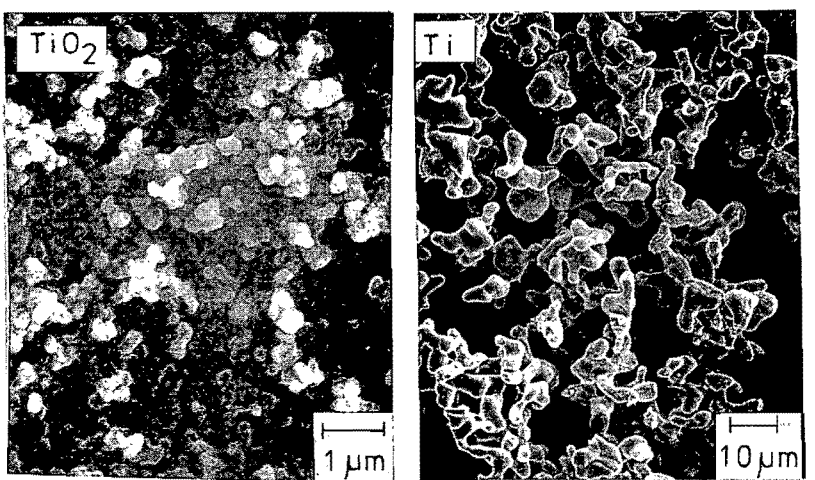

Figure 3: Micrographs showing the row material TiO_2 and the titanium metal reduced by pure Ca.

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

$$N_O = \frac{a_{CaO}}{a_{Ca}} \cdot \frac{1}{\gamma_O} \cdot \exp\left(\frac{\Delta G^O_{CaO}}{RT}\right) \quad (4)$$

where a_{Ca} and a_{CaO} are activities of Ca and CaO, γ_O activity coefficient of oxygen in Ti and $\Delta G^O_{(s)}$ 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 $CaCl_2$ as indicates the solubility of CaO in the liquid $CaCl_2$, 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.

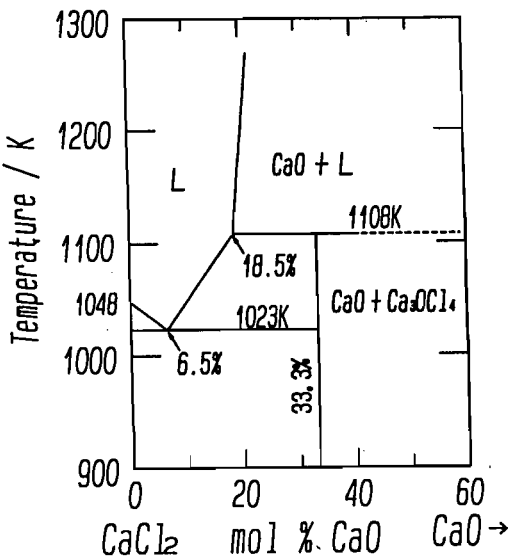

Figure 4: Phase diagram of the $CaCl_2$-CaO system[6].

On the above thermochemical basis, the molten Ca+$CaCl_2$ 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/$CaCl_2$ ratio, holding time and temperature. Further removal of oxygen was carried out by repeating the treatment with the Ca+$CaCl_2$ two-phase flux. Elaboration of extra-low-oxygen titanium are summarized in Table 1.

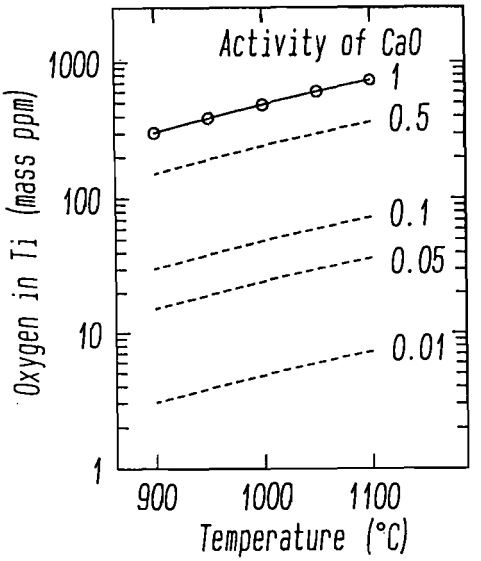

Figure 5: Equilibrium oxygen concentration in β-Ti under Ca existence.

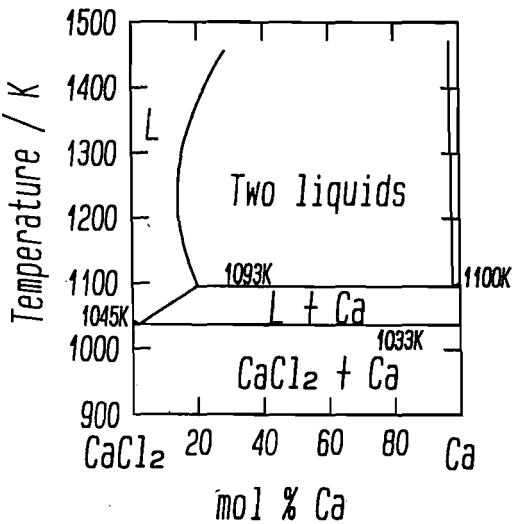

Figure 6: Phase diagram of the $CaCl_2$-Ca system[7].

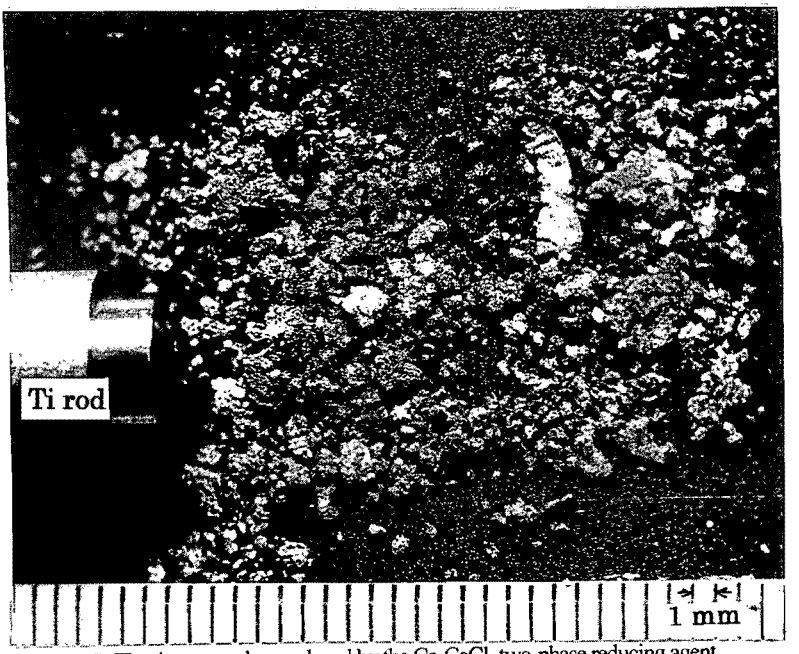

Figure 7: Titanium granules produced by the Ca-$CaCl_2$ two-phase reducing agent.

Table I. Elaboration of extra-low-oxygen titanium[8]

Exp. No.	Conditions	Oxygen content (mass ppm)	
	Flux Temperature Holding time	Initial	After deoxidation
1	Ca-$CaCl_2$ 1173K 220ks <Ca: Liquid>	200 720 1200 1270	30 40, 80 70, 100 60
2	Ca-$CaCl_2$ 1223K 180ks <Ca: Liquid>	200 720 1200	40, 90 30, 80 70, 90
3	Ca-$CaCl_2$ 1273K 86ks <Ca: Liquid>	200 720	70, 90 70, 80
4	Ca-$CaCl_2$ 1273K 86ks <Ca: Vapor>	200 720 1200	60, 70, 70 40 60
5	Ca-$CaCl_2$ 1273K 65ks <Ca: Vapor>	200 720	60, 70 40, 40, 60, 60, 70
6	Ca-$CaCl_2$ 1273K 65ks <Ca: Vapor>	200 720	60, 80 30, 50, 60, 60, 70, 80
7	Ca-$CaCl_2$ 1273K 86ks <Ca: Vapor> [vacuum dried flux]	200 720	70 60, 70, 70, 70
8	Ca-$CaCl_2$ 1273K 86ks <Ca: Vapor> [double deoxidation]	(200) (720)	60, 70 70, 70, 70

Fluidization of reduction medium

The reaction of TiO_2 with Ca is exothermic as the reaction of $MgCl_4$ with Mg:

$$TiO_2 + 2Ca = Ti + 2CaO\,; \qquad \Delta H^\circ_{1200K} = -340.3\ kJ \tag{5}$$

$$TiCl_4 + 2Mg = Ti + 2MgCl_2\,; \qquad \Delta H^\circ_{1200K} = -420.0 \tag{6}$$

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 by-product CaO, the direct contact being obstructed.

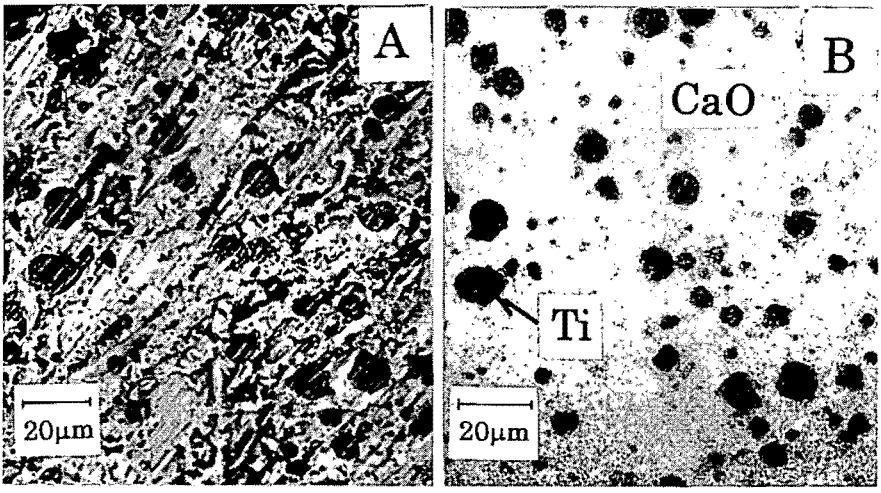

Figure 8: Micrographs showing the products of TiO_2 reduction by pure calcium.
A: As-reduced image. B: Secondary electron image of CaO and Ti particles.

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. Its

Fluidity depends on the $CaCl_2$ content, but addition of large amount of $CaCl_2$ 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 TiO_2 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 $CaCl_2$ as a flux is useful for the diminution of deoxidation limit by the reason that $CaCl_2$ 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 TiO_2 using the $Ca+CaCl_2$ 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 $CaCl_2$ in the feed and its mechanical mixing can realize fluidity .

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