A NEW CONCEPT OF SPONGE TITANIUM PRODUCTION BY CALCIOTHERMIC REDUCTION OF TITANIUM OXIDE IN THE MOLTEN $CaCl_2$

Ryosuke O. Suzuki and Katsutoshi Ono
Dept. Energy Sci. & Techn., Kyoto Univ.,
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501 JAPAN

A new cell concept for calciothermic reduction of titanium dioxide and an ongoing test program for its experimental verification are presented(1). The thermo-chemical background of this concept and a new cell design are described. The reduction system consists in a single cell, where both the reduction reaction and the electrolytic reaction for recovery of reducing agent coexist in the same molten calcium chloride bath, as shown in Fig.1.

Titanium dioxide powder is available from many worldwide sources, and directly top-charged into the molten $CaCl_2$. A few percent calcium dissolves in the molt, as shown in Fig.2, which constitutes the media with a strong reducing power. Sufficiently deoxidized titanium metal deposits agglomerate rapidly and form granular sponge, which sink down to the bottom of the cell.

The reducing agent is *in situ* recovered by electrolysis. Since the process is in continuous operation, the molten salt contains the reduction by-product CaO in solution. Molten $CaCl_2$ has also a relatively large solubility for CaO, so that the $CaCl_2$-CaO-Ca ternary system exhibits a homogeneous liquid region (Fig. 2).

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,

$$TiO_2 + 2\,\underline{Ca}^{+} + 2\,\underline{e}^{-} = Ti + 2\,\underline{Ca}^{2+} + 2\,\underline{O}^{2-} \qquad [1]$$

where $\underline{Ca}^{2+}$, $\underline{Ca}^{+}$, $\underline{O}^{2-}$ and $\underline{e}^{-}$ represent the calcium ions, oxygen ion and electron in solution in the salt, respectively. If TiO_2 particles meet liquid Ca droplets, they are also immediately reduced to metal by the thermochemical reaction

$$TiO_2 + 2\,Ca = Ti + 2\,\underline{Ca}^{2+} + 2\,\underline{O}^{2-} \qquad [2]$$

CaO in the both reactions dissolves into the bath, and it can be converted to $\underline{Ca}^{+}$, liquid Ca and CO_2 gas by electrolysis at temperatures over the melting point of Ca. Between a consumable carbon anode and a cathode both immersed in the bath, a voltage of 3.0V. has been applied, which is higher than the decomposition voltage of CaO (1.66V), but below that of $CaCl_2$ (3.2V). Under these conditions, CO_2 gas is emitted from the carbon anode and no chlorine gas evolves. The electrolytic reaction is described by,

$$\text{At the anode : } \quad C + 2\,\underline{O}^{2-} = CO_2 + 4\,e^{-} \qquad [3]$$

$$\text{At the cathode : } \quad \underline{Ca}^{2+} + e^{-} = \underline{Ca}^{+} \qquad [4]$$

The $\underline{Ca}^{+}$ ion leaves the cathode and migrates in the molten $CaCl_2$ bath, and when the melt is saturated, liquid Ca deposits on the cathode,

$$\text{At the cathode : } \quad \underline{Ca}^{2+} + 2\,\underline{e}^{-} = Ca \qquad [5]$$

$$\underline{Ca}^{+} + e^{-} = Ca \qquad [6]$$

It then detaches from the cathode surface as small calcium droplets. Oxygen in the reduced Ti particles, $[O]_{Ti}$, is removed by,

$$[O]_{Ti} + \underline{Ca}^{+} + \underline{e}^{-} = \underline{Ca}^{2+} + \underline{O}^{2-} \qquad [7]$$

$$[O]_{Ti} + \underline{Ca} = \underline{Ca}^{2+} + \underline{O}^{2-} \qquad [8]$$

The oxygen level attainable with this process depends on the equilibrium ratio of the activity of CaO and Ca in the bath, a_{CaO}/a_{Ca}. When both activities of CaO and Ca are unity, the ultimate oxygen content in Ti, i.e., the thermodynamic equilibrium value, is 347 mass ppm at 1200 K.

Sponge titanium containing 1000 ppm oxygen could be produced within 2 hours. from 10g TiO_2 powder. However, 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,

$$2\,\underline{Ca} + CO_2 = C + 2\,CaO \qquad [9]$$

$$\underline{Ca} + CO = C + CaO \qquad [10]$$

Carbon dust was observed in the upper part of the bath and froze as a crust layer. By analyzing the cell behavior, we believe that the cathode design is the key to solve the matter.

REFERENCES

1. K. Ono and R.O. Suzuki, J. of Metals, Feb. (2002) in press.

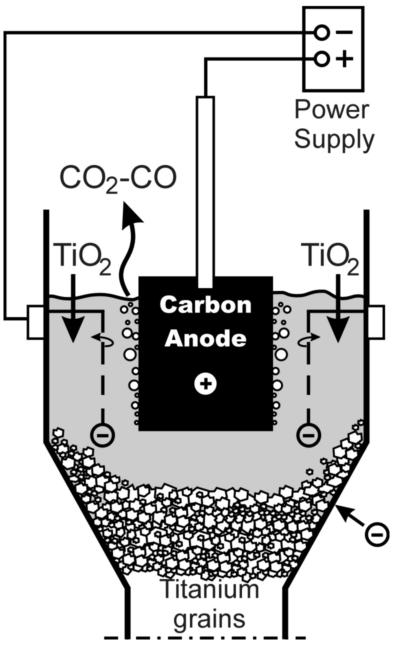

Fig.1 Concept of cell design

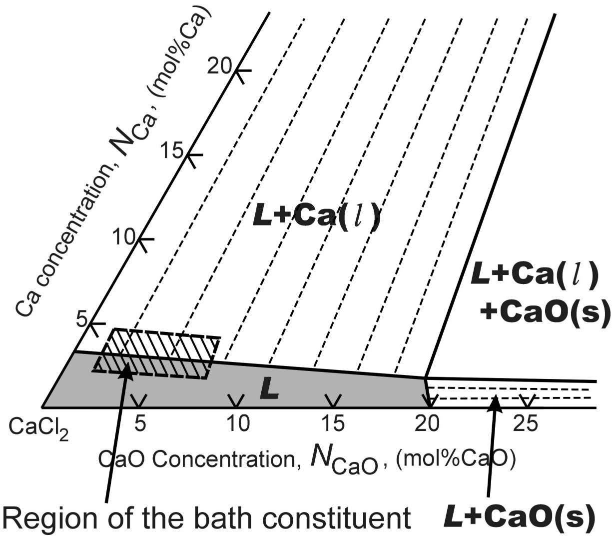

Fig.2 Isothermal cross-section of $CaCl_2$-CaO-Ca system at 1200K.