Carbon Dioxide (CO₂) Released in the Electrochemical Reduction of Titanium Dioxide (TiO₂) to Titanium Metal

Galam Govinda Rajulu¹,², M. Girish Kumar¹, K. Srinivas Rao¹, B. Hari Babu²,* and Chaganti RVS Nagesh¹,5

¹Defence Metallurgical Research Laboratory, Hyderabad, TS, 500058, India
²Department of Chemistry, Acharya Nágarjuna University, Guntur, AP, 522510, India

©2017 The Japan Institute of Metals and Materials

Materials Transactions, Vol. 58, No. 6 (2017) pp. 914 to 920

Studies pertaining to kinetic aspects of the direct electrochemical reduction process of titanium preparation from TiO₂ have not been substantial for determining the conversion time precisely. The solid state reduction process does not permit measuring either the rate of formation of product or the rate of depletion of the feed stock. In this work an attempt has been made to study the applicability of variation of CO₂ (the product gas) in the vent gases of the electrolytic cell to approximate the bulk process kinetics of the process. From the electrolysis current trend, it might be possible to estimate CO₂ profile during the electrolysis time so as to utilize the same for inferring optimal time of the electrochemical reduction process. [doi:10.2320/matertrans.MK201633]

(Received October 14, 2016; Accepted February 23, 2017; Published May 12, 2017)

Keywords: electrochemical reduction, titanium dioxide, solid state conversion, CO₂ in vent gases, reaction time estimation

1. Introduction

Extraction metallurgy of titanium has been very complicated and cumbersome mainly because of its high melting point (∼1663°C) and high chemical reactivity. Especially preparation of titanium metal directly from its widely occurring oxide (TiO₂) by employing all the conventional reduction techniques proved futile because of high stability of the oxide and affinity of the metal towards oxygen. The Kroll process, in which titanium tetrachloride is reduced by magnesium metal, has been the predominant method of titanium extraction. However, since the emergence of the electrochemical reduction process popularly known as FFC Cambridge process¹–³ wherein the metal oxide (TiO₂) is converted into metal through cathodic action, expectations have been high for realizing an alternate cost and energy effective method of preparing titanium metal of required purity. Hence the process has been widely pursued for greater understanding of the process and for scale up to produce the metal in larger batches.

In the electrochemical reduction of TiO₂, the overall conversion of the oxide to metal is described simply by removal of oxygen in ionic form, from the oxide which passes through the conducting electrolyte (molten calcium chloride at about 950°C) to a graphite anode to form CO/CO₂ as per the following:

\[ \text{TiO}_2 + 4e^- = \text{Ti} + 2\text{O}^{2-} \text{(at cathode)} \]  \hspace{1cm} (i)

\[ C + 2\text{O}^{2-} - 4e^- = \text{CO}_2 \text{(at anode)} \]  \hspace{1cm} (ii)

However, the actual mechanism of conversion of TiO₂ to titanium metal appears to be more complex with formation of several sub-oxides of titanium and calcium titanate as intermediate reaction species⁴–⁵. It has been convincingly explained that the calcium metal deposited (due to the electrolysis of CaO dissolved in the CaCl₂ electrolyte), on the cathode (TiO₂) can reduce the oxide into metal through various intermediate titanium suboxides. Lowering of activity of CaO (generated due to calciothermic reduction of oxide) as it dissolves in molten CaCl₂ circumvents the thermodynamic restrictions prevailing in the conventional calco-thermic reduction process in obtaining titanium sufficiently free from oxygen. Alternatively, the reduction process is also explained to be taking place through oxygen ion (generated due to applied DC voltage) transportation from the oxide through the electrolyte to form O/CO/CO₂ at the graphite anode, which is let out through the vent gases of the cell. Under experimental conditions, carbon dioxide is however, the predominant product gas of the overall electrochemical reduction process. Current exercise, aims at understanding the bulk process kinetics in terms of CO₂ release in the electrochemical reduction process. Based on experimental measurements and theoretical predictions on CO₂ content in the vent gases of cell, it is possible to understand the kinetic aspects of the conversion process in various stages of the experiment. Before discussing the results of these efforts, a review of current understanding on various kinetic aspects of the process is brought out in the following.

2. Mechanism and Kinetic Aspects of the Reduction Process

Several investigators have reported works related to the mechanism of the reduction process and tried to relate the influence of various experimental conditions such as type of pre form, applied voltage, current densities, temperature etc. on the mechanism and pathway of metal formation⁶–¹⁰. According to Schwandt and Fray⁹ the reduction of TiO₂ to Ti take place through formation and decomposition of calcium titanate and the conversion process is associated with substantial changes in the microstructure. Similar findings were also reported by Jayashree Mohanty et al¹⁰. Lebdev et al¹¹ discussed about possible mechanism and kinetics of processes occurring at TiO₂ cathode and graphite anode independently in CaCl₂-CaO melt. According to which the CaO concentration in the CaCl₂ melt does play a role on the kinet-
ic aspects of the process. Studies by Alexander et al.\textsuperscript{13}, indicated that the conversion of TiO$_2$ to titanium metal takes place through formation of several sub-oxides of titanium and calcium titanate though formed, can decompose into titanium sub oxide and calcium oxide. It is also said that the formation of calcium titanate can be minimized by the use of highly sintered/less porous TiO$_2$ pre-forms. Dring et al.\textsuperscript{19} dwelled into thermodynamic aspects of Ca-Ti-O-C-Cl system to propose predominance area diagrams for electrochemical reduction of titanium dioxide in molten calcium chloride. Interesting results/suggestions reported by this work include favourable conditions for producing low oxygen titanium metal. According to these studies higher pO$_2$- values in the melt are into thermodynamic aspects of Ca-Ti-O-C-Cl system to proposesubstitutes for TiO$_2$ pre-cursers on the rate of the electrochemical reduction process. Bhagat et al.\textsuperscript{10} conducted \textit{in situ} synchrotron diffraction to propose electrochemical pathway of TiO$_2$ re-
duction and discussed the kinetic aspects of oxygen ion generation at cathode and formation of CaO and other compounds. Hualin Chen et al.\textsuperscript{19} studied influence of graphite anode area on the oxidation kinetics of O$_2$ at the anode and suggested that a low anode current density is beneficial for reducing energy consumption. An elaborate review by Mohandas\textsuperscript{20} brings out summary of various developments that have been taken place over the years on understanding of the electrochemical conversion of oxides to metal in general.

From the above description, it is pertinent to state that simultaneous occurrence of various cathodic and anodic cell reactions and a set of chemical reactions associated with the species TiO$_2$, Ti, Ca, C CaO and CO/CO$_2$ would determine the bulk kinetics of the electrochemical reduction process of TiO$_2$ to titanium metal. As already presented earlier\textsuperscript{21}, the bulk kinetics of the reduction process can be determined from the rate constants of all the associated kinetic steps such as (i) oxygen ion generation at cathode and its transportation to cathode/electrolyte interface, (ii) transportation of oxygen ion through electrolyte to anode/electrolyte interface and (iii) evolution of O/CO/CO$_2$ at the anode. These kinetic steps however, additionally might depend on aspects such as dissolution kinetics of CaO in CaCl$_2$, solubility of calcium in CaCl$_2$, viscosity related surface flows, parameters related to gas evolution at the anode, solid state phase/crystalline changes in the cathode feed stock etc. In the earlier work\textsuperscript{21} an attempt has also been made to determine time of conversion of the oxide granule under an assumption that oxygen ion mobility from the bulk oxide to oxide/electrolyte interface as the predominant and rate controlling kinetic step.

As reported earlier\textsuperscript{21}, the overall reaction of conversion of TiO$_2$ to Ti can be expressed in terms of a set of thermodynamically possible chemical reactions involving sub-oxides of titanium as given below:

\begin{alignat}{1}
8\text{TiO}_2 + C & = 2\text{Ti}_4\text{O}_7 + \text{CO}_2 \\
\Delta G_{1200K}^\circ & = -863178\text{ J/mol} \tag{iii}
\end{alignat}

\begin{alignat}{1}
16\text{Ti}_4\text{O}_7 + C + 2\text{Ti} & = 22\text{Ti}_2\text{O}_5 + \text{CO}_2 \\
\Delta G_{1200K}^\circ & = -1124570\text{ J/mol} \tag{iv}
\end{alignat}

\begin{alignat}{1}
3\text{Ti}_2\text{O}_3 + C + \text{Ti} & = 7\text{TiO} + \text{CO}_2 \\
\Delta G_{1200K}^\circ & = -843871\text{ J/mol} \tag{v}
\end{alignat}

\begin{alignat}{1}
2\text{TiO} + C + \text{Ti} & = 3\text{Ti} + \text{CO}_2 \\
\Delta G_{1200K}^\circ & = -525832\text{ J/mol} \tag{vi}
\end{alignat}

Chemical reactions associated with calcium titanate might not be considered in representing the overall conversion process as it can exist only as reaction intermediate and is also expected to dissociate into titanium sub-oxide and CaO.

Thus the overall electrochemical reduction process can be represented as

\[ \text{TiO}_2(\text{in contact with CaCl}_2) + C(\text{graphite anode in contact with CaCl}_2) = \text{T}_3(\text{left behind in the starting material}) + \text{CO}_2(\text{anode gas}) \]

Since it is practically difficult to monitor the chemical changes taking place in the oxide during the process so as to correlate the experimental conditions with bulk process kinetics, study of CO$_2$ generation during the course of reduction process shall be useful in understanding the kinetic aspects of the overall conversion process. In this work an attempt has been made to understand kinetic aspects of the process with experimentally measured values of CO$_2$ content in the vent gases of the electrolytic cell during the course of reduction process. Measurements of CO$_2$ in the out gasses could be made at selected time intervals of the process in two different scales of operation viz. 500–1000 g cell and 5–8 kg cell.

3. Experimental

Experimental work on electrochemical reduction of titanium dioxide to titanium metal has been pursued on different scales of operation so as to develop improved understanding of the process. After establishing the feasibility of the process on 500–1000 g scale, scaled up experimentation on 5–8 kg per batch is continuing. Detailed description of experimental procedures pertaining to establishment of feasibility of the process from gram scale to 1000 gram scale is available elsewhere\textsuperscript{23–25}. In all the experimental works Merck make high purity titanium dioxide is used. Experimental set up employed for both the scales of operation are similar and comprise a cathode basket made of AISI 304 perforated sheet in which sintered TiO$_2$ granules are loaded. Electrolytic grade graphite plates (rectangular/curved shaped) are used as anode. The electrode lead rods are used both for holding the cathode basket and graphite anode plates in specified positions in the cell as well as for connecting to DC power source. Typical experimental procedure of 5–8 kg/batch experimentation includes preparation of titanium oxide granules in the size range of 8–12 mm which are sintered at 1000°C for 24 hours before taken into the cathodic basket which takes the
dimensions of $250 \times 450 \times 100$ mm. As shown in Fig. 1 (a), graphite plates of $250 \times 400 \times 15$ mm thick placed on either side of the cathode basket form anode and the cathode-anode assembly is placed inside a stainless steel reactor ($450$ mm ID $\times 1300$ mm height $\times 12$ mm thick), with the help of stainless steel lead rods. These are connected to a DC power source for applying DC voltage during the electrolysis. A $40$ kW three zone electrical resistance furnace is employed to provide heating requirements to heat the electrolyte and electrodes assembly along with stainless steel reactor to a temperature of $970^\circ$C and maintain the temperature all through the experimental period. Initially about $500$ kg of laboratory grade anhydrous calcium chloride is taken into the reactor and melted under argon gas atmosphere and then cooled to room temperature. At room temperature, after placing the electrodes assembly, the reactor is closed with a stainless steel lid that has necessary openings and nozzles for (i) taking out the electrode lead rods, (ii) for evacuation of the reactor system, (iii) argon gas supply and (iv) for the exit of vent gases. Pressure tightness of the assembly is achieved with the use of appropriate high temperature gaskets between the reactor flange and the lid flange (Fig. 1 (b)). The annular gap between the electrode lead rods and nozzles are filled with high temperature seals so as to ensure pressure tightness even at
the higher temperatures experienced during the experimentation. The system is evacuated with the help of an oil rotary vacuum pump to 10–15 mm of Hg and filled back with argon gas to about 2 psig. The evacuation and filling back with argon gas is repeated to ensure withdrawal of residual air (up to a lowest limit) that initially present in the system.

Before each experiment, samples of calcium chloride are analyzed for CaO content by titration with dilute acid and the data is recorded. As a general practice voltage drops associated with the given cell configuration are experimentally determined under ‘no load’ conditions (basket without TiO\textsubscript{2} granules) prior to the actual reduction experiment. Accordingly the experimental procedure pertaining to DC voltage application is evolved. This helps in understanding the applicable voltage window (avoiding CaCl\textsubscript{2} decomposition and chlorine generation) for the given experiment.

The experiment begins with the heating of the set up to a temperature of 970°C as measured at the reactor outer wall, under argon gas cover. After ensuring an electrolyte temperature of 930°C, application of DC voltage is initiated and increased stepwise from 2.0 to 4.5 V (Table 1). During the entire electrolysis period argon gas purge into the cell system is continued at a rate of 100–200 cc/min. The exit gases let out during the experiment are led through a copper/rubber tube to a CO\textsubscript{2} detection and monitoring system. A carbon dioxide transmitter cum infrared sensor, ADT-D3 1164, Intertek, Germany make of (i) 0–5000 and (ii) 0–50000 ppm range were employed for measuring CO\textsubscript{2} content in the exit gases at selected points of time during the experimentation (The higher range detector was used in the 5–8 kg experiment whereas the lower range one is used in the experiments on 5000–10000 g scale set up). Otherwise the vent gases pass through a set of baryta (barium hydroxide solution) bubblers which helps in detecting CO\textsubscript{2} in the gases qualitatively and enables monitoring of the same as formation of white barium carbonate precipitate indicates the presence of CO\textsubscript{2} in the gases. Table 2 presents typical operating conditions and important process parameters recorded during the course of electrolysis time. Figure 2 shows a photograph of the cathode basket loaded with the oxide granules employed in the experimentation.

After the electrolysis experiment, the entire assembly is cooled to room temperature under argon gas cover. Then the cathode basket is carefully taken out, examined and after visual inspection of the same, it is taken up for further handling. The granules are taken out from the cathode basket and are subjected to a series of washings with water, dilute acetic acid and dilute HCl solutions for completely removing the adhered electrolyte and other species. The anode after visual inspection is separately taken away and water washed. In every experiment new graphite plates are used as anode.

4. Prediction of CO\textsubscript{2} Profiles

As per the understanding of the mechanism of conversion of TiO\textsubscript{2} to titanium metal, the overall reduction process is described (as mentioned before) by eqs. (i) and (ii) and practically CO\textsubscript{2} can be considered as the predominant products gas. The essential requirement for CO\textsubscript{2} evolution at anode is oxygen ion transportation from cathode through molten calcium chloride which is governed by applied voltage and transport properties of the associated species. Electrolysis current in a way represents the rate of transportation of oxygen ions to anode and hence the DC current profile, recorded during the electrolysis time can be applied to infer the rate of CO\textsubscript{2} formation at the anode. However, CO\textsubscript{2} formation cannot be in proportion to the magnitude of electrolysis current as there can be many electron transfer subsidiary reactions that are not associated with the conversion of the oxide to metal/CO\textsubscript{2} formation. Still, the electrolysis current profile during the reaction time is expected to describe the trend of CO\textsubscript{2} formation. In a simple and preliminary approach, the electrolysis current variation is correlated to rate of formation of CO\textsubscript{2} and attempts have been made to predict CO\textsubscript{2} variation in the vent gases and compare with the experimental measurements.

5. Results & Discussion

It is generally observed that during the electrochemical reduction process, as the voltage is applied and increased say from 2.0 to 4.5 volts, DC current raises from a lower value to

---

**Table 1** Variation of applied DC voltage in the experiments.

<table>
<thead>
<tr>
<th>DC voltage (V)</th>
<th>Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2–4</td>
</tr>
<tr>
<td>2.6</td>
<td>4–6</td>
</tr>
<tr>
<td>2.8</td>
<td>4–6</td>
</tr>
<tr>
<td>3.2</td>
<td>4–6</td>
</tr>
<tr>
<td>3.8</td>
<td>6–10</td>
</tr>
<tr>
<td>4.5</td>
<td>Remaining period of experiment</td>
</tr>
</tbody>
</table>

---

**Table 2** Typical experimental operating conditions and important process parameters in a 5–8 kg experiment.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weight of TiO\textsubscript{2}</td>
<td>10–14 kg</td>
</tr>
<tr>
<td>2</td>
<td>Level of molten electrolyte</td>
<td>= 650 mm</td>
</tr>
<tr>
<td>3</td>
<td>DC voltage</td>
<td>2.5–5.2 V</td>
</tr>
<tr>
<td>4</td>
<td>Electrolysis temperature</td>
<td>960°C</td>
</tr>
<tr>
<td>5</td>
<td>Inert gas pressure in the cell</td>
<td>1.1 atm</td>
</tr>
<tr>
<td>6</td>
<td>Free (gas) volume in the cell</td>
<td>0.1 m\textsuperscript{3}</td>
</tr>
</tbody>
</table>
a higher value which continues predominantly over a period of time and then the current gradually decreases. As can be seen in Fig. 3 the DC current – time profile broadly consists of three phases viz initial phase during which current increases with voltage and in the second phase higher current persists at a constant applied higher voltage and this is followed by final phase during which current decreases to a lower value even at the highest applied voltage. This kind of current variation can be understood to represent the pattern of oxygen ion transportation from the cathode to graphite anode through the electrolyte resulting in the formation of CO2 which is detected in the exit gases. In Fig 4 (a) and (b), measured values of CO2 content in the exit gases at various selected points of electrolysis time are presented. In the first part of the experiment after reaching the applied higher cell voltage, CO2 content above 5000 ppm in the case of 500–1000 g experiment and above 50000 ppm in the case of 5–8 kg experiment were observed. In the second half of the experiment, the CO2 content is seen gradually reducing from 5000 ppm to as low as 300 ppm in the case of small scale experiment and from 50000 ppm to about 500 ppm in the case of 5–8 kg experiment. In both the scales of operation the last/terminal phase of electrolysis is denoted by a lower and constant CO2 value. It is interesting to note that the variation of CO2 content in the exit gases, with time during the experiment follows the trend similar to the DC current profile as can be seen in Fig. 5. At a given time in the midst of the experiment, it is seen that the CO2 content is increasing with the applied voltage as can be seen from Table 3. This indicates that the overall conversion rate could be increasing with increased voltage within the applicable voltage range.

The observations made on the conditions of electrodes after the experiment are highly informative. In Fig. 6 (a) and (b) photographs of graphite anode plates before and after the experiment are shown. The area of the anode immersed in the electrolyte is seen to be significantly corroded. The regions of the anode that are at the gas-electrolyte interface are generally seen to be highly corroded. The gas-electrolyte interface at the anode is apparently experiencing erosion due to intense gas evolution during the electrolysis time as was also observed and reported by Srimaha Vishnu et al\textsuperscript{26}.

<table>
<thead>
<tr>
<th>Applied DC voltage (V)</th>
<th>Measured CO2 content in the exit gases (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>2630</td>
</tr>
<tr>
<td>3.5</td>
<td>4130</td>
</tr>
<tr>
<td>3.8</td>
<td>5120</td>
</tr>
<tr>
<td>4.0</td>
<td>5310</td>
</tr>
<tr>
<td>4.2</td>
<td>6260</td>
</tr>
</tbody>
</table>

Fig. 3  Variation of electrolysis current with time (5–8 kg scale).

Fig. 4  (a): Measured CO2 content in the vent gases of 1 kg experiment, (b): Measured CO2 content in the vent gases of 5–8 kg experiment.

Fig. 5  Variation of Electrolysis current and CO2 in vent gases with time (5–8 kg batch).
As already brought out, the similar co-relative trends observed with the CO₂ – time profile and DC current – time profile, could be used for estimating CO₂ in the vent gases by simpler linear best fit methods. From the experimental data on DC current variation with time collected from different experiments, the average rate of CO₂ generation could be determined. In Fig. 7, predicted CO₂ content in the exit gases during the electrolysis period is compared with experimentally measured values. The predictions in general are found to be reasonably well though at times, the predicted values differ from the measured values significantly. The significant difference in predicted value and actual value is understandable because often the electrolysis current is masked by current spent in the side reactions such as calcium titanate formation process cycle time.

Acknowledgements

Authors wish to express their deep sense of gratitude to Dr. S.V. Kamat, Outstanding Scientist & Director, DMRL for the constant support and encouragement extended to this developmental activity and also for according permission to publish this technical paper. Authors also wish to acknowledge DRDO for providing funds to this R&D work on development of the electrochemical reduction process for titanium extraction.

REFERENCES

21) Ch. R.V.S. Nagesh extended abstracts, 64th Annual Technical Meeting, Indian Institute of Metals, Bangalore, (India): 2010