Compatiblity of TiO\(_2\) with a CaO–CaCl\(_2\) Melt

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Abstract—Interaction of TiO\(_2\) with a CaO–CaCl\(_2\) melt was studied to determine whether electrolytic production of titanium from oxide raw materials is possible.

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Titanium is among the most widely occurring metals and possesses a unique combination of properties. Its wide and efficient use in various fields of national economy is hindered by the high cost of the metal, which is due to the multistage and batch nature of the Kroll process employed in modern titanium industry. Numerous attempts to develop a continuous electrolytic technique for manufacture of titanium from titanium tetrachloride have failed to produce a widely used industrial technique because of the difficulties associated with the polyvalent nature of the metal, its high vapor pressure, and susceptibility of the tetrachloride to hydrolysis.

In recent years, a considerable interest has been observed in the possibility of electrolytic production of titanium from oxide raw materials. It has been found that understoichiometric titanium dioxide has high electrical conductivity and can serve as a cathode both in reduction of titanium oxides to the metal and in removal of dissolved oxygen from titanium.

It was suggested by Chen et al. [1, 2] to perform direct electrochemical reduction of TiO\(_2\) to titanium in molten CaCl\(_2\), which is the so-called FFC process. It was shown on laboratory scale that the reduction reaction occurs at 950°C on a cathode made of solid TiO\(_2\), with oxygen anions oxidized on a graphite anode to give CO\(_2\). Pure calcium chloride CaCl\(_2\) was chosen as a molten salt electrode because of the high solubility of calcium oxide in this compound.

Ono and Suzuki [3] studied the high-temperature calcium reduction of TiO\(_2\) and developed a process for continuous production of titanium. The electrolysis was performed at a voltage that was higher than the decomposition voltage of CaO, but lower than that of CaCl\(_2\). Ca\(^{2+}\) ions were reduced at the cathode to Ca; oxygen evolved at the anode reacted with carbon to give CO and CO\(_2\). A cell for continuous manufacture of titanium was developed and the possibility of using inert anode was discussed.

In [4], a TiO\(_2\) powder or a preform was placed in a holder, and a Ca + 18 wt % Ni alloy, onto the electrolyzer bottom. The reduction was carried out without a current, with the electrochemical circuit formed between the TiO\(_2\) cathode and the calcium alloy. In the process, TiO\(_2\) was reduced and calcium ions were deposited at the anode. The alloy was replenished with calcium at regular intervals of time.

It seems that the FFC process is the best developed and ready for implementation [1, 2, 5, 6].

In view of the possible use of CaO as the main component in electrolytic reduction of TiO\(_2\), it is necessary to substantiate the optimal CaO content and to analyze the oxidation kinetics of O\(^{2-}\) ions in relation to temperature and CaO concentration. It remains unclear whether TiO\(_2\) is compatible with the CaCl\(_2–\)CaO melt.

The rich experience of the electrometallurgy of aluminum indicates that the main reason for a decrease in the current efficiency is the reverse reaction of the electrolysis products (aluminum and CO\(_2\)), which may lead to contamination of the metal by carbon via formation of carbides. This issue has not been studied for the materials under consideration. Possibly, it is necessary to choose a stable porous diaphragm for separating the cathode and anode spaces in electrolysis. The aim of this study was to elucidate these issues.
Table 1. Gibbs energy of formation of calcium and titanium oxides and chlorides

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\Delta G^0), cal mol(^{-1}), at indicated (T), K, according to indicated reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>1100</td>
</tr>
<tr>
<td>CaO</td>
<td>124700</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>152800</td>
</tr>
<tr>
<td>TiO</td>
<td>98900</td>
</tr>
<tr>
<td>Ti(_2)O(_3)</td>
<td>290600</td>
</tr>
<tr>
<td>Ti(_3)O(_5)</td>
<td>471050</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>178000</td>
</tr>
<tr>
<td>TiCl(_2)</td>
<td>85100</td>
</tr>
<tr>
<td>TiCl(_3)</td>
<td>115600</td>
</tr>
<tr>
<td>TiCl(_4)</td>
<td>150050</td>
</tr>
</tbody>
</table>

The previously published reports have virtually disregarded the mechanism, and presented no results of analysis, of the reaction between TiO\(_2\) of varied origin with CaCl\(_2\)-CaO melts of various compositions. At the same time, the possible formation of TiOCl\(_2\), CaO-TiO\(_2\), and 2CaO-TiO\(_2\) can strongly affect the parameters and results of the electrolysis.

The solubility of TiO\(_2\) in molten CaCl\(_2\) is low, and that of metallic titanium reaches 0.5 wt% at 850°C [7].

The authors of [8] attributed the high residual currents in cathodic deoxidation of titanium in molten calcium chloride to the noticeable solubility of lower titanium oxides in CaCl\(_2\).

It has been suggested [9], in an analysis of voltammetric data for oxidized titanium in a molten calcium chloride, that fast oxidation of oxygen ions from the oxide phase causes supersaturation of the CaCl\(_2\) melt in CaO, which can react with partly reduced titanium oxide to give titanates of variable composition. The suggestions made in the studies mentioned above have not been directly confirmed.

To elucidate these issues, we made a thermodynamic assessment of the possibility of occurrence of various reactions in the system TiO\(_2\)-CaO-CaCl\(_2\) and carried out chemical and X-ray phase analyses of the reaction products.

Table 1 lists the standard Gibbs energy of formation of calcium and titanium oxides and chlorides at 1100, 1200, and 1300 K according to [10, 11].

The values recommended by the authors are in reasonable agreement. To determine whether a reaction between titanium oxides and molten CaCl\(_2\) is possible, we calculated, using the data in Table 1, the Gibbs energy of the corresponding reactions, \(\Delta G^0\). The results of these calculations for the temperatures of 1100, 1200, and 1300 K are listed in Table 2.

According to two references, the calculated results virtually coincide. The high positive values of \(\Delta G^0\) indicate that there is no interaction in the systems under standard conditions. Judging from the decreasing value of \(\Delta G^0\), calculated per gram-atom of titanium, the probability of a reaction with the CaCl\(_2\) melt increases in the order TiO\(_2\), Ti\(_3\)O\(_5\), Ti\(_2\)O\(_3\), and TiO, in qualitative agreement with the suggestions made in [8].

In the system under consideration, perovskite CaTiO\(_3\) can be formed in accordance with the equation

\[
3\text{TiO}_2 + 2\text{CaCl}_2 = 2\text{CaTiO}_3 + \text{TiCl}_4. \tag{1}
\]

Table 3 list thermodynamic parameters of the substances involved in reaction (1), according to the reference book [12].

The enthalpy of reaction (1) can be found using the equation

\[
\Delta H^0_r = 2\Delta H^0_{\text{CaTiO}_3,298} + \Delta H^0_{\text{TiCl}_4,298} - 3\Delta H^0_{\text{TiO}_2,298} - 2\Delta H^0_{\text{CaCl}_2,298} = 2 \times 1661.7 - 805.96 + 3 \times 944 + 2 \times 797.17 = 297 \text{ kJ mol}^{-1}. \tag{2}
\]

The value of \(\Delta H^0_r\) at a temperature \(T\) is given by

\[
\Delta H^0_r = \Delta H^0_{298} + \int_{298}^{T} \Delta C_p \, dT. \tag{3}
\]