Electrowinning Molten Titanium from Titanium Dioxide

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CSIR
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Conceptual Process

\[ \text{Graphite Anode} \quad \text{CO} \quad \text{TiO}_2 \]

\[ + \]

\[ \text{Molten Salt} \quad \text{Molten Ti} \]

\[ - \]

\[ \text{Ti}^{4+} + 4e^- \leftrightarrow \text{Ti} \]

\[ \text{O}^2- + \text{C} \leftrightarrow \text{CO(g)} + 2e^- \]

\[ \text{TiO}_2 + 2\text{C} \leftrightarrow \text{Ti} + 2\text{CO(g)} \]
### Rationale – Titanium Cost Build-up

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost</th>
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</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>$0.27/kg Ti sponge</td>
</tr>
<tr>
<td>Titanium slag</td>
<td>$0.75/kg Ti Sponge</td>
</tr>
<tr>
<td>TiCl₄ and TiO₂</td>
<td>$3.10/kg Ti Sponge</td>
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<tr>
<td>Ti Sponge raw materials costs</td>
<td>$5.50/kg Ti Sponge</td>
</tr>
<tr>
<td>Total Ti Sponge cost</td>
<td>$9-$11/kg Ti Sponge</td>
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<tr>
<td>Ti ingot</td>
<td>$15-17/kg Ti</td>
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<tr>
<td>Aluminium</td>
<td>$1.7/kg Al</td>
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Rationale - Advantages

- Feed: Safe, transportable, alternative supplies (sulphate and chloride routes), decoupled from TiCl₄ production
- Direct use of electricity instead of firstly making Mg or Na and recycling of MgCl₂ or NaCl as in Kroll and Hunter processes with recycling of these
- Direct production of ingot or equivalent instead of making sponge first
- Continuous instead of batch operation
- Fewer process steps
- Scale-up by addition of more pots
Problems

- High temperature (1670 to 1800°C)
- Limited electrolyte choices
  - Low vapour pressure
  - Lower density than titanium
  - Inert towards titanium
  - $\text{CaF}_2$, $\text{SrF}_2$, $\text{BaF}_2$ and $\text{YF}_3$
- High affinity of Ti for $\text{O}_2$, C and $\text{N}_2$ and stringent specifications severely limits the choice of suitable materials of construction
- Melting point of Ti is about 300 to 400°C higher than suitable electrolytes. Complicates the use of protective freeze linings
- Choice of anode – Propensity of graphite for C contamination
- 4 Different oxidation states of titanium giving rise to different oxides with different physical and chemical properties and also affecting current efficiencies
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**Apparatus**

- Graphite anode
- Tungsten/rhenium thermocouple
- Electrolyte \((\text{CaF}_2/\text{TiO}_2)\)
- Optical Pyrometer
- Alumina
- Insulation board
- Carbon element
- Graphite Tube
- Graphite stand
- Electrical Insulation
- Molybdenum
- Cell lining
- Alumina tube insulation sleeve
- High temperature insulation material
- Graphite anode
- Tungsten/rhenium thermocouple
- Graphite anode
- Electrolyte \((\text{CaF}_2/\text{TiO}_2)\)
- Graphite tube
- Argon gas
- DC power supply
- Cathode
- Anode
- Alumina tube insulation sleeve
- Carbon Insulating board
- Carbon Insulating board
- Electrical Insulation
- Graphite crucible
Typical Contents of Cell after Experiment
Evidence of Gas Blanket
TiO Interspersed in CaF$_2$
Limited Evidence of Coalescence
Typical XRD
Titanium Oxygen Phase Diagram
Conclusions

- Conceptually, electrolytic production of molten titanium from TiO$_2$ is very attractive.
- The process is hampered by many engineering problems that might be overcome.
- Fundamental process problems that must be overcome before scaling up the process are:
  - Prevention of carbon contamination
  - Termination of the electrolysis reaction when deoxidising TiO

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