THE PRODUCTION OF LIQUID TITANIUM BY MOLTEN OXIDE ELECTROLYSIS

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ELECTROLYTIC PRODUCTION OF TITANIUM

“It might, however, be fair to say, that titanium will be made competitively by fusion electrolysis within the next 5 to 10 years”

W. J. Kroll-1959 at American Institute of Mining, Metallurgy & Petroleum Engineers
ADVANTAGES OF HIGH TEMPERATURE ELECTROLYSIS

- Production of molten titanium results in complete physical separation of metal and electrolyte
- Electrolysis is continuous in contrast to batch nature metallothermic reduction
- Possibility of major cost reductions
ELECTROLYTIC REDUCTION OF TiO$_2$ IN OXIDE MELTS

- direct use of beneficiated ores
  $\Rightarrow$ avoiding halide metallurgy
  $\Rightarrow$ environmental advantages

- higher solubility of TiO$_2$ $\Rightarrow$ higher throughput

- possibility of
  \[ 2O^- \rightarrow O_2 + 2e^- \] on an inert anode
MATERIALS CHALLENGES IN ULTRA-HIGH-TEMPERATURE ELECTROCHEMISTRY

special conditions:
- high melting point of titanium (1675°C)
- aggressive solubilizing power of oxide melts

special needs:
- chemical and electrochemical stability
- electronic conductivity
HOST ELECTROLYTE

• Low melting temperature
• Wide potential window
• Good ionic conductivity
• Electronically insulating
• Capable of dissolving TiO$_2$

Al$_2$O$_3$-aO-MgO
EMF SERIES AT 1700°C(V)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>1.53</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.80</td>
</tr>
<tr>
<td>MgO</td>
<td>1.98</td>
</tr>
<tr>
<td>CaO</td>
<td>2.18</td>
</tr>
</tbody>
</table>
EXPERIMENTAL SETUP

Reference

WE

CE

Gas Outlet/Inlet

Crucible

Molten Electrolyte
Learn to crawl before you learn to run

- D.R. Sadoway
CYCLIC VOLTAMMETRY AT 1550 °C

WE: Mo
RE: Ti
CE: Mo

Ti deposition

Ti⁴⁺ + 4e → Tiₐ

Ti stripping
CYCLIC VOLTAMMETRY OF THE ELECTROLYTE

WE: Mo
RE: Ti
CE: Mo
CYCLIC VOLTAMMETRY AT 1700 °C

WE: Mo
RE: Mo
CE: Mo

Ti^{4+} + 4e \rightarrow Ti_{(l)}
ELECTROLYTIC PRODUCTION OF SOLID TITANIUM

Cathode: Mo
Anode: C
Current Density ~ 1A/cm²
ELECTROLYTIC PRODUCTION OF LIQUID TITANIUM

Cathode: Mo
Anode: C
Current Density $\sim 1 \text{ A/cm}^2$
XRD ANALYSIS
SUMMARY

• cyclic voltammetry investigations at white heat
• electrolysis of TiO$_2$ in oxide solvent melt produces metallic Ti
• current densities as high as $\sim 5$ A/cm$^2$ observed
THE JOURNEY TO ULTRA-HIGH TEMPERATURE

magnesia tube

lanthanum chromite heating element

alumina crucible

carbon crucible