Direct Electrochemical Production of Titanium
Thermodynamics- and electrochemistry-based metallurgy

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3rd Reactive Metals Workshop
Acknowledgements

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- SINTEF
- Norsk Hydro
Alf Bjørseth, founder of REC
History of Norsk Titanium

- **December 2004**: founded by Alf Bjørseth (former research director - Norsk Hydro and founder of REC).
- Norsk Titanium AS is 100% owned by Scatec AS.
- **Medio 2005**: Discussions with British Titanium to sub-sub-license FFC in Norway
  - No agreement could be reached
- **June 2005**: Contract signed with Hydro Research Centre to develop the De-Ox Process for commercial production of titanium.
- **February 2006**: Patent applications for NTi’s De-Ox Process using inert anodes.
Pictures of titanium applications

PRIVATE SECTOR:

AIRCRAFTS:

MILITARY SECTOR:
Alternative Titanium Technology

Direct reduction of (blended) oxide feedstock may be an alternative metal production route.

Electrolysis using molten alkali earth halide electrolytes

\[ \text{TiO}_2 (\text{+MO}) \rightarrow \text{Ti-M} + \text{O}_2 \]
NTi Metals AS – Simplified De-Ox Process

Cathode

\[ \text{Ca}^{2+} + 2e \rightarrow \text{Ca} \]

\[ \text{Ca} + \text{TiO}_2 \rightarrow \text{Ti} + \text{CaO} \]

Inert Anode

\[ \text{CaO} \rightarrow \text{Ca}^{2+} + \frac{1}{2}\text{O}_2(g) \]

Molten salt electrolyte
De-Ox Experimental Setup

2 cells - operable in parallel

Testing electrodes – both cathodes and anodes

Online current efficiency monitoring

Off-gas monitoring

Side-lining tests

Electrolyte composition analyses

Raw-material feeding tests

Refractory materials for casting furnaces, tools etc.

Local and remote experiment control and monitoring
Overview of efforts

● Cathodic studies
  - Reduction pathway
  - Kinetics
  - Optimisation of precursor composition/morphology

● Alloy production
  - Process capabilities: alloys (new and complex), composites
  - Changes to reduction rate
  - Modified/novel microstructures

● Inert anode development
  - Thermodynamic considerations
  - Electrical properties
  - Solubility measurements
  - Electrolysis performance
Success: Cathodic Studies – TiO$_2$ Films

CaCl$_2$-NaCl eutectic w/ 1 wt% CaO, 800 °C

High cathodic currents on bare W electrode $\rightarrow$ indicative of Ca formation at $a_{\text{Ca}} < 1$

Absence of C2 in reverse scan due to insufficiently positive final potentials

Weak shift in peak potentials with increasing sweep rate

![Graph showing cathodic studies](image-url)
Success: Cathodic Studies – TiO$_2$ Films

C4: $D_L = 2.5 \times 10^{-8}$ cm$^2$·s$^{-1}$
C3: $D_L = 1.5 \times 10^{-7}$ cm$^2$·s$^{-1}$

C2$: D_L = 8.8 \times 10^{-8}$ cm$^2$·s$^{-1}$
C2: $D_L = 8.3 \times 10^{-7}$ cm$^2$·s$^{-1}$
Success: Complex Titanium Alloy (Ti 10V-2Fe-3Al)
Success: Novel titanium alloy

Ti - 10W

Impossible to produce via Kroll method

Uses in bio-medical applications

Diffusion of oxygen in $\beta$ is about 1-2 orders of magnitude higher than in $\alpha$
Setback: Carbon contamination at cathode

- 1-2 wt% carbon is enough to make the electrolyte “sludgy”.  
- Carbon can be burned off by purging air through the electrolyte.  
- Need to shield graphite to prevent excessive anode consumption.  
- Carbon anode is not well suited.

\[
\text{CO}_3^{2-} + 4e^- \rightarrow C + 3\text{O}^{2-}
\]
Setback: C and Ca problems

- Both C and Ca accumulate under conditions needed to produce titanium
  - C due to carbonate reduction from reaction of CO₂ with CaO
  - Ca due to the high solubility and negative potentials to deoxidize Ti
Challenges: Lack of prior art
Success?: Oxygen evolving "inert" anode

High background currents
Nucleation loops at reversing potential

Oxygen evolution peak

Anode chlorination?
Due to low $a_{\text{CaO}}$

- Cl₂/Cl⁻ @ 0mV
- MO₂ + Cl₂ = MOCl₂ + 1/2 O₂ @ -83mV
- CaMO₃ + Cl₂ = MO₂ + 1/2 O₂ + CaCl₂ @ -246mV
- $1/2$ MO₂ + Cl₂ = 1/2 O₂ + 1/2 MCl₄ @ +39mV
- O₂/O²⁻ @ -354mV, $a_{\text{CaO}} = 0.01$
- O₂/O²⁻ @ -460mV, $a_{\text{CaO}} = 0.1$
- O₂/O²⁻ @ -566mV, $a_{\text{CaO}} = 1$
- M⁴⁺/M²⁺ @ -680mV
Conclusions and Further Work

- Development of inert anodes is necessary prerequisite to commercialisation
- Interaction between operability and anode/cathode materials stability is critical
- Ca formation at activities less than unity can consume high currents and effect titanium reduction

Further work…

**Anodic process:**
Characterise the change in composition/morphology during operation

**Cathodic process:**
Understand the ingress/egress of CaO during initial stages of reduction
Optimise the precursor composition for rapid reduction $\rightarrow \beta$-alloys