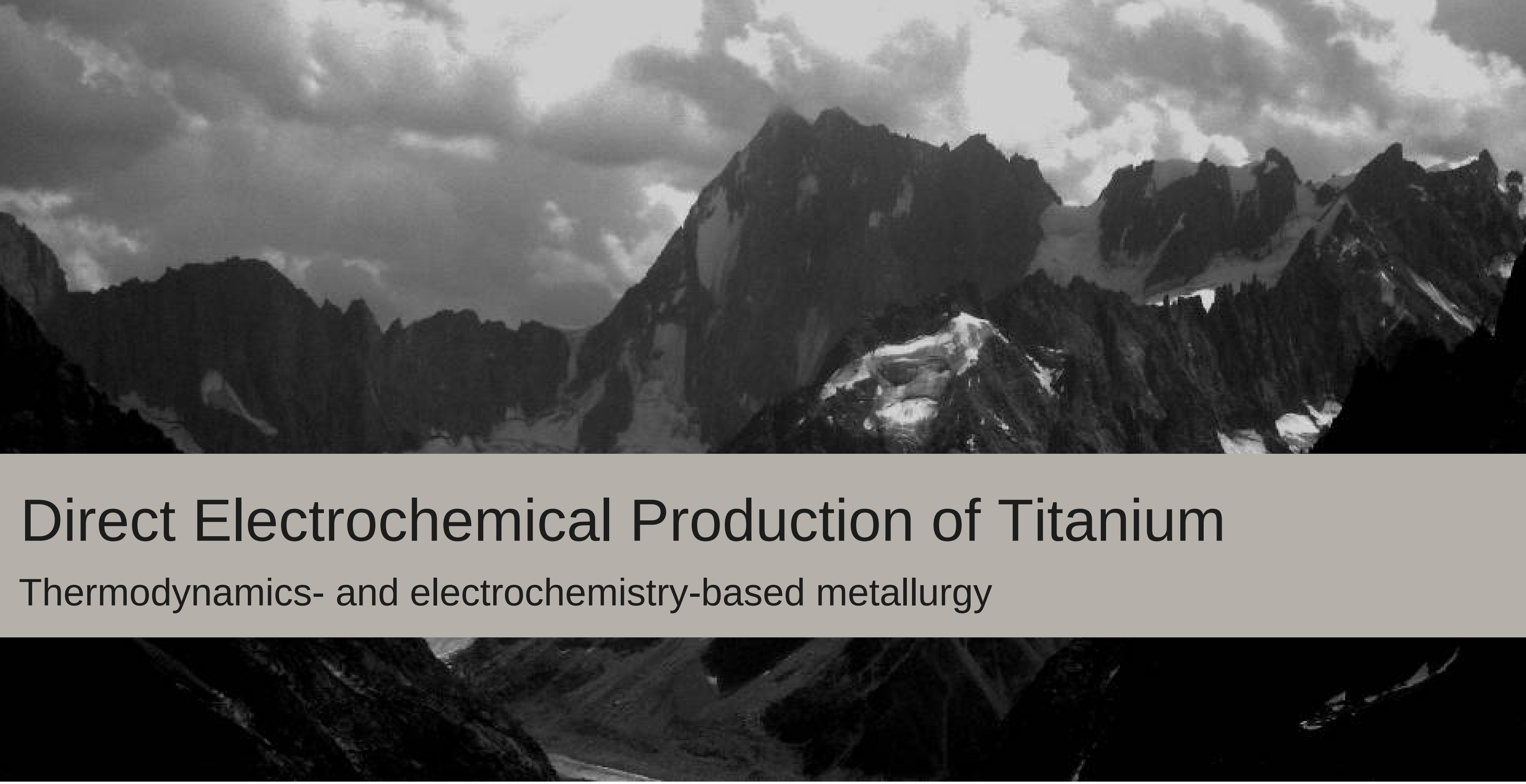


Direct Electrochemical Production of Titanium

Thermodynamics- and electrochemistry-based metallurgy

Dr. K. Dring

3rd Reactive Metals Workshop

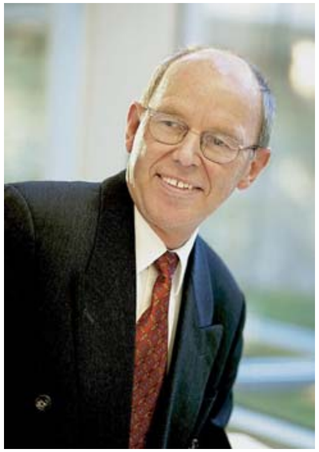
MIT – 2-3.March.2007

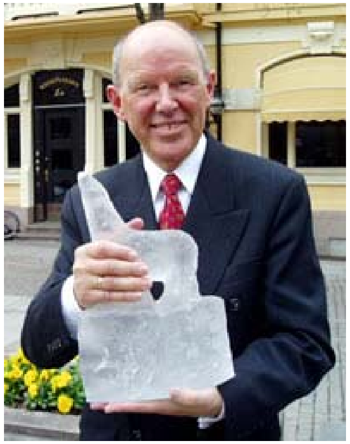
Norsk Titanium
Scandinavian Advanced Technology

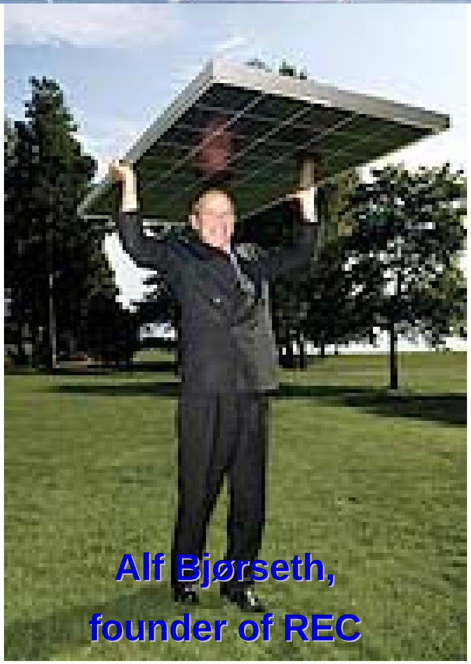
Acknowledgements

- Imperial College London
- University of Cambridge
- NTNU
- SINTEF
- Norsk Hydro

NorSun | Norsk Titanium | n-Tec | Carbon Cones | Thor Energi | PowerFluid







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.
- **June 2006:** Patent applications for De-Ox-Process concept.

Pictures of titanium applications

PRIVATE SECTOR:



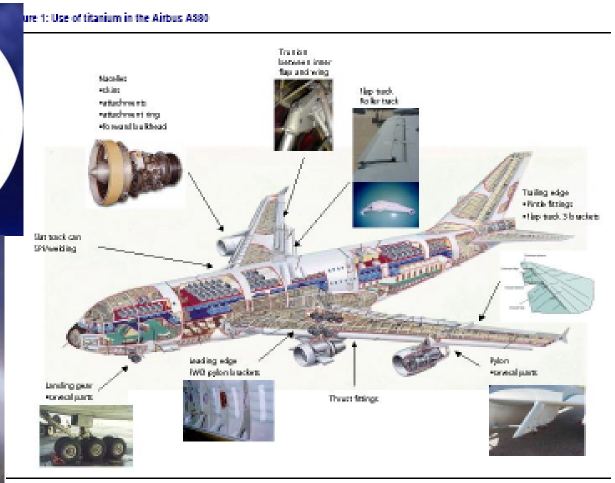



MILITARY SECTOR:



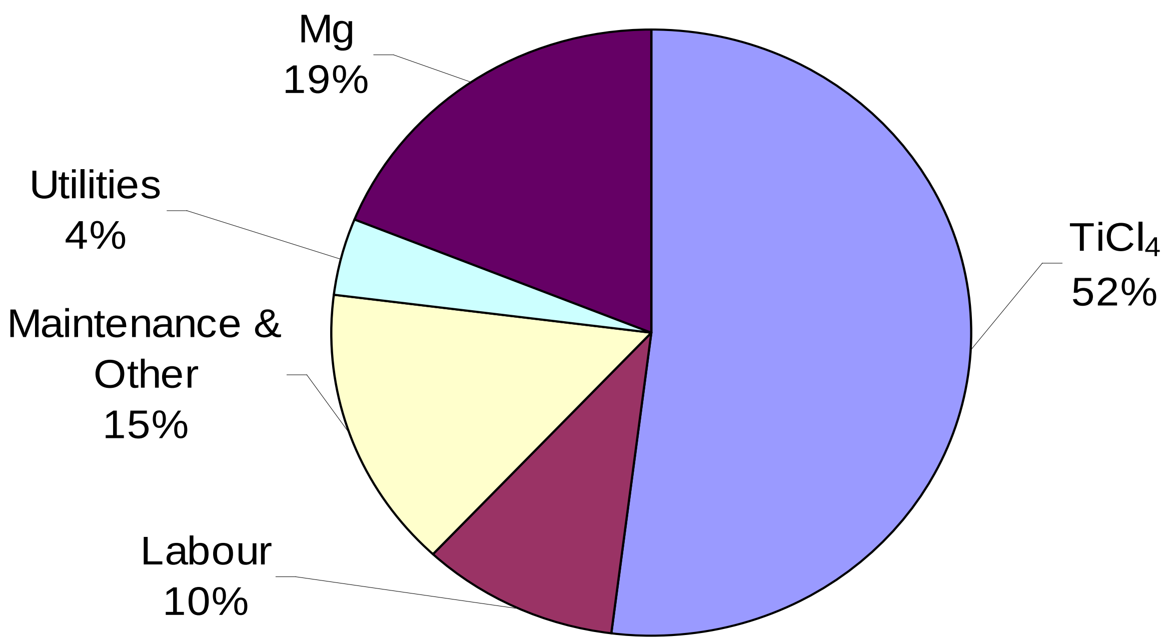
AIRCRAFTS:

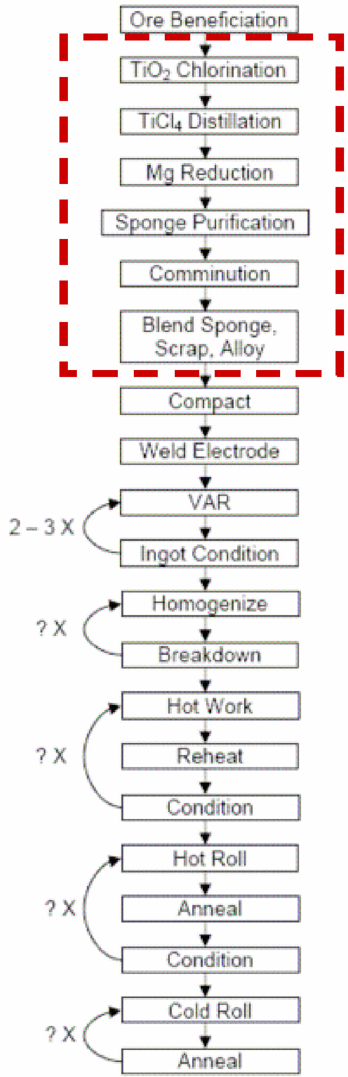




Norsk Titanium

Alternative Titanium Technology





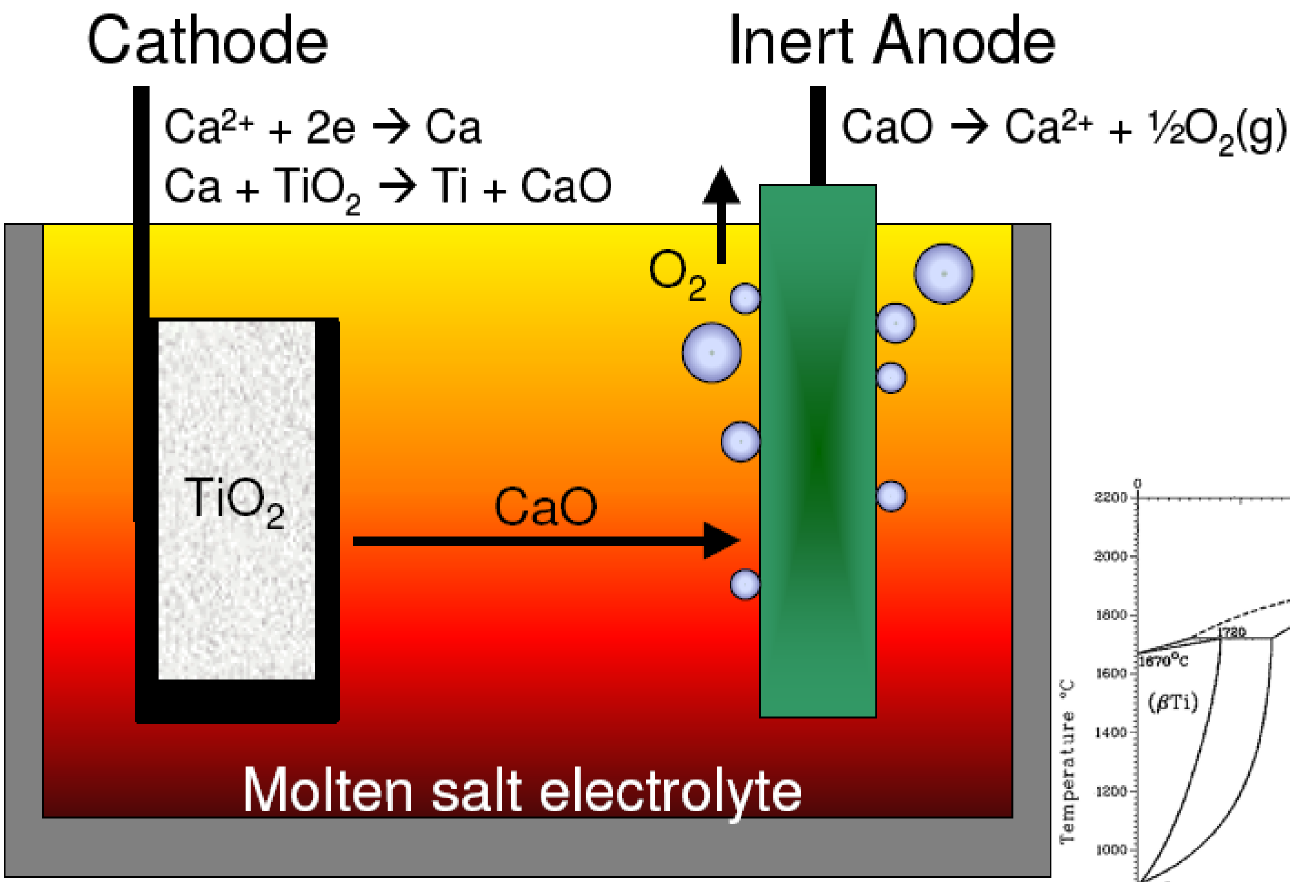
Direct reduction of (blended) oxide feedstock may be an alternative metal production route

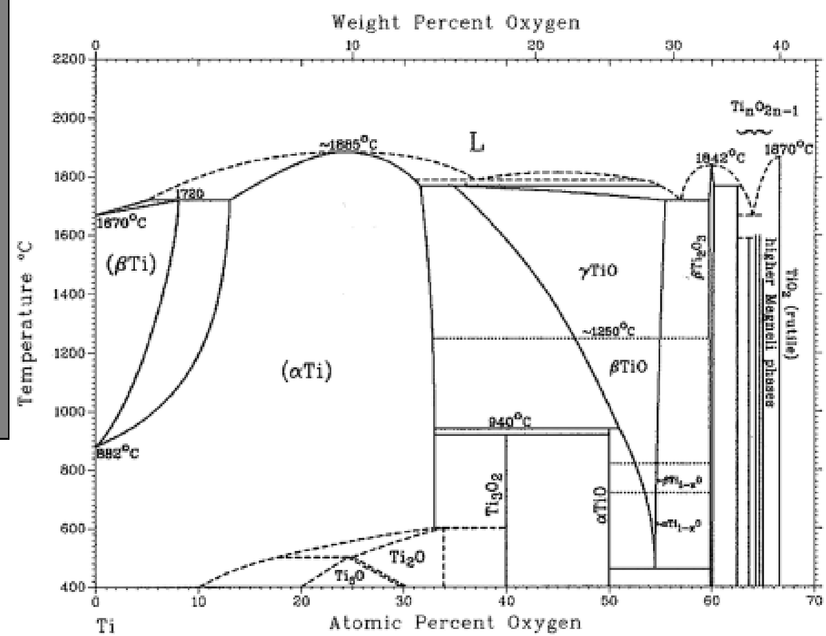
Electrolysis using molten alkali earth halide electrolytes

$$TiO_2\ (+MO) \rightarrow Ti\text{-}M + O_2$$

Norsk Titanium

NTi Metals AS – Simplified De-Ox Process

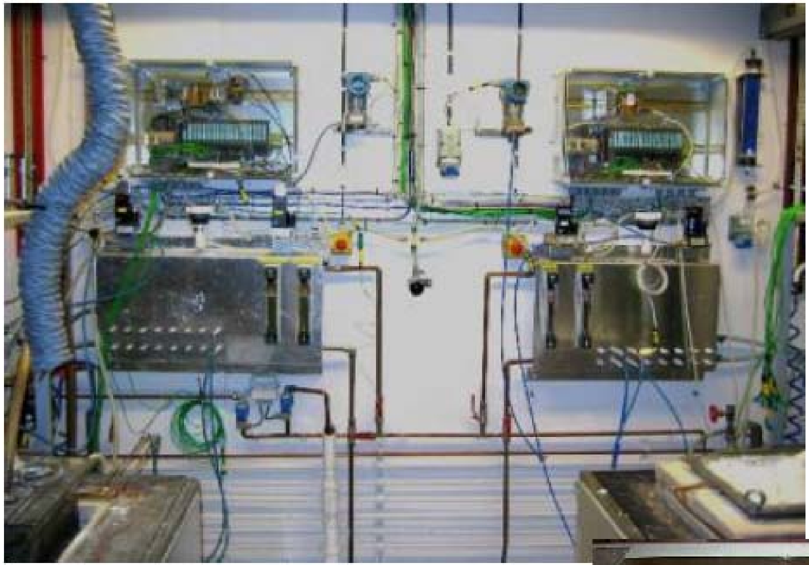


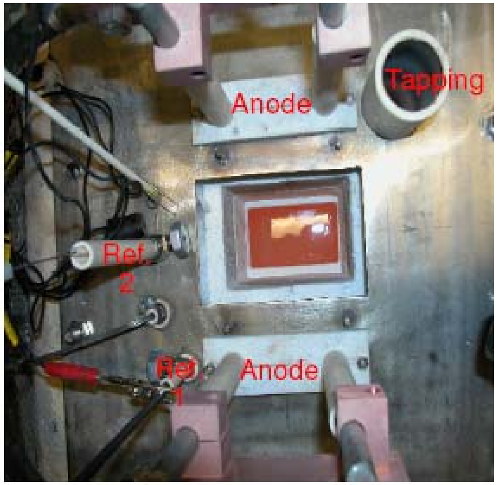


Norsk Titanium

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





Norsk Titanium

Overview of efforts

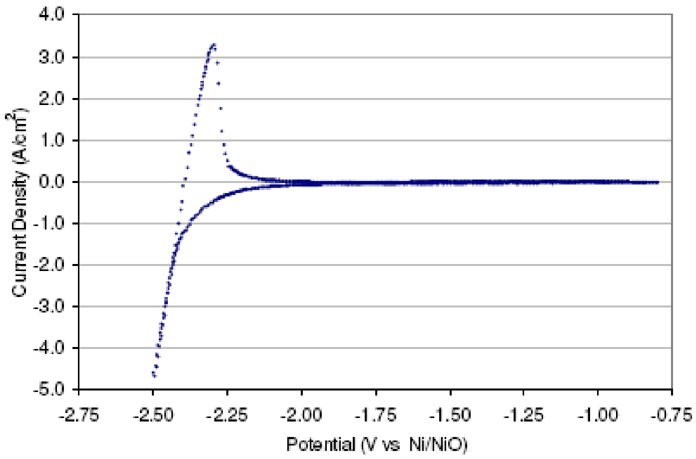
- Cathodic studies
  - Reduction pathway
  - Kinetics
  - Optimisation of precursor composition/morphology

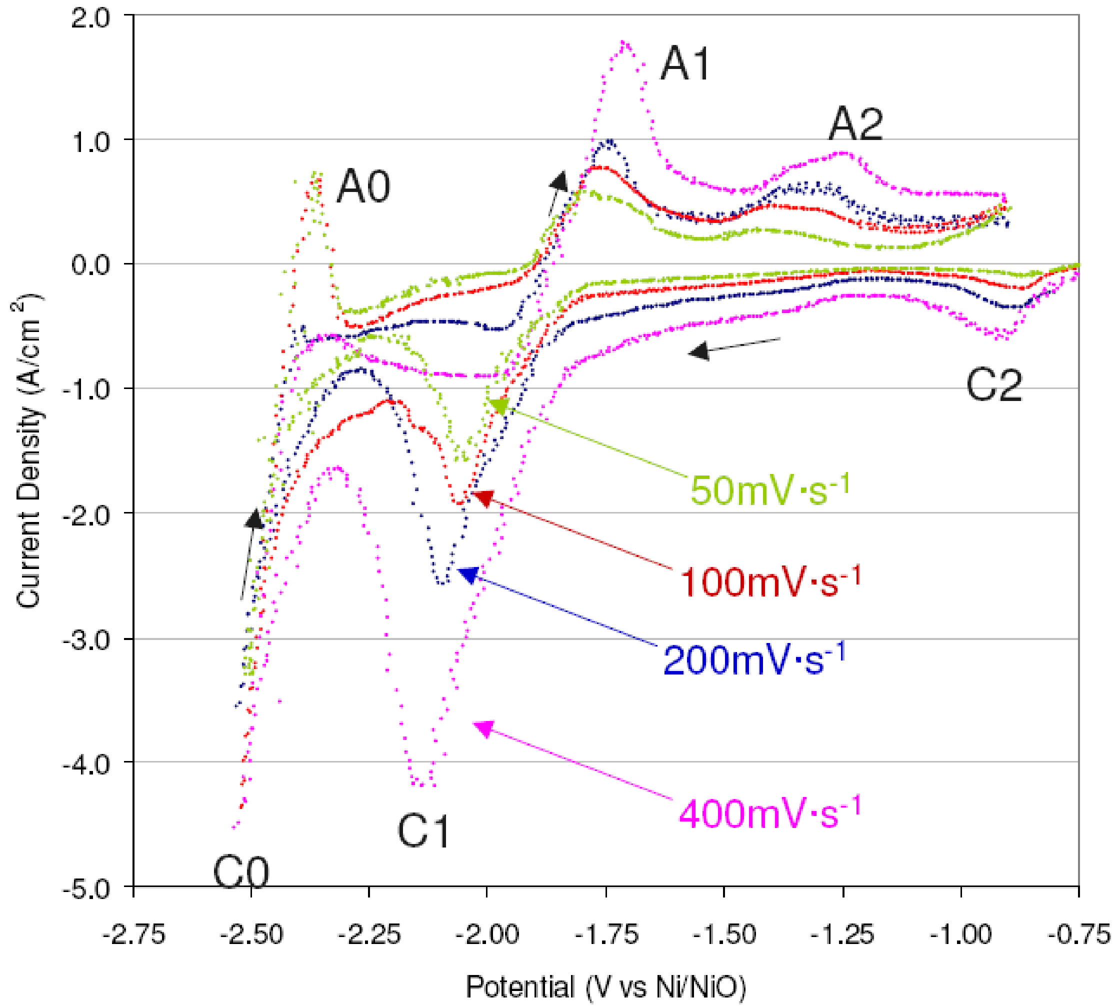
- Alloy production
  - Process capabilities: alloys (new and complex), composites
  - Changes to reduction rate
  - Modified/novel microstructures

- Inert anode development
  - Thermodynamic considerations
  - Electrical properties
  - Solubility measurements
  - Electrolysis performance

Success: Cathodic Studies – TiO_2 Films

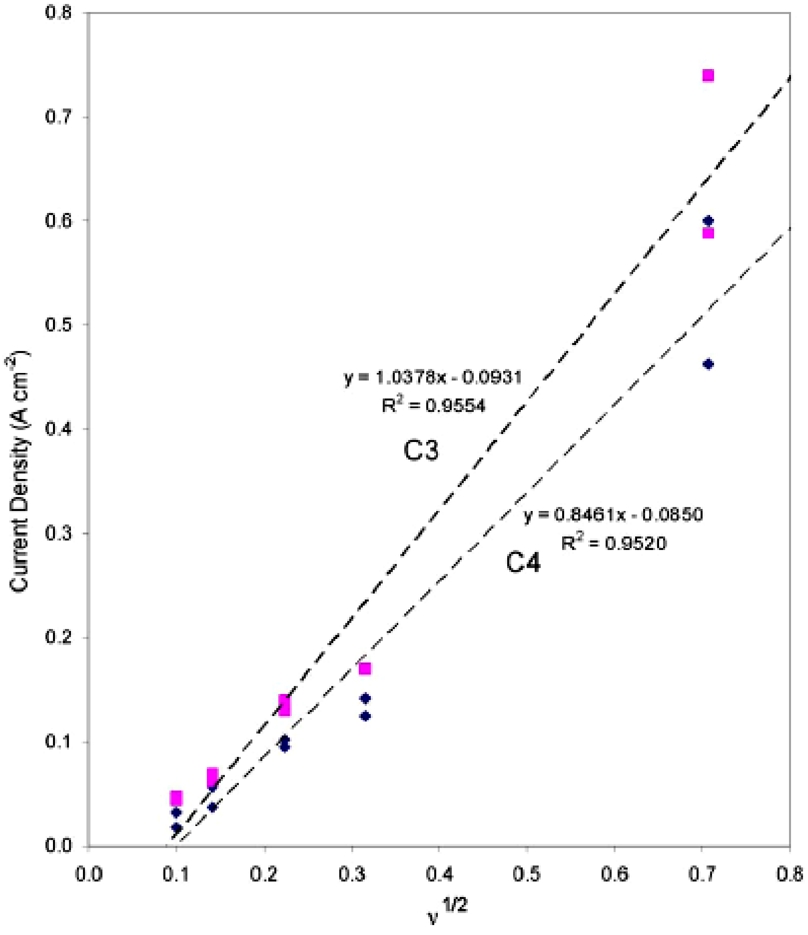
- $CaCl_2$-NaCl eutectic w/ 1 wt% CaO, 800 ºC
- High cathodic currents on bare W electrode → indicative of Ca formation at $a_{Ca} < 1$
- Absence of C2 in reverse scan due to insufficiently positive final potentials
- Weak shift in peak potentials with increasing sweep rate

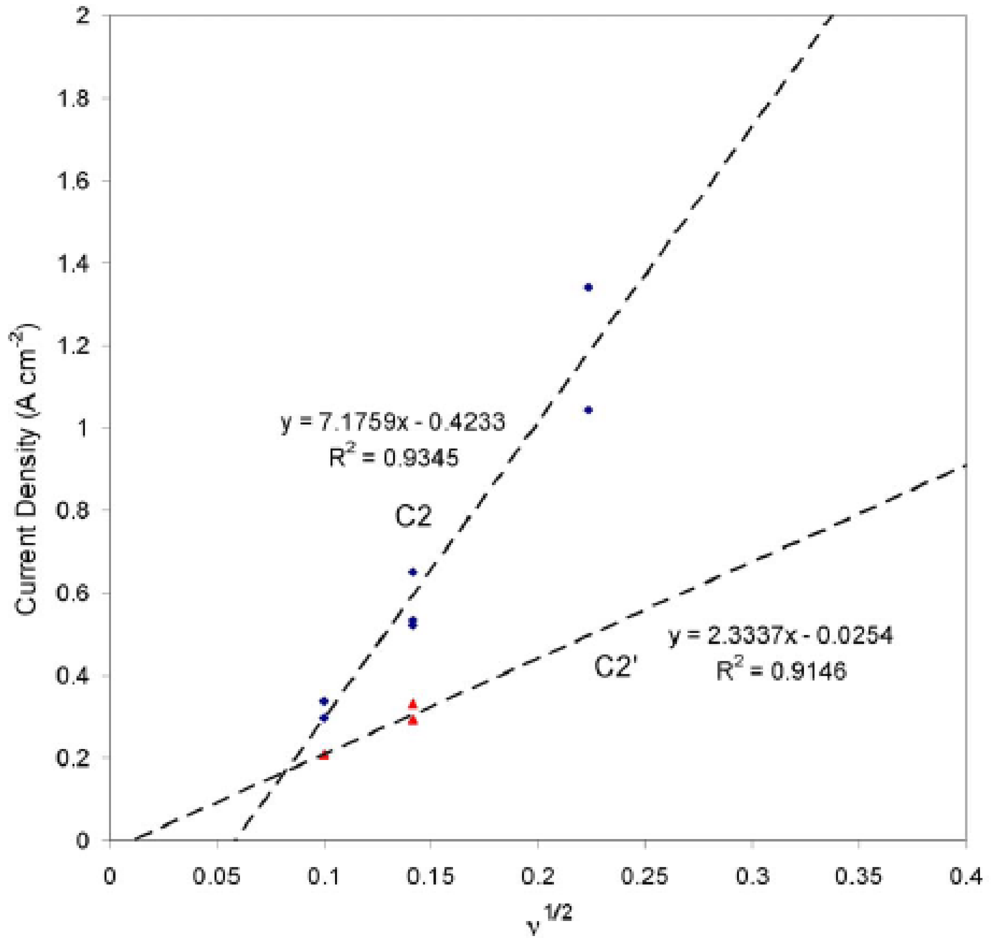




Norsk Titanium

Success: Cathodic Studies – TiO_2 Films





C4: $D_L = 2.5 \times 10^{-8}\ cm^2 \cdot s^{-1}$

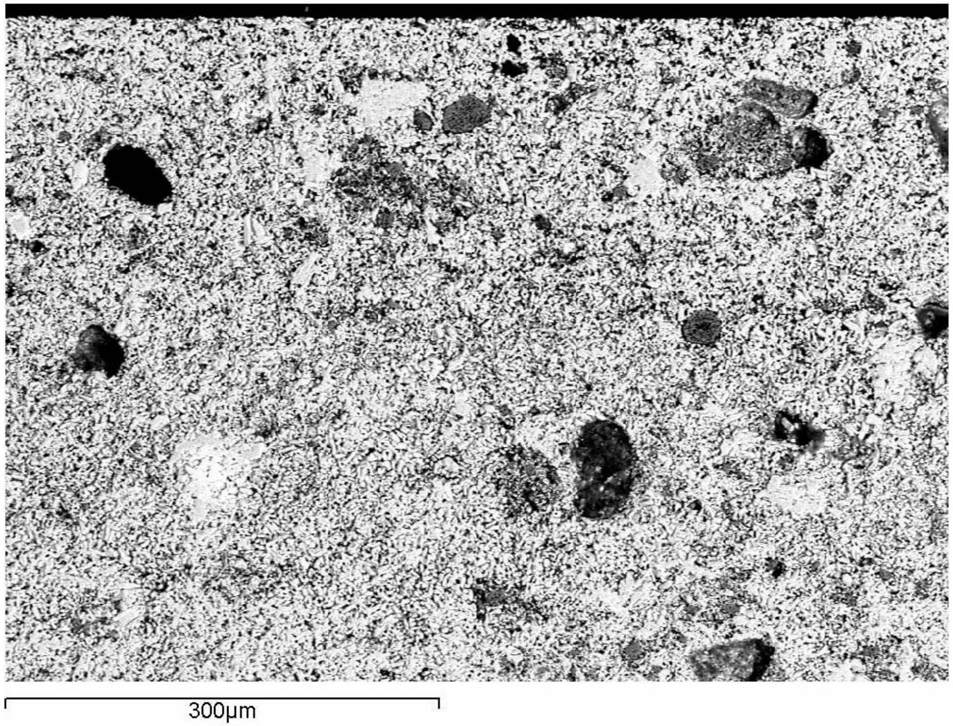
C3: $D_L = 1.5 \times 10^{-7}\ cm^2 \cdot s^{-1}$

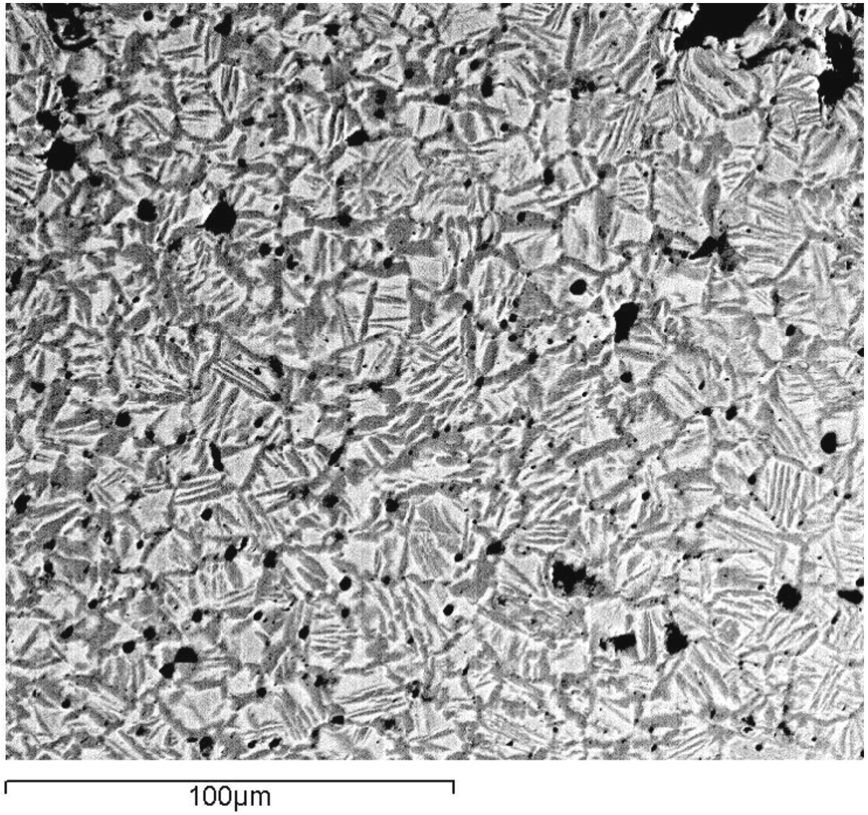
C2': $D_L = 8.8 \times 10^{-8}\ cm^2 \cdot s^{-1}$

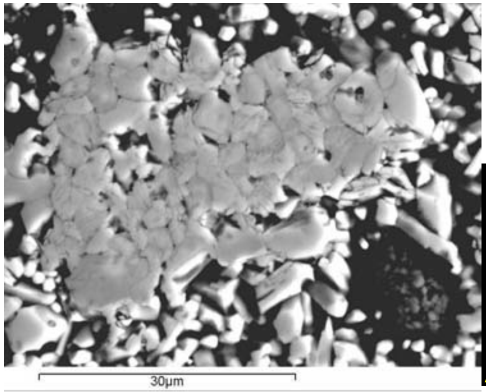
C2: $D_L = 8.3 \times 10^{-7}\ cm^2 \cdot s^{-1}$

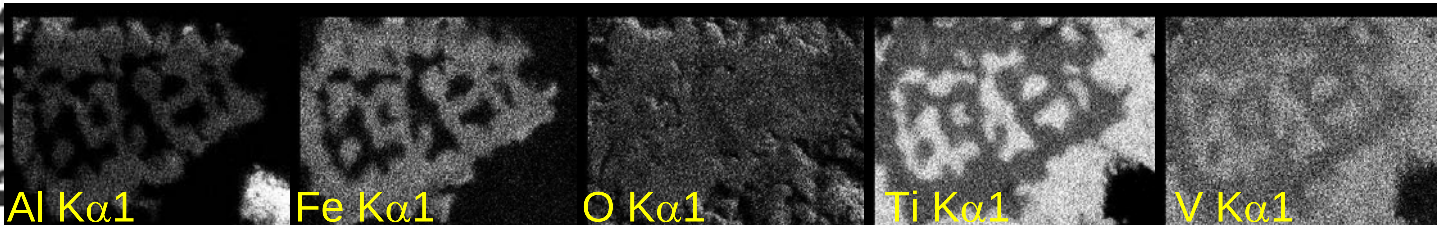
Norsk Titanium

Success: Complex Titanium Alloy (Ti 10V-2Fe-3Al)









Norsk Titanium

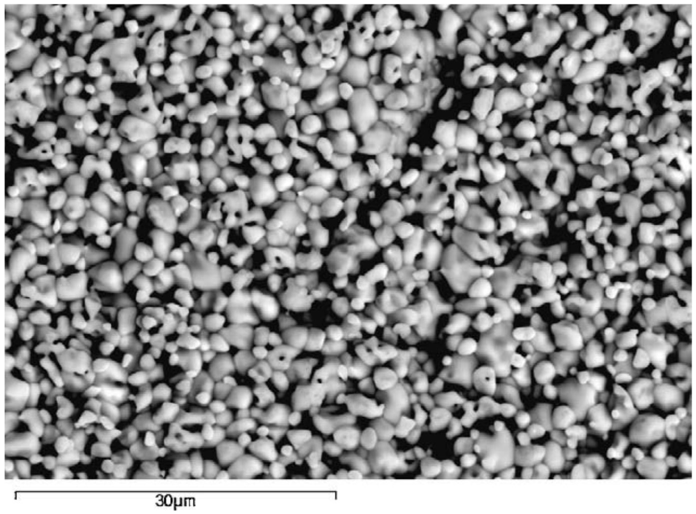
Success: Novel titanium alloy

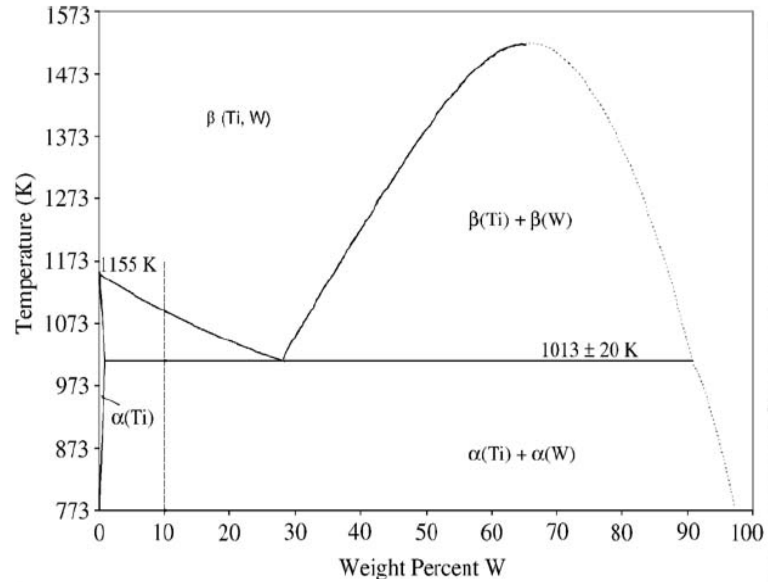
Ti - 10W

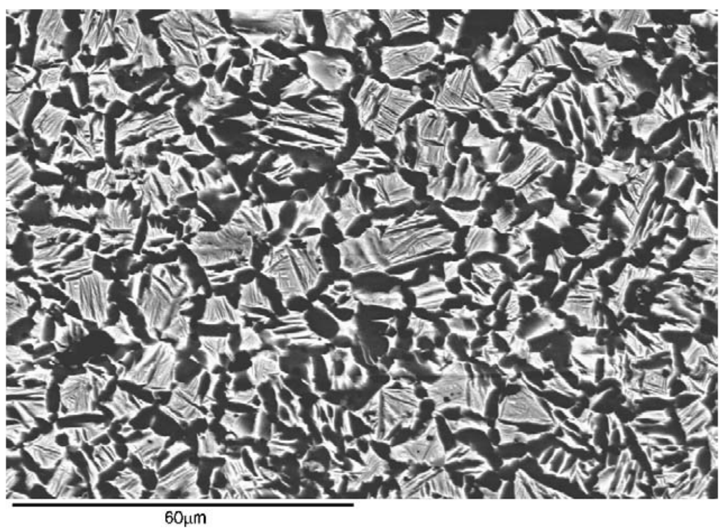
Impossible to produce via Kroll method

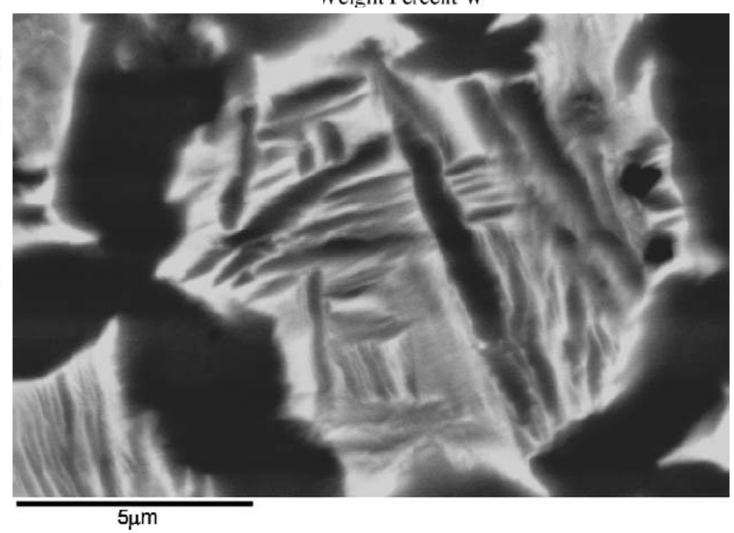
Uses in bio-medical applications

Diffusion of oxygen in β is about 1-2 orders of magnitude higher than in α







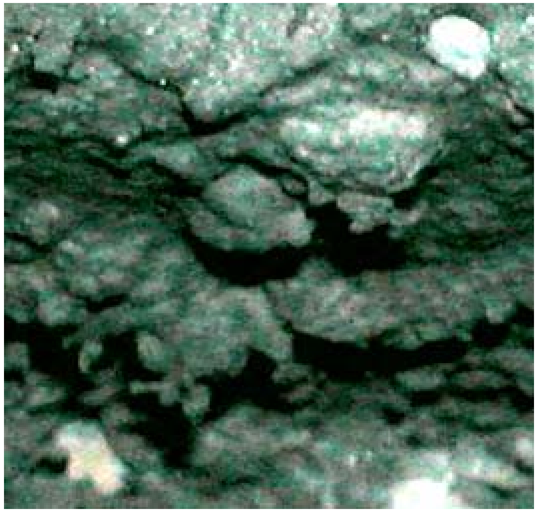


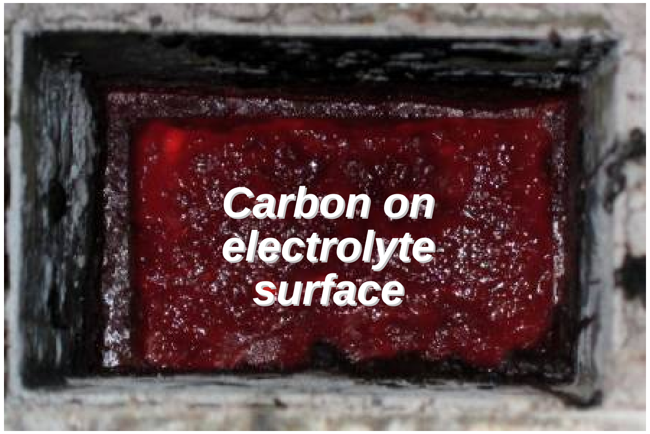
Norsk Titanium

Setback: Carbon contamination at cathode

~1 cm

$CO_3^{2-} + 4e^- \rightarrow C + 3O^{2-}$

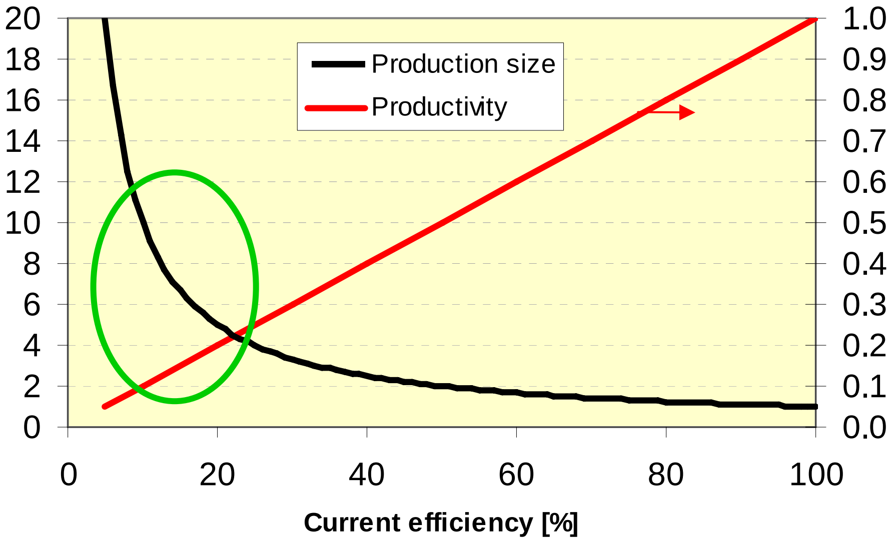




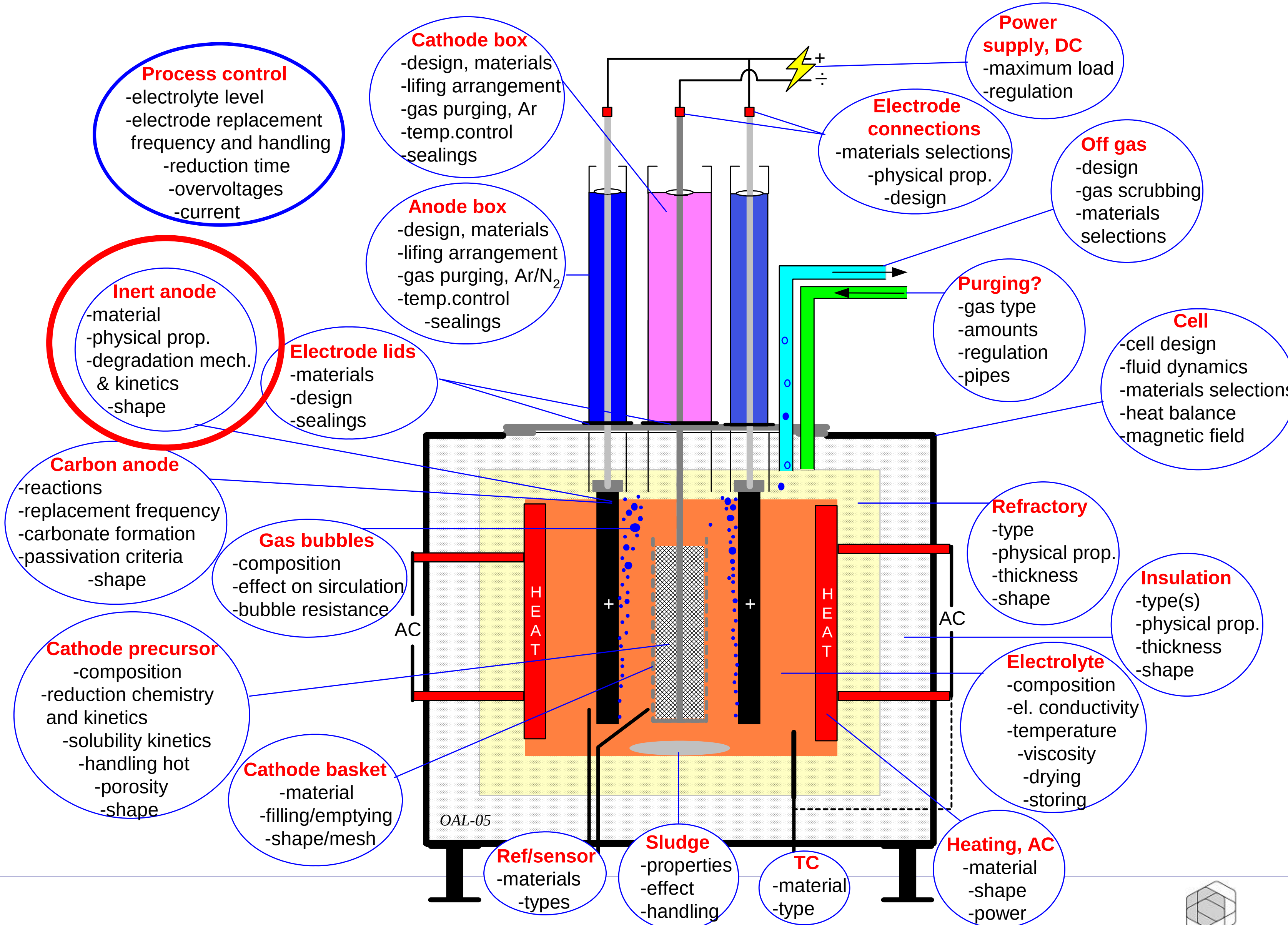
- 1-2 wt% carbon is enough to make the electrolyte “sludgy”.
- Carbon can be burned off by purging air through the electrolyte.
- Need to shield graphite to prevent excessive anode consumption.
- Carbon anode is not well suited.

Setback: C and Ca problems

- Both C and Ca accumulate under conditions needed to produce titanium
  - C due to carbonate reduction from reaction of CO_2 with CaO
  - Ca due to the high solubility and negative potentials to deoxidize Ti

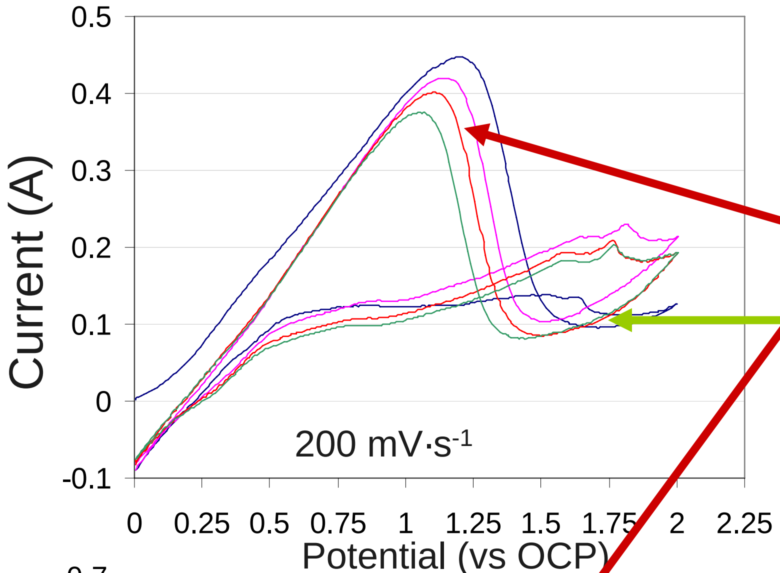


Challenges: Lack of prior art



Norsk Titanium

Success?: Oxygen evolving ”inert” anode



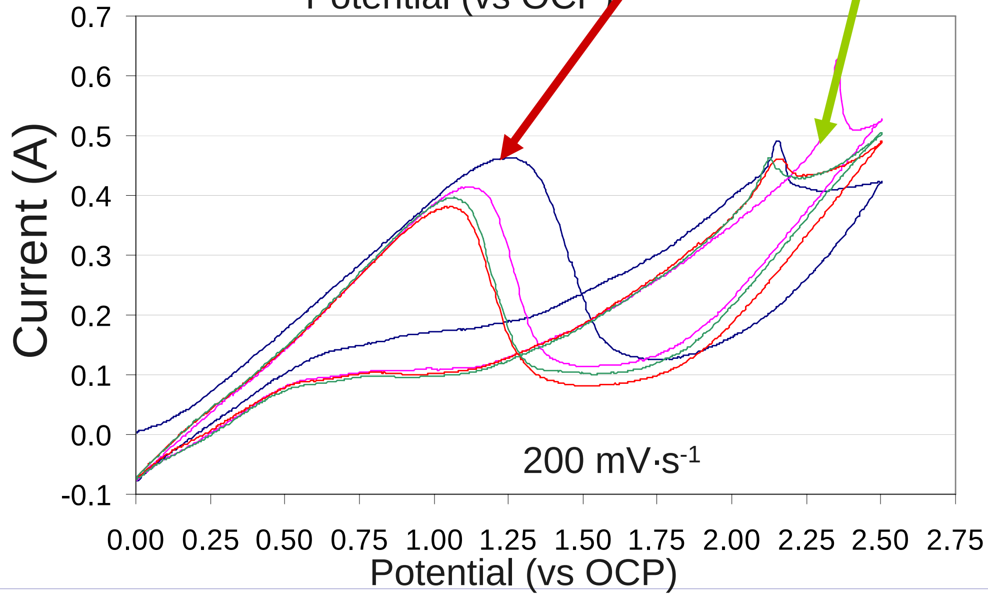
High background currents

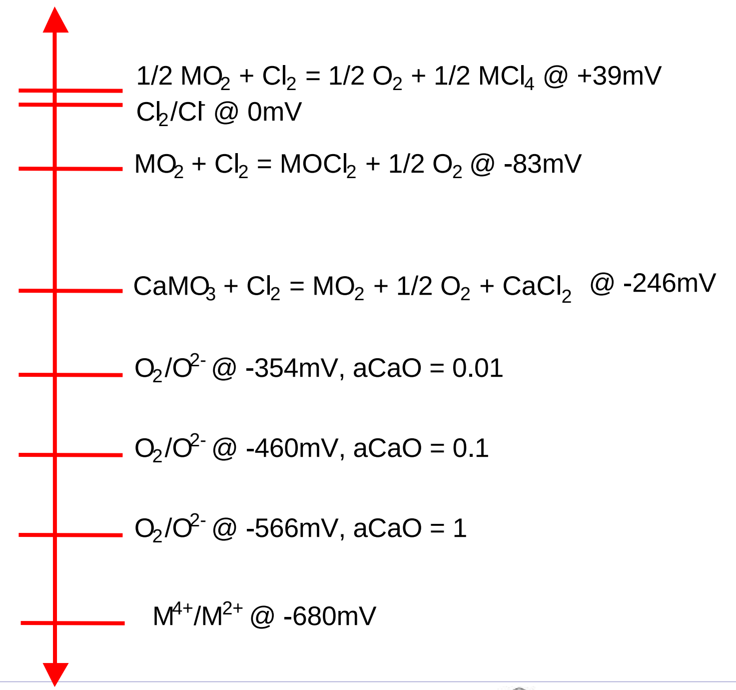
Nucleation loops at reversing potential

Oxygen evolution peak

Anode chlorination?

Due to low a_{CaO}





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…

<u>Anodic process:</u>

Characterise the change in composition/morphology during operation

<u>Cathodic process:</u>

Understand the ingress/egress of CaO during initial stages of reduction

Optimise the precursor composition for rapid reduction → β-alloys

Norsk Titanium

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