Electrowinning Molten Titanium from Titanium Dioxide

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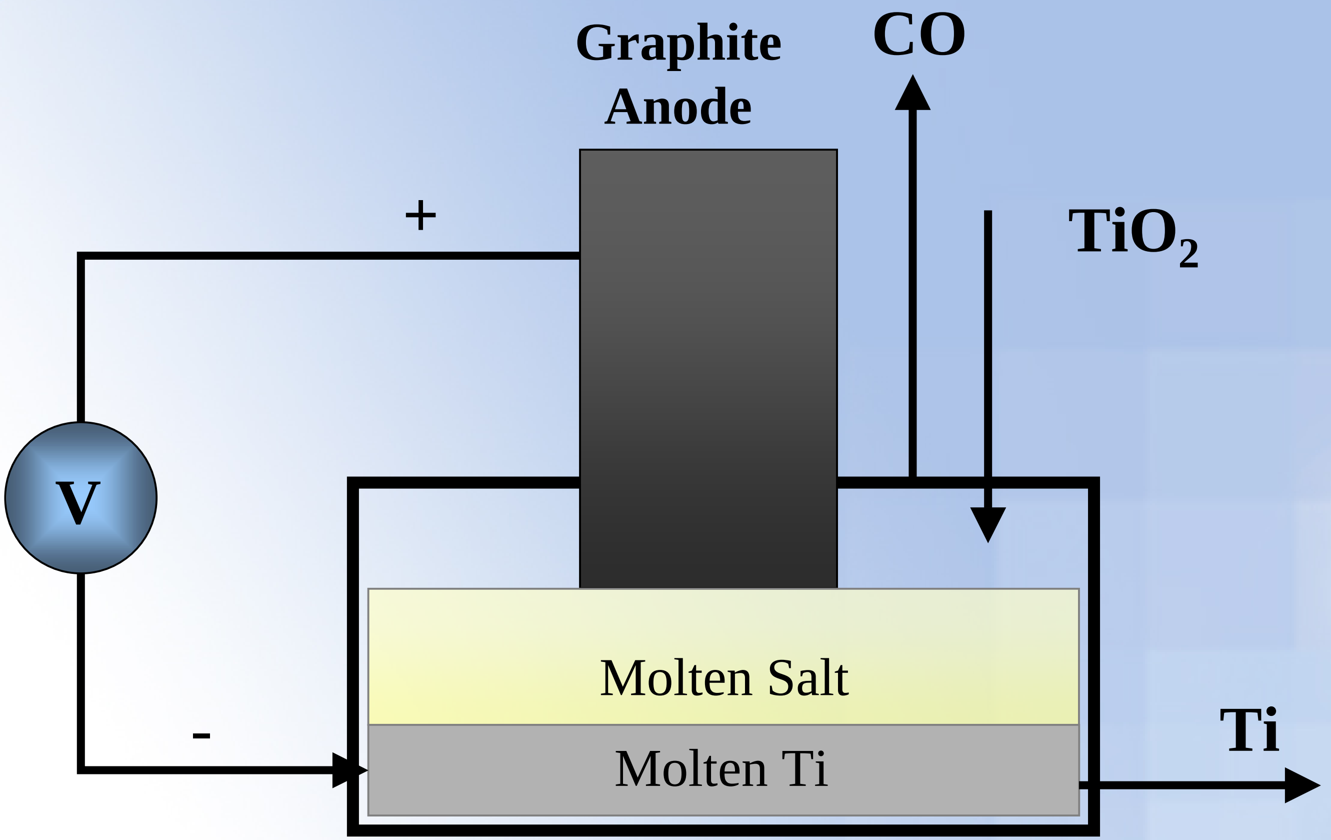
Conceptual Process



$$Ti^{4+} + 4e^{-} \leftrightarrow Ti$$

$$O^{2-} + C \leftrightarrow CO(g) + 2e^{-}$$

$$TiO_2 + 2C \leftrightarrow Ti + 2CO(g)$$

Rationale – Titanium Cost Build-up

Material	Cost
Ilmenite	\$0.27/kg Ti sponge
Titanium slag	\$0.75/kg Ti Sponge
$TiCl_4$ and TiO_2	\$3.10/kg Ti Sponge
Ti Sponge raw materials costs	\$5.50/kg Ti Sponge
Total Ti Sponge cost	\$9-\$11/kg Ti Sponge
Ti ingot	\$15-17/kg Ti
Aluminium	\$1.7/kg Al

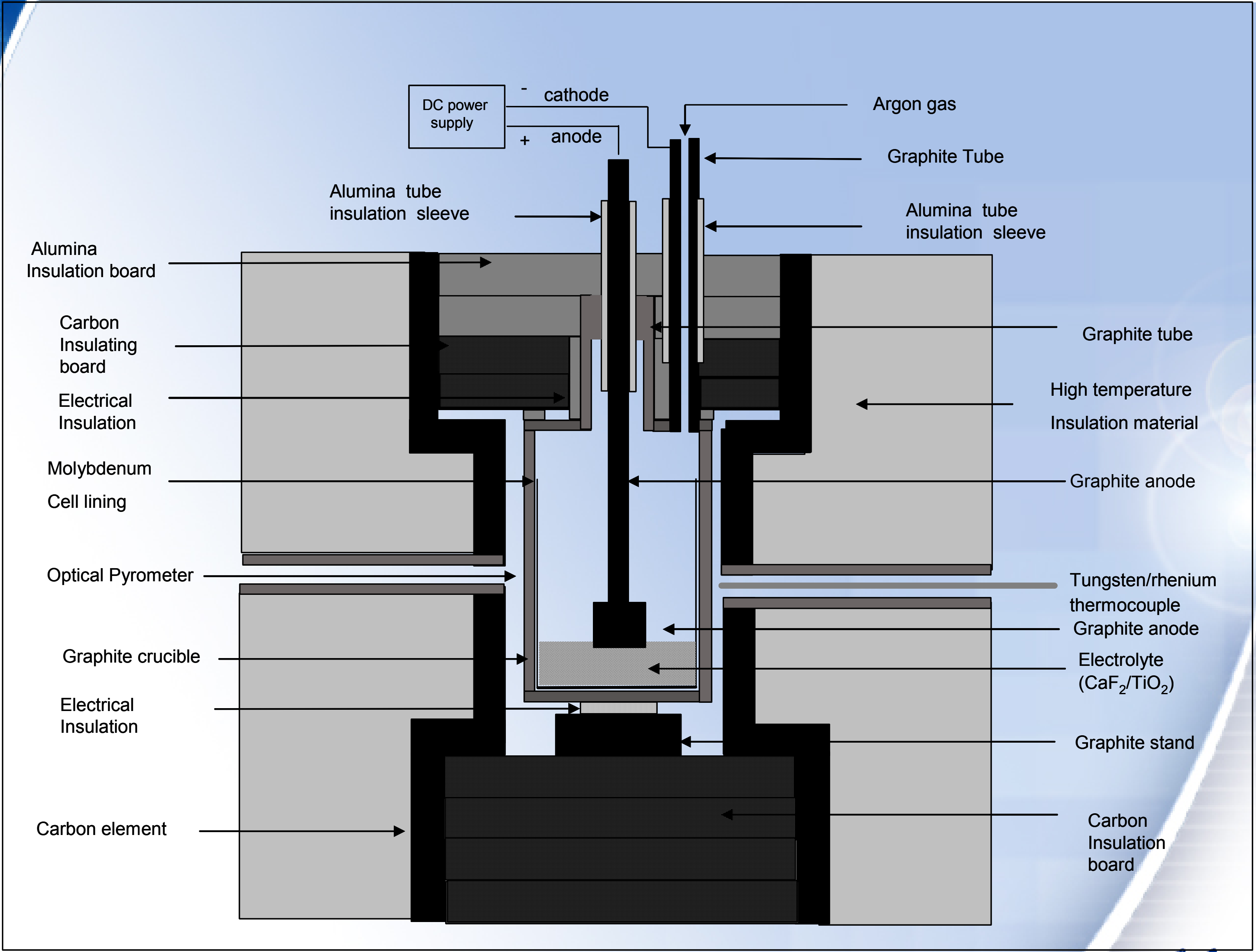
Rationale - Advantages

- Feed: Safe, transportable, alternative supplies (sulphate and chloride routes), decoupled from $TiCl_4$ production
- Direct use of electricity instead of firstly making Mg or Na and recycling of $MgCl_2$ 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*
  - *CaF_2, SrF_2, BaF_2 and YF_3*
- High affinity of Ti for O_2, C and 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

Apparatus

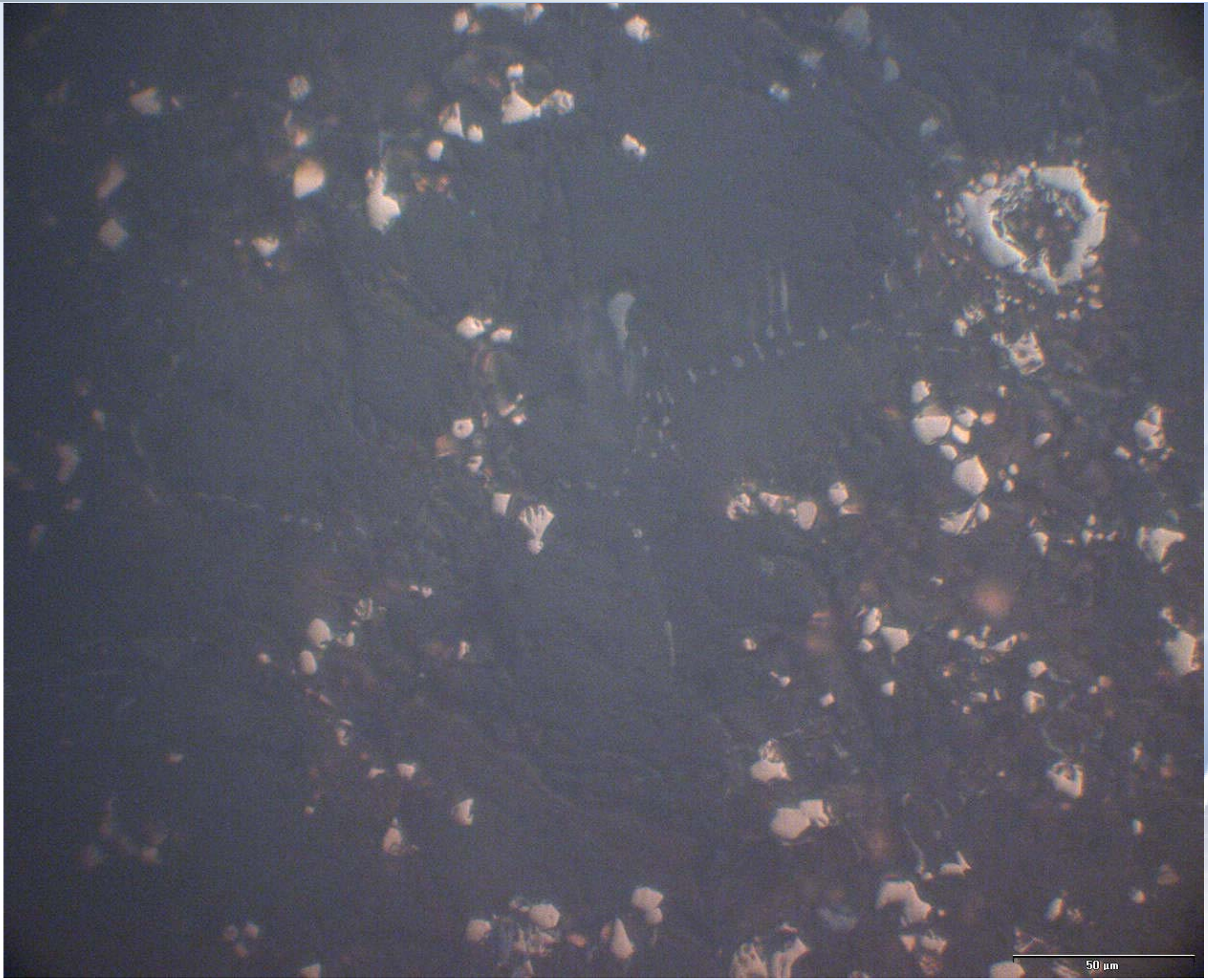

DC power supply
- cathode
+ anode
Argon gas
Graphite Tube
Alumina tube insulation sleeve
Alumina tube insulation sleeve
Alumina Insulation board
Carbon Insulating board
Electrical Insulation
Molybdenum
Cell lining
Optical Pyrometer
Graphite crucible
Electrical Insulation
Carbon element
Graphite tube
High temperature
Insulation material
Graphite anode
Tungsten/rhenium thermocouple
Graphite anode
Electrolyte (CaF_2/TiO_2)
Graphite stand
Carbon Insulation board

Typical Contents of Cell after Experiment

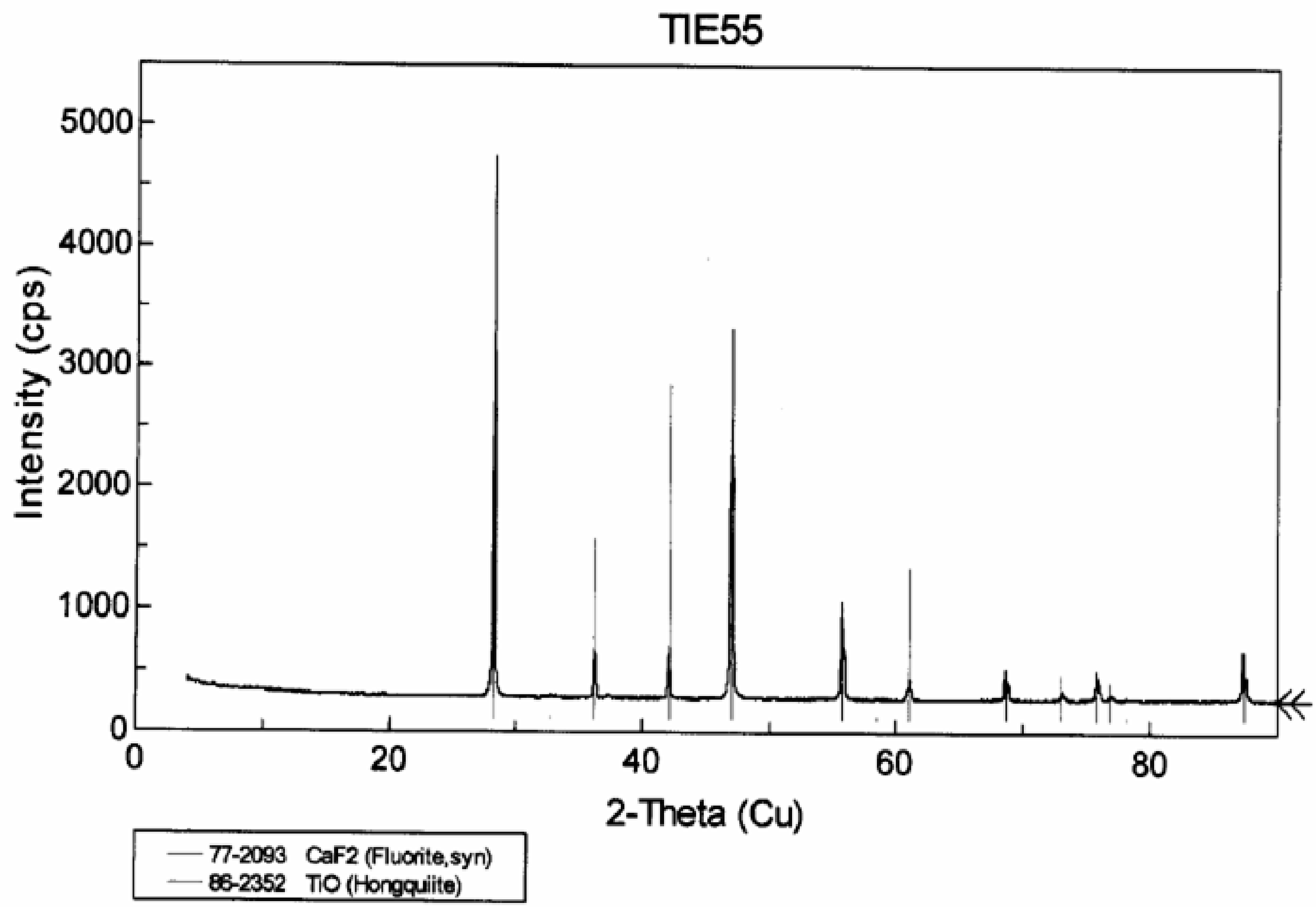
Evidence of Gas Blanket

TiO Interspersed in CaF_2

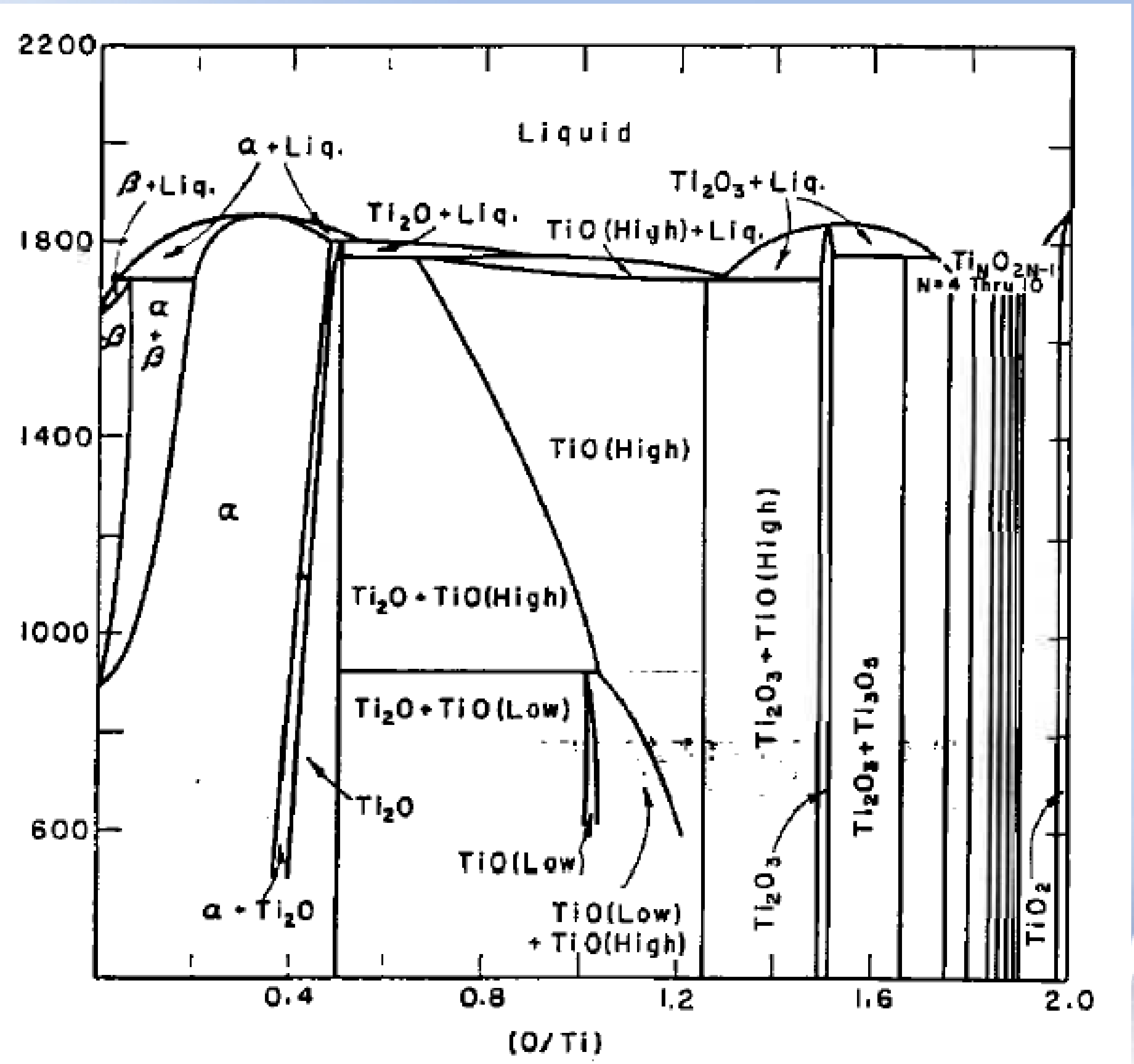
Limited Evidence of Coalescence



Typical XRD


TIE55
Intensity (cps)
5000
4000
3000
2000
1000
0
0
20
40
60
80
2-Theta (Cu)
77-2093 CaF2 (Fluorite,syn)
86-2352 TiO (Hongquiite)

Titanium Oxygen Phase Diagram



- 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*

Acknowledgements:

Sponsors: Innovation Fund, BHPBilliton, Kumba Resources

Partners: Mintek, UP, Risimati Engineers

The Minerals, Metals and Materials Society