NEW PROCESSES FOR TITANIUM PRODUCTION – from swarf to moon dust

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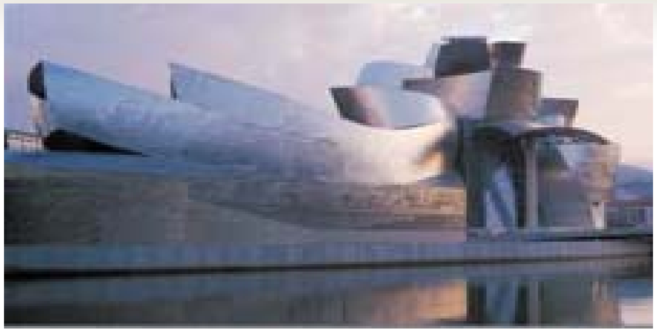
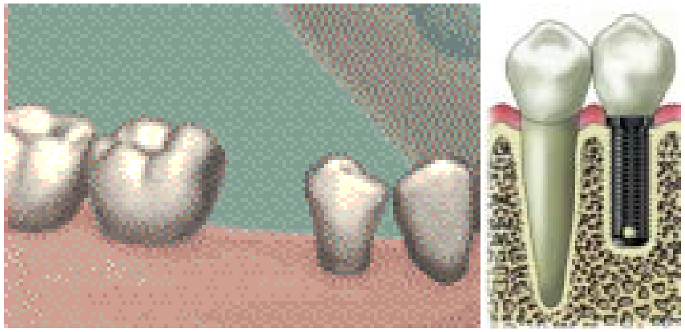




Marine applications

Corrosion resistance

Fouling resistance

Shock absorption

Cost sensitivity

New stainless steels

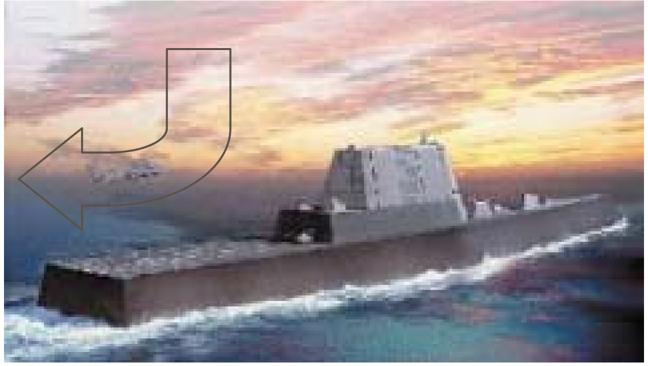
Testing and certification

Offshore Oil & Gas

Pipe work

Propellers

Hulls



Titanium’s appeal rests on its corrosion resistance coupled with its strength and lightness

TITANIUM

1. **Titanium is 0.44% of the earth's crust**

2. **Titanium is the 9th most abundant element and the 4th most abundant metal after aluminium, iron and magnesium. It is far more abundant than copper, nickel, zinc and other common metals.**

3. **Market use is 40% aerospace (aero-engines, aircraft), 50% industrial (power, chemical pulp and paper, desalination), and 10% emerging sectors (land based military equipment, architectural, sporting goods).**

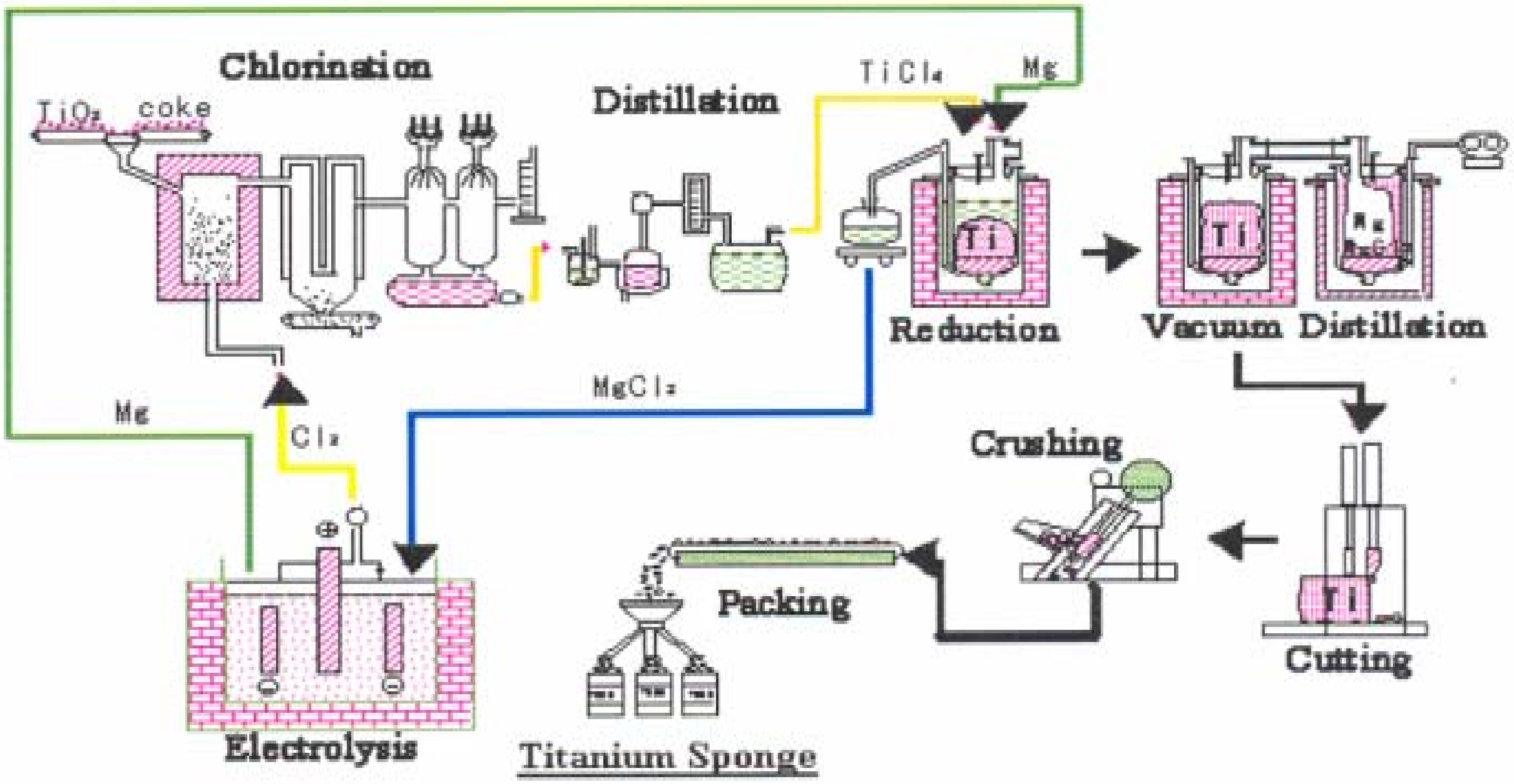
4. **Titanium alloys have an outstanding combination of properties, including high strength, a density 40% less than steel, elevated temperature capability up to 600˚C and a corrosion resistance four times better than steel.**

5. **Titanium alloys are typically £20,000–£35,000/tonne compared with £500–£5,000/tonne for aluminium alloys and steels.**

6. **Present production of titanium is 60,000 tonnes/annum compared to 25 million tons of aluminium.**

Price reduction would lead to a much more rapid increase in usage, with long term potential similar to that of stainless steel (13 million tonnes).

KROLL PROCESS



REQUIREMENTS OF NEW PROCESS

- Remove oxide layer and alpha case from recycled titanium, including swarf
- Reduce titanium compounds, oxide or halide, to pure titanium with about 1000 ppm oxygen
- Ability to produce alloys directly
- Waste products should not harm the environment

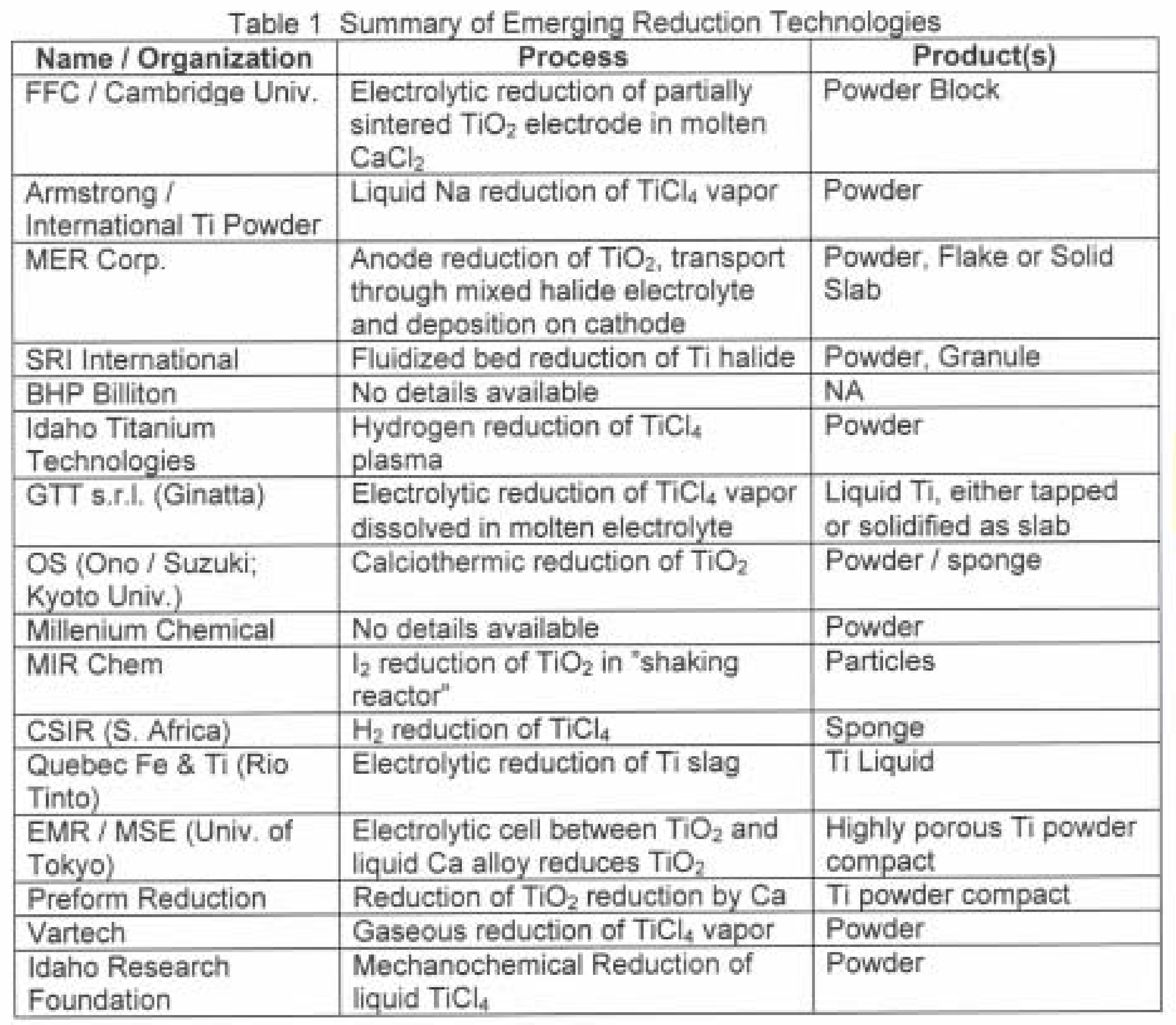


Table 1 Summary of Emerging Reduction Technologies

Name / Organization	Process	Product(s)
FFC / Cambridge Univ.	Electrolytic reduction of partially sintered TiO_2 electrode in molten $CaCl_2$	Powder Block
Armstrong / International Ti Powder	Liquid Na reduction of $TiCl_4$ vapor	Powder
MER Corp.	Anode reduction of TiO_2, transport through mixed halide electrolyte and deposition on cathode	Powder, Flake or Solid Slab
SRI International	Fluidized bed reduction of Ti halide	Powder, Granule
BHP Billiton	No details available	NA
Idaho Titanium Technologies	Hydrogen reduction of $TiCl_4$ plasma	Powder
GTT s.r.l. (Ginatta)	Electrolytic reduction of $TiCl_4$ vapor dissolved in molten electrolyte	Liquid Ti, either tapped or solidified as slab
OS (Ono / Suzuki; Kyoto Univ.)	Calciothermic reduction of TiO_2	Powder / sponge
Millenium Chemical	No details available	Powder
MIR Chem	I_2 reduction of TiO_2 in "shaking reactor"	Particles
CSIR (S. Africa)	H_2 reduction of $TiCl_4$	Sponge
Quebec Fe & Ti (Rio Tinto)	Electrolytic reduction of Ti slag	Ti Liquid
EMR / MSE (Univ. of Tokyo)	Electrolytic cell between TiO_2 and liquid Ca alloy reduces TiO_2	Highly porous Ti powder compact
Preform Reduction	Reduction of TiO_2 reduction by Ca	Ti powder compact
Vartech	Gaseous reduction of $TiCl_4$ vapor	Powder
Idaho Research Foundation	Mechanochemical Reduction of liquid $TiCl_4$	Powder

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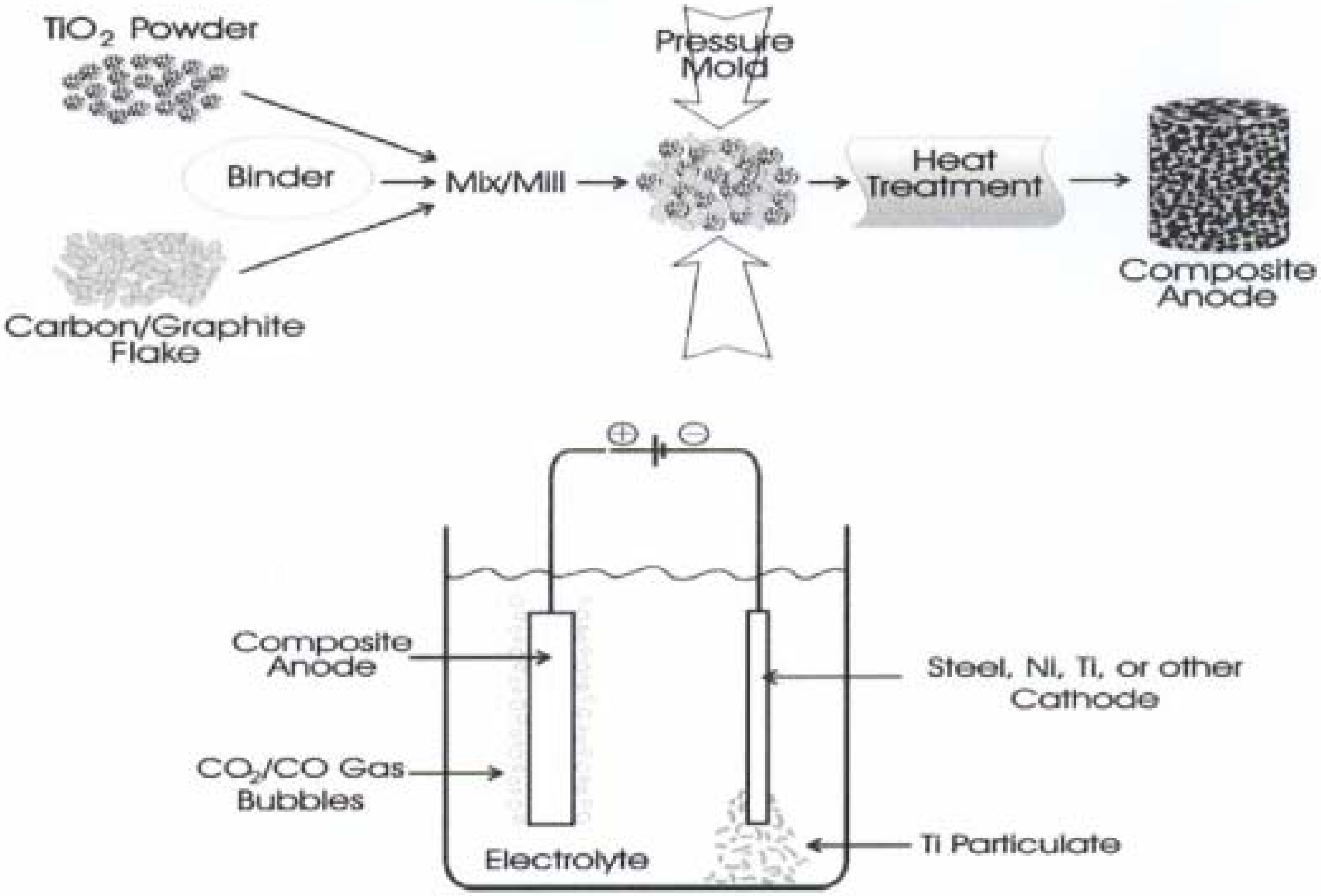
MER PROCESS



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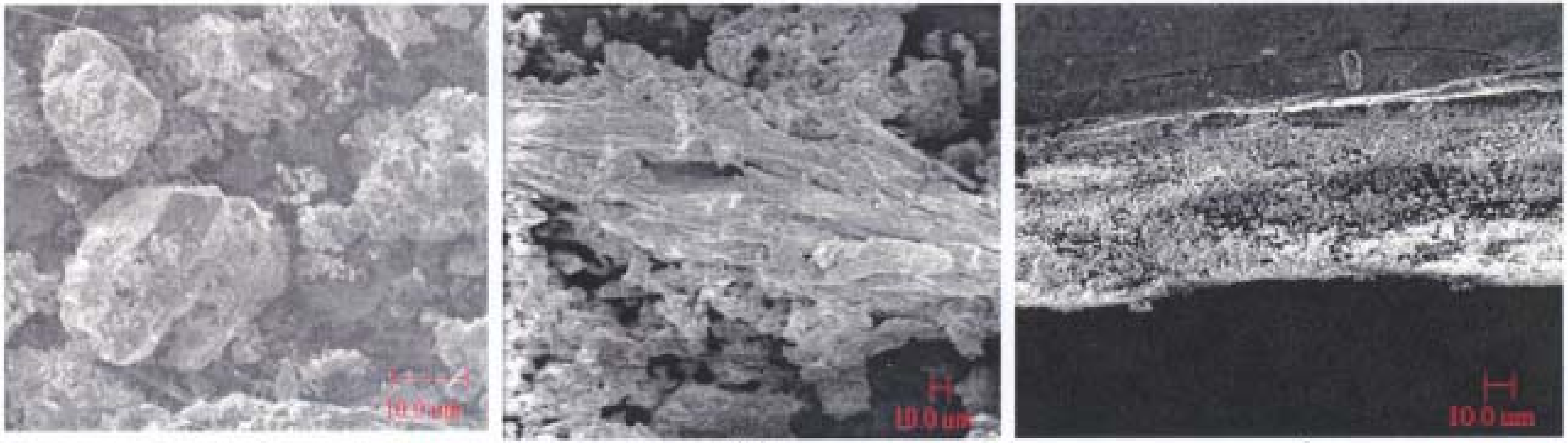
Anodic Reaction

$TiO.TiC = 2Ti^{2+} + CO + 4e^{-}$

Cathodic Reaction

$2Ti^{2+} + 4e^{-} = 2Ti$



a) b) c)

MER PROCESS

ADVANTAGES

*Pure titanium with low oxygen content has been produced.

*Current efficiency is about 90%

DISADVANTAGES

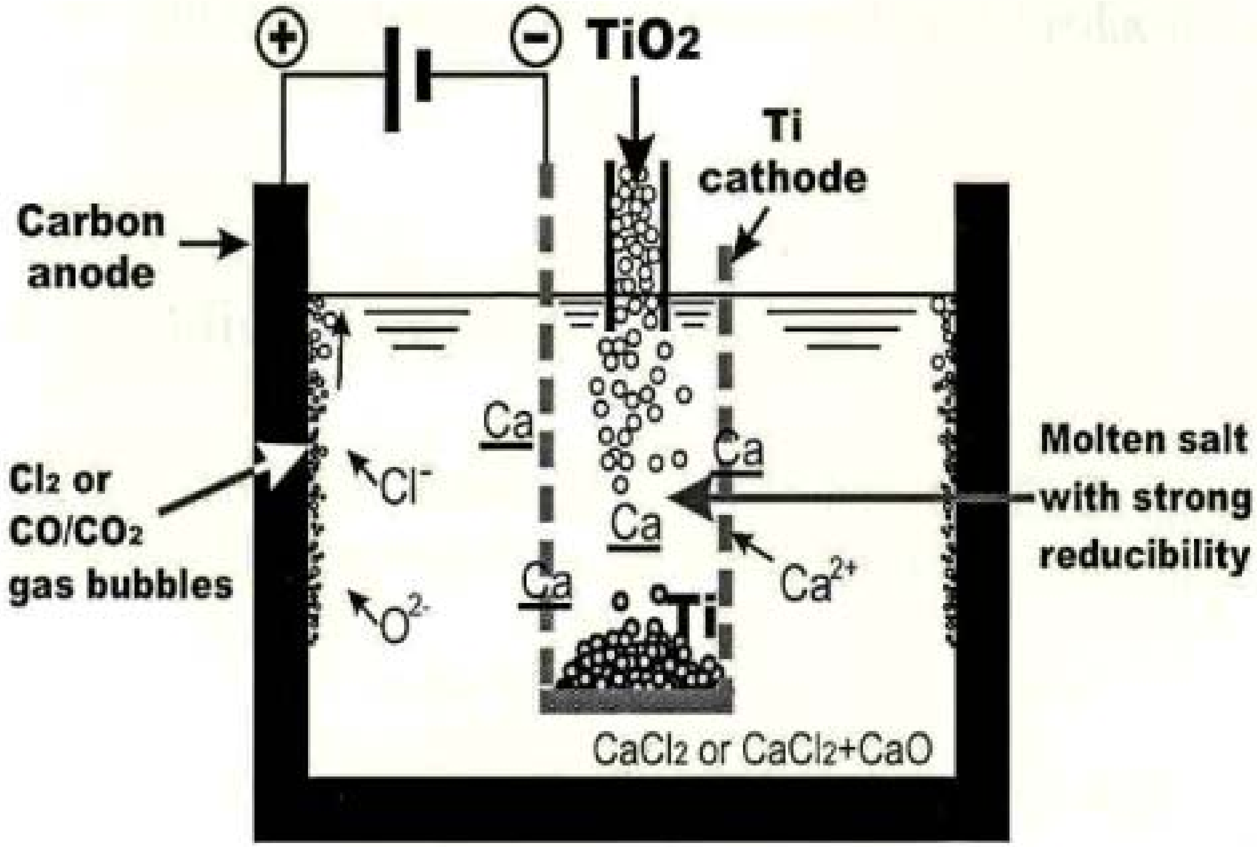
*Treatment of swarf will require complete dissolution of titanium

*May be difficult to produce alloys

*Anode may not be mechanically stable

* CO is evolved

ONO AND SUZUKI CELL FOR THE PRODUCTION OF CALCIUM AND THE SUBSEQUENT REDUCTION OF TiO_2



ONO and SUZIKI PROCESS

ADVANTAGES

*As calcium is a very electropositive element, it is capable of producing both titanium and its alloys from oxides and also reducing oxide layers

DISADVANTAGES

*Calcium is soluble in molten calcium chloride which increases the electronic conductivity of the melt, decreasing the current efficiency

* Consumable anode with CO/CO_2 evolution

BHP PROCESS

- BHP Process is claimed to work in the same way as the OS Process
- Calcium is thought to deposit from the electrolyte and this reduces the oxide
- 2kg/day of titanium are being produced with 100 kg/day plant being designed

Attributes of the experimental facilities – main reactor

REACTORS

- Containment of up to 1 t of molten salt ($CaCl_2$).
- $CaCl_2$ preheating and melting plant for reactor startup (patented).
- Molten $CaCl_2$ salt temperature up to 150°C of salt superheat (i.e. to 930°C in-salt temperature).
- Variable reduction power to 4800 A, or to a potential of 16 V.
- Off gas handling facilities and reactor shrouding to 28 $m^3 \, min^{-1}$ (1000 cfm). Off gas scrubbing facilities for HCl, Cl_2, and $CaCl_2$ fume.
- Inert gas (Ar) shielding for mitigation of metal re-oxidation.

PROCESS CONTROL & MONITORING

- Cascaded, multi-zone, flux-limited control for near isothermal furnace heating.
- Individual current and voltage monitoring for every electrode.
- Real-time product gas analysis (CO, CO_2, and O_2).

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The Polar™ Titanium process is based on reduction of TiO_2 to Ti using molten salt electrochemistry

Cathodic reactions

$CaO_{(in\ salt)} + 2e^- = Ca_{Met\ (in\ salt)} + O^{2-}$

$TiO_2 + 2Ca_{(in\ salt)} = Ti + 2CaO_{(in\ salt)}$

Anodic reactions

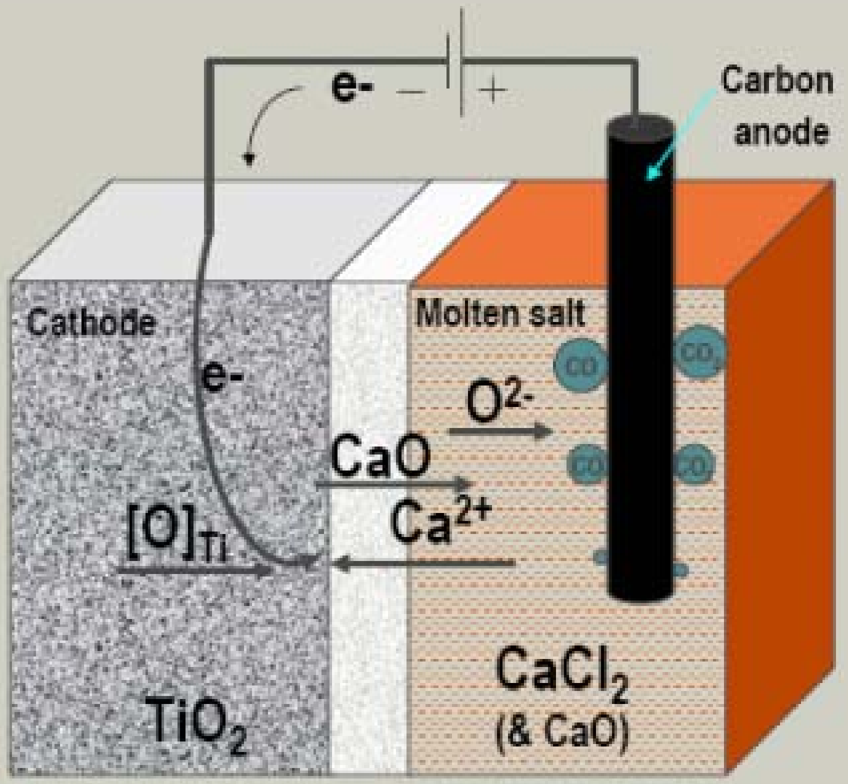
$O^{2-} + C_{(anode)} = CO_{(gas)} + 2e^-$

$2O^{2-} + C_{(anode)} = CO_{2(gas)} + 4e-$

$TiO_2 + C = Ti + \{CO_{(gas)} + CO_{2\ (gas)}\}^*$

Kinetics of the reaction are important – key parameters for investigation include:

- Reactor temperature,
- Applied voltage,
- Electrolyte composition
- Feed properties



* *Stoichiometry not shown, CO/CO_2 ratio varies with process conditions*

Titanium 2005 – 21st Annual ITA Conference, Scottsdale, AZ, USA – 25-27 September 2005

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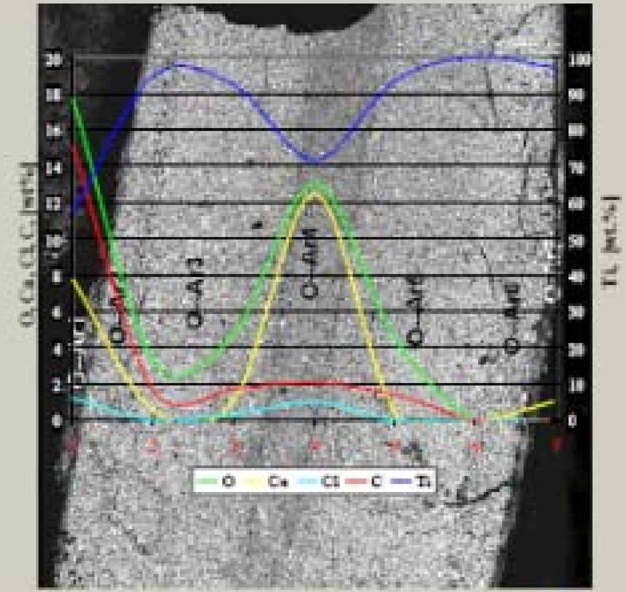
Typical product chemistry

Product analysis comments

- As reduction reactions proceed, the feed form progressively attains final product specifications, moving through a series of transitions to produce Ti:
  $TiO_2 \Rightarrow Ti_4O_7 \Rightarrow Ti_3O_5 \Rightarrow Ti_2O_3 \Rightarrow Ca_xTi_yO_z \Rightarrow TiO \Rightarrow$ Ti metal $_{(0\ to\ 15\%\ O)}$

- Potential for a range of products: ingot, sheet, or powder.
- Product quality from the reactor can be varied to suit market requirements.
- Quality achieved to date
  - Oxygen < 0.05%;
  - Carbon < 0.02%;
  - Nitrogen < 0.009%
  - Hydrogen < 0.01%



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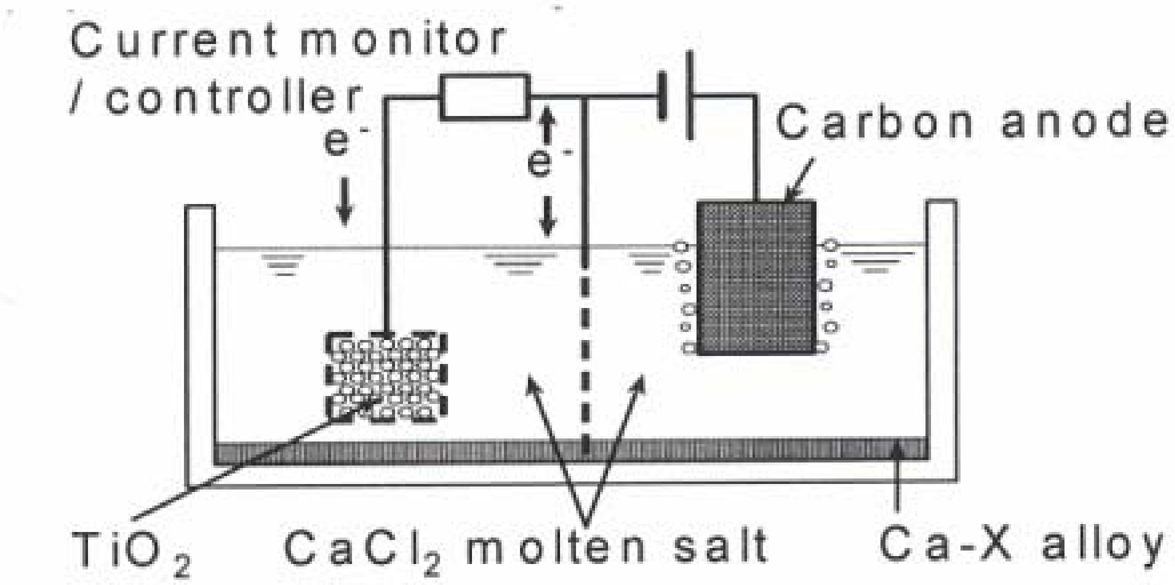
EMR/MSE PROCESS



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EMR/MSE PROCESS

ADVANTAGES

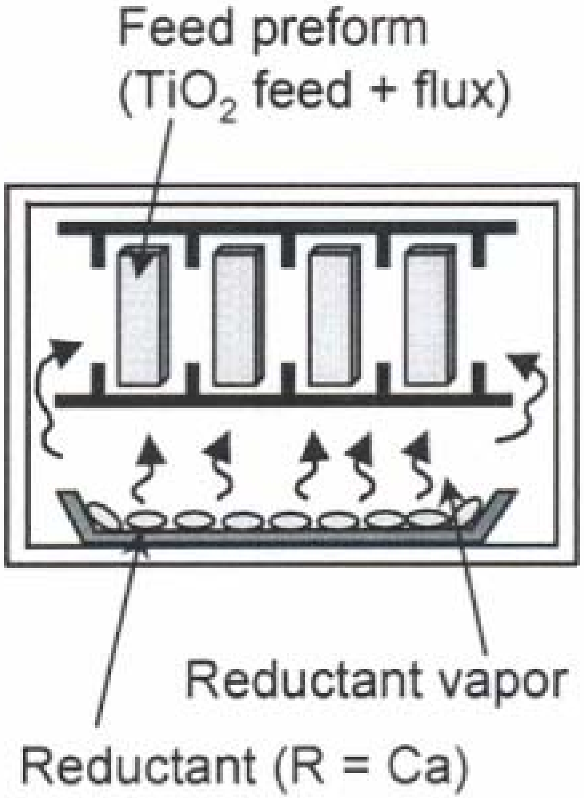
*Can use off-peak electricity

DISADVANTAGES

*Due to calcium solubility in calcium chloride, current efficiency is very low

* Consumable anode

PREFORM REDUCTION PROCESS



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PREFORM REDUCTION PROCESS

ADVANTAGES

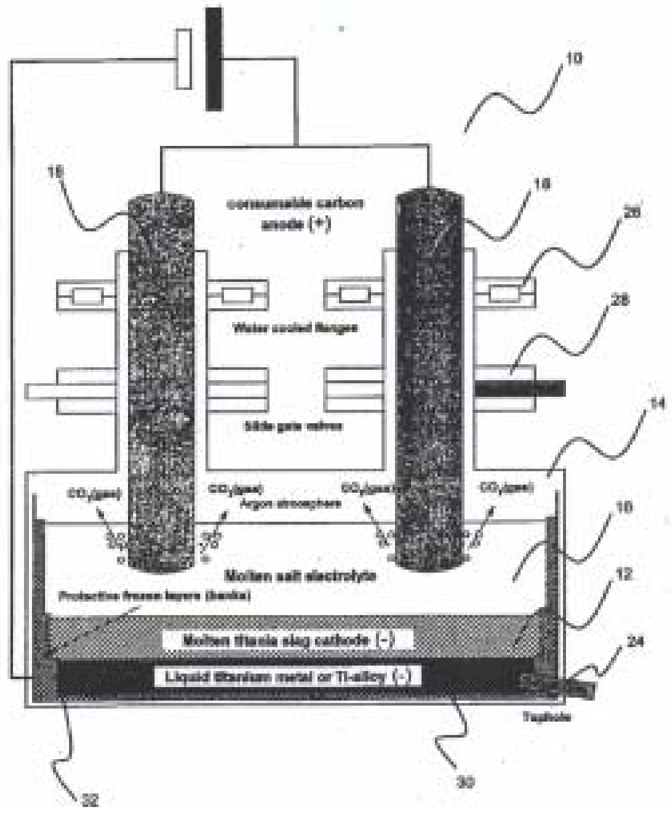
*Calcium is a well known reductant and the oxide produced dissolves in the $CaCl_2$ flux.

*Alloys could be prepared

DISADVANTAGES

*Calcium is very expensive

QIT PROCESS



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QIT PROCESS

ADVANTAGES

*Produces liquid titanium

DISADVANTAGES

*Process operates at at very high temperature

*Separation of three liquid layers?

FFC CAMBRIDGE PROCESS

Electrode Potentials in Fused Chlorides, calculated from thermodynamic data ($E_{Na} = 0$ at 973 K)

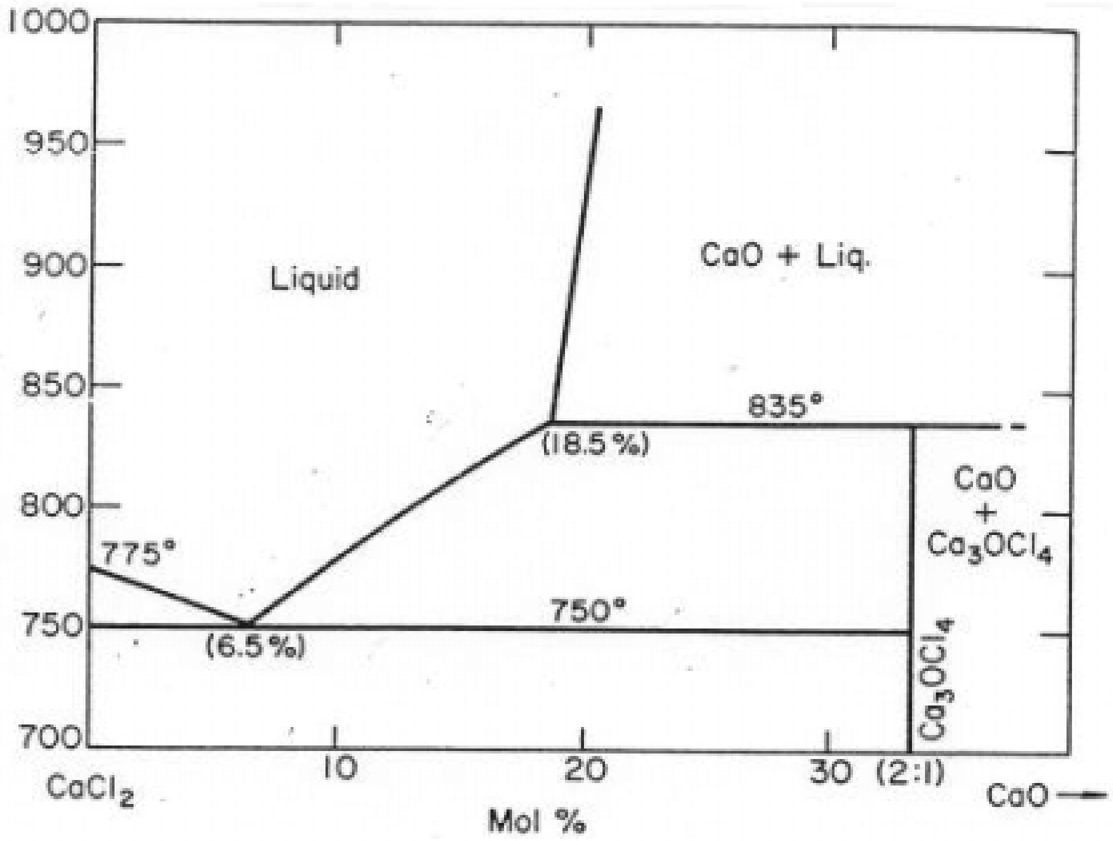
■ $O_2 + 4e^- = 2O^{2-}$	$E^o = 2.713$ V
■ $TiO_2 + 4e^- = 2O^{2-} + Ti$	$E^o = 0.750$ V
■ $Ca^{2+} + 2e^- = Ca$	$E^o = - 0.06$ V

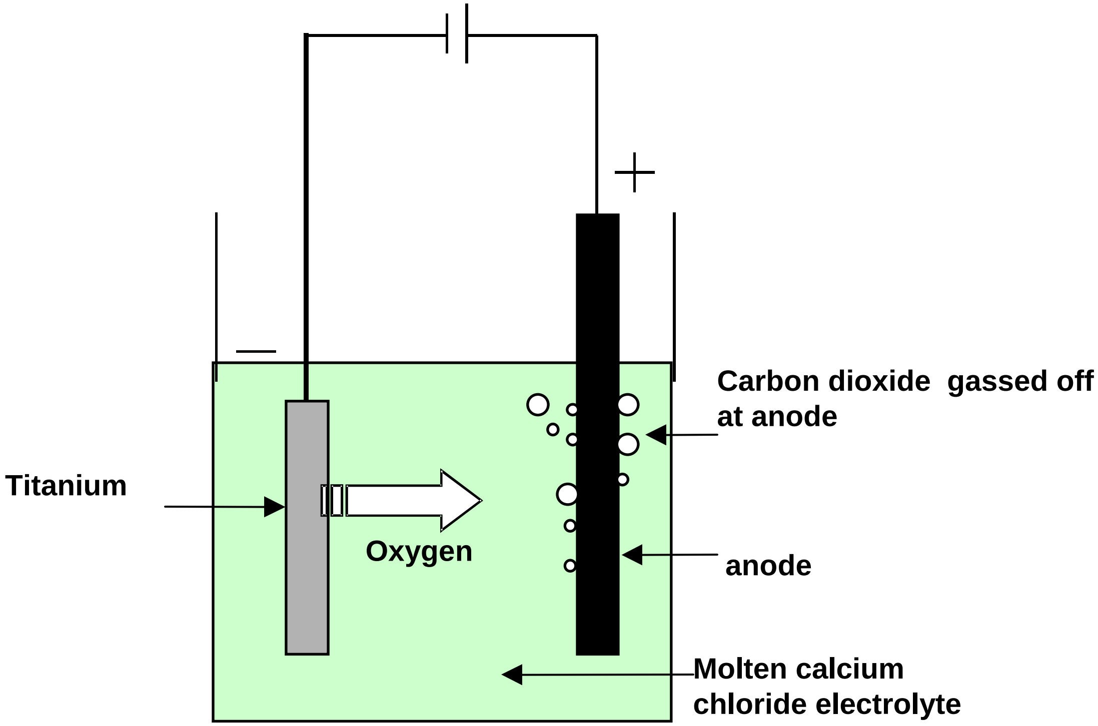
Methods for Titanium Deoxidation

- Molten calcium
- Grinding away surface layer
- Dissolving surface layer in acid

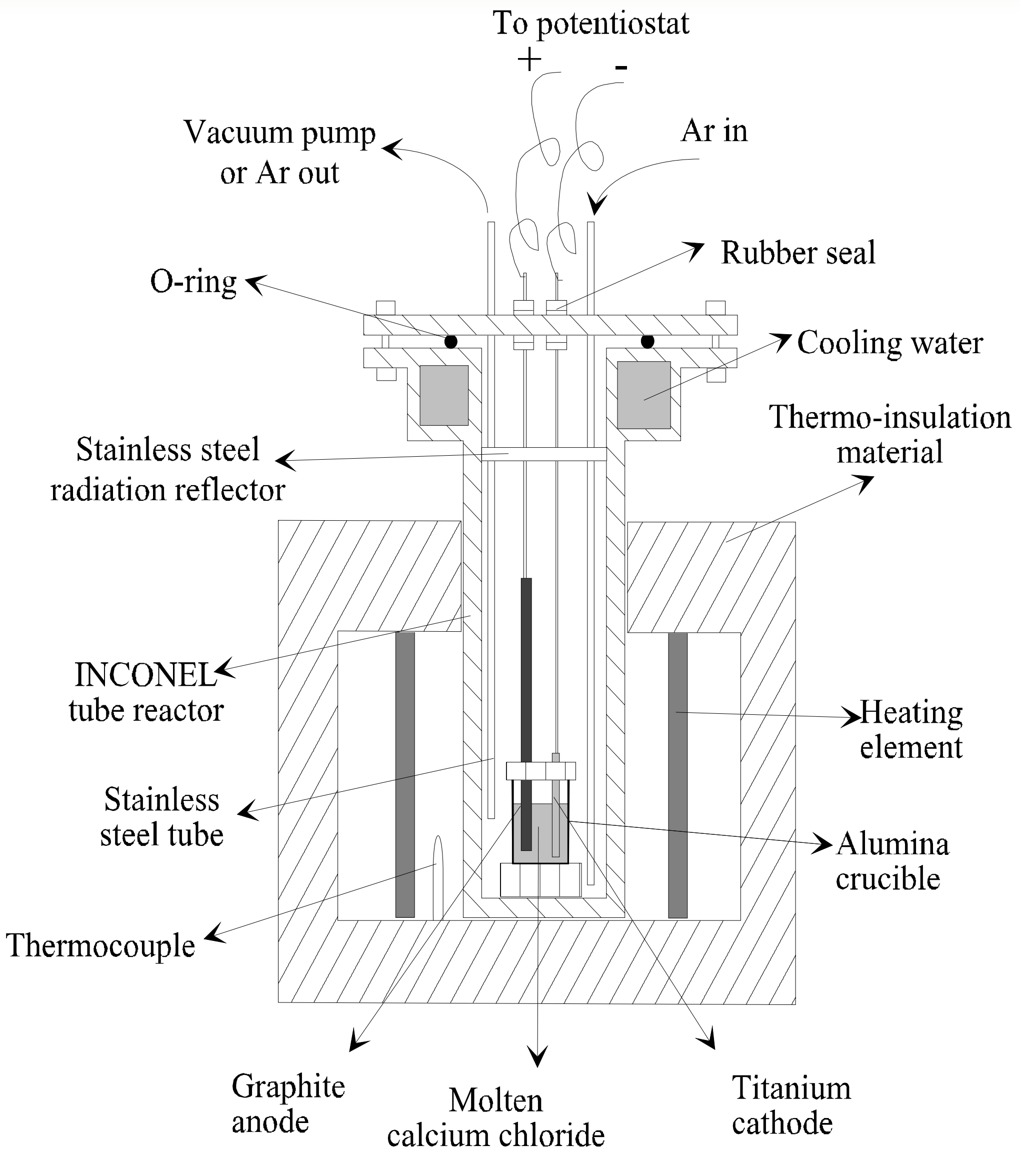
Removal of Oxygen from Solid Titanium

- $O_{(metal)} + 2e^{-}_{(Power\ source)} = O^{2-}_{(molten\ salt)}$


1000
950
900
850
800
750
700
Liquid
CaO + Liq.
835°
(18.5%)
CaO
+
Ca_3OCl_4
775°
750°
(6.5%)
Ca_3OCl_4
$CaCl_2$
10
20
30
(2:1)
$CaO \rightarrow$
Mol %


+
—
Carbon dioxide gassed off at anode
Titanium
Oxygen
anode
Molten calcium chloride electrolyte

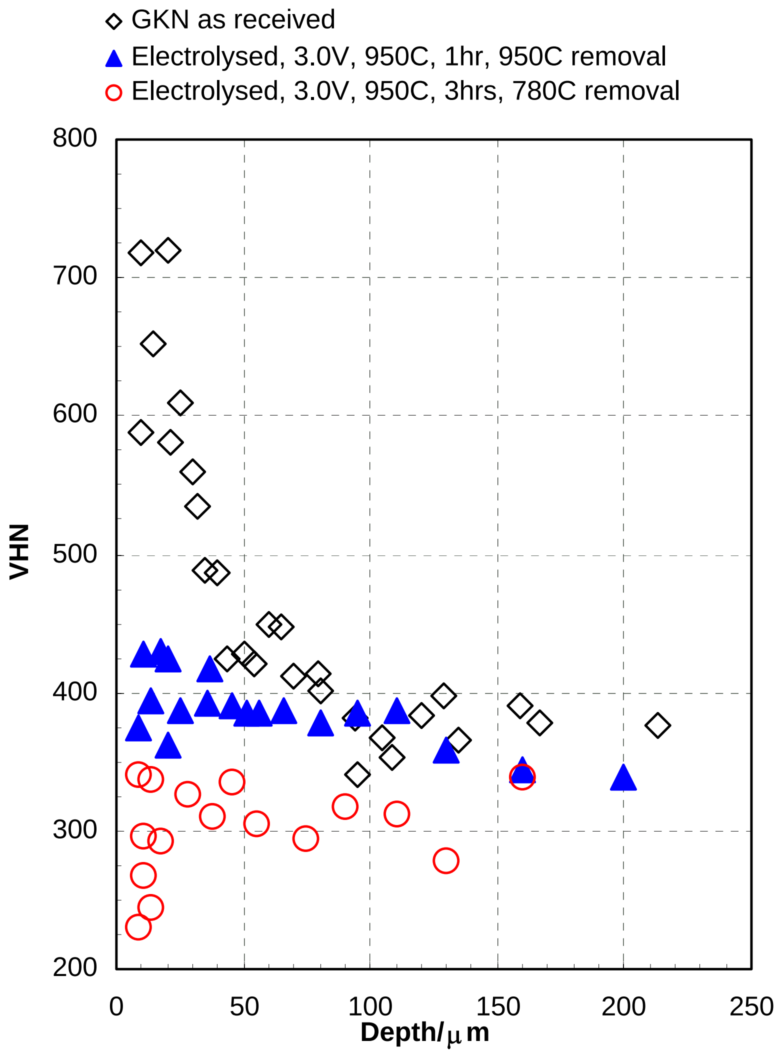
Furnace



To potentiostat
+
-
Vacuum pump or Ar out
Ar in
Rubber seal
O-ring
Cooling water
Thermo-insulation material
Stainless steel radiation reflector
INCONEL tube reactor
Heating element
Stainless steel tube
Alumina crucible
Thermocouple
Graphite anode
Molten calcium chloride
Titanium cathode

View of Apparatus

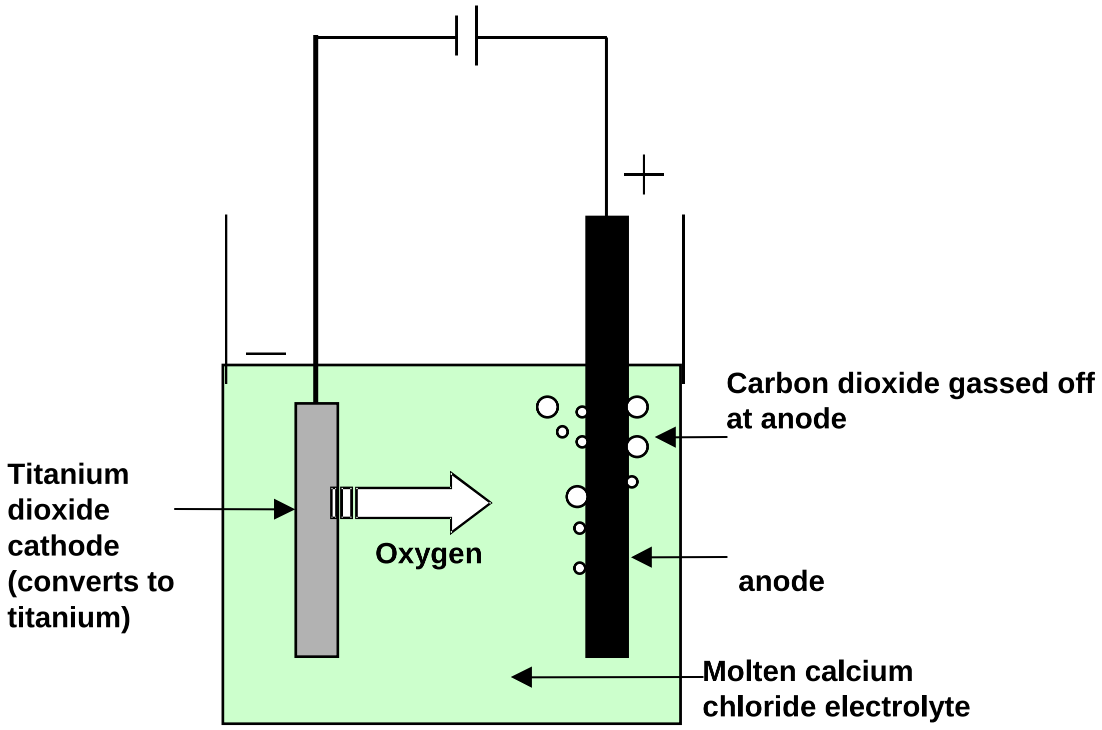
Microhardness Profiles

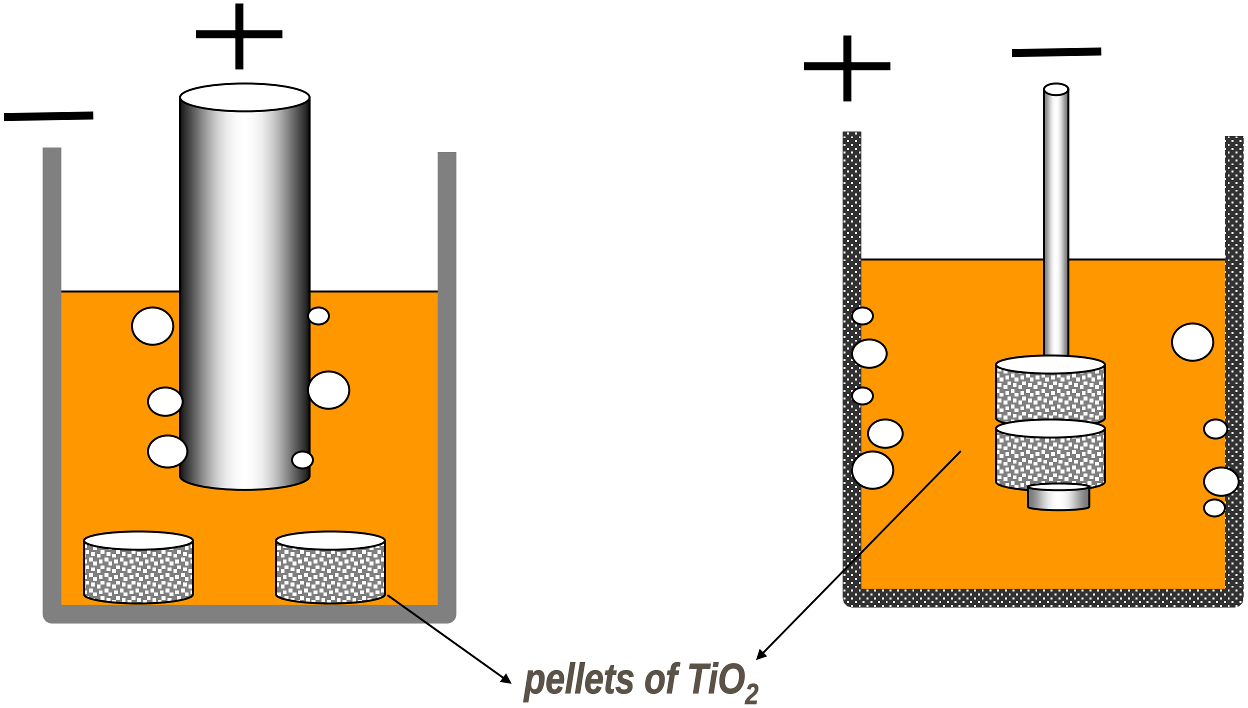


Oxygen Contents of De-oxidised Titanium

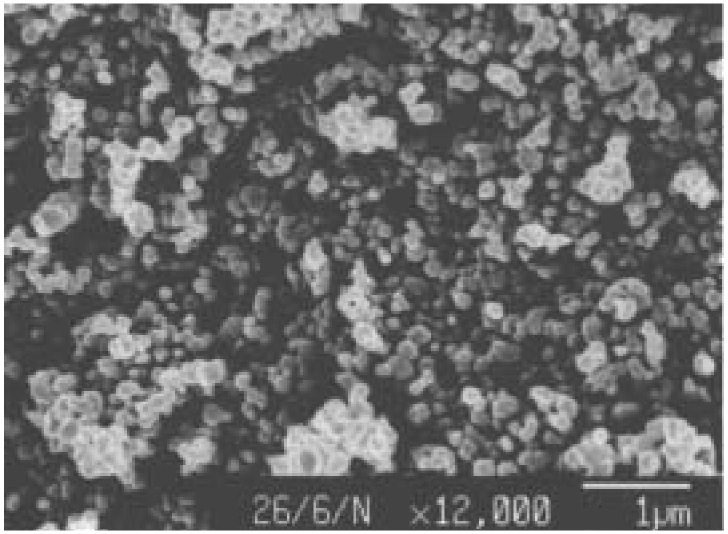
3.0 V	<200 ppm
3.3 V	<200 ppm
2.8 V	<200 ppm
3.1 V	<200 ppm

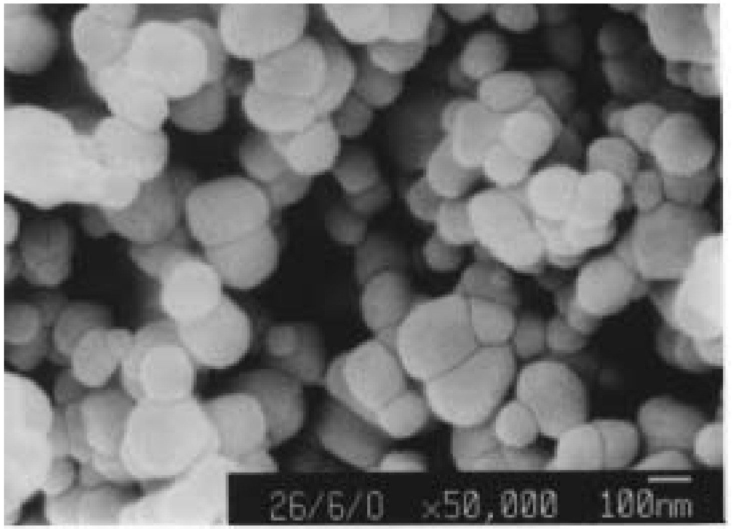
Removal of Oxygen from Titanium dioxide


+
—
Carbon dioxide gassed off at anode
Titanium dioxide cathode (converts to titanium)
Oxygen
anode
Molten calcium chloride electrolyte

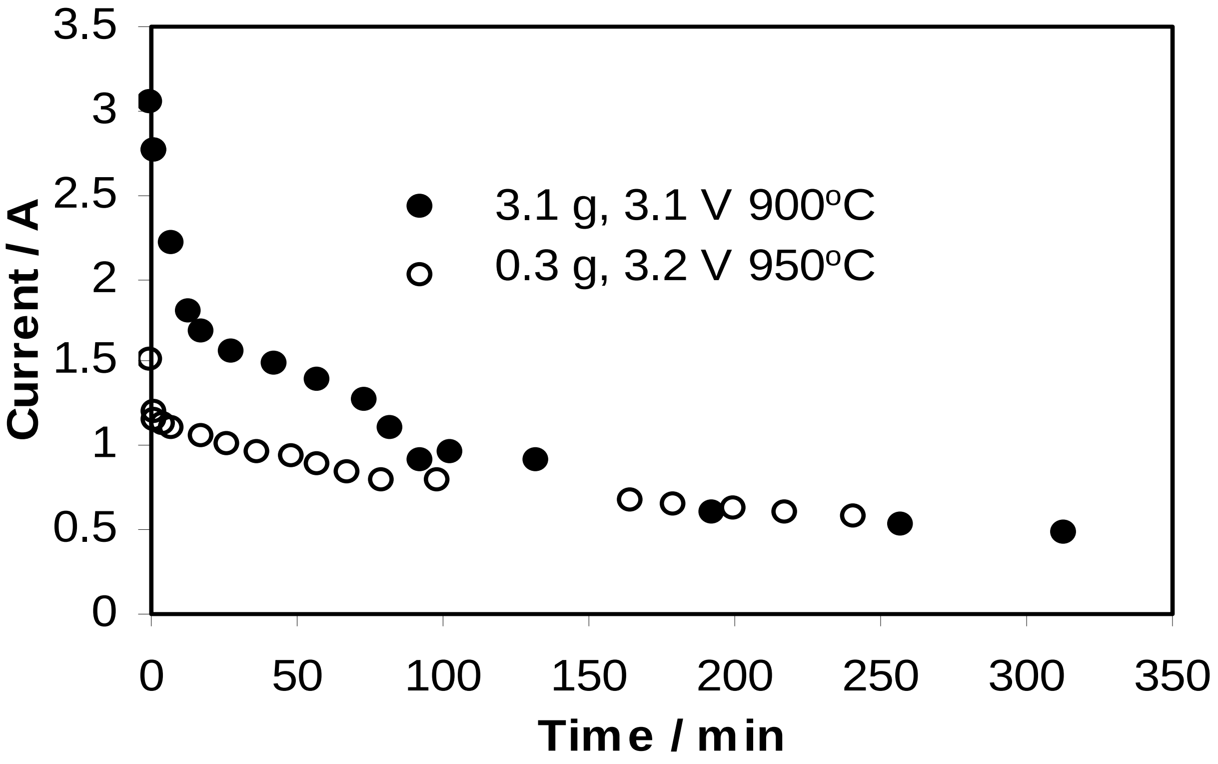

+
–
+
–
pellets of TiO_2

Starting Material

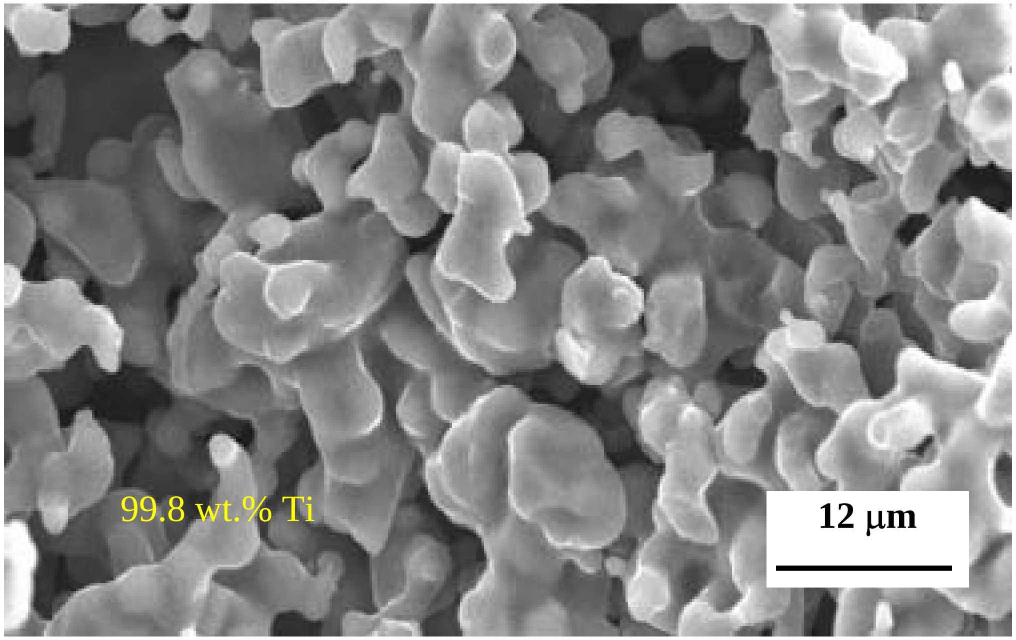




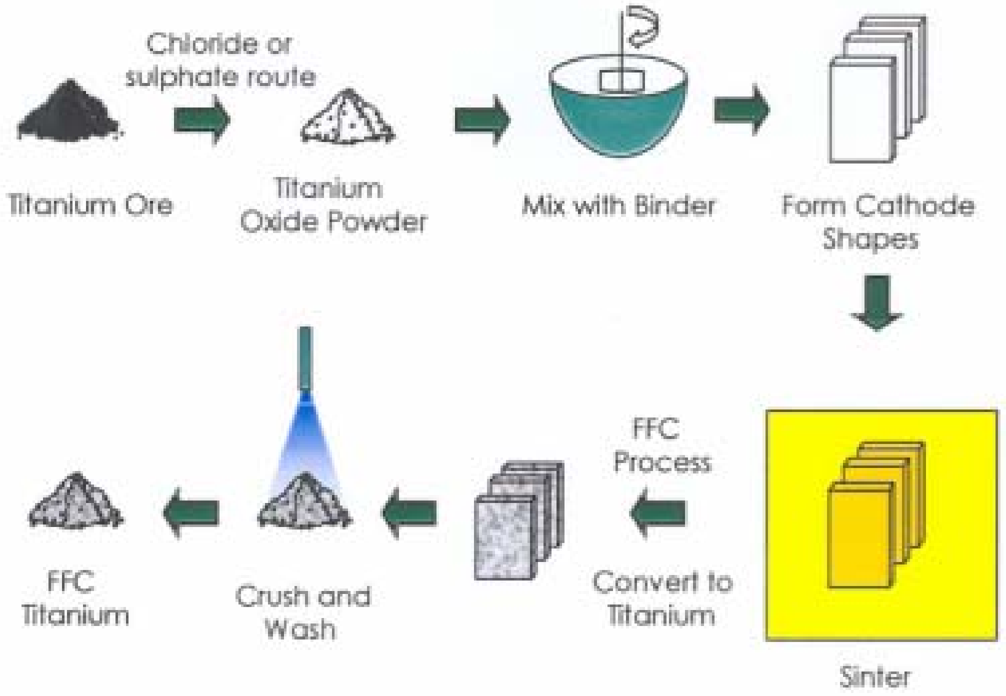
Current-Time Plot



Titanium Product



CAMBRIDGE FFC PROCESS

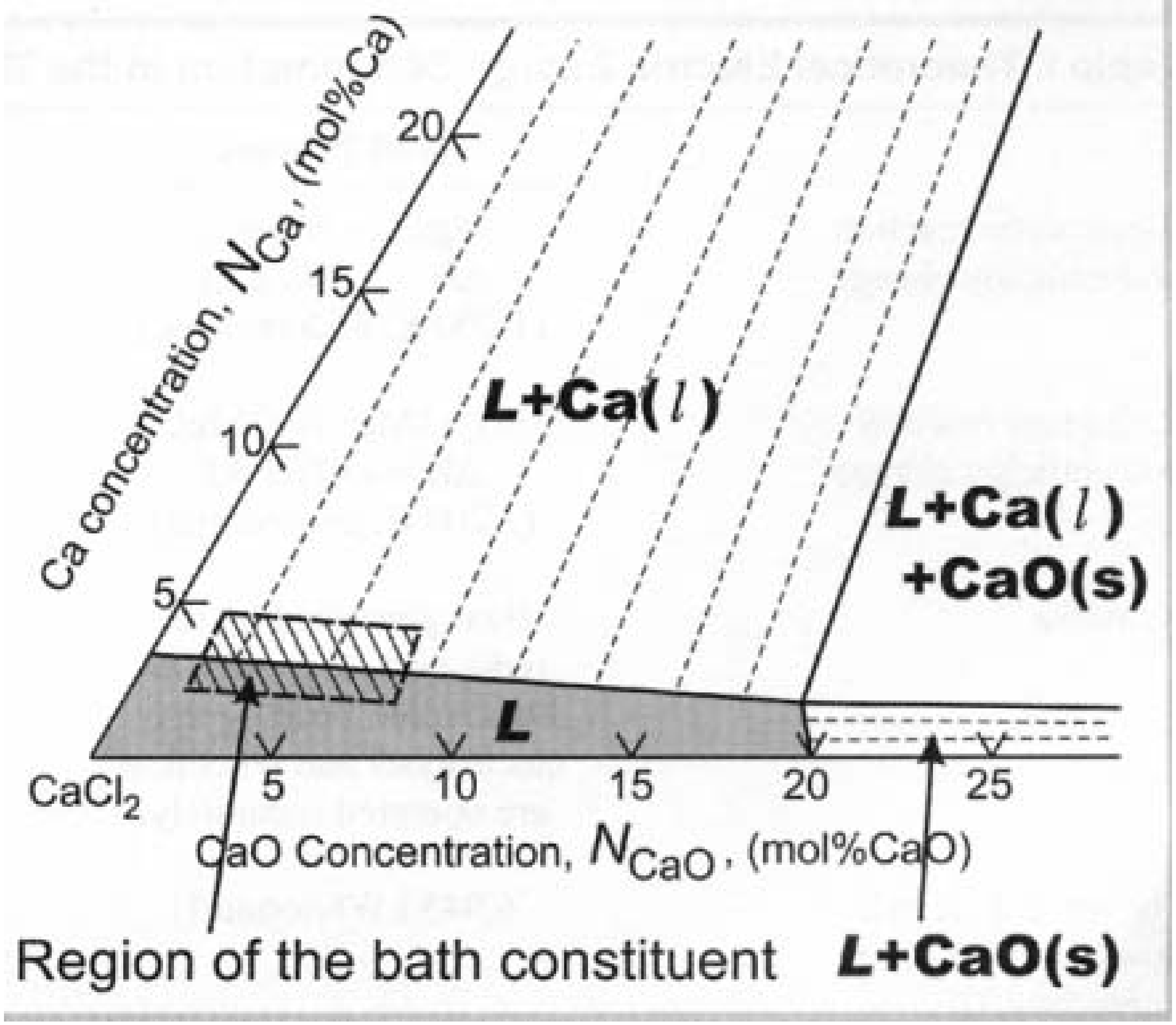


PROBLEMS

- Current efficiency relatively low at the end of the process
- Substantial amounts of carbon present in vicinity of cathode
- Consumable anode with CO/CO_2 evolution

EFFECT OF DISSOLVED CALCIUM

CALCIUM – CALCIUM OXIDE – CALCIUM CHLORIDE PHASE DIAGRAM

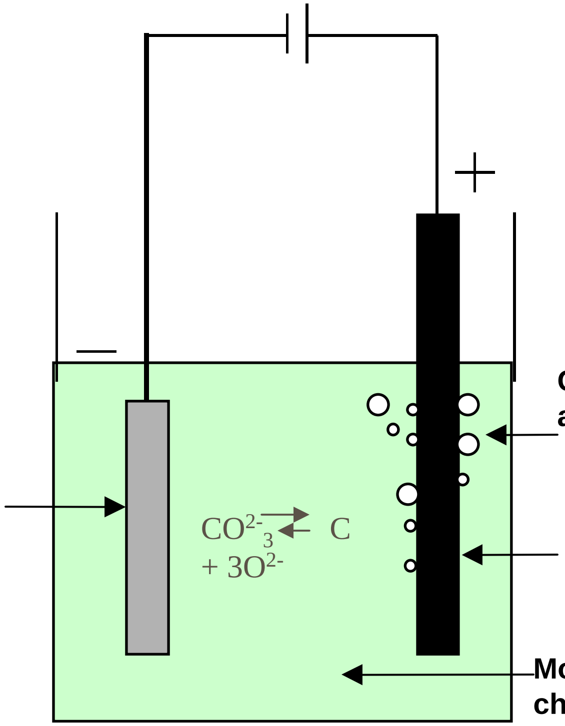


CALCIUM ACTIVITIES AT POTENTIALS FOR THE REDUCTION OF TITANIUM DIOXIDES

- $Ca^{2+} + O^{2-} + 2e = Ca + O^{2-}$ $E = 0$ V
  $a_{Ca} = 1$
- $O_{(500\ \text{ppm in Ti})} + 2e = Ti + O^{2-}$ $E = 0.029$ V
  $a_{Ca} = 5.63 \times 10^{-1}$
- $TiO + 2e = Ti + O^{2-}$ $E = 0.43$ V
  $a_{Ca} = 2.0 \times 10^{-4}$
- $Ti_2O_3 + 2e = 2TiO + O^{2-}$ $E = 0.92$ V
  $a_{Ca} = 1.2 \times 10^{-8}$
- $2TiO_2 + 2e = Ti_2O_3 + O^{2-}$ $E = 1.275$ V
  $a_{Ca} = 1.1 \times 10^{-11}$

FORMATION AND REACTION OF CARBONATE ION

- $3O^{2-} + C = CO^{2-}_3 + 4e^-$
- CO^{2-}_3 ion diffuses to cathode
- $CO^{2-}_3 + 4e^- = 3O^{2-} + C$
- O^{2-} ion diffuses back to anode where it can react again
- This may be the major loss of current efficiency



Carbon dioxide gassed off at anode

Titanium

$CO_3^{2-} \rightleftarrows C + 3O^{2-}$

anode

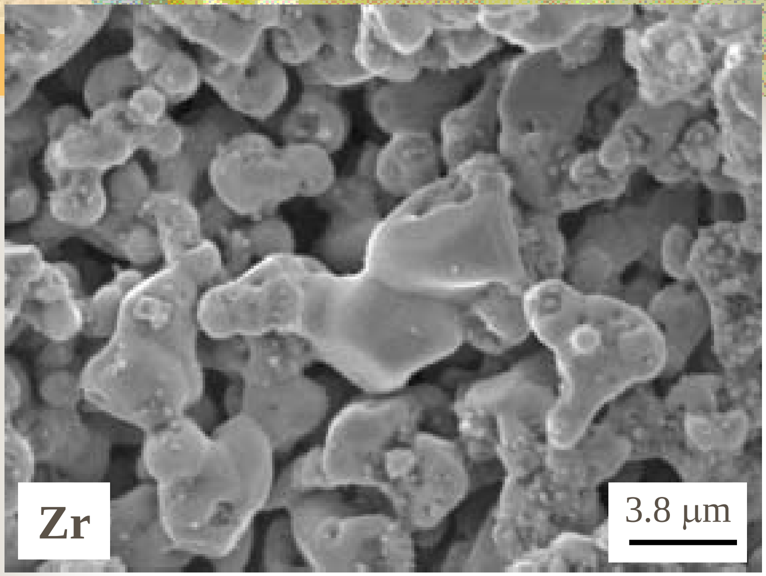
Molten calcium chloride electrolyte

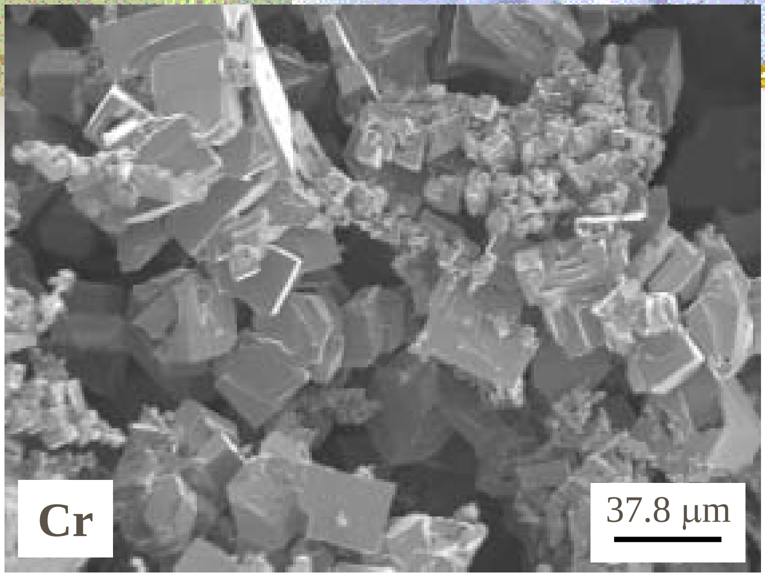
Reduction of other Metal Oxides

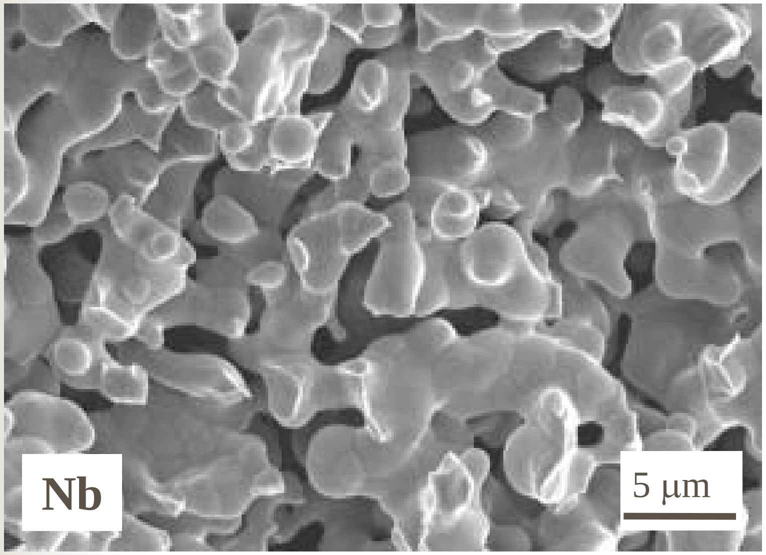
- Zirconium oxide
- Hafnium oxide
- Samarium oxide
- Uranium oxide
- Neodymium oxide
- Niobium oxide
- Chromium oxide
- Tantalum oxide

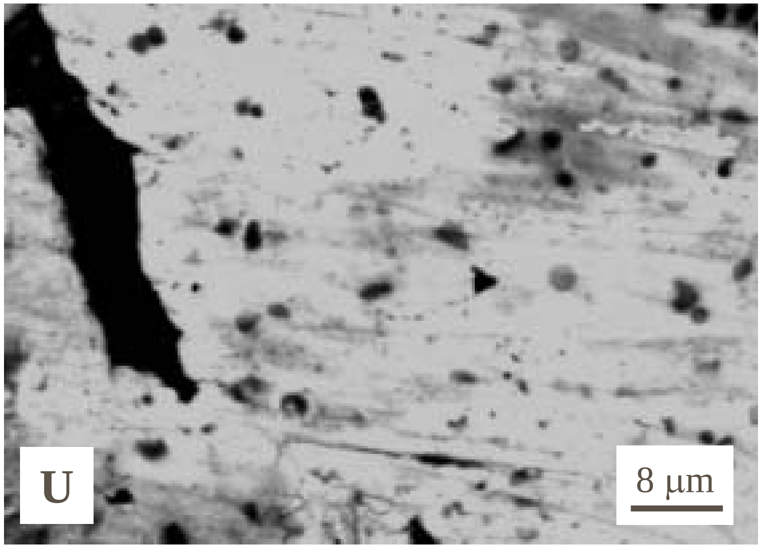
Electrode Potentials in Molten Calcium Chloride, calculated from thermodynamic data (E_{Na} = 0 at 973 K)

$O_2 + 4e^- = 2O^{2-}$	$E^0 = 2.713\ \mathrm{V}$
$2PbO + 4e^- = 2O^{2-} + 2Pb$	$E^0 = 2.082\ \mathrm{V}$
$SnO_2 + 4e^- = 2O^{2-} + Sn$	$E^0 = 1.734\ \mathrm{V}$
$MoO_2 + 4e^- = 2O^{2-} + Mo$	$E^0 = 1.650\ \mathrm{V}$
$\frac{2}{5}\,Nb_2O_5 + 4e^- = 2O^{2-} + \frac{4}{5}\,Nb$	$E^0 = 1.209\mathrm{V}$
$\frac{2}{3}\,Cr_2O_3 + 4e^- = 2O^{2-} + \frac{4}{3}\,Cr$	$E^0 = 1.189\mathrm{V}$
$\frac{2}{5}\,Ta_2O_5 + 4e^- = 2O^{2-} + \frac{4}{5}\,Ta$	$E^0 = 1.038\mathrm{V}$
$TiO_2 + 4e^- = 2O^{2-} + Ti$	$E^0 = 0.750\mathrm{V}$
$ZrO_2 + 4e^- = 2O^{2-} + Zr$	$E^0 = 0.349\mathrm{V}$
$\frac{2}{3}\,Al_2O_3 + 4e^- = 2O^{2-} + \frac{4}{3}\,Al$	$E^0 = 0.348\mathrm{V}$
$2TiO + 4e^- = 2O^{2-} + Ti$	$E^0 = 0.338\mathrm{V}$
$UO_2 + 4e^- = 2O^{2-} + U$	$E^0 = 0.337\mathrm{V}$
$HfO_2 + 4e^- = 2O^{2-} + Hf$	$E^0 = 0.211\mathrm{V}$
$2MgO + 4e^- = 2O^{2-} + 2Mg$	$E^0 = 0.143\mathrm{V}$
$2Ca^{2+} + 4e^- = 2Ca$	$E^0 = -0.06\mathrm{V}$

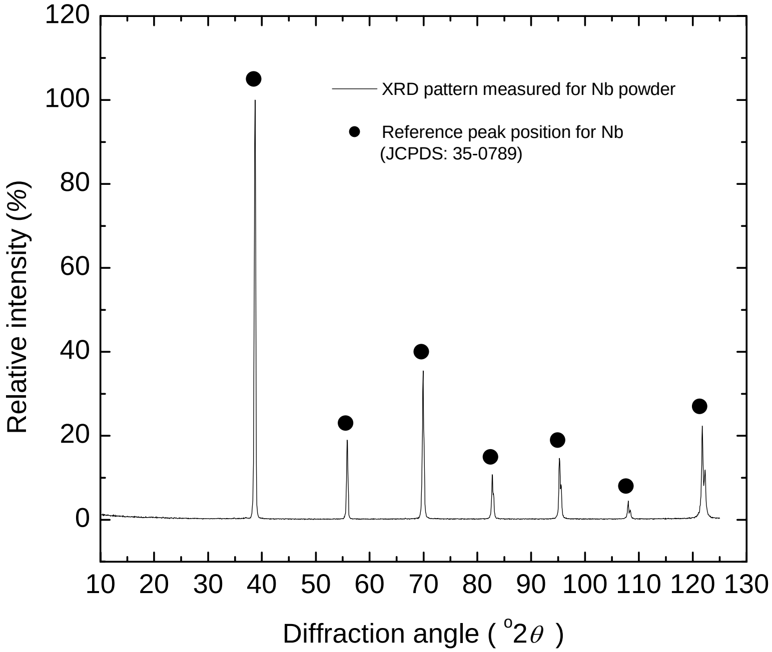

Zr
3.8 μm


Cr
37.8 μm


Nb
5 μm


U
8 μm

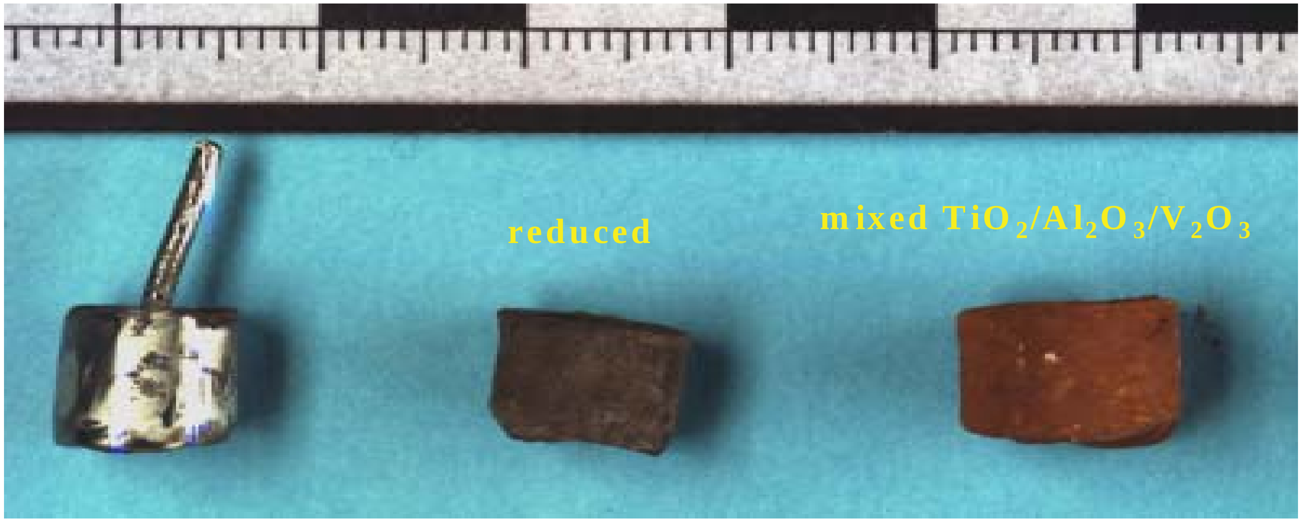
X-ray Spectra of Niobium

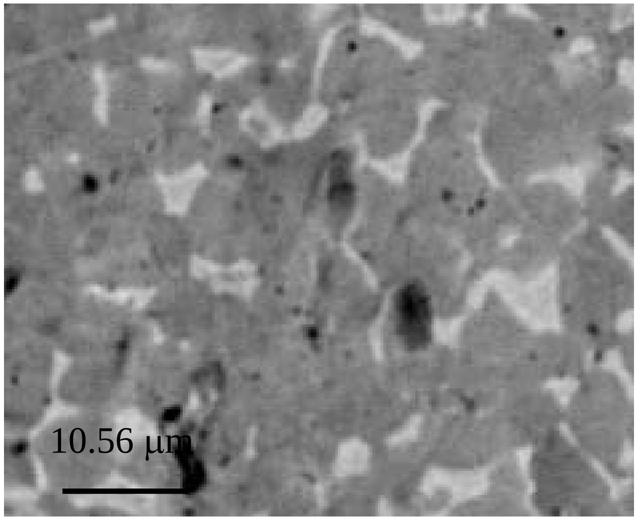


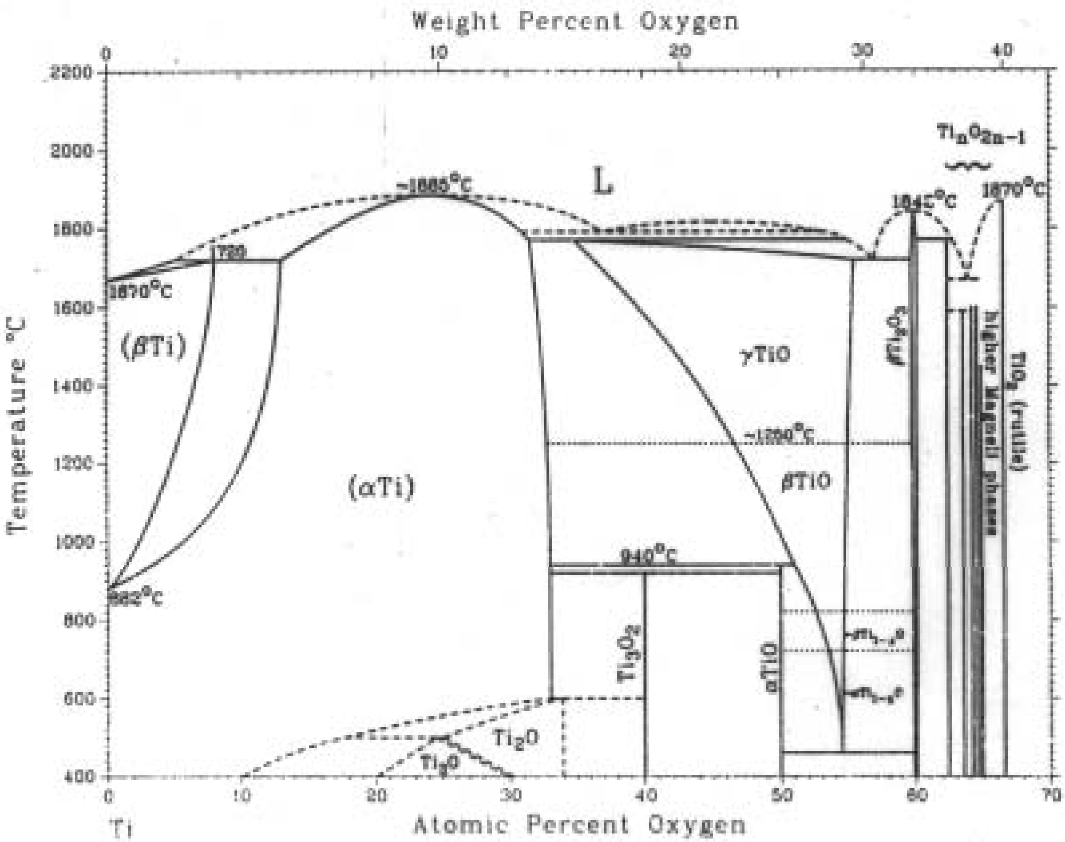
Preparation of Alloys and Intermetallic Compounds

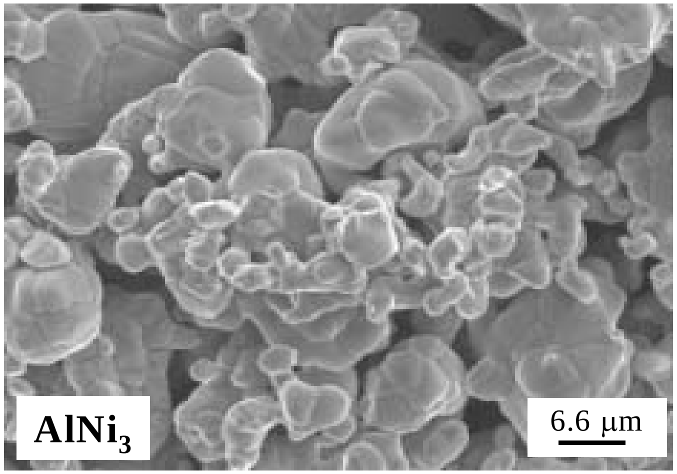
- Ti-6Al-4V
- TiAl
- $AlNi_3$
- NbTi
- NiTi

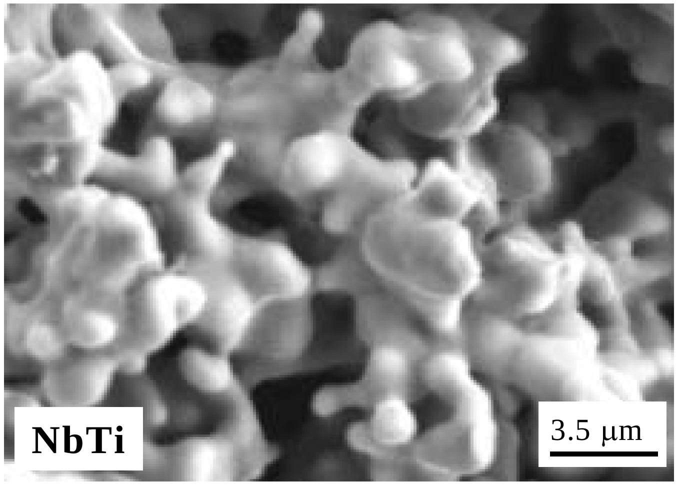
Ti-6Al-4V

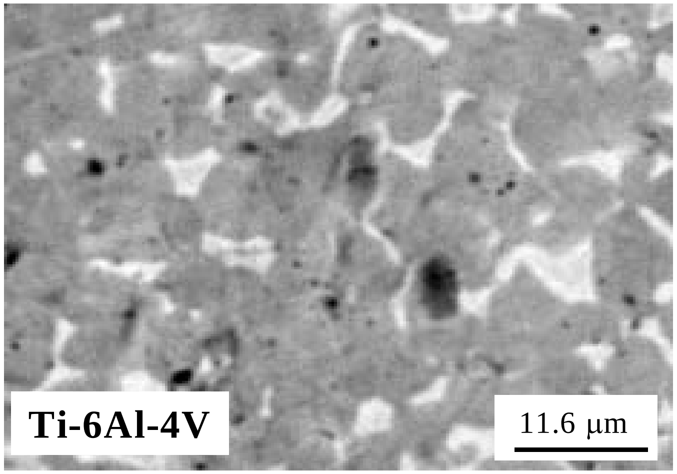


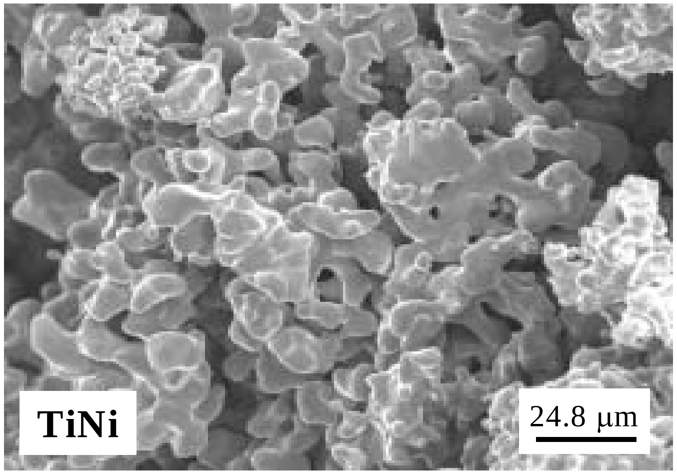



Weight Percent Oxygen
0
10
20
30
40
2200
2000
1800
1600
1400
1200
1000
800
600
400
Temperature °C
L
~1885°C
1870°C
1842°C
Ti_nO_{2n-1}
1720
1670°C
(βTi)
(αTi)
γTiO
~1250°C
βTiO
940°C
Ti_3O_2
αTiO
βTi_2O_3
higher Magneli phases
TiO_2 (rutile)
882°C
Ti_2O
Ti_3O
0
10
20
30
40
50
60
70
Ti
Atomic Percent Oxygen


AlNi$_3$
6.6 µm

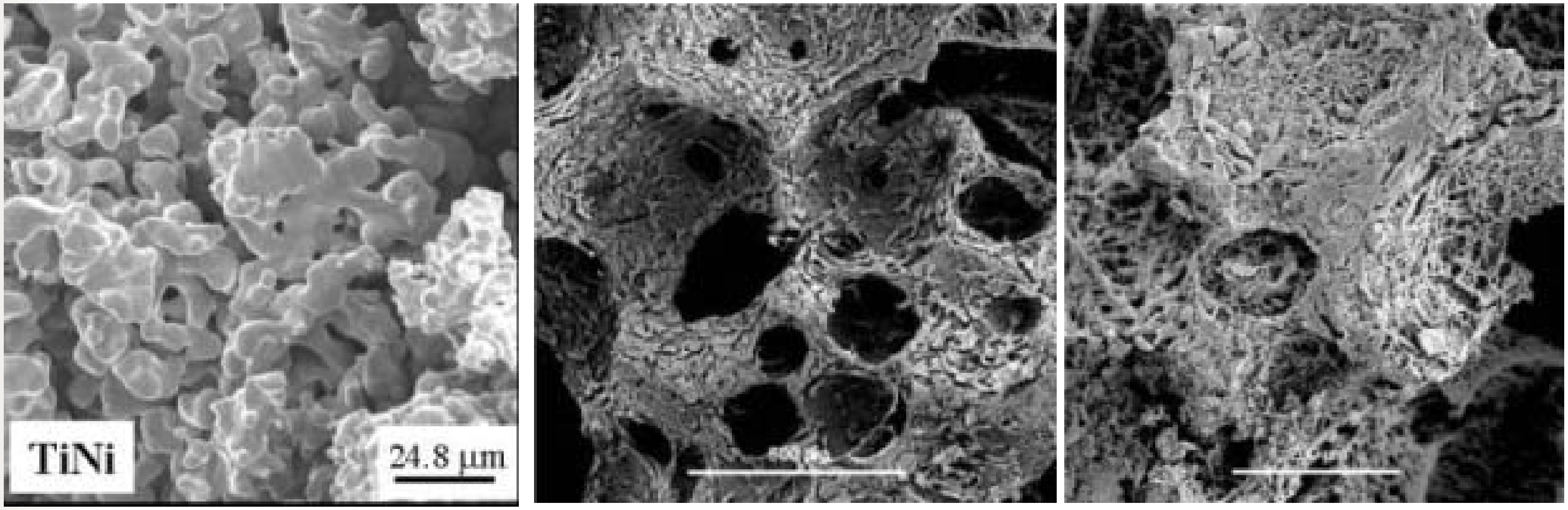

NbTi
3.5 µm


Ti-6Al-4V
11.6 µm


TiNi
24.8 µm

Ni-Ti Spectacle Frames

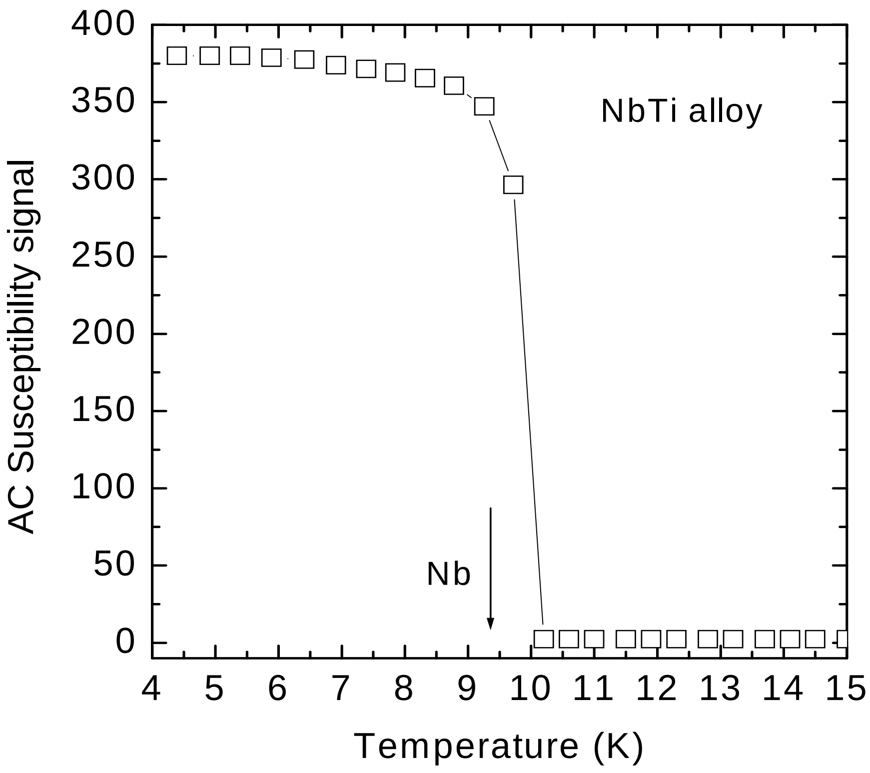
Bio-compatibility of Porous NiTi Alloys



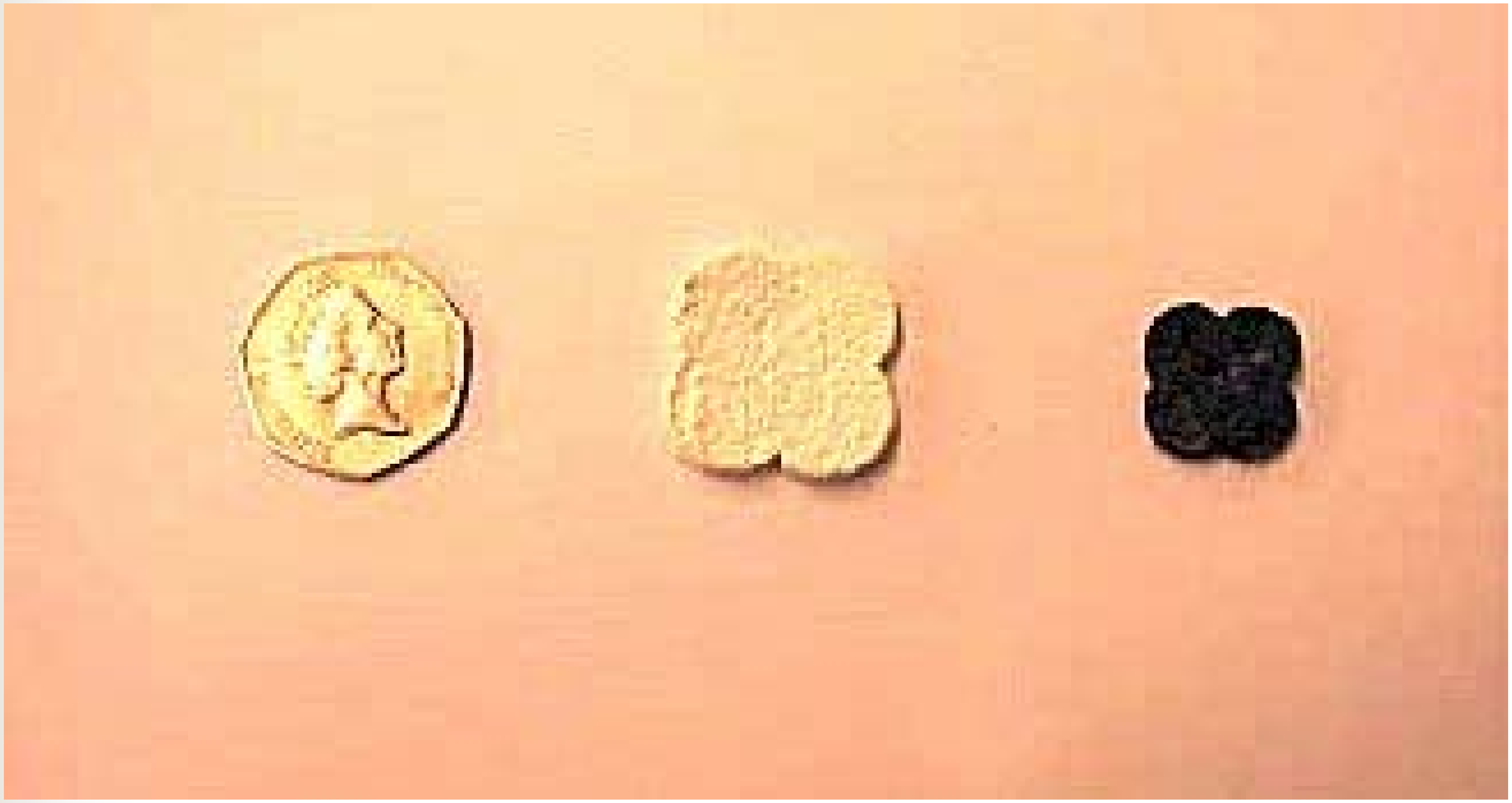
Human MG63 Cells Grown on FFC NiTi

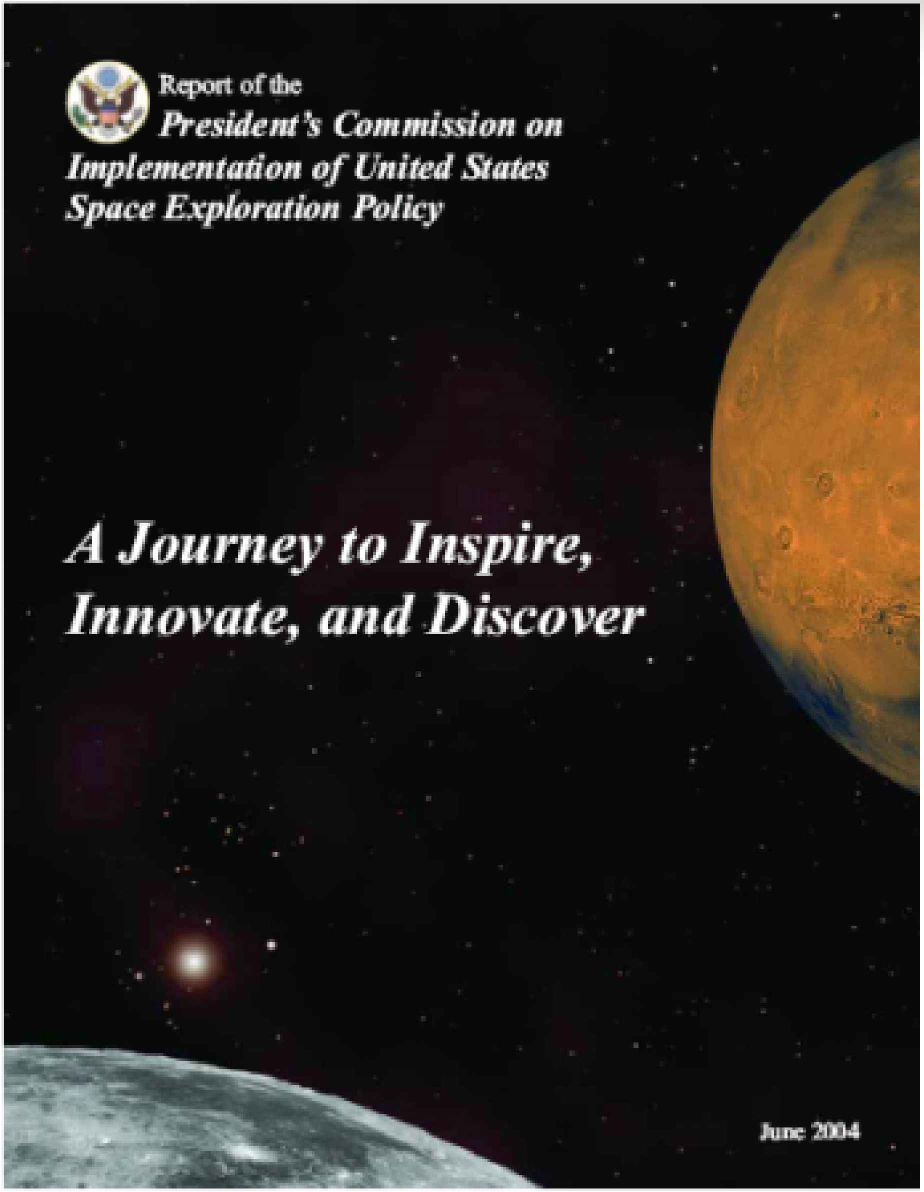
MRI Scanner

Superconductivity of niobium-titanium




BRITISH TITANIUM
55

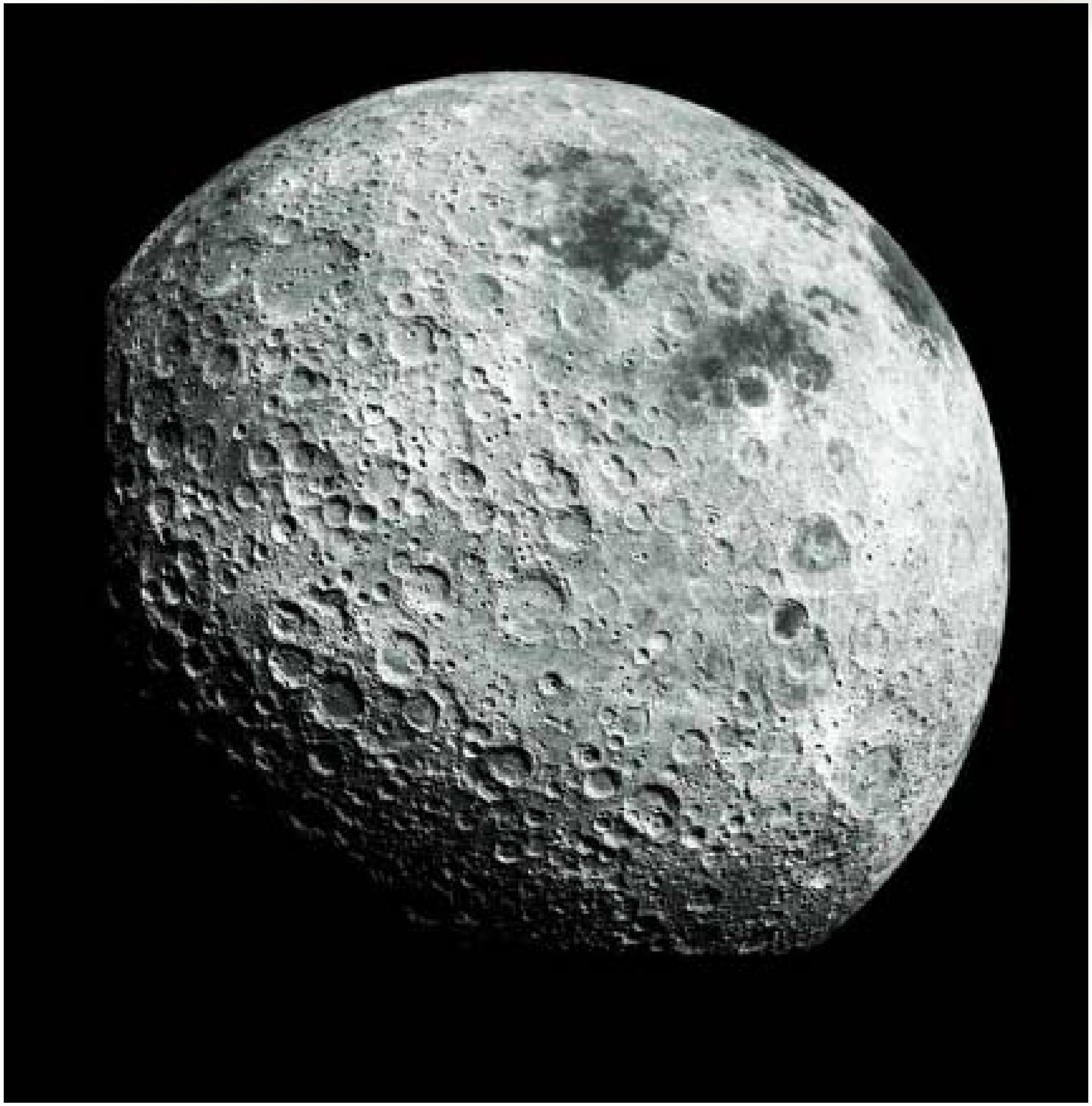




Report of the
President's Commission on
Implementation of United States
Space Exploration Policy

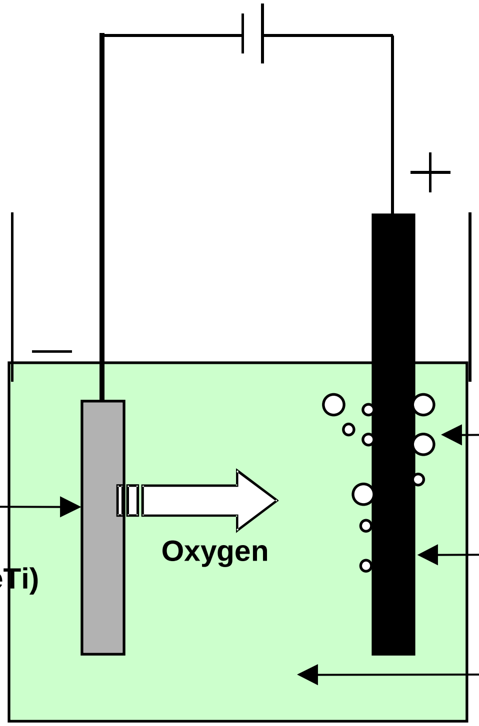
A Journey to Inspire,
Innovate, and Discover

June 2004



LUNAR ROCKS

- $FeTiO_3$
- Electro-deoxidise in molten calcium chloride to liberate oxygen for fuel for rockets
- Metals can be used as materials for construction



Oxygen gassed off at anode

$FeTiO_3$ Cathode (converts to FeTi)

Inert anode

Molten calcium chloride electrolyte

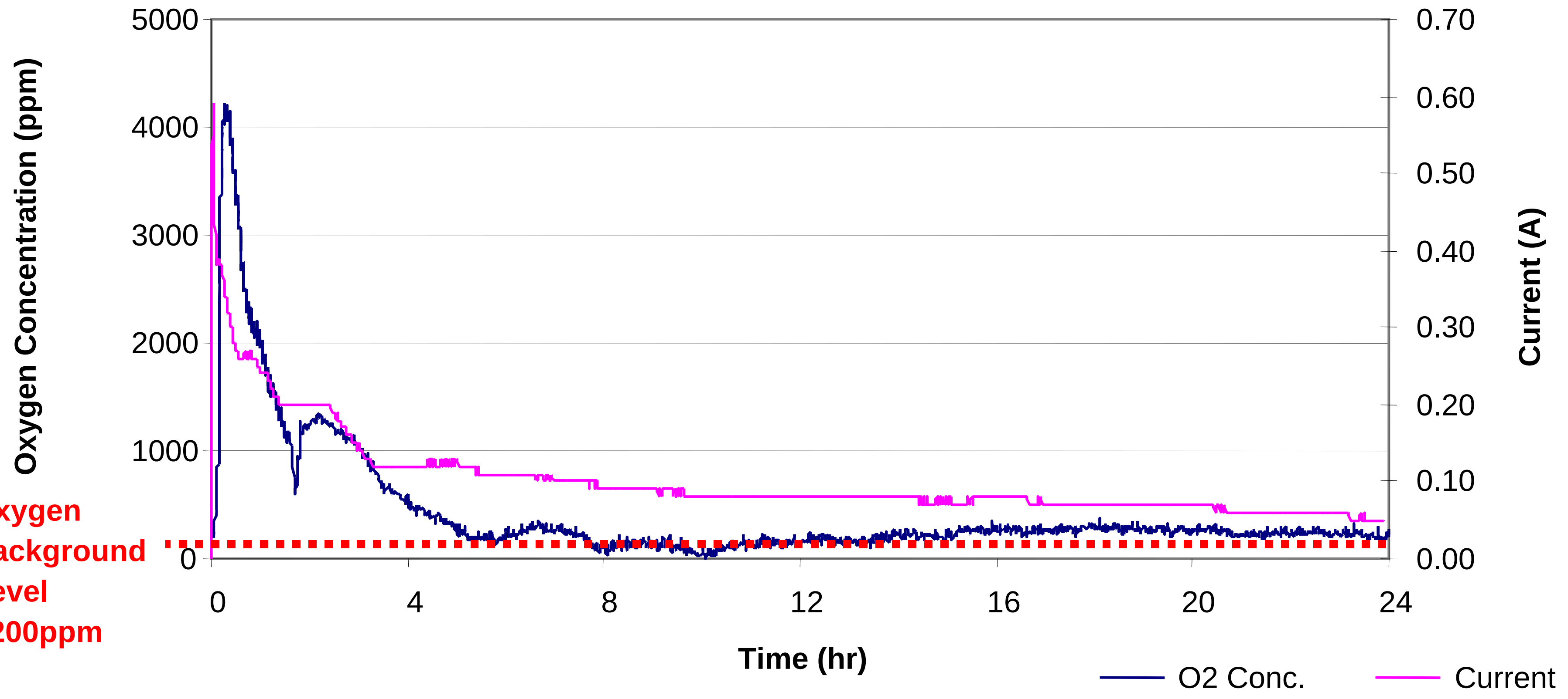
What does FFC produce?

The FFC Reduction from A (Ilmenite powder) or B (Ilmenite tiles) to
C (95% reduced), D (99% reduced, sintered) and E (melted tiles).
The FFC Process can remove >99% oxygen from metal oxide feedstock.

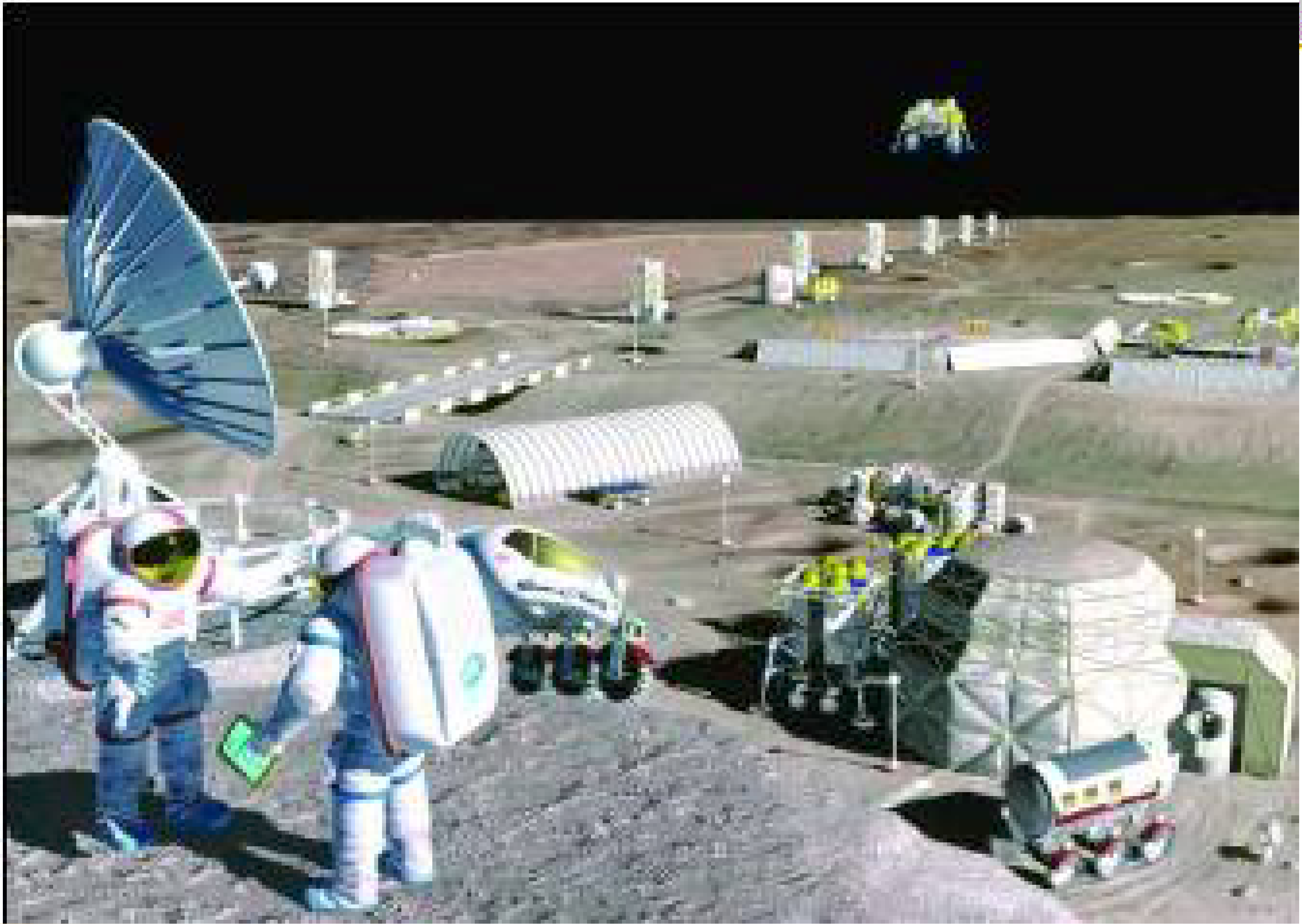
POSSIBLE INERT ANODE MATERIALS

- Conducting ceramics – SnO_2, ferrites
- Alloys – Aluminium bronzes
- Coatings – CeO_2
- Cermets – Nickel ferrites plus copper or silver

Oxygen Concentration and Current Profiles for an inert anode- TiO2 cathode Sytem (CaCl2; 550C; 3V Constant)



Oxygen Background Level ~200ppm



FFC PROCESS INCORPORATING INERT ANODE

- Remove oxide and alpha case layers
- Reduce titanium dioxide
- Reduce many other metal oxides
- Produce alloys directly
- Produce oxygen at the anode rather than carbon dioxide or carbon monoxide

Conclusions

- There are about 15 new processes for the production of titanium although none have gone beyond the pilot plant stage.
- Some processes can produce other metals, alloys and intermetallic compounds
- The FFC Cambridge Process has moved from solving a metallurgical problem, through a new method of reducing metal oxides to high technology materials and space exploration
- This could result in a process that simply takes a metal oxide and converts into the metal and oxygen

Acknowledgements

- I am grateful to Dr Tom Farthing for introducing me to the problem of oxygen contamination of titanium, Dr George Chen for playing a major part in the development of the concept of electro-deoxidation and Drs Duncan Alexander, Robert Copcutt, Tony Cox, Greg Doughty, Stuart Finch, Carsten Schwandt , Yong Yan and Kamal Tripuraneni for carrying out the scientific investigations and for financial support from EPSRC, DERA, DARPA, EAORD, ONR, British Titanium plc and the University Challenge Fund