Challenges and Opportunities in Titanium Metal Production

Is there still any interest/need to replace Kroll production?

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Presentation outline

- Brief introduction to Scatec and Norsk Titanium
- Market and applications of titanium
- Extractive and physical metallurgy
- Conventional processing of Ti via the Kroll process
- Alternative extraction methods for Ti metal
  - Possible reagents and reductants
- Detailed discussion of selected processes
- Conclusions

The Scatec Platform

Vision

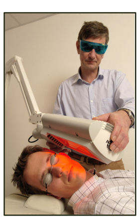
To be profitable and make the world a little cleaner

Business Idea

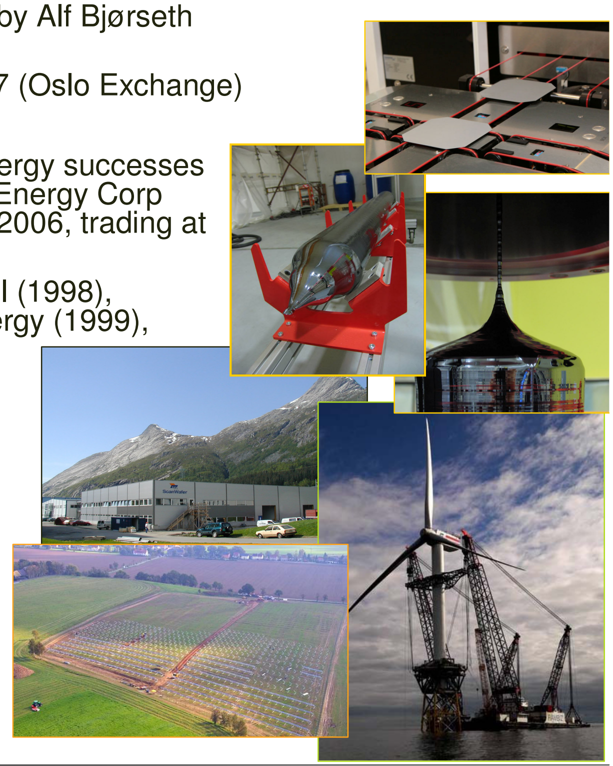
Develop new technology to produce renewable energy and advanced materials

History of Scatec

Norsk Titanium



- SCATEC established in 1987 by Alf Bjørseth (100%)
- PhotoCure established in 1997 (Oslo Exchange)
- SCATEC established solar energy successes which merged as Renewable Energy Corp (REC) in 2000, went public in 2006, trading at Oslo Exchange
  - ScanWafer (1994), ScanCell (1998), ScanModule (1998), SolEnergy (1999), SiTech (2004)
- Established:
  - Norsk Titanium in 2004
  - NorSun in 2005
  - Thor Energy in 2006
  - Scatec Solar in 2007
  - Scatec Adventure in 2007
  - NorWind in 2007
  - OceanWind 2008
  - Scatec Power 2008

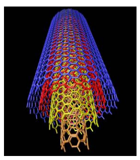


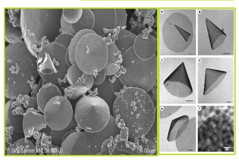
Industrial Macro Trends

Norsk Titanium

Advanced materials

- *Titanium*
- *Nano carbon*





Climate neutral energy

- *Solar energy*
- *Thorium*
- *Offshore wind*
- *CO_2 capture*

Electrification of transport

- *El car*
- *Battery technology*

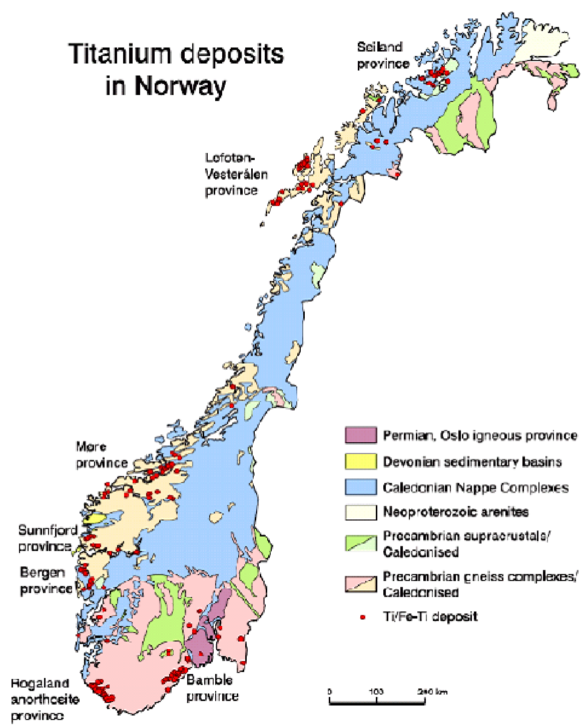
Why Norway?

Norsk Titanium

Norwegian Titanium mineral resources are LARGE

- Igneous deposits composed of ilmenite, magnetite and apatite
- Rutile-bearing eclogites in western Norway
- Proterozoic Rutile-bearing rocks in the Bamble region

Tellnes ilmenite deposit is the largest Ti-Fe orebody in Europe and 2nd most important in the world (after Lake Tio in Québec, Canada)



Ti Market and applications

Mechanical:

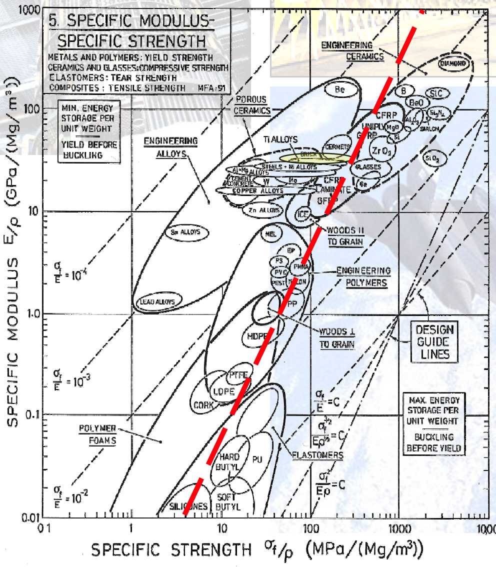
specific strength, fatigue

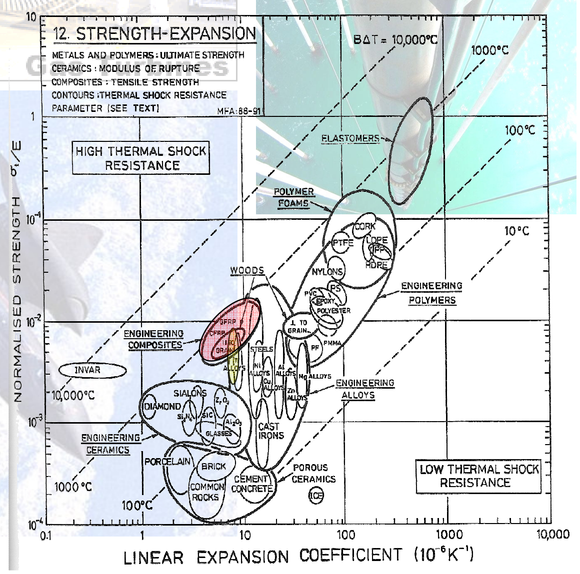
Chemical:

corrosion resistance & biocompatibility

Physical:

CTE similar to composites, non-magnetic, shape memory effect



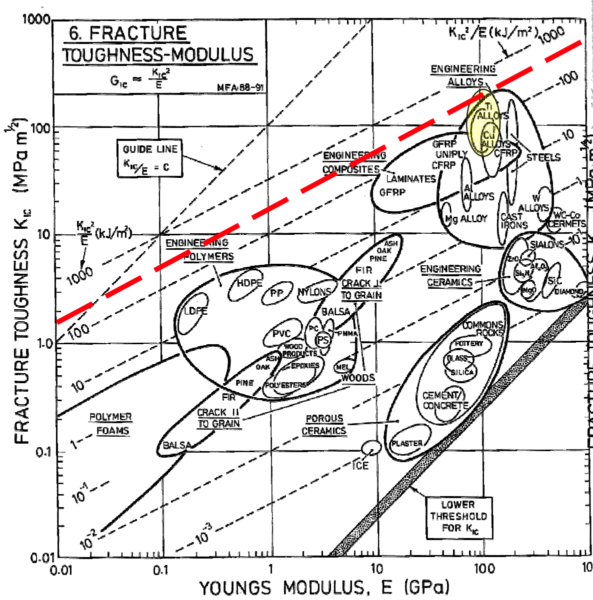


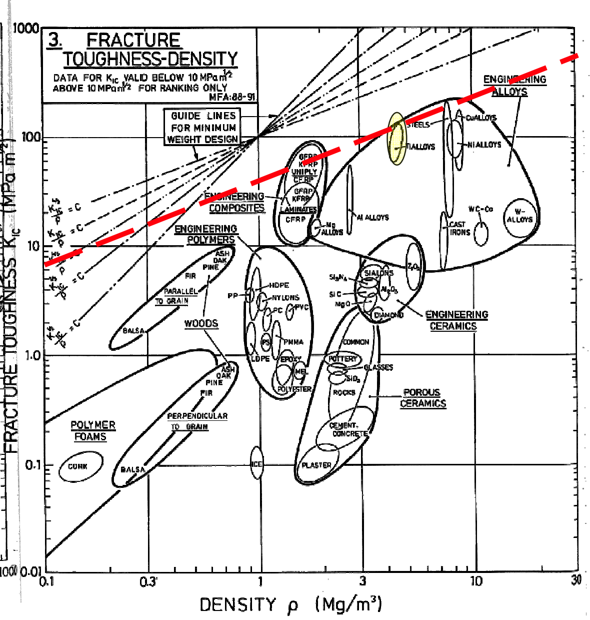
Ashby diagrams

Norsk Titanium
Scandinavian Advanced Technology

Titanium microstructures can be optimised to suit the application:

HCF & LCF versus K_{IC} & dA/dN versus static properties





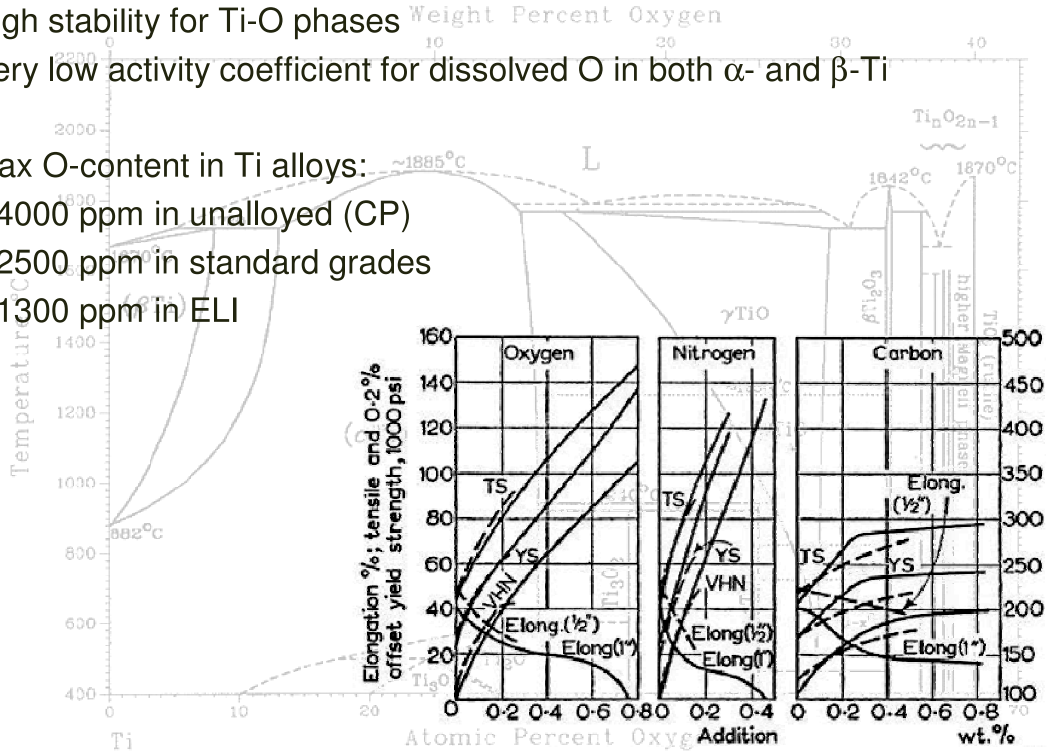
Ti metallurgy

High stability for Ti-O phases

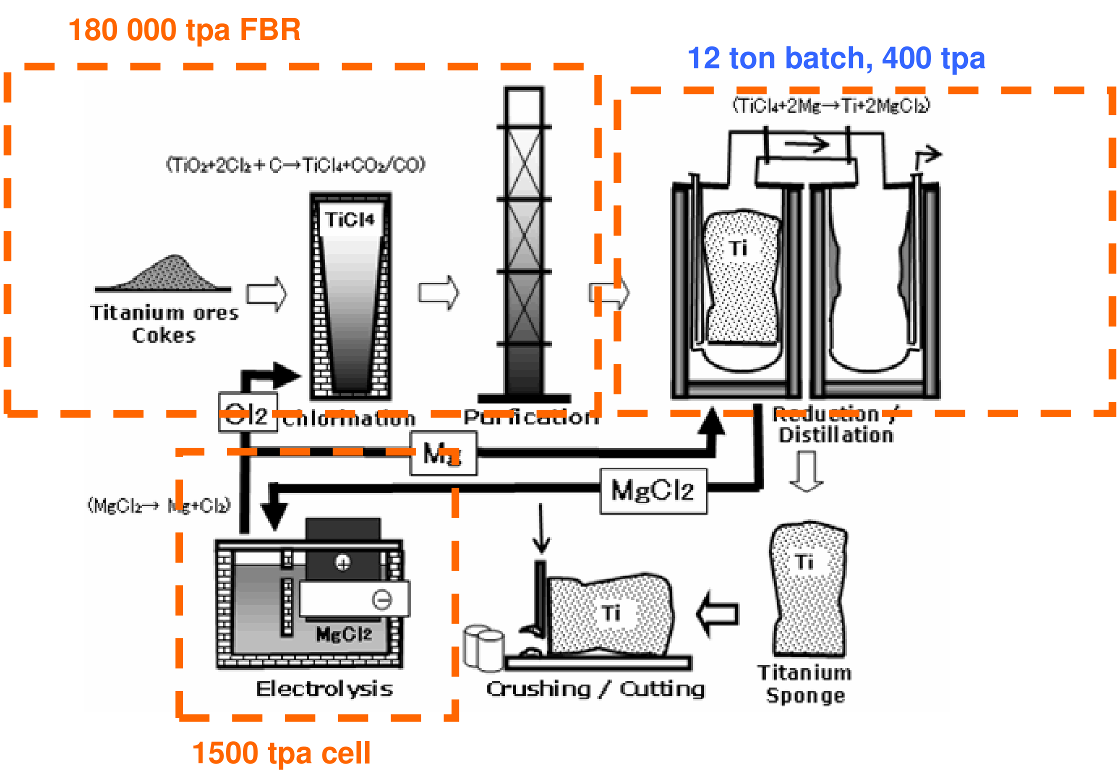
Very low activity coefficient for dissolved O in both α- and β-Ti

Max O-content in Ti alloys:

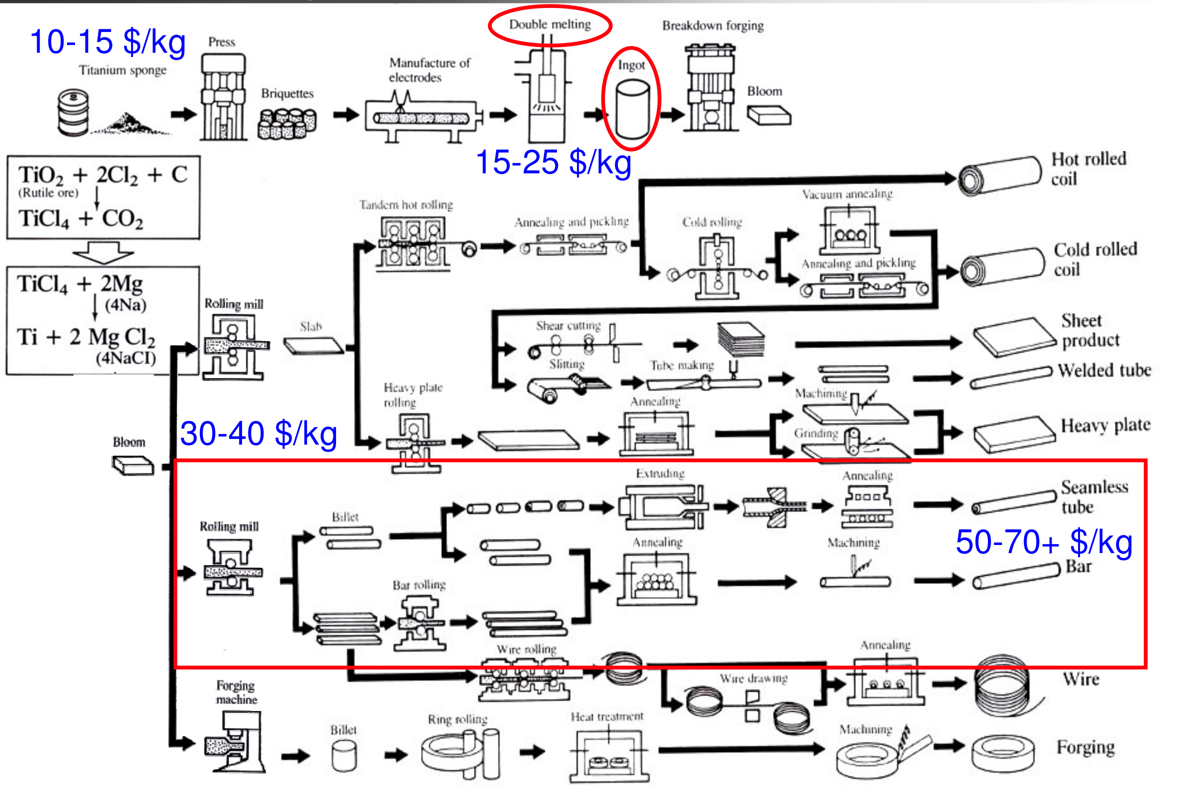
- 4000 ppm in unalloyed (CP)
- 2500 ppm in standard grades
- 1300 ppm in ELI



Kroll production of Ti metal



Conventional production



Alternative processes

Norsk Titanium

Reagent	Comments	Reductant	Process	Product
TiO_2	Via $TiCl_4$? – pigment Limited availability Environmentally friendly?	[Ca], Ca(liq)	OS/BHP	Powder
		Ca(g)	PRP	Powder
		e^- - low T	FFC	Powder, sponge
		e^- - high T	MIT/QIT	Liquid
Impure TiO_2	May use cheaper feedstock? Suitable for inert anode?	e^-	MER	Dendrites
		Al	various	Granules
$TiCl_4$	CO/CO_2/CHC emissions? High purity (5N+) Restricted feedstocks	Mg	Kroll	Sponge
		Na - batch	Hunter	Sponge
		Na - cont	ITP	Powder
		Ca	JTS	Powder
		H_2	SRI	Granules
$TiCl_x$	Via $TiCl_4$? Ti recycling?	Mg	Sub-chloride	Powder
		e^-	GTT/EW	Dendrites

Alternative processes

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		Ca(g)	PRP	Powder
		e^- - low T	**FFC**	**Powder, sponge**
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		Na - batch	Hunter	Sponge
		Na - cont	**ITP**	**Powder**
		Ca	**JTS**	**Powder**
		H_2	SRI	Granules
$TiCl_x$	Via $TiCl_4$? Ti recycling?	**Mg**	**Sub-chloride**	**Powder**
		e^-	GTT/EW	Dendrites

Internation Titanium Powder

Norsk Titanium

Continuous Na reduction of $TiCl_4$

Pros: Simplistic process (equip & chem)

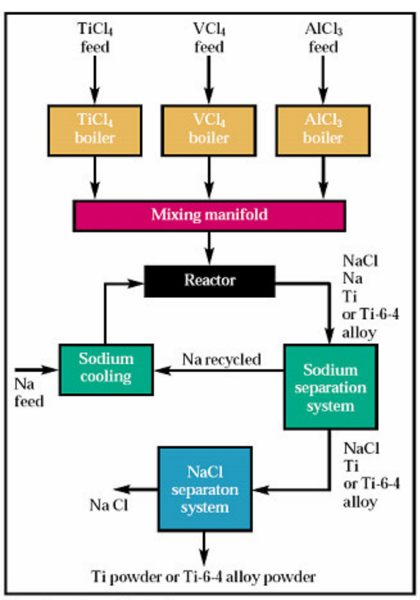
$TiCl_4 + 4Na \rightarrow Ti + 4NaCl$

T_{mp} NaCl = 801 ℃ T_{bp} Na = 883 ℃

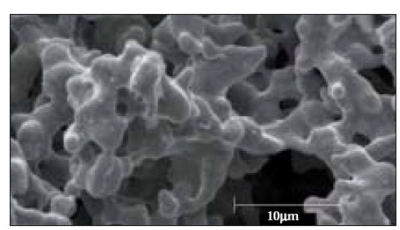
Cons: Post-processing to increase p.s.

Na-loop may be uneconomic

Status: Scaled up to tonne production



The Armstrong direct alloy process.



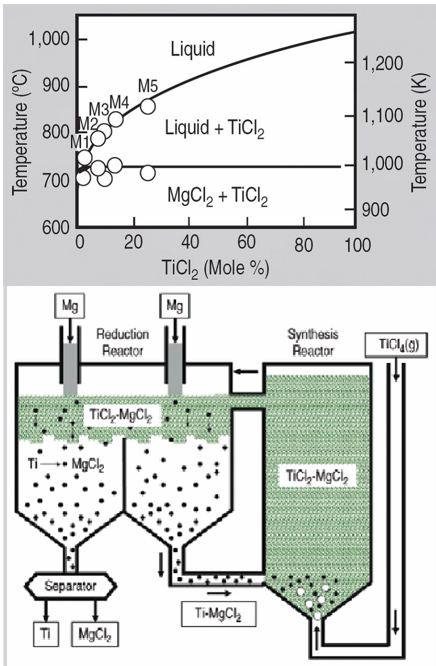
Scanning electron microscope (SEM) image of the titanium product of the Armstrong process.

Apparent		Particle Size Analysis			Chemical Analysis		
Density		Mean	d50	d90	O2	N2	H2
g/cc	%	um	um	um	%	%	%
0.27	5.95	Raw powder (not milled)			0.175	0.003	0.0032
1.13	24.89	91.26	46.06	176.6	0.275	0.009	0.0038
0.82	18.06	187.8	102	386.2	0.238	0.01	0.0032

Reference: Crowley 2003

Sub-chloride process

Mg reduction of $TiCl_2$ investigated at University of Tokyo (IIS) & Waseda



Pros: Relatively "known" process

High purity reagents

$Ti + TiCl_4 \rightarrow$ in $MgCl_2 \rightarrow 2TiCl_2$

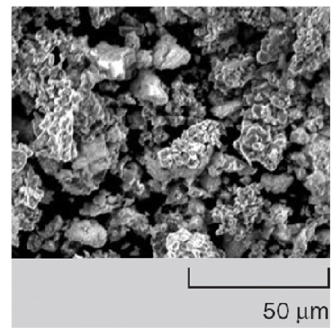
$2Mg + 2TiCl_2$ (in $MgCl_2$) $\rightarrow 2Ti + 2MgCl_2$

Cons: $TiCl_x$ generation

Ti product morphology & recycle

Status: Lab scale

The impurity constituents in the button-melted specimen are, in weight percent, O-0.22 N-0.34 Fe-0.104 Ni-0.145 Cr-0.048 Ti-99.4. It appears that the titanium

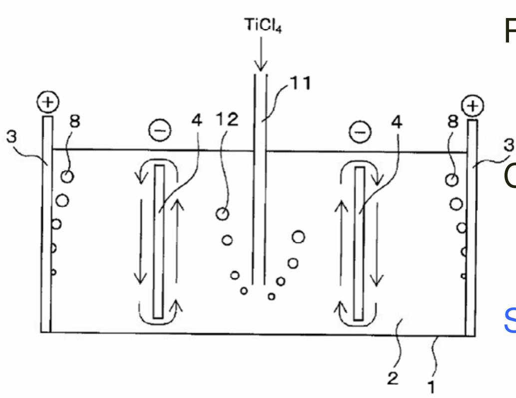


Reference: Fuwa 2005

JTS – Osaka/Toho Titanium

Norsk Titanium
Scandinavian Advanced Technology

Ca reduction of $TiCl_4$ through modified OS process



Pros: High purity Ti feedstock

Powder product

$2\underline{Ca} + TiCl_4 \rightarrow Ti + CaCl_2$

Cons: Max solub 1wt% $TiCl_4$ in $CaCl_2$

C.E. of $CaCl_2$ electrolysis

Ti particle size (<1µm)

Status: No announcement of scale-up

11. The process for production of a metal by molten-salt electrolysis according to claim 1,

wherein the molten salt consists of calcium chloride, sodium chloride, barium chloride, and lithium chloride.

12. The process for production of a metal by molten-salt electrolysis according to claim 1,

wherein a titanium tetrachloride supplying pipe is arranged in the inner area in which the metal is generated by the molten-salt electrolysis,

Reference: WO 06/040978

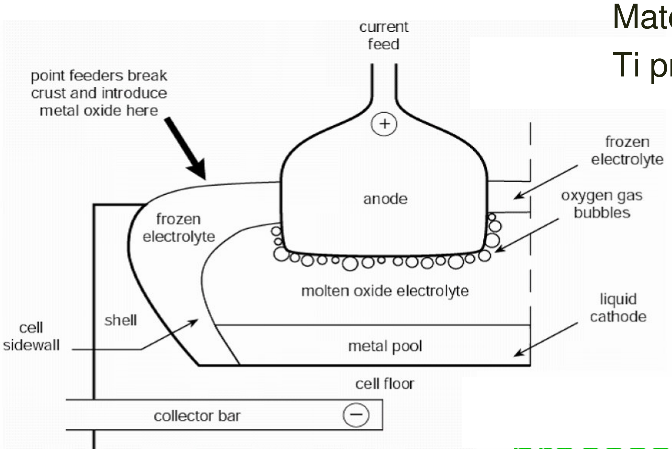
MIT – Elkem process

Norsk Titanium

Dissolved TiO_2 in O & F-based melt

Pros: Liquid product
Possible use of cheaper feedstocks
Amenable to inert anode
$TiO_2 + 4e^- \rightarrow Ti(liq) + 2O^{2-}$

Cons: e^- conductivity of Ti_2O_3 & Ti_3O_5
Materials of construction
Ti product purity

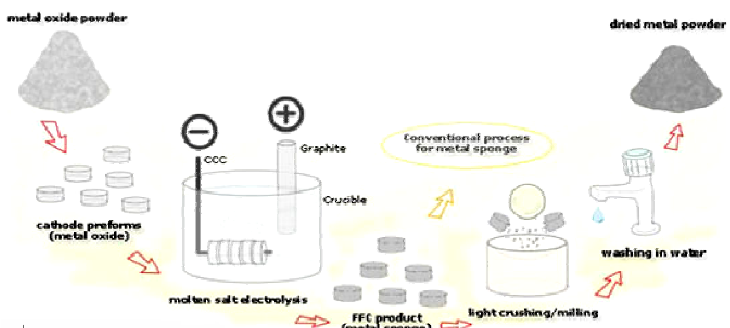


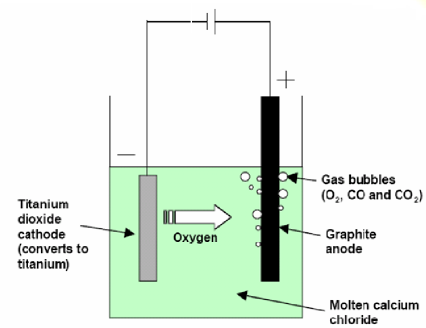
Status: Bench scale

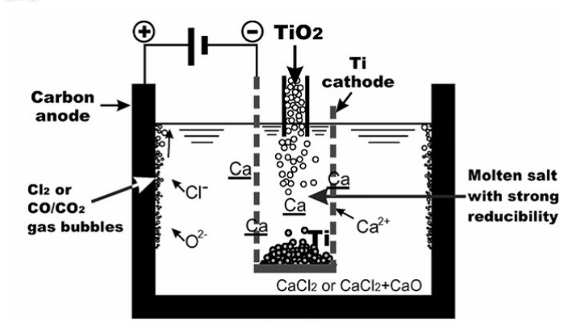
OS/FFC/BHP/DeOx

Norsk Titanium

Solid state reduction of TiO_2-MO_x in fused salt electrolyte



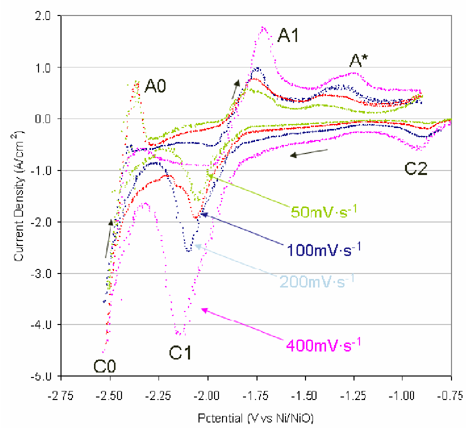




Reference: Kraft 2004, Metalysis 2009

OS/FFC/BHP/DeOx

- β-Ti has order of magnitude higher oxygen diffusion coefficient than α
- Common β stabilising elements:
  - V - costly, $VOCl_2$ removed during distillation of $TiCl_4$
  - Mo - difficult to alloy due to melting point difference with Ti
  - Zr - cost of Zr metal
  - Nb - cost of Nb metal
  - Fe - contaminant from Kroll production (fast diffuser, same as Ni)
- Composite formation also possible
- Advantages of mixed oxides/ceramics



C2: $2TiO_2 + 2e^- \rightarrow Ti_2O_3$

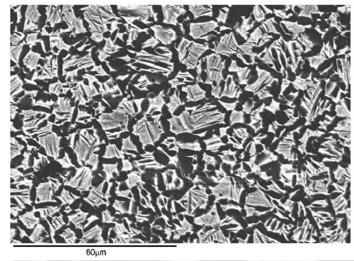
C1: $Ti_2O_3 + 2e^- \rightarrow 2TiO$

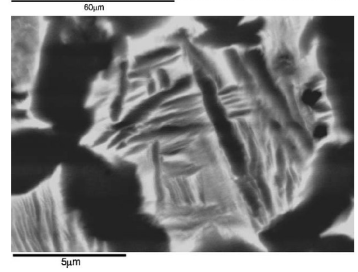
C0: $Ca^{2+} + 2e^- \rightarrow Ca$ (a=1)

A0: $Ca \rightarrow Ca^{2+} + 2e^-$

A1: $2TiO \rightarrow Ti_2O_3 + 2e^-$

A*: ?





OS/FFC/BHP/DeOx

Pros: Novel alloying capabilities
Possible alternative feedstock materials (non-pigment ores)
Low oxygen contents

Cons: Low current efficiency and cathodic current density
Solid state diffusion of oxygen rate limiting

Status: Scaled-up for Ta, Ti research ongoing at Metalysis

Ongoing research: Intermetallic inert anode $Al_{70}Ti_{25}Cu_5$

> 2-12 wt% Fe, Ni → 2+ phases from SEM

> Loss of $AlCl_3$ via gas phase

Boron Doped Diamond (BDD)

> Expensive production method

> Low current density and high background currents

Reference: Jha 2008, Kudo 2008

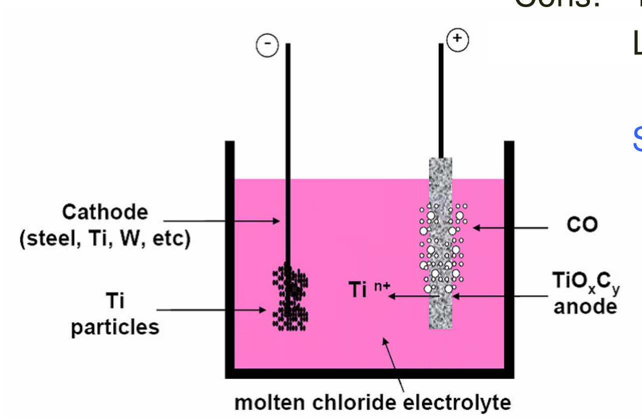
Oxycarbide anode

Anodic dissolution of carbothermically reduced Ti ores

Pros: Cheaper feedstocks
High purity product

$TiO_2 + C \rightarrow TiO_xC_y + CO$ (x≈y ≈0,5)
$TiO_xC_y \rightarrow Ti^{n+} + ne^- + CO_x$ (anode)
$Ti^{n+} + ne^- \rightarrow Ti$ (cathode)

Cons: Ti product morphology
Low cathod current density



Status: MER scale-up to 50kg/d

Oxycarbide anode

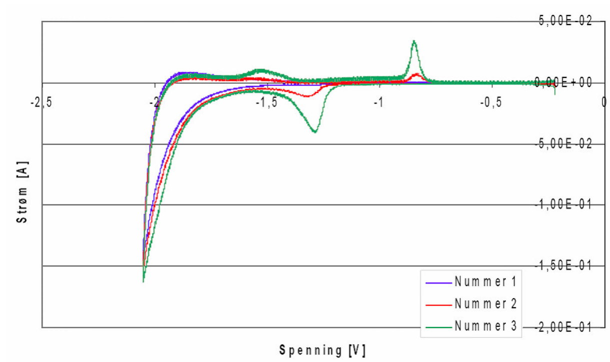
Effect of $TiCl_3$ additions to NaCl-KCl melt at 1073K

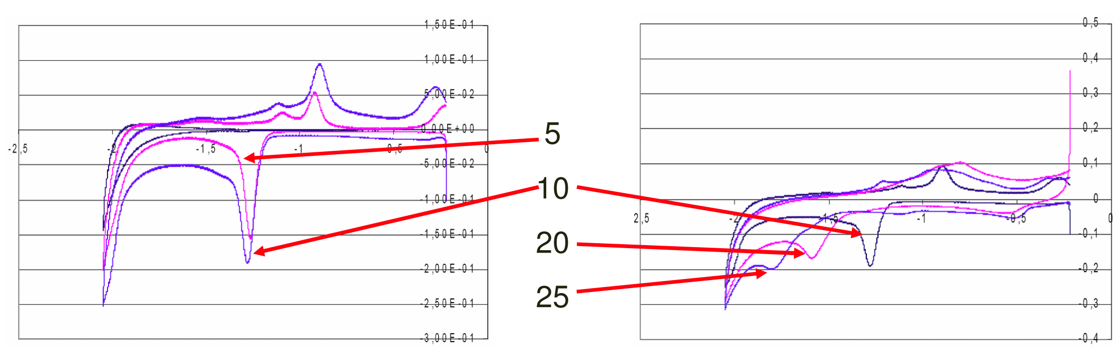
5-electrode configuration

Potential controlled bulk electrolysis

- voltammetry to analyse melt

Clear shift from Ti^{3+} to Ti^{2+}





Oxycarbide anode

Norsk Titanium

☺ Succcessful **manufacture** of TiO_xC_y anodes in laboratory scale from **TiO_2 slag** (TINFOS), with the **optimal properties** to be used in an electrolytic process for titanium production

☺ Production of **titanium metal** (laboratory scale) from the equimolar mixture NaCl-KCl using Ti cathodes and TiO_xC_y anodes made from **TiO_2 slag** powders

☺ Very **low oxygen** content of the metal product

☺ Develop a **vacuum destillation** process of the cathode product

☺ Cathode product from Ti(II) ions gave titanium particles 30-40 μm size, with some "fines" (1-5 μm) ⇨ very reactive cathode product ☹

☹ Cathode product from Ti(III) ions gave **small particle size** (it is mainly "fine" powder, 1-5 μm, with some "flakes" ca 40μm length)

😐 Purity of the Ti obtained with respect to other metals (V, Si and Fe) and C is still an open question

😐 CE (Ti^{3+} basis and recovered product at the cathode): 30-40%

	Raw material	T= 1600ºC, esteq. C	
		reduction	"washing" HCl+NaOH
% TiO_2*	86.50	82.8	96.9
% FeO	9.70	9.5	<0.2
% MnO	2.10	1.68	0.4
% CaO	0.13	0.24	0.06
% MgO	0.66	0.6	0.6
% SiO_2	1.60	1.6	<0.2
% Al_2O_3	0.90	2.3	2.3
% Cr_2O_3	0.03	0.1	<0.02
% V_2O_5	0.28	0.27	0.31
% Nb	0.180	0.18	0.23
TOTAL	102.0	99.2	100.8

* Total Ti content (TiO_2+Ti_2O_3) calculat

NTNU SINTEF

Conclusions

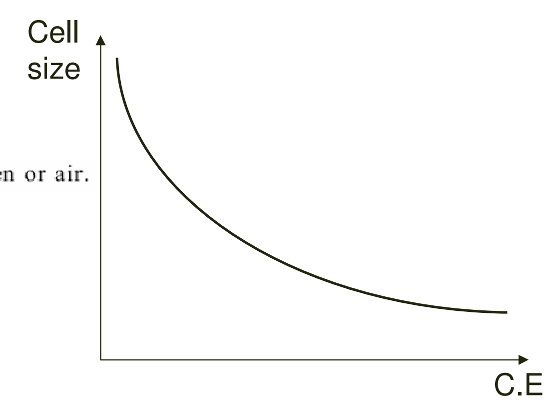
Norsk Titanium

- Kroll process has not been replaced
- New processes have largely been tested only at lab scales
- Ti particle size and specific energy consumption (kWh/kg Ti) have not been satisfactory for existing applications

MATERIAL SAFETY DATA SHEET

Flammable solid in powdered form

May burn in an atmosphere of carbon dioxide, nitrogen or air.



Future research

- Ore selection dependent on upgrading operation
  - Chlorination flash vs fluid bed
  - Carbothermic presence of alloying elements, radioactive species

- Chloride-based routes offer highest purity (metallothermic or EW)
- Parallels to Al- and Mg- electrolysis? Liquid product?

- Or… Kroll with incremental changes?
  - Larger batch sizes with better heating/cooling
  - Modified reactor design

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- NTNU: Geir Martin Haarberg, Ole S Kjos

- Norwegian Research Council Project 176734/i40 "Miljøvennlig produksjon av metaller basert på ny deoksyderingsprosess"

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World Patent 06/040978 – *"Metal Producing Method and Producing Device by Molten Salt Electrolysis"*

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Upcoming conferences

TMS 2010 - Lower Cost Titanium Symposium

- explore all areas of the Ti metal production process to lower costs
  - Upstream: ore & metal extraction
  - Downstream: melting, non-melt processing, post-production operations
- 5-6 symposia, 14-18 February, 2010, Seattle

2nd International Round Table on Titanium Production in Molten Salts

- Fall 2010, Trondheim, Norway
- Exact date to be determined