Challenges and Opportunities in Titanium Metal Production

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

Kevin Dring
Chief Technology Officer
kevin.dring@scatec.no

Norsk Titanium AS
Sommerrogaten 13-15
NO-0255 Oslo
Norway

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
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

- 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
- 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

**Advanced materials**
- Titanium
- Nano carbon

**Climate neutral energy**
- Solar energy
- Thorium
- Offshore wind
- CO₂ capture

**Electrification of transport**
- El car
- Battery technology

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Why Norway?

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 Bambrie region

Tellines ilmenite deposit is the largest Ti-Fe orebody in Europe and 2nd most important in the world (after Lake Tío 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

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**Ashby diagrams**

Titanium microstructures can be optimised to suit the application:

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

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Reference: Ashby 1992
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

Reference: Murray 1987, Donachie 1988

Kroll production of Ti metal

180 000 tpa FBR
12 ton batch, 400 tpa

1500 tpa cell

Reference: Toho 2009
**Conventional production**

**10-15 $/kg**

- Titanium sponge
- Pressing
- Rolling
- Forging

**15-25 $/kg**

- Manufacture of electrodes
- Double rolling
- Bloating

**30-40 $/kg**

- Rolling mill
- Slab
- Hot rolled coil

- Cold rolled coil

- Sheet product
- Welded tube
- Heavy plate

**50-70+ $/kg**

- Seamless tube
- Bar

**Alternative processes**

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<thead>
<tr>
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<td>Limited availability</td>
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<td>Environmentally friendly?</td>
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Internation Titanium Powder

Continuous Na reduction of TiCl₄

Pros: Simplistic process (equip & chem)
\[
\text{TiCl}_4 + 4\text{Na} \rightarrow \text{Ti} + 4\text{NaCl}
\]
\(T_{mp} \text{ NaCl} = 801^\circ \text{C} \quad T_{bp} \text{ Na} = 883^\circ \text{C}\)
Cons: Post-processing to increase p.s.
Na-loop may be uneconomic
Status: Scaled up to tonne production

Reference: Crowley 2003
**Sub-chloride process**

Mg reduction of TiCl₂ investigated at University of Tokyo (IIS) & Waseda

Pros:  
Relatively "known" process  
High purity reagents  

\[ \text{Ti} + \text{TiCl}_4 \rightarrow \text{MgCl}_2 \rightarrow 2\text{TiCl}_2 \]

\[ 2\text{Mg} + 2\text{TiCl}_2 \, (\text{in MgCl}_2) \rightarrow 2\text{Ti} + 2\text{MgCl}_2 \]

Cons:  
\[ \text{TiCl}_4 \] generation  

Ti product morphology & recycle  

Status: Lab scale

The impurity constituents in the button-melted specimen are, in weight percent, 0.022 N, 0.34 Fe, 0.104 Ni, 0.145 Cr, 0.048 Ti, 99.4. It appears that the titanium

Reference: Fuwa 2005

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**JTS – Osaka/Toho Titanium**

Ca reduction of TiCl₄ through modified OS process

Pros:  
High purity Ti feedstock  
Powder product  

\[ 2\text{Ca} + \text{TiCl}_4 \rightarrow \text{Ti} + \text{CaCl}_2 \]

Cons:  
Max solub 1wt% TiCl₄ in CaCl₂  
C.E. of CaCl₂ electrolysis  

Ti particle size (<1μm)  

Status: No announcement of scale-up

Reference: WO 06/040978

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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,
MIT – Elkem process

Dissolved TiO$_2$ in O & F-based melt

Pros:
- Liquid product
- Possible use of cheaper feedstocks
- Amenable to inert anode

\[ \text{TiO}_2 + 4e^- \rightarrow \text{Ti(liq)} + 2\text{O}^2- \]

Cons:
- e$^-$ conductivity of Ti$_2$O$_3$ & Ti$_3$O$_5$
- Materials of construction
- Ti product purity

Status: Bench scale

OS/FFC/BHP/DeOx

Solid state reduction of TiO$_2$-MO$_x$ in fused salt electrolyte

Reference: Kraft 2004, Metalysis 2009
**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 $\text{Al}_{70}\text{Ti}_{25}\text{Cu}_5$  
$>2$-$12$ wt% Fe, Ni $\rightarrow$ 2+ phases from SEM  
Loss of $\text{AlCl}_3$ via gas phase  
Boron Doped Diamond (BDD)  
Expensive production method  
Low current density and high background currents

Oxycarbide anode

Anodic dissolution of carbothermically reduced Ti ores

Pros: Cheaper feedstocks
       High purity product

\[ \text{TiO}_2 + C \rightarrow \text{TiO}_x\text{C}_y + \text{CO} \quad (x \approx y \approx 0.5) \]
\[ \text{TiO}_x\text{C}_y \rightarrow \text{Ti}^{n+} + n\text{e}^- + \text{CO}_x \quad \text{(anode)} \]
\[ \text{Ti}^{n+} + n\text{e}^- \rightarrow \text{Ti} \quad \text{(cathode)} \]

Cons: Ti product morphology
       Low cathod current density

Status: MER scale-up to 50kg/d

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Effect of TiCl\textsubscript{3} additions to NaCl-KCl melt at 1073K
5-electrode configuration
Potential controlled bulk electrolysis
- voltammetry to analyse melt

Clear shift from Ti\textsuperscript{3+} to Ti\textsuperscript{2+}

Reference: Kjos 2008
Oxycarbide anode

• Successful manufacture of TiO$_2$C$_x$ anodes in laboratory scale from TiO$_2$ slag (TINIOS), 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$_2$C$_x$ anodes made from TiO$_2$ slag powders.

• Very low oxygen content of the metal product.

• Develop a vacuum distillation process of the cathode product.

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

• Cathode product from Ti(III) ions gave small particle size (it is mainly "fine" powder, 1-3 µm, with some "flakes" as 40-µm length).

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

• CE (Ti® basis and recovered product at the cathode): 30-40%.

Reference: Martinez 2008

Conclusions

• 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.
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

Acknowledgements

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• Norwegian Research Council Project 176734/i40 “Miljøvennlig produksjon av metaller basert på ny deoksyderingsprosess”
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A M M Martinez, NFR Project Meeting - 176734/i40 Miljøvennlig produksjon av metaller basert på ny deoksideringsprosess


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