The Processing to Win Titanium and Make Parts

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The Processing to Win Titanium and Make Parts

Is there Magic?

Ore → purification → carbo-chlorination (800-1000°C) → purification → TiCl₄ → Kroll reactor → MgCl₂ → Vacuum Separation of MgCl₂ → Mg electrolysis → TiCl₄ → Kroll reactor → MgCl₂ → Vacuum Separation of MgCl₂ → Mg electrolysis

High Cost Route

Melt 1 → Melt 2 → Melt 3 → High Cost Parts

Ingot → multiple conventional processing steps
Low Cost Processing to Produce Primary Titanium Metal

Ore

(carbothermic reduction) Ti₂OC + Cl₂ → TiCl₄

400°C electrolysis

vacuum powder

metal

low cost

lower cost than standard Kroll sponge

batch

continuous
Low Cost Processing to Finished Components

low cost electrolytic powder → Metal → Plasma Transferred Arc (PTA)

Kroll sponge fines (low cost) → alloying elements, powder → Near Net Shapes

Net Shape Armor
Other Net Shapes

hot/cold roll → low cost sheet

Surface Finish → low cost parts
The DARPA Initiative in Titanium to Reduce the Cost of Kroll Sponge

- DARPA Initiative in Titanium in 2003 had a goal to produce titanium, alternative to the Kroll process, in a billet form for under $4/lb with an oxygen content under 600 ppm oxygen.
- DARPA sponsored four programs to demonstrate producing low cost titanium.
- One of the DARPA programs was with MER to utilize TiO₂/ore as a feed to produce titanium electrolytically.
- Many others proceeding Kroll (Hupperty 1905) through the early 90’s investigated producing titanium electrolytically that has been the scaled to limited production.
- The military would like to utilize titanium extensively to reduce the weight from steel and because of titanium’s excellent corrosion resistance.
- Compared to steel, aluminum and most structural metals, titanium’s cost is prohibitive except in special cost insensitive applications.
Challenges to Electrolytically Produce Titanium

- Disproportionation and re-oxidation reactions between Ti\(^{+4}\), Ti\(^{+3}\), Ti\(^{+2}\) and Ti\(^{0}\) that reduce Faradic efficiency
- Disproportionation reactions generate a colloidal metal fog that can remain suspended in the fused salt leading to electronic conductivity versus ionic conductivity as well as a settled mud (poor efficiency and/or stops processing)
- Exchanging large cathode sheets of the deposited titanium out and into the electrolytic cell operating 500 – 900°C which has a necessity to maintain a highly inert atmosphere
- Removing the titanium deposit from the metal cathode and separating a multiple component salt containing TiCl\(_x\) from the deposited titanium
  - Water washing a multicomponent salt
    - Presents environmental issues
    - Oxidizes titanium fines above 600 ppm oxygen
    - Oxidizes and loses Ti ion concentration necessary for electrolytic deposition
  - MgCl\(_2\) from the Kroll process can be vacuum evaporated to low residual chlorides
  - Only MgCl\(_2\), KCl and LiCl meet vapor pressure requirements that can be evaporated to low residual chlorides at 900°C in a reasonable vacuum level
  - KCl-LiCl forms an azeotrope that can reduce temperature to 800-850°C
Approach to DARPA Program to Electrolytically Produce Titanium from a TiO$_2$/Ore Feed

- Since TiO$_2$ has insufficient solubility in any identified fused salt, TiO$_2$ must be reacted to produce a feed to a fused salt that electrolytically produces titanium.

- Carbothermic reduction of TiO$_2$/ore produces a suboxide-carbide with the general composition TiO$_x$C$_y$
  - Carbothermic processing provides control of $x$ and $y$.

- Fused salt electrolytes consisting only of KCl, LiCl, MgCl$_2$ provides vacuum separation from titanium particles analogous to MgCl$_2$ separation from sponge.
  - Provides separated salt direct recycle to electrolysis cell.
  - Preserves Ti ion concentration in salt recycle.
Approach to DARPA Program to Electrolytically Produce Titanium from a TiO2/Ore Feed (Continued)

- TiOxCy used in anodic circuit in chloride electrolyte replenishes Ti ion in the electrolyte that is being deposited at the cathode

- Ti$^{+2}$ ion concentration in the fused salt electrolyte >2 wt% electrolytically produces titanium at high efficiency
  - Consistent with all electrolysis reported over the past century

- Pumping of electrolyte over cathode surface strips deposited titanium particulate which is separately collected and harvested
  - Provides continuous operation
  - **Electrolysis cell never opened, electrolysis never stops**
    - Highly purified electrolysis environment maintained
Examples of the Best Crystalline Morphologies of Titanium Particulate
Status of DARPA Program

- Continuous hot wall cells with mechanical pumping have operated at the rate of 50 lbs/day
- Cold wall cell in self sustaining heat balance from electrolysis with mechanical pumping has capacity of 100 lbs/day and intermediately at higher rates
- A 500 lbs/day cold wall self sustaining heat balance from electrolysis with mechanical pumping for harvesting is under construction at Timet, Henderson, Nevada
Processes to Produce “Alloy” Titanium

- Chloride based processing (Kroll) when carried out in an oxygen free system produces high quality titanium.

- Electrodeposition from fused salts containing TiCl₂ and alloying metal chlorides such as AlCl₃ and VCl₄ or VCl₂ can make Ti-6Al-4V alloy powder.

- Co-reduction of mixed metal chlorides with alkali and/or alkaline earth metal reductants:
  - TiCl₄ – AlCl₃ – VCl₃ + MR = Ti-6Al-4V + MRCIₓ
  - MR = metal reductant, x = 1 or 2

- Continuous processing provides potential to produce Ti Alloy powder at substantially lower cost than standard process now used to produce powder.
Standard Processing Typically used for Producing Titanium Powder

1. Kroll Sponge
2. E-Beam or Plasma Melter and Alloying
3. Ingot
4. Ingot Melting, Gas Blowing To Powder
5. Ti Alloy Powder

Industry quoted prices well over a hundred $/lb
Background Relevant to Titanium Powder Production

- Ti powder is not the general morphology from Kroll processing
- Ti alloy is not generally produced from Kroll processing
- Burner style reactors for mixing metal reductant (i.e. Mg, Na, Ca, etc.) and TiCl₄ in a nozzle characteristically produce quite small particles under 10µ to submicron
  - No time for particles to grow in a burner type reactor head
  - Small Ti particles pick-up excessive passivation oxygen and can be pyrophoric
- Most powder metallurgy processing prefers particle sizes in the 25 to 250µ size range
When TiCl$_4$ is Passed into a Liquid Fused Salt, Bubbles of TiCl$_4$ are Formed

- Bubbles are rarely greater than 100µ diameter
- The amount of titanium in a TiCl$_4$ bubble is on the order of 10^{-10} grams which is a very small particle
  - Unless additional TiCl$_4$ contacts an already nucleated particle and builds-up the particle size, only small size particles will be produced

Schematic illustrating the titanium particle growth with TiCl4 gas introduced within the salt below the Mg layer.

Reactor Design Criteria to Produce Ti-Alloy Particles from Chloride Precursors

- Maintain precursor chlorides in a gas phase in uniform non-segregated mix

- Provide reductant in liquid phase in a discrete architecture to reduce TiCl$_4$ and alloying chloride precursors to the metallic state

- Provide opportunity for continued nucleation and reduction to build particles >25µ <250µ

- Provide for separation of by-product reductant chloride/MgCl$_2$ from interfering with reductant processing and separation from produced alloy particle
Reactor Types to Produce Ti-Alloy Powder Directly from Chloride Precursors

- Stirred gas phase and agitated reductant

- Reductant in discrete architecture in free space for sufficient time to reduce mixed chloride precursors in gas phase

- Reductant in controlled film thickness over large area containing mixed chlorides precursors in gas phase
Example Ti-Al-V Alloy Particles

Ti-Al-V alloy particulate produced with Mg reductant of the chloride precursors

Higher Magnification

Ti-Al-V alloy particulate produced by Mg reductant of the chloride precursors

Ti-Al-V alloy particulate produced by Ca reduction of the chloride precursors
Example Ti-Al-V Alloy Particles

Higher Magnification of Ti-Al-V Particles with a General Spheroidal Morphology
Other Interesting Processing Routes

Ore

(can be perovskite)

1. Carbothermic reduction
2. Purify
3. TiO<sub>x</sub>C<sub>y</sub> / Ti<sub>2</sub>O<sub>C</sub>
4. X & Y <<
5. Ca

Ti/CaO/CaC<sub>2</sub>

- Acetylene/fuel
- Anhydrous rinse
- Ti powder
- CaOH

Kroll
- Metal sponge
- Electrolysis
- Low cost metal powder

Pigment
- CO<sub>(g)</sub> + TiCl<sub>4</sub>

400°C
+ Cl<sub>2</sub>

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Transforming Titanium into Low Cost Products

Ti Alloy Powder
Over a Hundred Dollars per Pound

High Cost Ti Alloy Parts

Ti Sponge Fines
Very Low Cost

Plasma Transferred Arc (PTA)
(very low cost processing)

Al / V alloy
Cr or other alloying

Near Net Shape Parts / Ingot

low cost

Fraction of Conventional Processing Cost

hot/cold roll sheet
0.02 to inches thick
Low cost

PRODUCTION READY
MER PTA
Example Titanium Components
Produced by the Rapid Manufacturing
Plasma Transferred Arc System