HOW TO MAKE AND USE TITANIUM

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Background for Titanium Production

• All commercial titanium is produced by the Kroll processing consisting of molten magnesium metal reducing $\text{TiCl}_4$ resulting in a sponge morphology product.

• A powdered titanium morphology has a higher value than sponge morphology as powder can be used directly in powder metallurgy processing to produce meltless componentry as well as feeds for the various additive manufacturing processes.
Background for Titanium Production

• What are processes to produce titanium and titanium alloy powder
  – Sieved sponge fines with vacuum processing to remove all traces of Mg/MgCl₂
  – Hydride-dehydride (HDH) process
    • Kroll sponge
    • Turnings from machining
    • Segregated scrap
  – Several variations of gas blowing molten streams from billots/ingots and arced wires which feed is made from sponge fusion processing
Using titanium sponge as a source for titanium powder, the below pie chart is utilized.
Background for Titanium Production

• A powdered morphology can be produced using Kroll chemistry of Mg reduction of TiCl$_4$ and alloy using mixed metal chlorides (TiCl$_4$ – AlCl$_3$ – VCl$_4$)

• In a continuous flow reactor, as contrasted to batch sponge production, a powder morphology can be produced for equivalent to a lesser cost than sponge
Example of Metallothermically Produced Ti-6Al-4V Alloy Powder from a Continuous System Flow

Mg reduced mixed streams of TiCl$_4$/AlCl$_3$ and TiCl$_4$/VCl$_4$

Larger alloy Ti-Al-V particles from Mg reduction of mixed streams of TiCl$_4$/AlCl$_3$ and TiCl$_4$/VCl$_4$
Background for Titanium Production

• Research from many sources for over a half century has shown it is possible to produce titanium powder electrolytically from TiCl$_4$ feed into a fused salt with cost projections to be less than Kroll sponge.
• The covalently bonded TiCl$_4$ as a feed to fused salts has virtually no solubility and must be electrolytically reduced to a lower chloride that complexes with the fused salt that can lead to complete electrolytic reduction to titanium.

• Electrolytic reduction of TiCl$_4$ to Ti metal is fraught with disproportionation reactions that reduces Faradic efficiencies and produces very small Ti powder that clogs the cell and is explosive when harvested and exposed to air.

• Ti metal is electrolytically reduced from Ti$^{++}$ (TiCl$_2$).

• Production of Ti$^{++}$ (TiCl$_2$) is enabling to electrolytically produce Ti metal/powder free from disproportionation reactions at lower cost than a TiCl$_4$ feed.
• MER demonstrated TiO$_2$ can be carbothermically treated to produce Ti$_2$OC which has the electrical conductivity approximately the same as dense high grade graphite.
• Highly electrically conductive Ti$_2$OC can be used as an anode in a fused salt.
• Ti$_2$OC as an anode electrically reduces to directly produce Ti$^{++}$ (TiCl$_2$).
• Control of electrolysis parameters, Ti$^{++}$ ion concentration, fused salt type and temperature produce Ti powder in control morphologies in size ranges from approximately 25-250µ with a capability up to 500µ.
An example of electrolytically produced Ti powder from a Ti$_2$OC anode
The process of electrolytically producing Ti powder from Ti$_2$OC anode feed is being scaled to commercial demonstration size of approximately 50 tons/year.
**Electrolytic Production of Titanium Alloy Powder**

- Elements with an electrolytic decomposition potential near that of titanium from TiCl$_2$ (1.9 V) can be co-deposited with titanium to produce alloy powder.
- Aluminum from AlCl$_3$ (2 V) and vanadium from VCl$_3$ (1.8 V) with controlled activity coefficient in the salt electrolyte can produce Ti-6Al-4V electrolytic powder.
- The feed of Al$^{+3}$ and V$^{+3}$ into the titanium ion electrolyte can be from their chlorides or as the metal ion from a metal anode.
**Electrolytic Production of Titanium Alloy Powder**

- The alloy composition of Ti-6Al-4V is controlled via cell voltage and activity coefficient of the alloying ions in the electrolyte.
- Since electrolytic Ti powder can be projected to be produced substantially less than Kroll sponge, the cost of the alloying elements of Al and V added to the Ti cost suggest the alloy Ti-6Al-4V powder can be electrolytically produced for approximately the same cost as sponge.
- Bench scale tests have verified Ti-6Al-4V powder can be electrolytically produced.
Other Uses of Ti$_2$OC

- In addition to the use of Ti$_2$OC as an anode to electrolytically produce Ti powder, Ti$_2$OC is an excellent feed to produce TiCl$_4$.
- Ti$_2$OC begins to react with Cl$_2$ as low as 180°C and becomes a self-sustaining reaction at approximately 300°C in contrast to chlorinating TiO$_2$ and C at 800-1000°C.
  - No phosphine is coproduced with the TiCl$_4$
- TiCl$_4$ can be used as a Kroll sponge feed, oxidized to pigment or sundry uses of TiCl$_4$. 
Applications for Low Cost Titanium Powders

- Metal additive manufacturing (AM) is widely beginning to be investigated and utilized to produce titanium alloy componentry.
- The low cost titanium powder feeds translate to low cost titanium componentry.
- Sponge fines after further treatment to remove residual Mg and MgCl₂ remains low cost and produces low cost AM products.
- Kroll chemistry of Mg reduction of TiCl₄ or mixed metal chlorides in a continuous reactor provides a desirable powder morphology equivalent to less than cost of sponge as a feed to powder metallurgy or additive manufacturing.
Applications for Low Cost Titanium Powders

- Electrolytically produced powders co-fed with alloying elements to fusion type AM produces standard and custom alloy low cost componentry.
- Select alloy compositions produced via AM can be lower cost than Ti-6Al-4V with enhanced mechanical properties and over 20% ductility.
- High modulus alloy in the 137-165 Gpa (20-24 MSi) range produced by fusion AM that retains up to 4 – 6% ductility are in extensive test as automotive connector rods.
- Modified gamma alloys produced by fusion AM from low cost powders are under wide spread tests as disc brakes.
- Low cost Ti powder has made possible graded Ti cermet encapsulated armor using AM processing with exemplary ballistic performance.
Applications for Low Cost Titanium Powders

- Non-fusion processing such as friction stir processing (FSP) as repair or AM produces micro/nano-grain sizes that result in enhanced mechanical properties over standard wrought produced material.

Illustration of a FSP repair

An illustration of friction stir additive manufacturing
(a) $\alpha+\beta$ Ti-6-4 alloy showing strength levels equivalent of $\beta$ alloys with significant ductility

(b) Strength levels of near $\beta$ Ti-6-2-4-6 FSP processed alloy produced strengths 2X up to 2GPa
Conclusions

• Electrolytic produced titanium powder is lower cost than Ti sponge and has a higher value.
• Lower cost electrolytic Ti powder is derived from Ti$_2$OC.
• The electrolytic Ti$_2$OC process is being scaled to production demonstration at 50 tons/yr. to define a basis for a 10,000 tons/yr. plant.
• Ti$_2$OC coupled with Al and V ion feeds can electrolytically produce Ti-6Al-4V powder projected to cost approximately the same as Ti sponge.
• Ti$_2$OC can be chlorinated at very low temperatures to TiCl$_4$.
• A continuous flow system using Mg reduction of TiCl$_4$ produces a powder morphology versus the typical sponge.
Conclusions

• Low cost sponge fines and electrolytic Ti powder are excellent feeds for fusion additive manufacturing (AM) to produce low cost componentry.

• Fusion AM can produce custom alloys from low cost powders including high modulus compositions for varieties of automotive applications.

• Low cost electrolytic Ti powders coupled with AM leads to lower cost titanium componentry than standard processing.

• Non-fusion AM of FSP produces Ti with a fine microstructure resulting in much higher mechanical properties.

• Non-fusion FSP processing is excellent as a repair process.