ELECTROLYTIC Ti POWDER PRODUCTION FROM ORE SOURCES
Outline

• Ways to produce titanium powder

• Metallothermic reduction to produce Ti and Ti alloy

• Electrolytic processing to produce powders

• Ore to intermediate feeds

• Electrolytic alloy powder production
Background

Titanium and alloys of titanium powders are enabling to meltless powder metallurgy parts fabrication and feeds for the many additive manufacturing processes to produce parts.

Cost associated with the various processing steps involved in producing titanium by Kroll processing:
- Unalloyed sponge fines (powder) are nearly 40% of the cost;
- Alloy powder is 53% of the cost plus the transformation of the ingot product to powder (very expensive)

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Background

• Titanium powder is produced by:
  - Sieving fines from Kroll sponge (but contains residual Mg and MgCl₂)
  - Several variations of gas blowing from a billet/ingot melt
  - Hydride-dehydride (HDH) from turnings or segregated scrap

• Titanium alloy powder produced from an alloy billet/ingot melt via several variations of gas blowing
  - Today’s titanium alloy powder cost is in the approximate price range of a high-end restaurant meal cost to more than twice that meal cost per pound, whose cost does not seem to be sensitive to volume

• Research has shown it is possible to produce titanium and alloy titanium powder electrolytically with cost projections to be similar to Kroll sponge
Low Cost Non-electrolytic Process to Produce Titanium Alloy Powder

Plasma transferred arc (PTA) process produces alloy melt directly from a sponge and alloying elements feed.

Cost is 3-5X of Kroll sponge + alloying elements 1/10 – 1/15 current cost of spherical alloy titanium powder.
Titanium and Titanium Alloy Powder via Metallothermic Reduction

• The Kroll process is metallothermic Mg metal reduction of TiCl₄ (tickle) which produces sponge morphology

• In a unique innovative continuous flow of molten Mg metal contacting TiCl₄, Ti powder (not sponge) can be produced in controlled particle size achieved via providing sufficient time in the nucleation/reaction zone to build the particle size suitable for powder metallurgy e.g. ≥ 25 µ

• Co-feeding AlCl₃ and VCl₄ with TiCl₄ in the continuous flow reactor produces Ti-6Al-4V powder

• Pure Ti powder ready for powder metallurgy processing can be produced for about the same cost as sponge

• Alloy powder e.g. Ti-6Al-4V is about the same cost of sponge plus the cost of the alloying chlorides e.g. AlCl₃ and VCl₄
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$_4$
• For more than a half-century investigations have been conducted to electrolytically produce titanium from a TiCl$_4$ feed
  ➢ Morphology is dendritic to irregular powder
  ➢ Electrolytic processing has been batch offering little incentive to replace batch Kroll processing
• MER discovered in the late 1990’s TiO$_2$ and ore containing TiO$_2$ could be carbothermically treated to produce Ti$_2$OC
  ➢ Ti$_2$OC chlorinates beginning at 180°C and is a self-sustaining reaction at 300+°C producing TiCl$_4$
Low cost TiCl$_4$ can be used to:
- Electrolytically produce Ti powder,
- Kroll process to produce sponge
- Oxidized to pigment

Ti$_2$OC is highly electrically conductive and can be used as anode feed to electrolytically produce titanium powder

Continuous electrolytic processing has been demonstrated with powder harvesting/separation of salt and powder separately to the electrolytic cell

- Continuous electrolytic processing predicts Ti powder at substantially lower cost than batch produced Kroll sponge
Electrolytically Produced Ti Powder

System for continuous electrolytic production of titanium with harvesting/separation of powder and salt remotely to electrolysis cell

Examples of good crystalline morphologies of electrolytically produced titanium particulate
**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.
Conclusions

- Kroll chemistry of Mg reduction of TiCl₄ can be performed in a continuous flow system to produce both Ti powder and the alloy Ti-6Al-4V

- TiO₂ and ore containing TiO₂ can be carbothermically reduced to Ti₂O₃ which can be chlorinated at 180 – 400°C to produce low cost TiCl₄
  - Low cost TiCl₄ can be used as a feed to electrolytically produce Ti powder on a continuous basis
  - Low cost TiCl₄ can be used as a feed for Kroll sponge production
  - Low cost TiCl₄ can be oxidized to pigment
Conclusions

- Ti$_2$OC is very electrically conductive and can be used as an anode to electrolytically produce Ti powder on a continuous basis at a projected cost less than Kroll sponge.

- Electrolytic process provides control to produce Ti powders in preferred sizes directly useable in powder metallurgy processing.

- The electrolytic process has demonstrated it is possible to produce alloy powder such as Ti-6Al-4V at a cost near that of sponge.

- A low cost Ti or Ti-6Al-4V alloy powder provides a paradigm for powder metallurgy to produce meltness Ti componentry as well as an enabling feed for the various additive manufacturing processes.