

TITANIUM METAL PRODUCTION VIA OXYCARBIDE ELECTROREFINING

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ABSTRACT

A combined electroreduction and refining process has been employed to produce pure titanium metal from an impure feedstock. The process involves the anodic dissolution of titanium oxycarbide with cathodic deposition of titanium in a eutectic mixture of NaCl:KCl at 973-1173K. Characterisation includes scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction, and inductively coupled plasma. Deposits consisted of pure titanium metal crystallites, sponge, or powder with a particle size range of 1-30 μ m.

INTRODUCTION

Global titanium sponge consumption is currently estimated at 150 kTpa and is predicted to grow by 6% annually until 2015 to >200 kTpa. This growth has resulted from an unprecedented worldwide demand for high-performance materials with titanium offering a unique combination of extremely desirable properties; these include its high strength-to-weight ratio, corrosion resistance, refractory nature, biocompatibility, and cryogenic capabilities^[1].

Although titanium is plentiful (it is the 4th most abundant engineering material in the Earth's crust^[2]) and despite its many advantages, the cost of extraction has so far remained a barrier for all but the most demanding applications (e.g. Aerospace). Consequently, the Kroll Process has dominated as the industrial scale extraction method for over 60 years, despite more than a century of research into the topic. Of the potential successors, electro-extractive processes are considered the most likely both technologically and economically.

In addition to the expensive reduction, a significant contributor to the cost of extraction is the requirement for a highly purified titanium tetrachloride (TiCl₄) feedstock to ensure complete removal of impurities present in the original ore. Whilst some high purity (>92%) TiO₂ ores do exist (e.g. Rutile), the vast majority of global resources (>90%) are present as FeTiO₃ (Ilmenite) which has a TiO₂ content of just 35-60%. Figure 1 shows the global production of these titanium ores with the insert providing a breakdown by country.

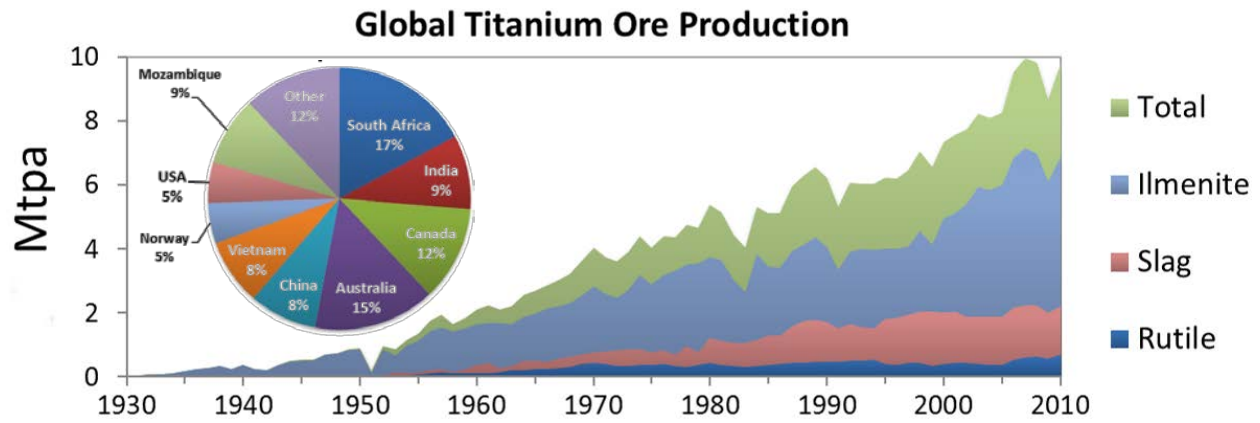


Figure 1. Historical global titanium ore production data [USGS Minerals Information]

Since the publication of the FFC-Cambridge Process^[3] in 2000, an intensive worldwide research programme was undertaken to develop novel titanium extraction techniques^[4]. A decade on, only limited progress been made and many of the proposed processes still necessitate similarly expensive feedstock to the Kroll Process, severely limiting their cost reduction potential. As an example, the electro-extractive FFC-Cambridge Process, the flagship Kroll replacement technology, is unable to accept any significant cationic impurities in the feed stock as these would be retained in the final product. It should be noted, however, that whilst this is a bane for pure metal production, it is a boon for producing alloys, where the FFC-Cambridge process understandably excels.

A promising competitor is the Chinuka Process^[5] which is a novel hybrid electroreduction-refining method: the process is illustrated schematically in Figure 2.

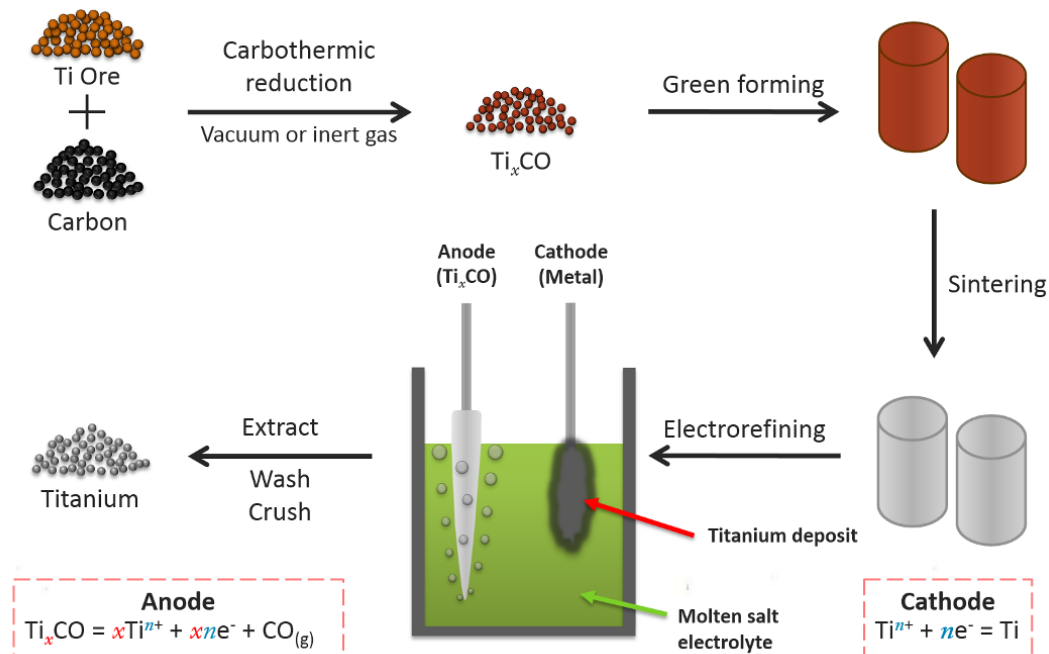


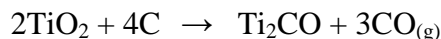
Figure 2. Schematic illustration of the Chinuka Process for titanium

Historically, titanium oxycarbide (Ti_xCO) has typically been prepared by solid state carbothermic reduction of pigment grade TiO_2 . Several researchers have subsequently electrolysed this material in a molten eutectic bath of $\text{NaCl}:\text{KCl}$ at temperatures of $\geq 973\text{K}$ ^[6-22]. Anodic dissolution of the Ti_xCO produces either Ti^{2+} ^[8] or Ti^{3+} ^[9, 12] ions which are plated out at the cathode to generate a powder, sponge, or dendritic product. The Chinuka Process extends this concept by utilising impure titanium ores as a feedstock and thereby integrating electrolysis into the reduction process. Elements more noble than titanium can be selectively retained at the anode to form an extractable sludge, whilst those less noble can be retained in the electrolyte. A particular advantage is the ability to use lower grade ores that are prohibitively impure for other titanium extraction methods, including the capability to handle both cationic and anionic impurities. In addition the Chinuka Process is able to treat ores that exhibit particular physical or chemical characteristics, such as small particle size or significant CaO concentrations, which would otherwise prevent them from being upgraded to pigment grade TiO_2 . The possibility to directly produce titanium powders is also extremely attractive due to their significant premium.

In this paper, results are presented from ongoing research on the Chinuka Process at the University of Cambridge. The production and electrolysis of oxycarbide anodes is discussed together with analysis of the anode and cathodic products by SEM/EDX and XRD. ICP analysis of the salt is also discussed.

EXPERIMENTAL

Magnetically separated rutile TiO_2 ores (White Mountain Titanium Corp.) with an average particle size of $70\mu\text{m}$ were blended with graphite powders ($1\text{-}2\mu\text{m}$, Aldrich) in a 1:2 mole ratio. This mixture was then dry ball milled with ZrO_2 media for 24 hours, to an average particle size of $5\text{-}15\mu\text{m}$. These powders were loaded into an alumina crucible and reacted at $1773\text{-}1873\text{K}$ for 4 hours under a vacuum or flowing argon to generate titanium oxycarbide (Ti_2CO) according to the following reaction:



The Ti_2CO products were dark red/orange friable agglomerates which were crushed to a powder before being uniaxial pressed. These green preforms were sintered at $>1873\text{K}$ for 4 hours under vacuum or flowing argon to produce the final anodes for electrolysis. Due to pore formation during the carbothermic reduction stage, densification sintering was performed separately to improve the mechanical strength and reduce the porosity of the anode. Final porosities were between 25-40% based on external measurements with an estimated theoretical density of 4.94gcm^{-3} ^[11]. Figure 3 shows a photograph of a Ti_2CO anode (left) and an SEM micrograph of the interior (right).

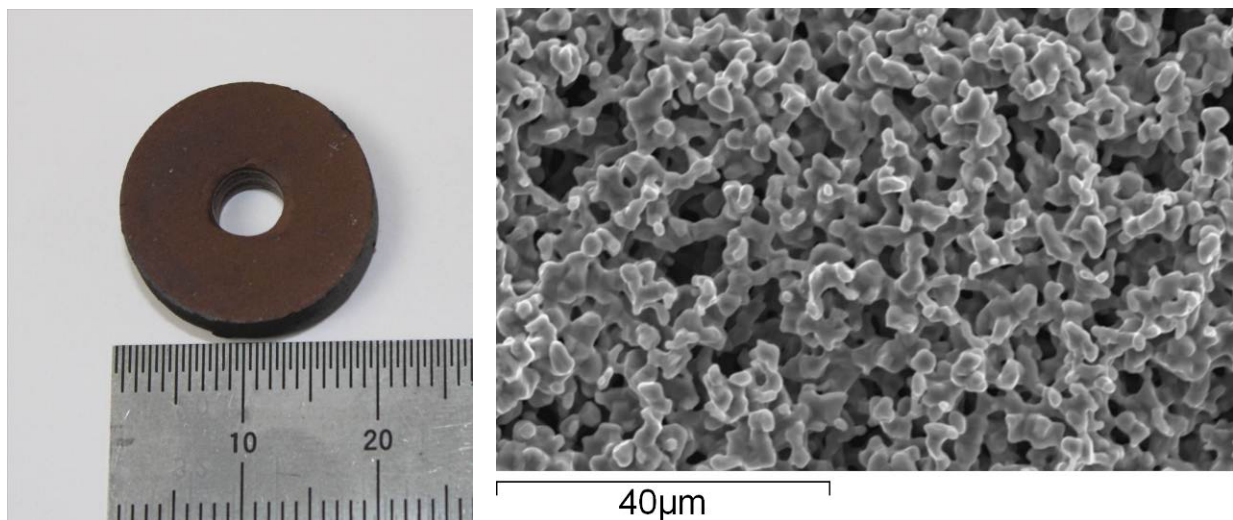


Figure 3. Photograph (left) and SEM micrograph (right) of a Ti_2CO pellet anode

A eutectic mixture of 44% by mass of NaCl and 56% by mass KCl was loaded into an alumina crucible which was placed in a water cooled Inconel retort and heated under vacuum to 723K. The retort was then flushed with argon at 200ml/min and heated to the process temperature. Pre-electrolysis was conducted at 2.8V between two graphite rods (HK-0, Tokai Carbon Europe) until a low and stable background current was achieved, normally ~20mA.

Oxycarbide electrolysis was typically conducted in a 2-electrode arrangement although a AgCl reference electrode or a graphite, molybdenum or titanium pseudo-reference electrode was often employed to monitor the achieved potentials. The anode was either a pure Ti_2CO rod or a carbon based conductive holder containing Ti_2CO pellets (Figure 4). The cathode was a rod of steel, titanium, nickel, or molybdenum.

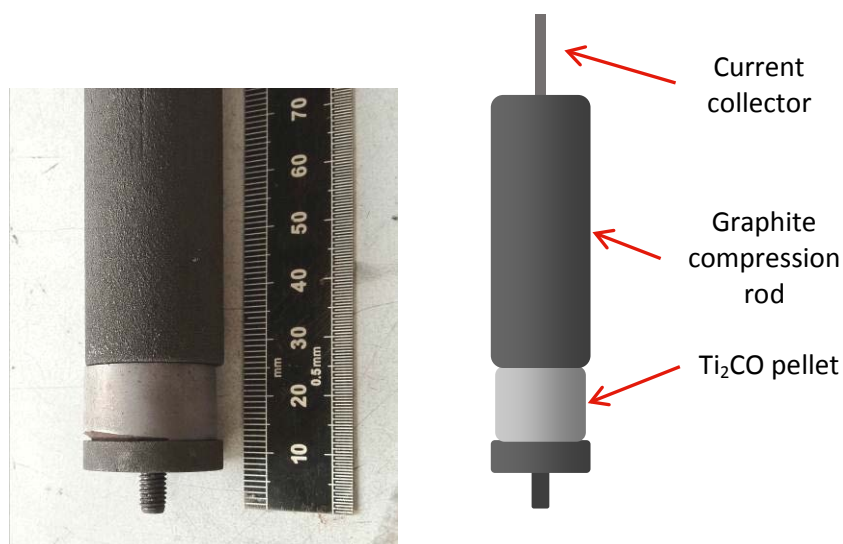


Figure 4. Photograph (left) and schematic (right) of an anode setup for Ti_2CO electrolysis

Electrolysis was performed at 1.8-3.0 V for 4–24 hours. Following electrolysis the electrodes were raised from the salt under argon and the furnace cooled. The electrodes were then washed in water, filtered, dried and analysed.

RESULTS AND DISCUSSION

Ti_2CO formation was validated by XRD analysis of feedstock materials sintered at different temperatures for 4 hours under vacuum (Figure 5). Starting with an admixture of carbon and TiO_2 , reduction can be seen to go through the formation of Ti_2O_3 at temperatures below 1673K, followed by the formation of a single phase $\text{TiC}_x\text{O}_{1-x}$ with excess carbon. Further elevation of temperatures above 1773K consumes the free carbon with a detectable peak shift in the single phase to the left. The $\text{TiC}_x\text{O}_{1-x}$ peaks are found to lie between those of TiC and TiO as would be expected with a solid solution $\text{TiC}:\text{TiO}$ phase. The products have been confirmed by carbon and oxygen analysis (combustion and Leco respectively) and are additionally supported by mass loss measurements. No additional products were detected at temperatures up to 2373K.

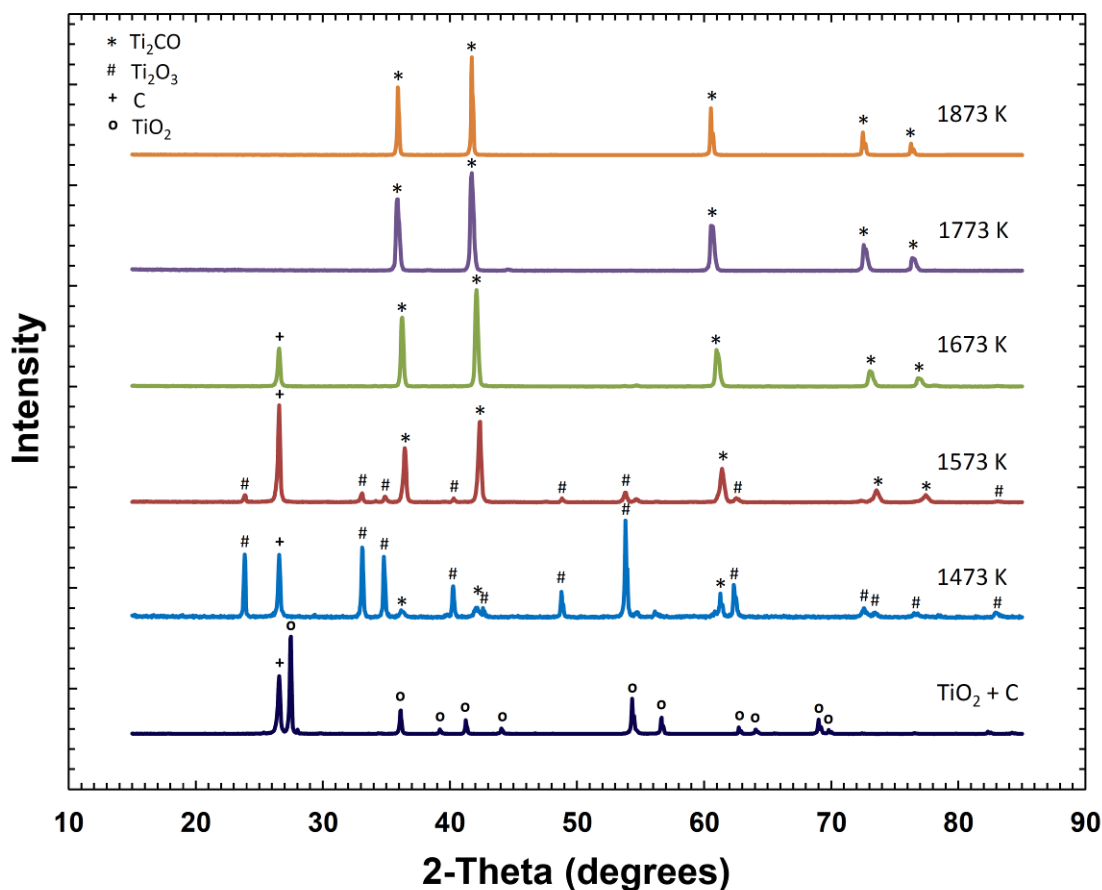


Figure 5. XRD patterns of 1:2 mole ratio rutile ore/C mixtures, sintered at various temperatures for 4 hours under vacuum

Ti_2CO electrolysis followed the previously outlined methodology. A typical chronoamperogram is given in Figure 6, obtained during electrolysis at applied cell voltage of 3.0V with a molybdenum rod cathode. An initially high electrolysis current is seen to decline to a baseline plateau value indicating the complete consumption of the Ti_2CO .

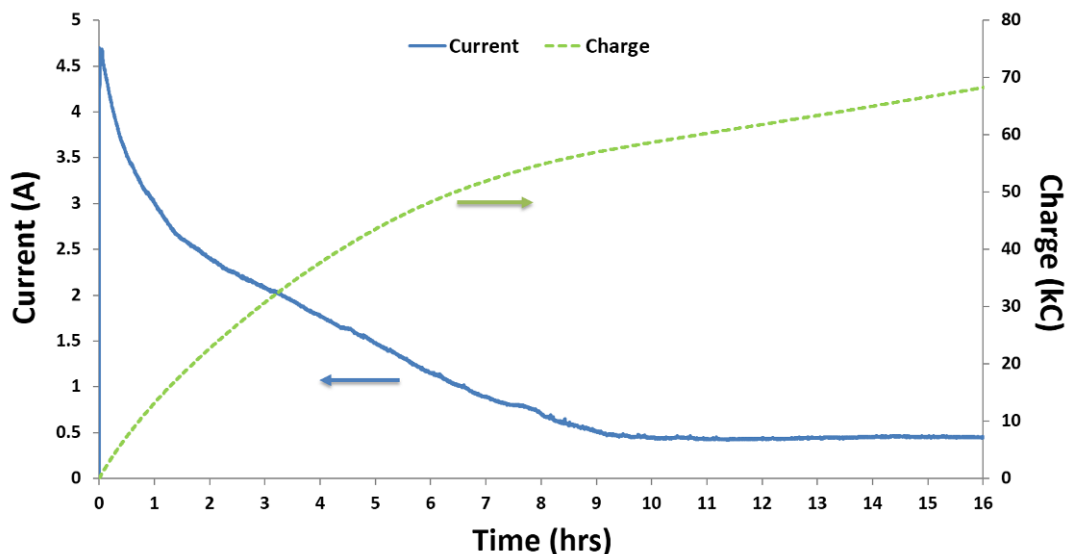


Figure 6. Chronoamperogram showing electrolysis of Ti_2CO at 3.0V

Figure 7 (left) shows an SEM micrograph of a titanium deposit obtained through electrolysis which exhibits a somewhat crystalline microstructure. The crystallites are approximately 20-30 μm . XRD analysis in Figure 7 (right) confirms a pure titanium metal is obtained.

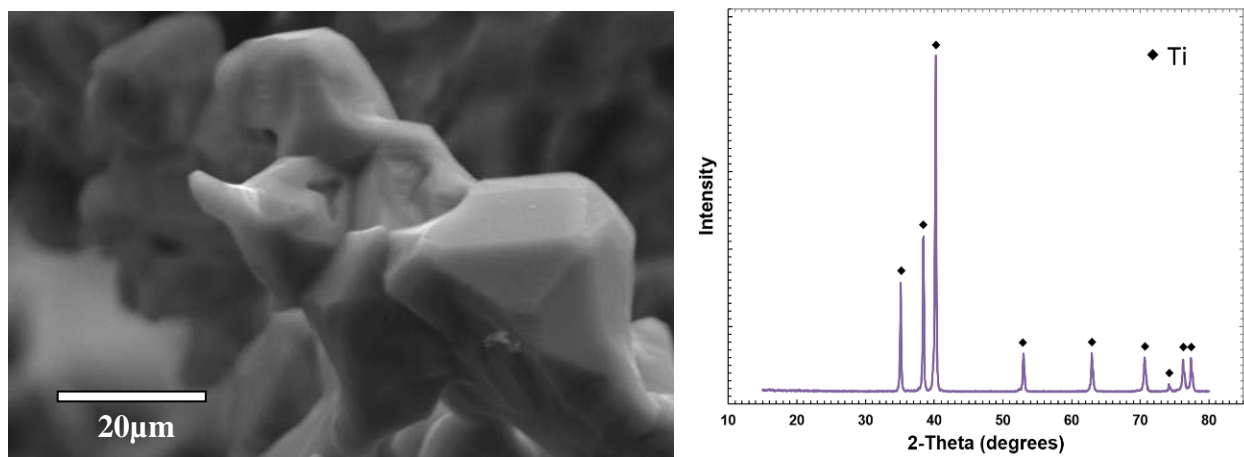


Figure 7. SEM micrograph of titanium deposit (left) and XRD showing pure titanium (right)

Figure 8 shows the Inductively Coupled Plasma (ICP) analyses of a rutile feedstock and a cathodic product. A significant reduction in the concentration of all major impurities can be seen in the product by contrast to the feedstock material. The titanium content has been upgraded from ~96.4% in the ore to >99.7% in the deposit. The retention of comparatively high iron levels is thought to have arisen from the use of a steel cathode in this case.

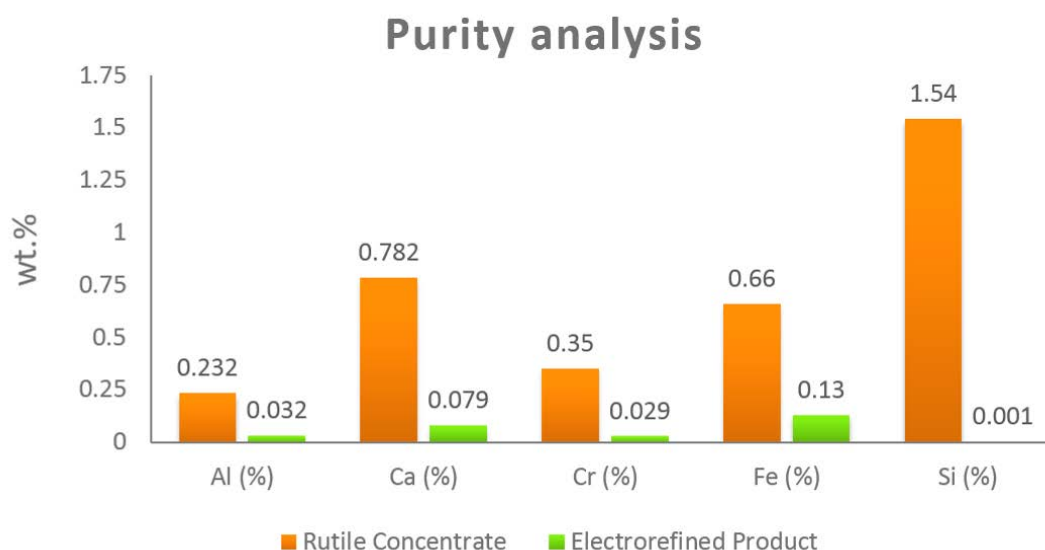


Figure 8. Composition of impurities in feedstock and electro-refined product

Given that the feedstock impurities are not transferred to the cathodic product, ICP was conducted on the salt over the course of 4 consecutive electrolyses (Table 1). The low concentrations of the impurities probably prevents their co-deposition, but their gradual build-up will eventually necessitate salt exchange or cleaning, e.g. by titanium gettering. Concentrations may also be kept low through the formation of volatile chlorides, such as AlCl_3 or SiCl_4 .

Sample	Al (ppm)	Ca (%)	Cr (%)	Fe (%)	Si (%)
Blank	0	0	0	0	0
Electrolysis 1	0.00176	0.33831	0.00558	0.00104	--
Electrolysis 2	0.00122	0.76268	0.03040	0.00098	0.04148
Electrolysis 3	0.00166	1.38767	0.03570	--	0.05111
Electrolysis 4	0.00219	1.62361	0.03753	0.00407	0.05483

Table 1. Composition of impurities in salt following consecutive electrolyses analysed by ICP

CONCLUSIONS

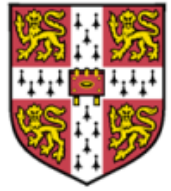
Impure ores can be partially carbothermally reduced to form Ti_2CO with some residual impurities. Electrolysis of this Ti_2CO in a molten eutectic mixture of $\text{NaCl}:\text{KCl}$ at 973-1183K, a method known as the Chinuka Process, can produce a titanium product with a significantly lower impurity content than that of the feedstock. This patented combined electroextraction-refining process permits the use of lower cost feedstocks than competing titanium extraction methods, whilst offering the potential for direct titanium powder production.

ACKNOWLEDGEMENTS

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White Mountain Titanium Corporation

Titanium Metal Production via Oxycarbide Electrorefining

The Chinuka Process: Electroextraction-refining

Daniel Jewell, Mike Kurtanjek, and Derek Fray

Who are we?



UNIVERSITY OF
CAMBRIDGE

Department of Materials Science and Metallurgy



Professor Derek Fray
Director of Research

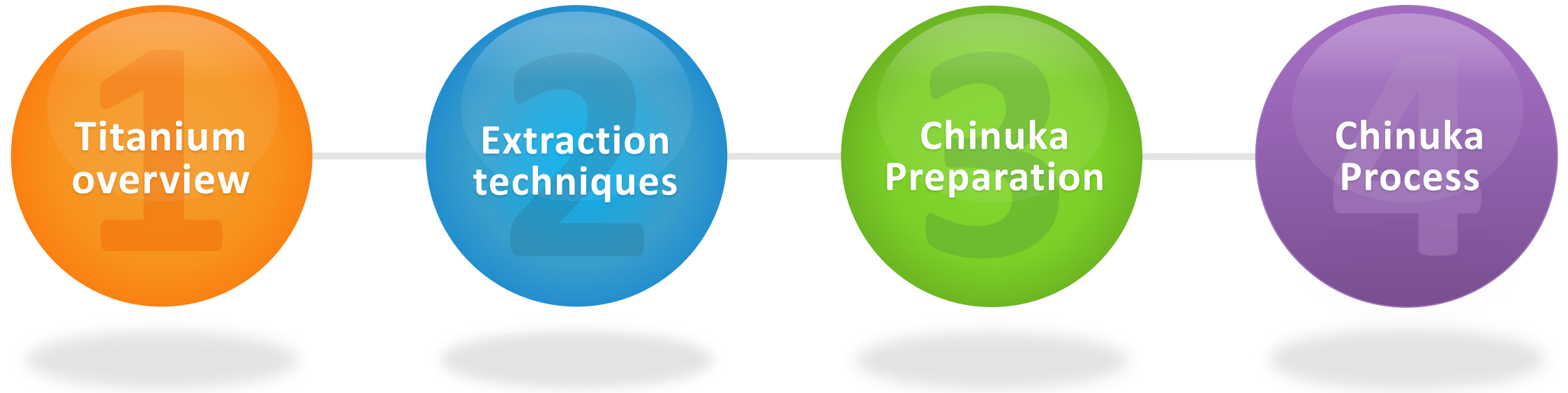


Dr Daniel Jewell
Research Associate

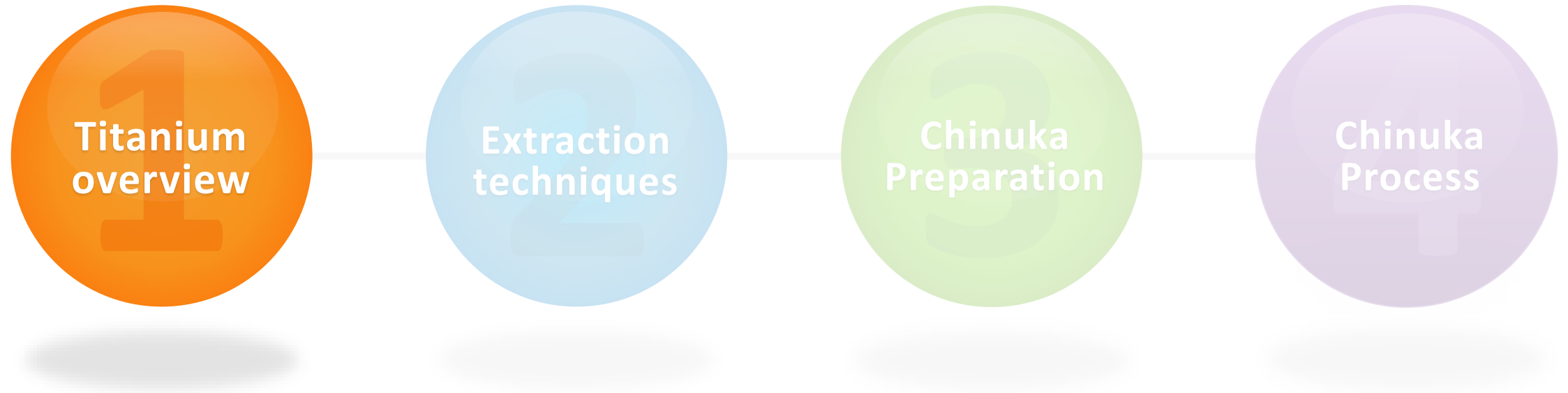


- Founded in 2003, White Mountain Titanium Corporation (WMTC), an exploration stage titanium mining company, is the parent company of Chinuka Ltd.
- WMTC is developing the Cerro Blanco Project; over 8,225 hectares located west of Vallenar in the Atacama region, northern Chile
- The mine has 32.9 Mt of measured & indicated resources at 2.1% TiO_2 ; mine life of 6-7 yrs, up to 17.5 kt/day
- Rutile and Ilmenite ores available

Agenda

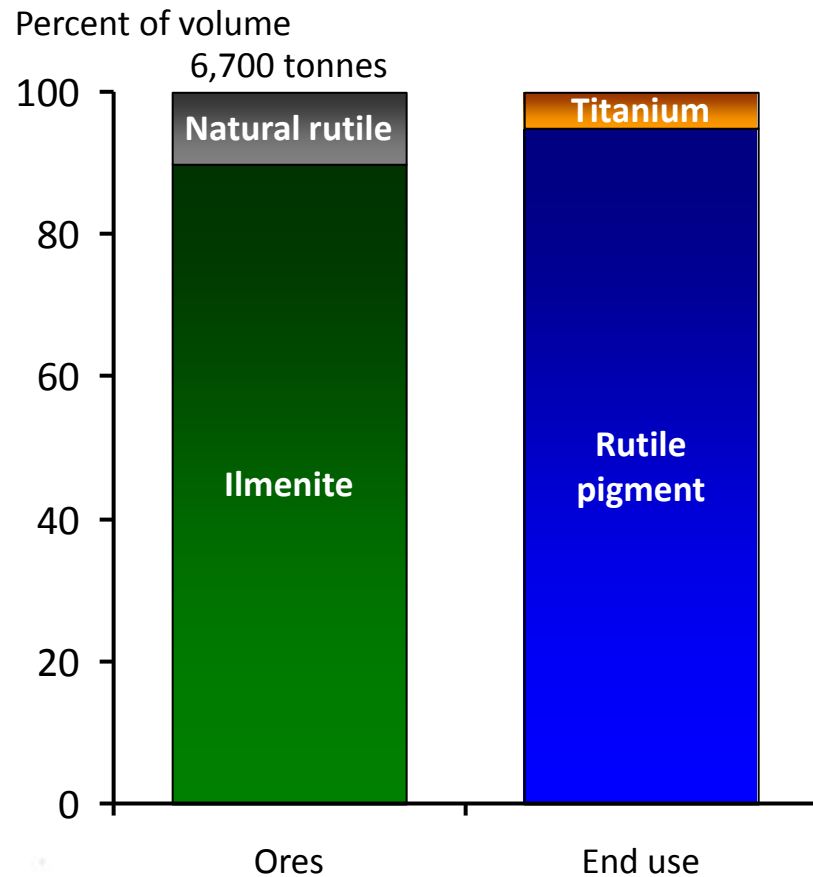


Agenda



Overview of titanium market

Titanium ores by supply and end usage (2011)



Ilmenite – Largest feedstock

- Total world resources more than 1.8bn tons
- 90% of global titanium mineral consumption
- Ores typically contain 35-60% TiO_2
- Ilmenites containing $>60\%$ TiO_2 are known as Leuxoxene
- Largest producer is South Africa

Rutile pigment – Largest product

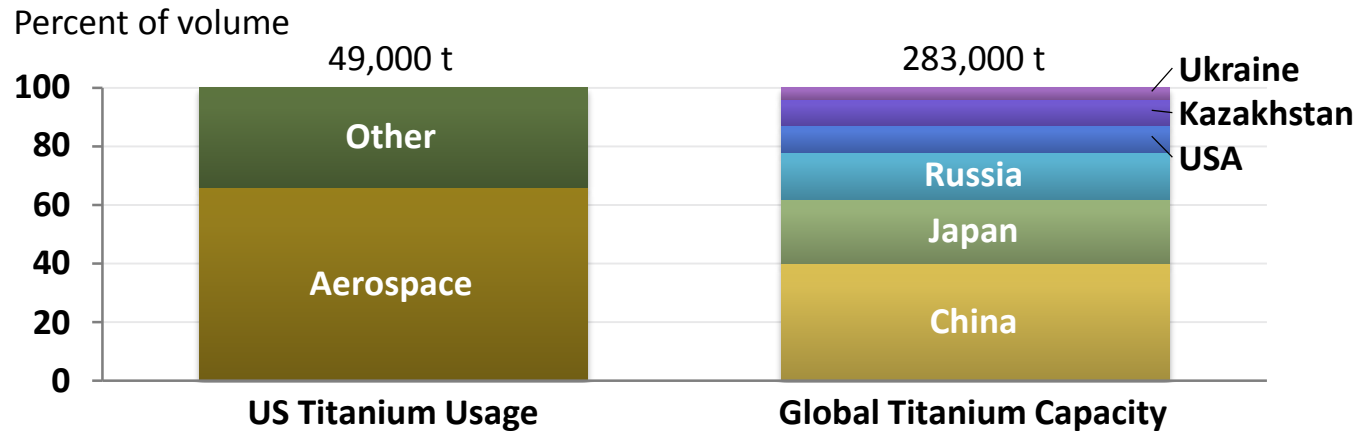
- Global demand over 5.7 million tonnes p.a.
- Accounts for 95% of global titanium ore end use
- Growing demand; up 8% from 2010 – 2011
- Predominantly used in paints, coatings, plastics, & paper
- Largest producer is the United States



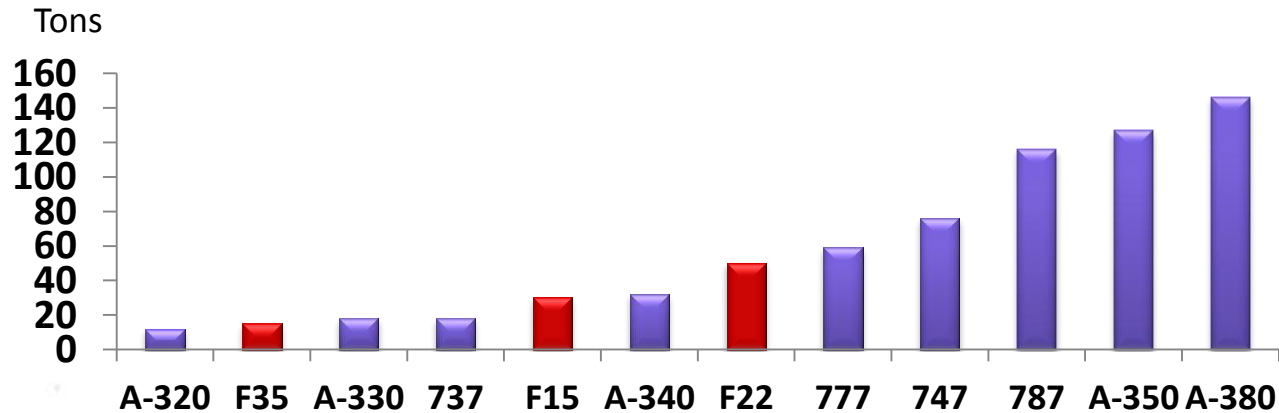
Titanium metal market

Data Sources: USGS Minerals Information, 2012
Titanium Metals Corporation Annual Report 2010
Titanium, S. Seong, O. Younossi & B. Goldsmith, 2009
Photograph Source: www.3d-aviation.com

US Titanium metal usage and world capacity (2011)



Titanium minimum buy weight in aircraft



Titanium metal sponge

- 5% of world titanium ore usage
- Fast growing (6% p.a.) market
- 283,000 tpa worldwide capacity
- Largest producer is China



787 Dreamliner – 116 tonnes titanium

But the real question is...

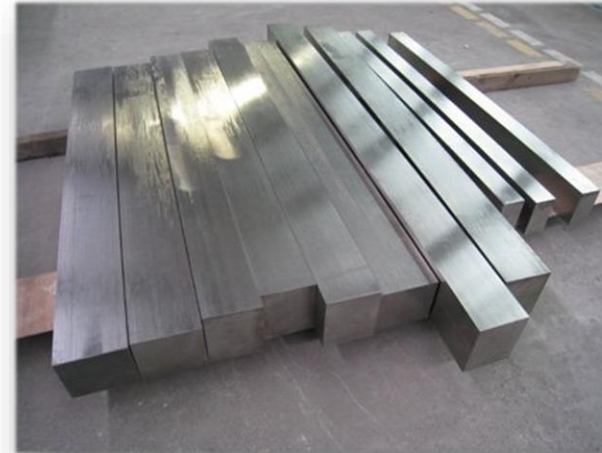
Photograph Sources:
Ilmenite – irocks.com
Titanium – balticnordic.com

How do you get from this...



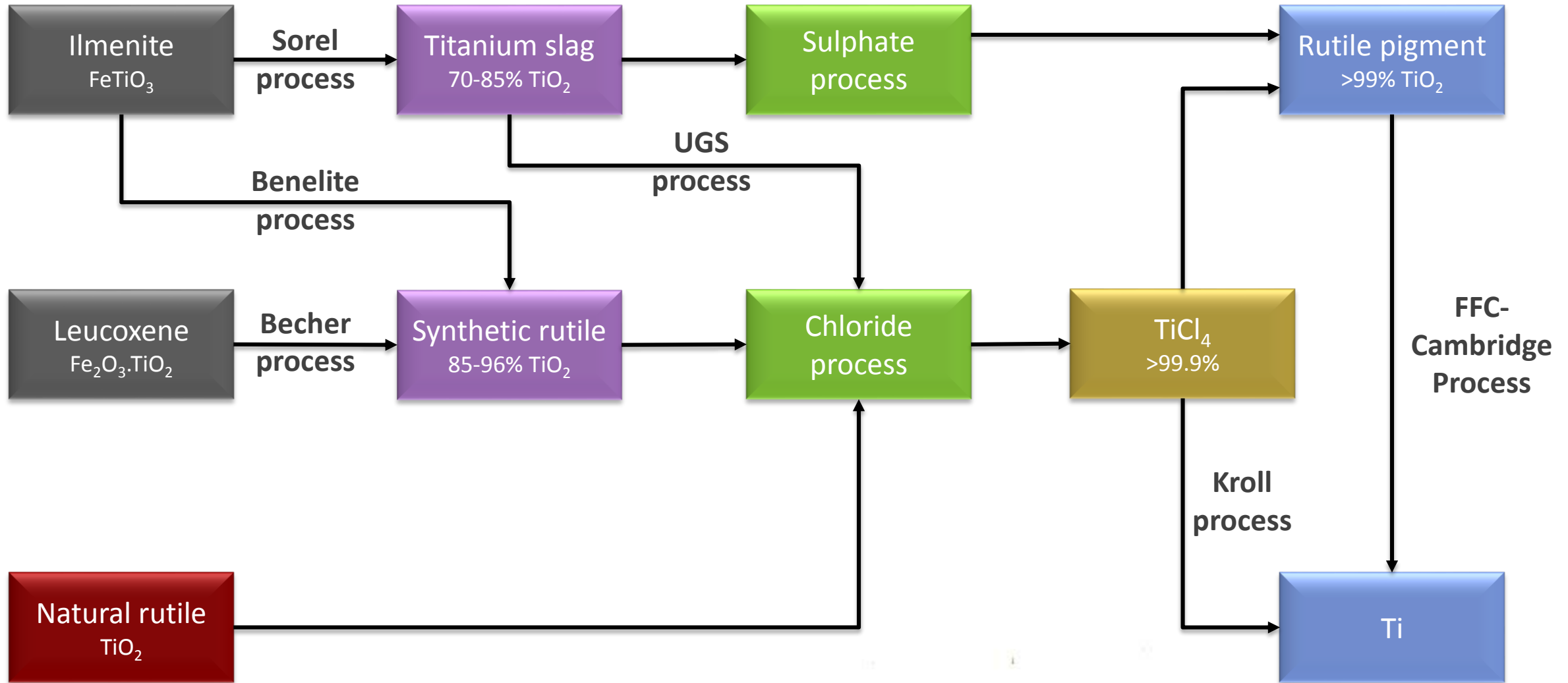
Titanium
ore

...to this?



Titanium
metal

Titanium: From ore to pure



Our challenge

XRF analysis of Cerro Blanco ores

	Rutile (wt. %)			Ilmenite (wt%)
	Standard	Fine	Ultrafine	
TiO ₂	96.4	97.2	97.5	51.2
FeO/Fe ₂ O ₃	0.66	0.77	0.97	48.7
SiO ₂	1.13	0.88	0.62	1.11
MgO	0.04	0.02	0.02	0.66
Al ₂ O ₃	0.30	0.18	0.12	0.62
MnO ₂	<0.01	0.01	<0.01	0.37
V ₂ O ₅	0.28	0.30	0.30	0.19
Nb ₂ O ₅	0.30	-----	0.39	0.15
CaO	0.06	0.12	0.20	0.12
Cr ₂ O ₃	0.34	0.34	0.35	0.05

Challenge #1:

At <53µm, ultrafine rutile is too fine for the chloride route as it is lost from the fluidised bed

This is important as it comprises ≈10% of the deposit

Challenge #2:

Calcium oxide content is too high for conventional processing

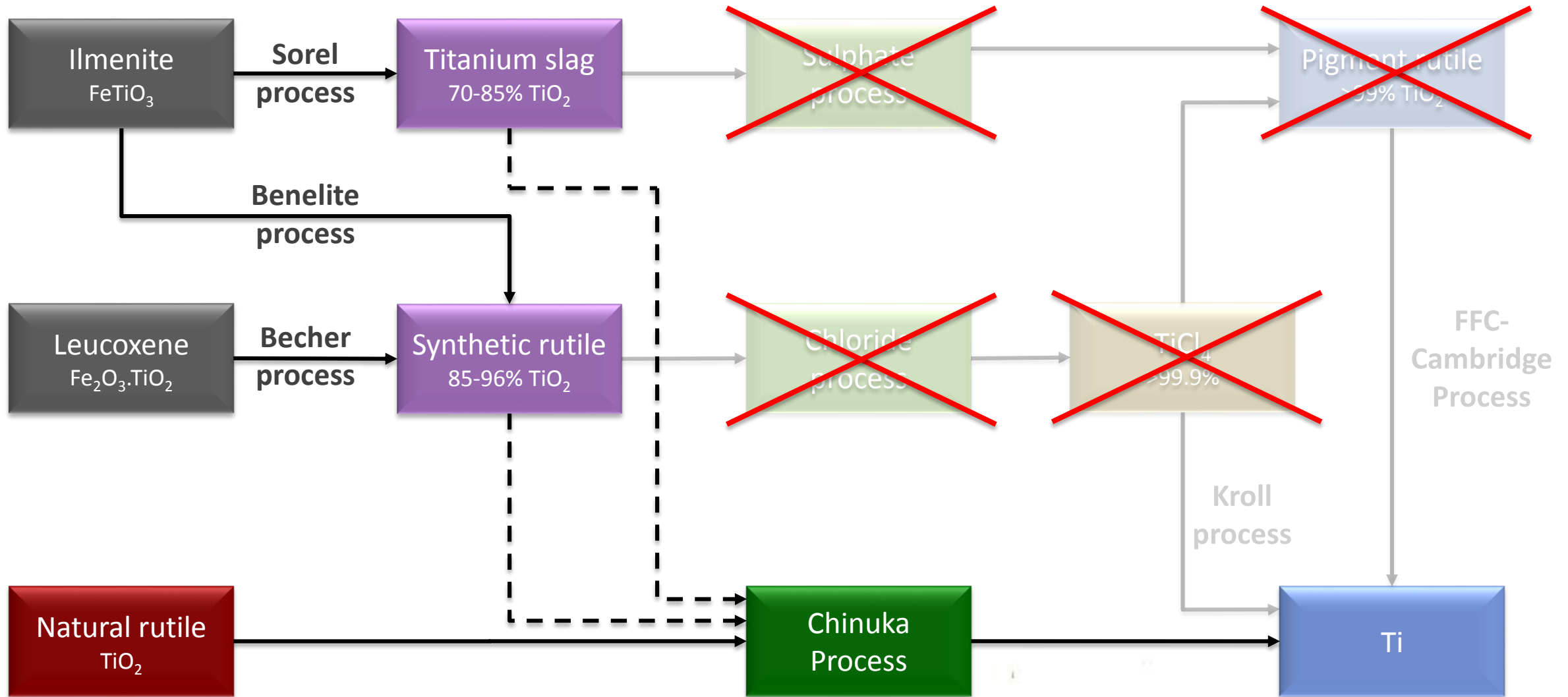
Chloride route:

CaCl₂ formation defluidises bed

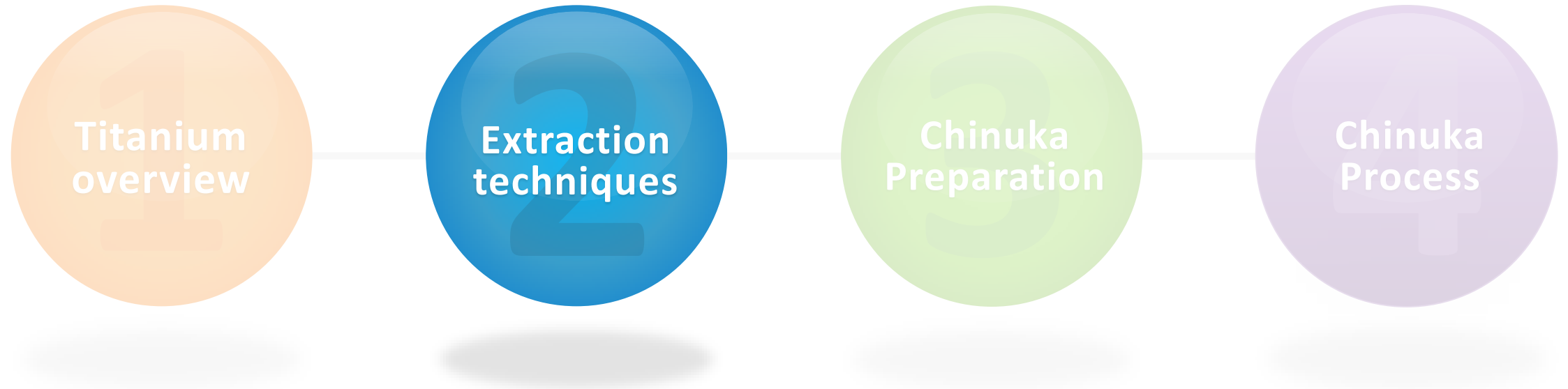
Sulphate route:

CaSO₄ formation is problematic

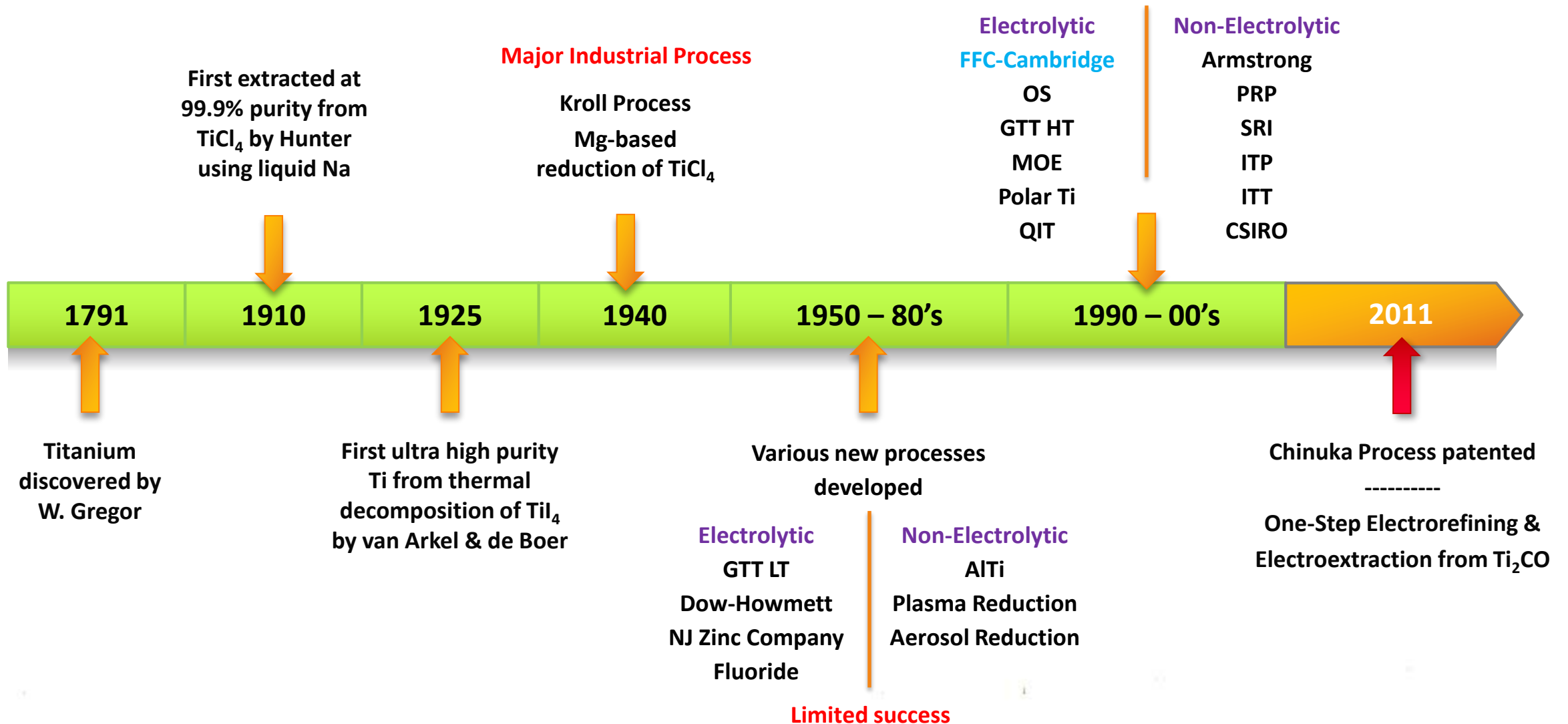
Chinuka: Ore to metal



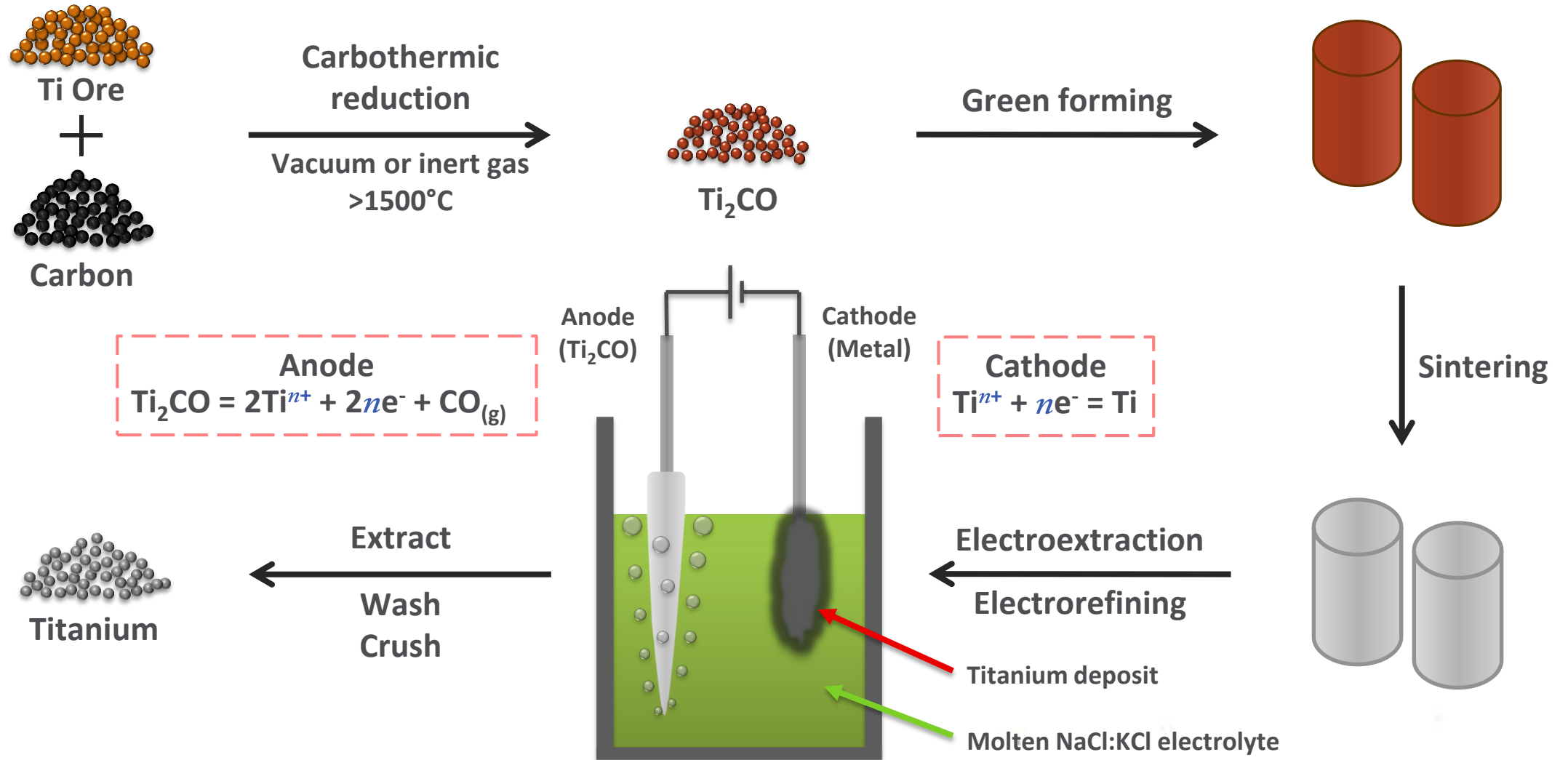
Agenda



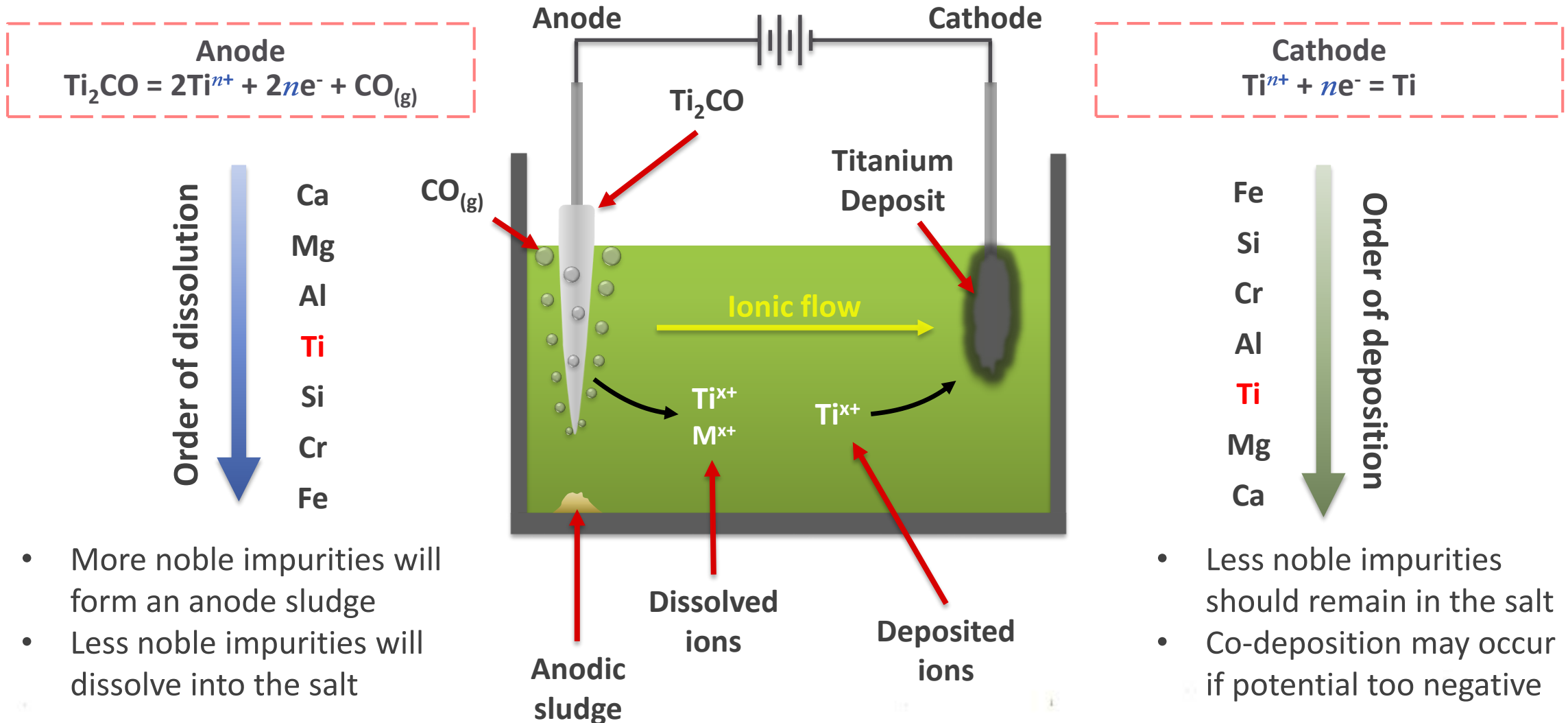
Titanium extractive history



The Chinuka Process



A closer look at electrorefining



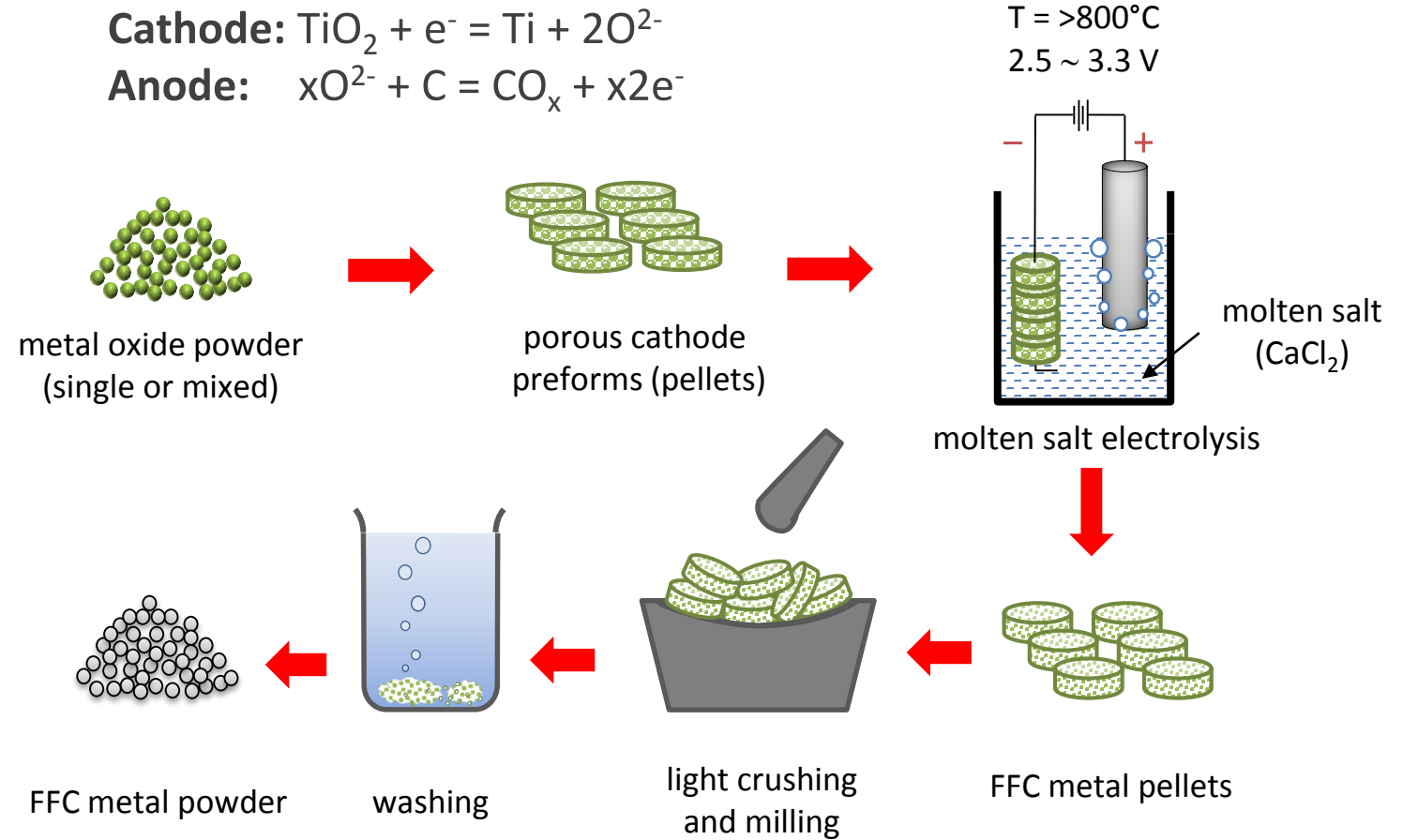
The FFC-Cambridge Process

Overview

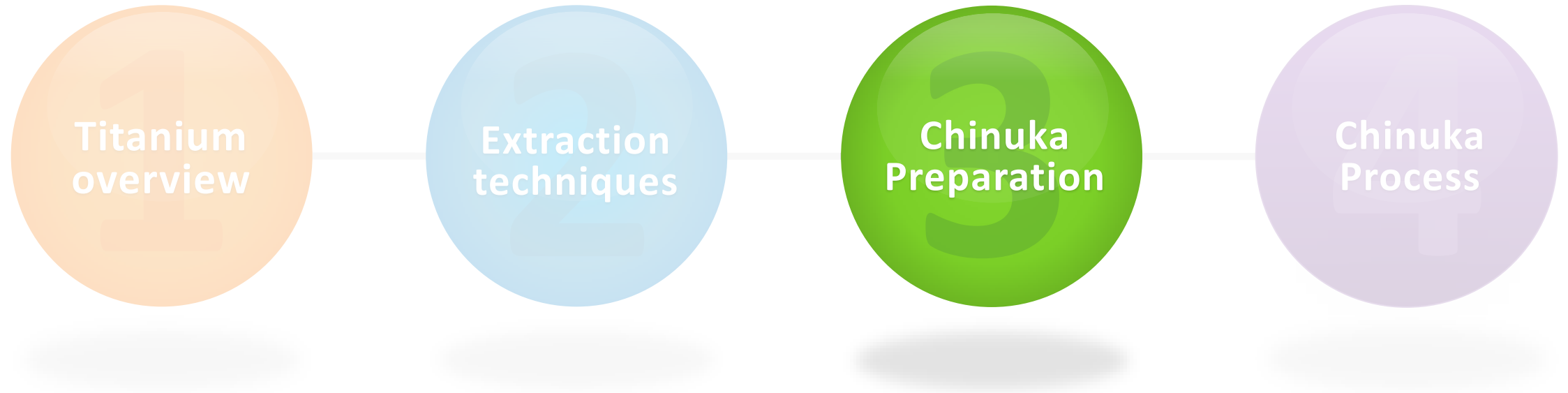
- Invented in 1996 by Derek Fray, Tom Farthing and George Chen at the University of Cambridge
- Electro-deoxidation of metal oxides in a CaCl_2 electrolyte
- Flagship replacement technology for the Kroll Process

Important notes

- Requires pure oxide feedstocks; particularly sensitive to cationic impurities
- Excels in the production of high value metals and alloys
- Employs CaCl_2 which has a high oxygen solubility and is highly hygroscopic

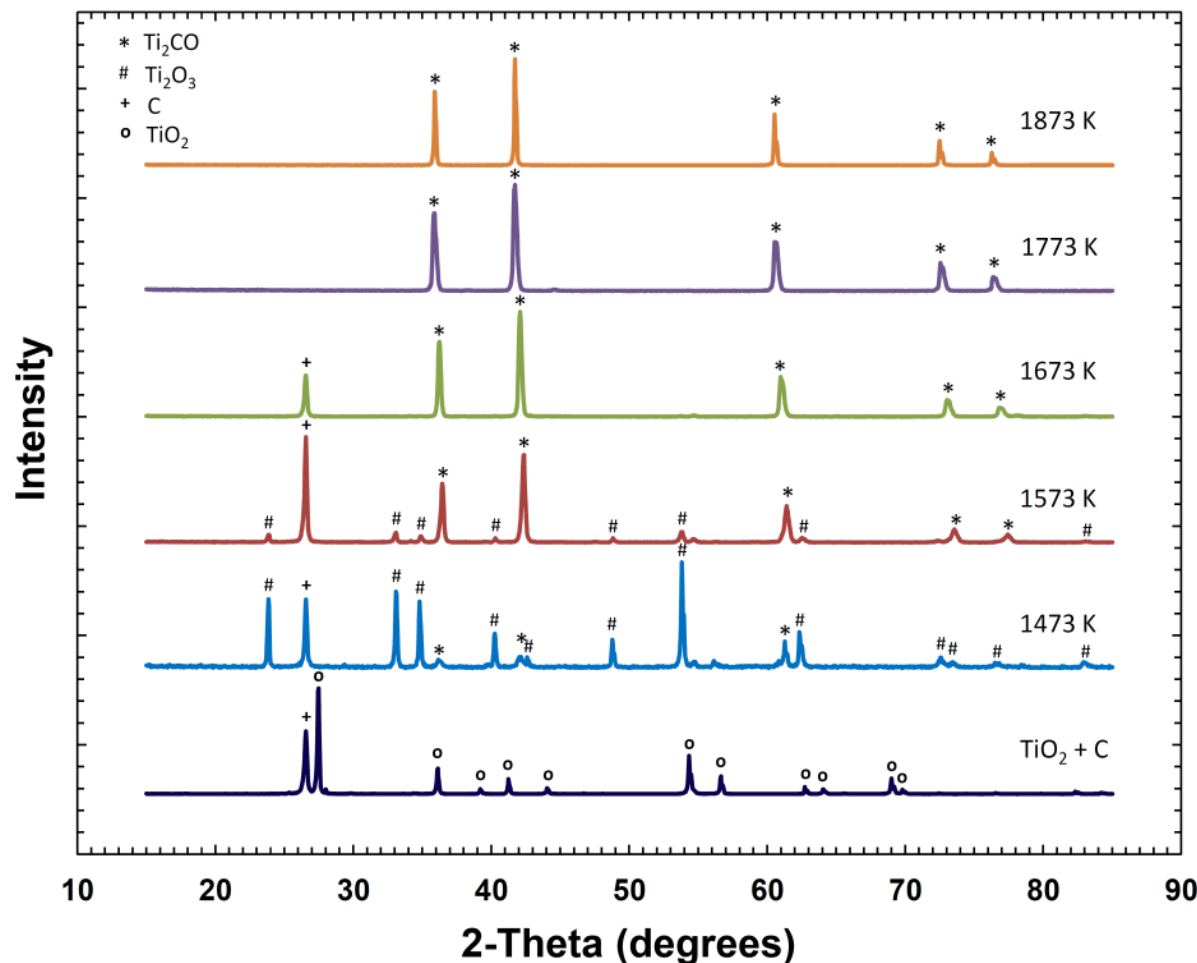


Agenda



Ti₂CO produced from rutile

Effect of temperature (4 hours under vacuum)



Stage 1:

Partial carbothermic reduction of rutile ores under a vacuum or inert atmosphere at >1500°C



Stage 2:

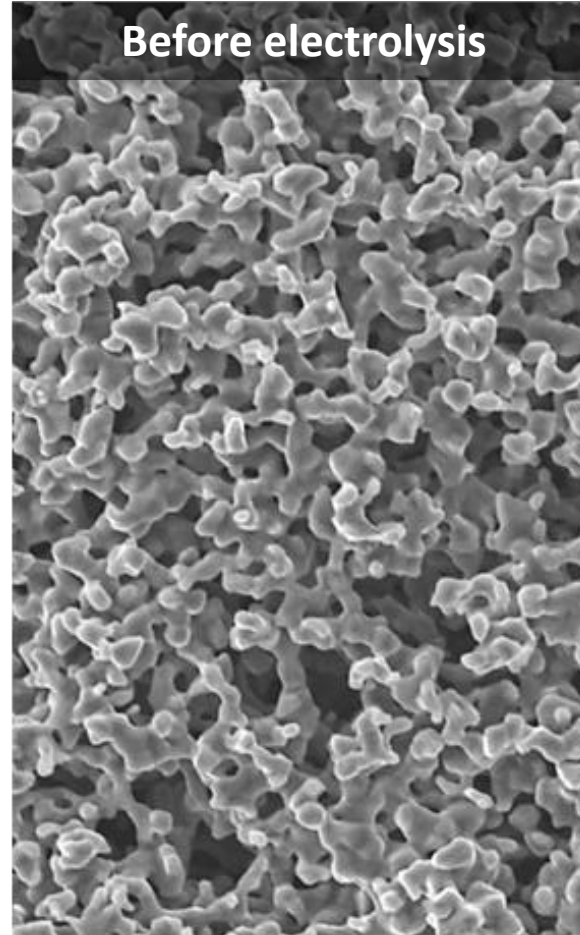
Anode green forming from oxycarbide followed by sintering ; usually performed above >1600°C

Ti₂CO anode microstructure

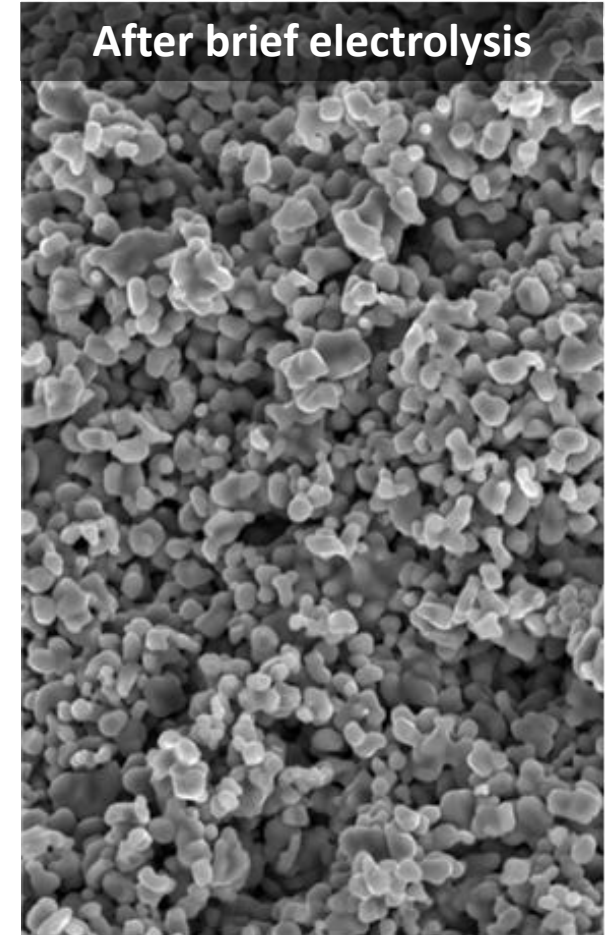


Effect of electrolysis on microstructure

Before electrolysis



After brief electrolysis



Key points

- Ti₂CO is a good electrical conductor
- Strongly interconnected nodular network provides good mechanical strength
- Low porosity is key to microstructural stability during electrolysis; currently <25% porosity is achieved at 1700°C

What about the impurities?

Issue?

In addition to Ti_2CO formation, impurity reaction products need to be considered

Solution?

Depending on level of impurity these can either be handled in electrolysis, or post-sinter processing can include magnetic separation and acid leaching

Exceptions?

Ilmenite contains so much iron that slagging can occur

	Reaction at 1500°C	Post-reaction processing
TiO_2	$2\text{TiO}_2 + 4\text{C} = \text{Ti}_2\text{CO} + 3\text{CO}_{(\text{g})}$	Desired product
FeO	$\text{FeO} + \text{C} = \text{Fe} + \text{CO}_{(\text{g})}$	Magnetic separation or acid leach
Fe_2O_3	$\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO}_{(\text{g})}$	
SiO_2	No Reaction	Retained in anode
MgO	No Reaction	Acid leach (HCl)
Al_2O_3	No Reaction	Retained in anode
MnO	$3\text{MnO} + 4\text{C} = \text{Mn}_3\text{C} + \text{CO}_{(\text{g})}$	Retained in anode
V_2O_5	$\text{V}_2\text{O}_5 + 6\text{C} = \text{V}_2\text{C} + 5\text{CO}_{(\text{g})}$	Retained in anode
Nb_2O_5	$\text{Nb}_2\text{O}_5 + 7\text{C} = 2\text{NbC} + 5\text{CO}_{(\text{g})}$	Retained in anode
CaO	No Reaction	Acid leach (HCl)
Cr_2O_3	$1.5\text{Cr}_2\text{O}_3 + 6.5\text{C} = \text{Cr}_3\text{C}_2 + 4.5\text{CO}_{(\text{g})}$	Retained in anode

A possible solution to the Ilmenite problem: blending

The approach

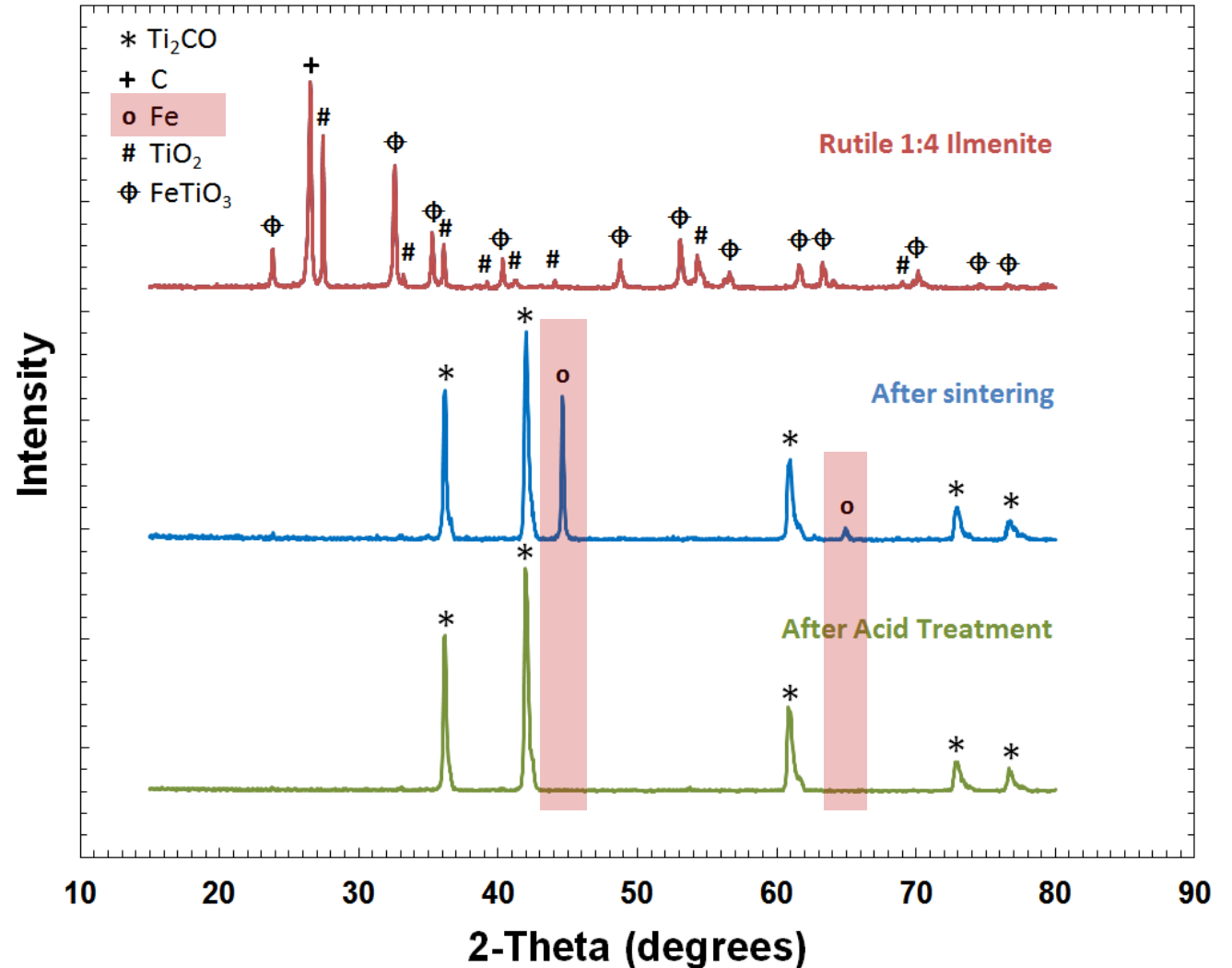
By blending rutile and ilmenite ores, the average iron concentration can be controlled

Advantages

- Eliminates slagging
- Provides tunable impurity levels
- Dilutes feedstock cost

However...

Significant iron contents are still problematic to electrolysis and should be reduced post-reaction



Another aspect of electrorefining: Electrolyte enrichment

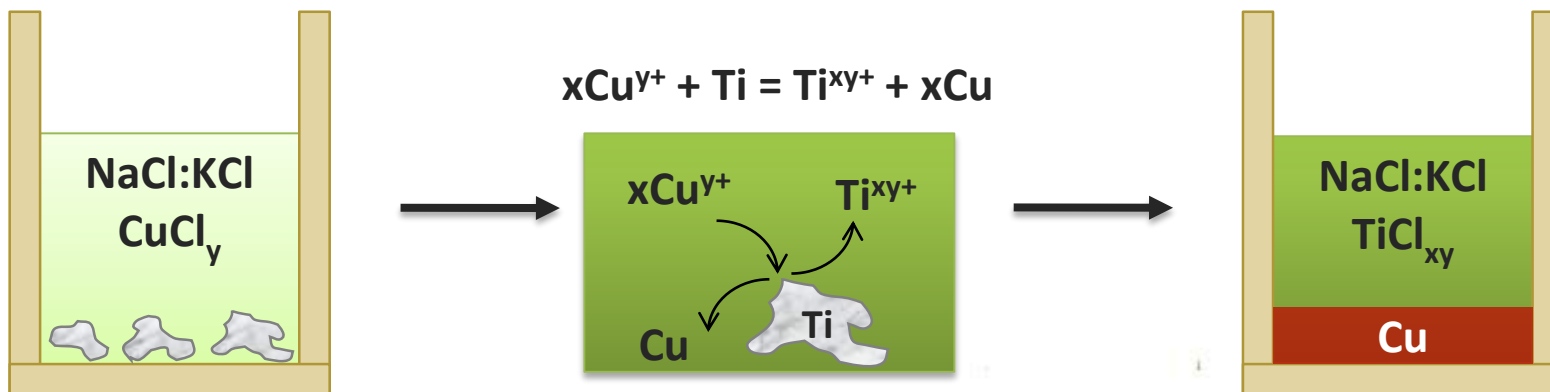
Pre-enrichment of electrolyte is typically employed in electrorefining to:

- Reduce deposition overpotential
- Provide sufficient relevant ions to support current
- Prevent decomposition of electrolyte
- Affect electrodeposited product morphology

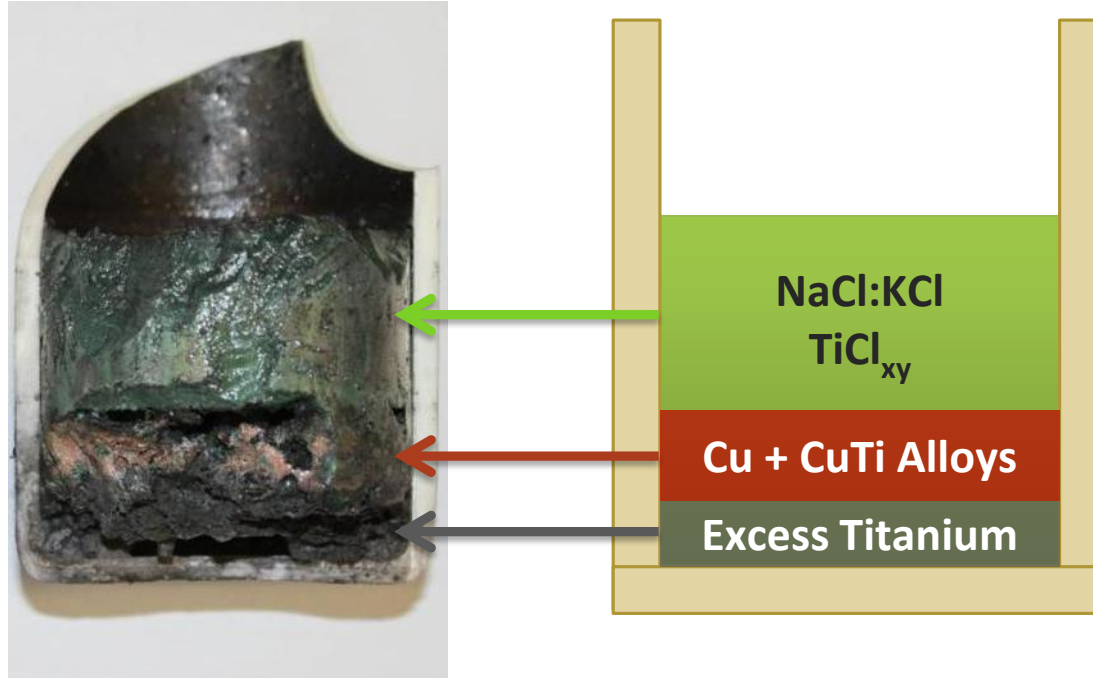
— This is **not essential** for process operation, but is preferred

For titanium, typically achieved by high temperature in-situ reaction: $\text{TiCl}_{4(g)} + \text{Ti}_{(s)} = \text{TiCl}_{2} - \text{Safety Issues!}$

— **Alternative?** – Use reactive chlorides of Sn, Ni, Co, Zn, **Cu** etc.



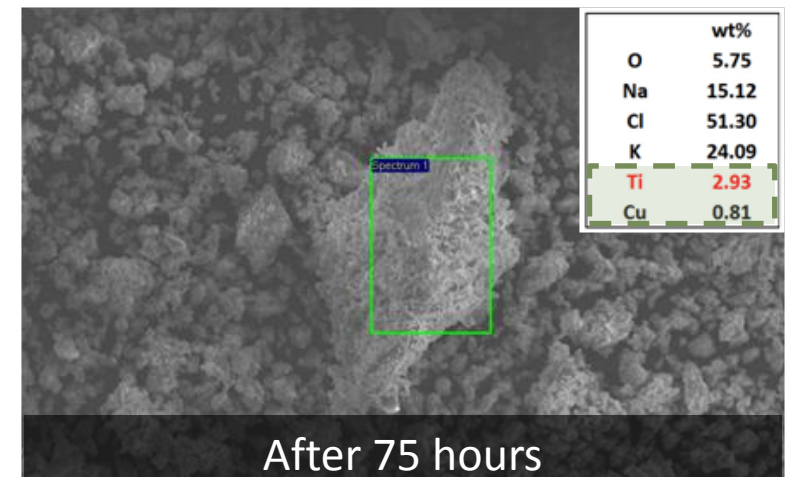
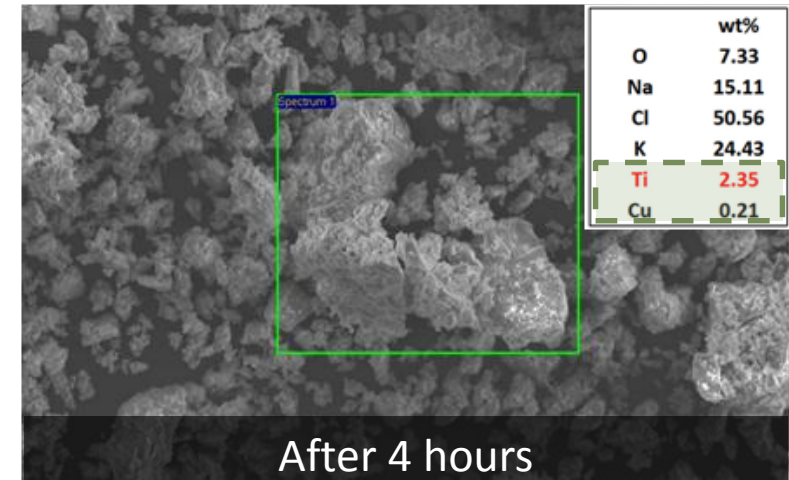
Experimental results of copper chloride reaction



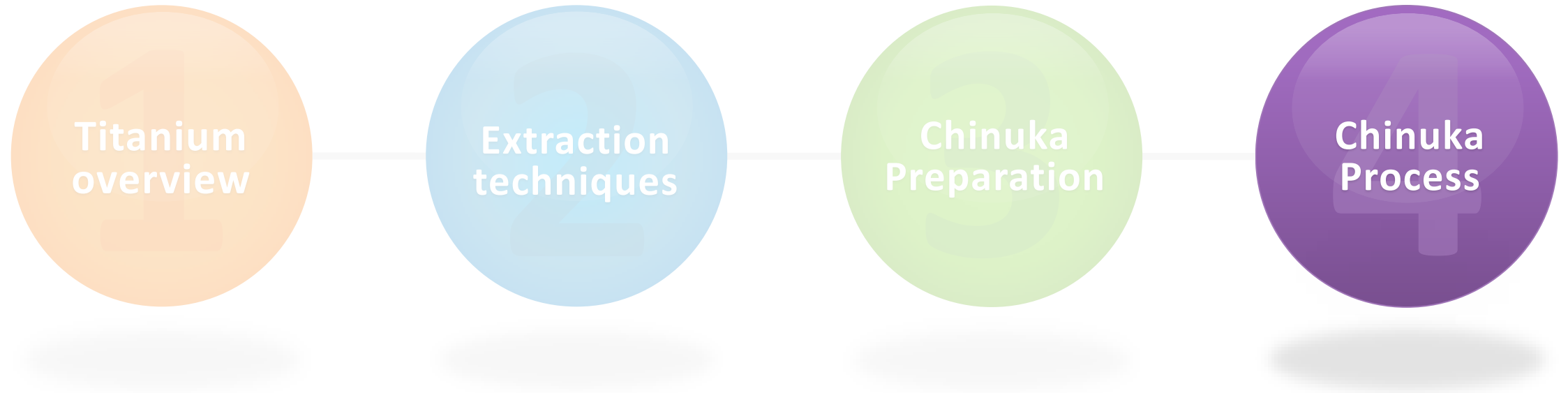
Conclusions

- Enrichment successful up to at least 10wt%
- Low copper impurities with good physical separation
- Dissolved titanium stable over very long periods

Stability test

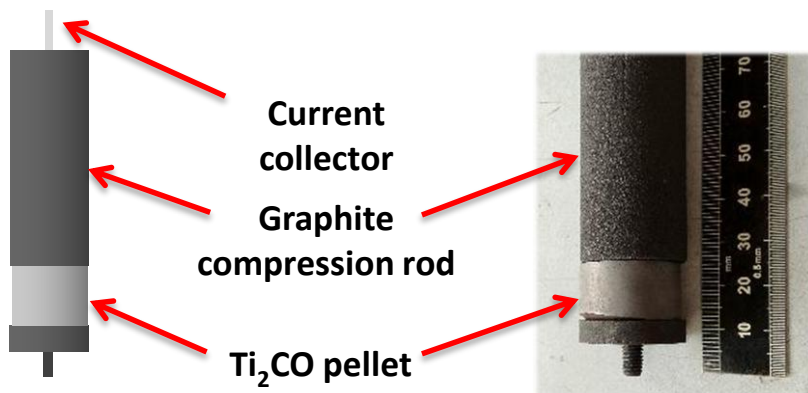


Agenda



Electrolysis of Ti_2CO

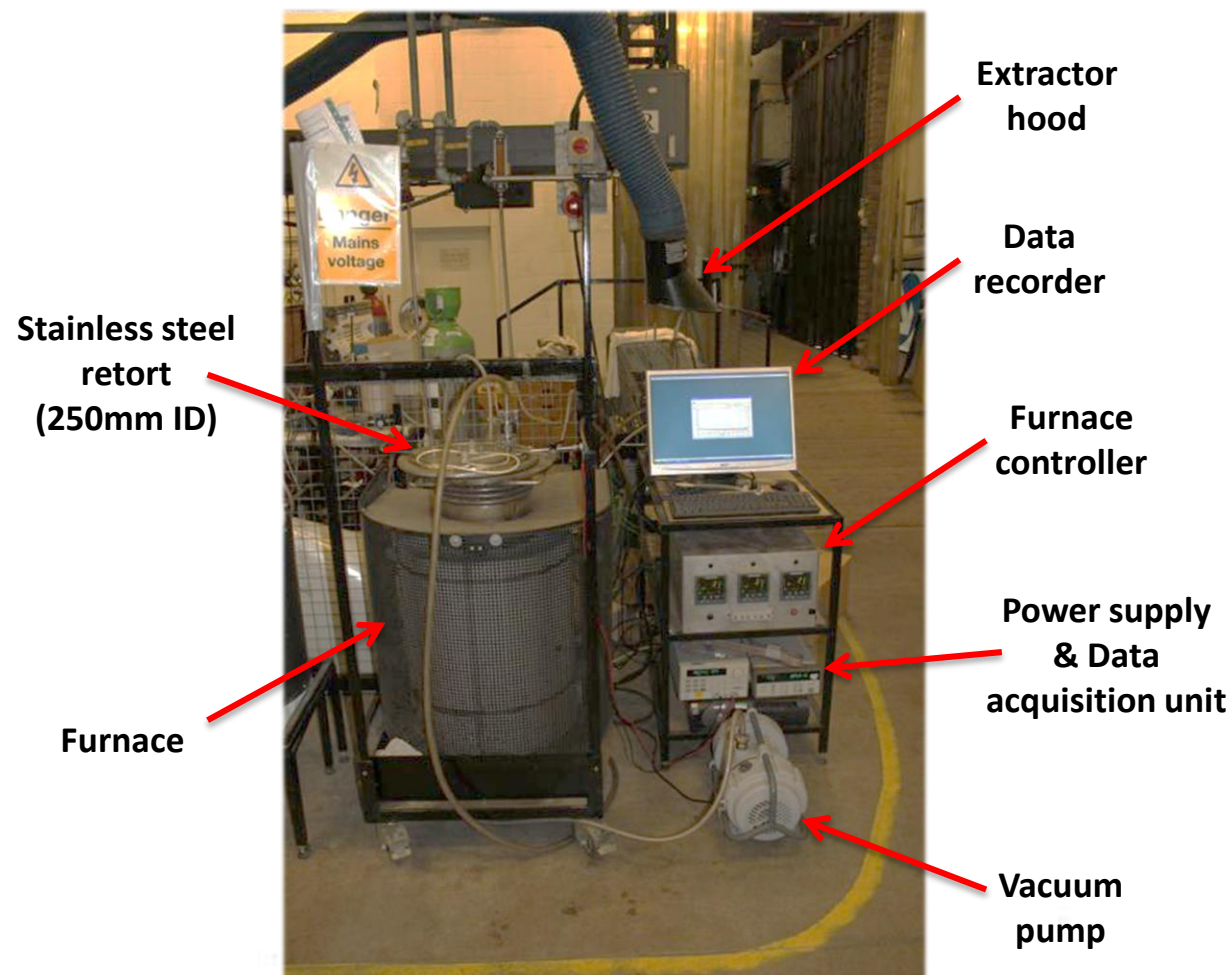
Ti_2CO anode



Experimental conditions

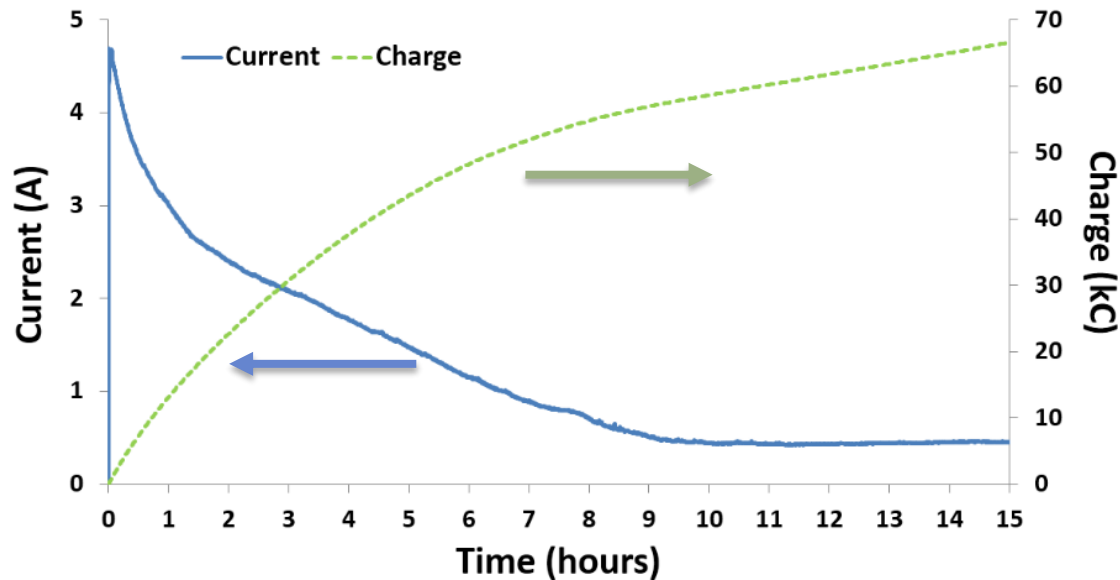
- Electrolyte : Eutectic $\text{NaCl}:\text{KCl}$
- WE = Mo ; CE = Ti_2CO ; RE = Ti
- Temperature : 700 - 900°C
- Time : 2 - 24 hrs
- Voltage : 1.8 V – 3.0 V
- Current density : 50 – 500 mA/cm^2
- Current efficiency : 15 - 50%

Experimental setup

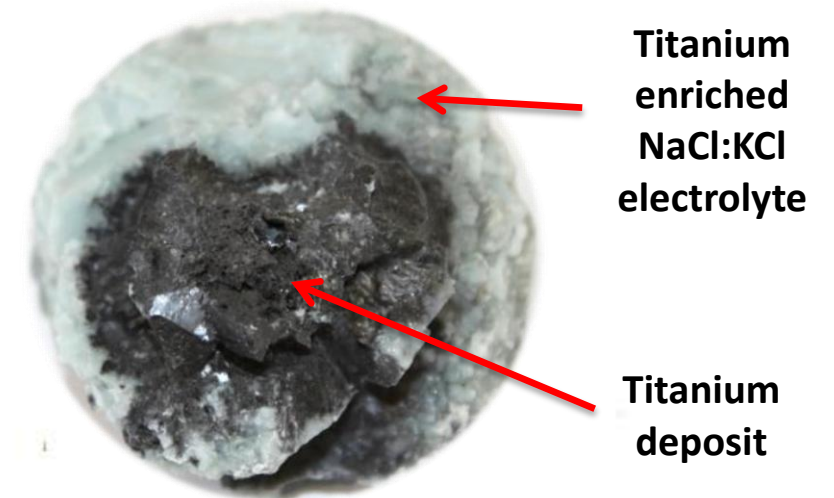
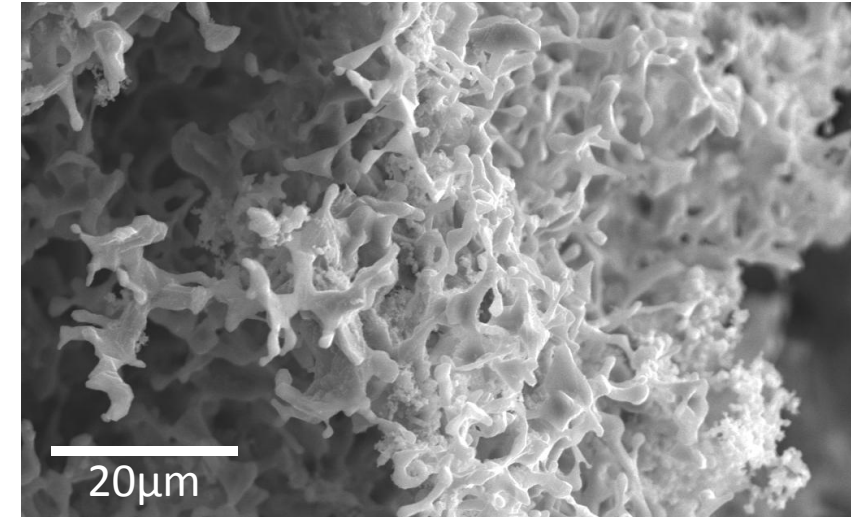


Observations and results

Constant cell voltage graph



- Anodic gas bubbling observed throughout electrolysis
- Ti sponge-like product adhered to cathode or retained in crucible
- Widely variable product form and size – for nodules typically 1-5 μ m
- Following washing (H₂O), 'sponge' readily crushed to powder
- Salt enriched with Ti – green (Ti²⁺) or blue (Ti³⁺)
- Oxygen content around 1wt.% for these samples*



Comparison of products - Macroscopic

Cathodic deposit - Ti Anode

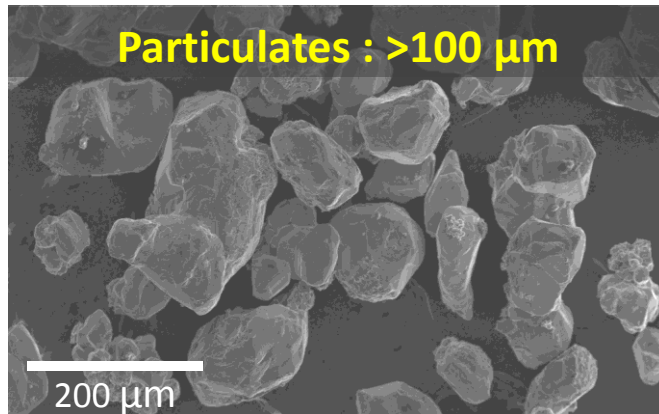
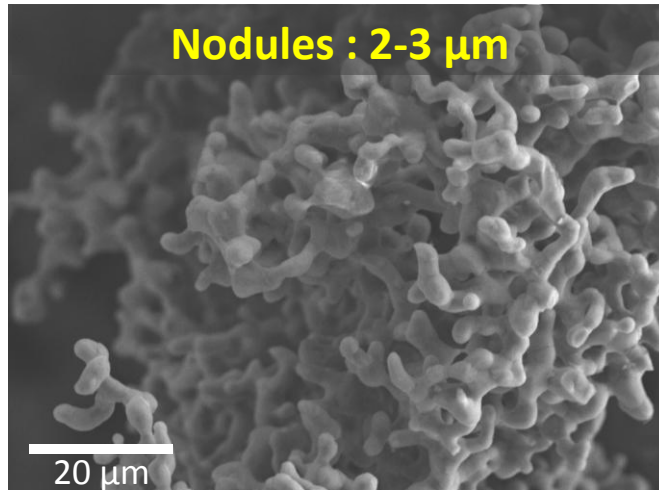


Cathodic deposit - Ti_2CO Anode

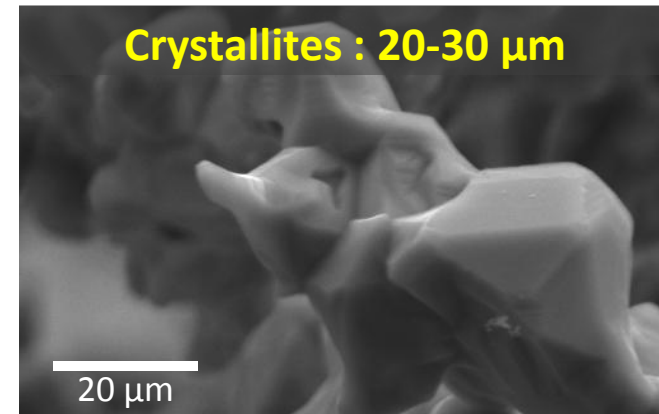
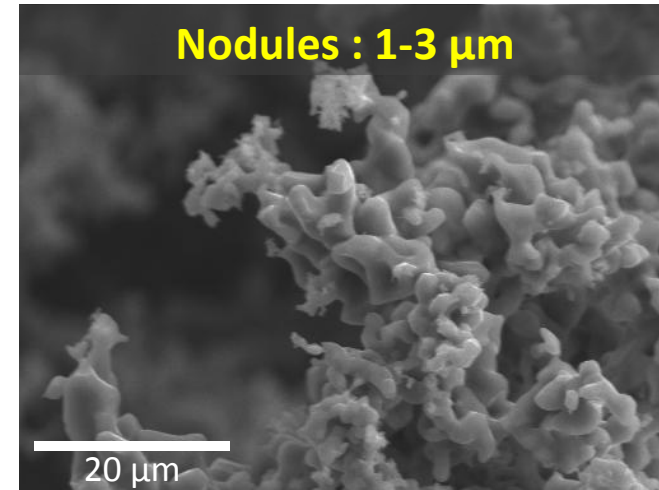


Comparison of products - Microscopic

Cathodic deposit - Ti Anode

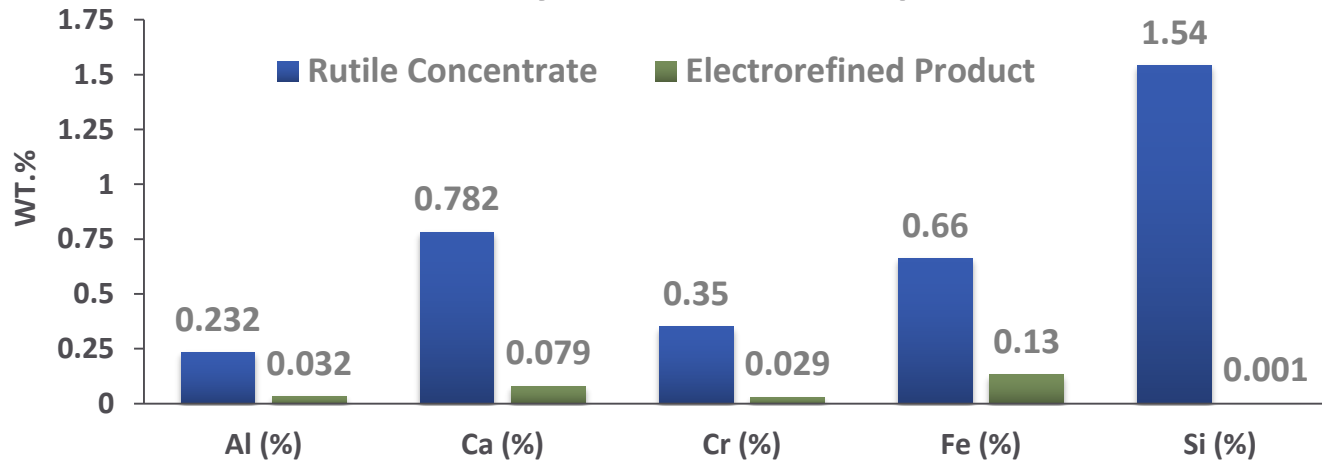


Cathodic deposit - Ti_2CO Anode



Experimental post-mortem

ICP analysis of feed and product



ICP analysis of electrolyte

Sample	Al (ppm)	Ca (%)	Cr (%)	Fe (%)	Si (%)
Blank	0	0	0	0	0
Electrolysis 1	0.00176	0.338	0.0056	0.00104	--
Electrolysis 2	0.00122	0.763	0.0304	0.00098	0.0415
Electrolysis 3	0.00166	1.388	0.0357	--	0.0511
Electrolysis 4	0.00219	1.623	0.0375	0.00407	0.0548

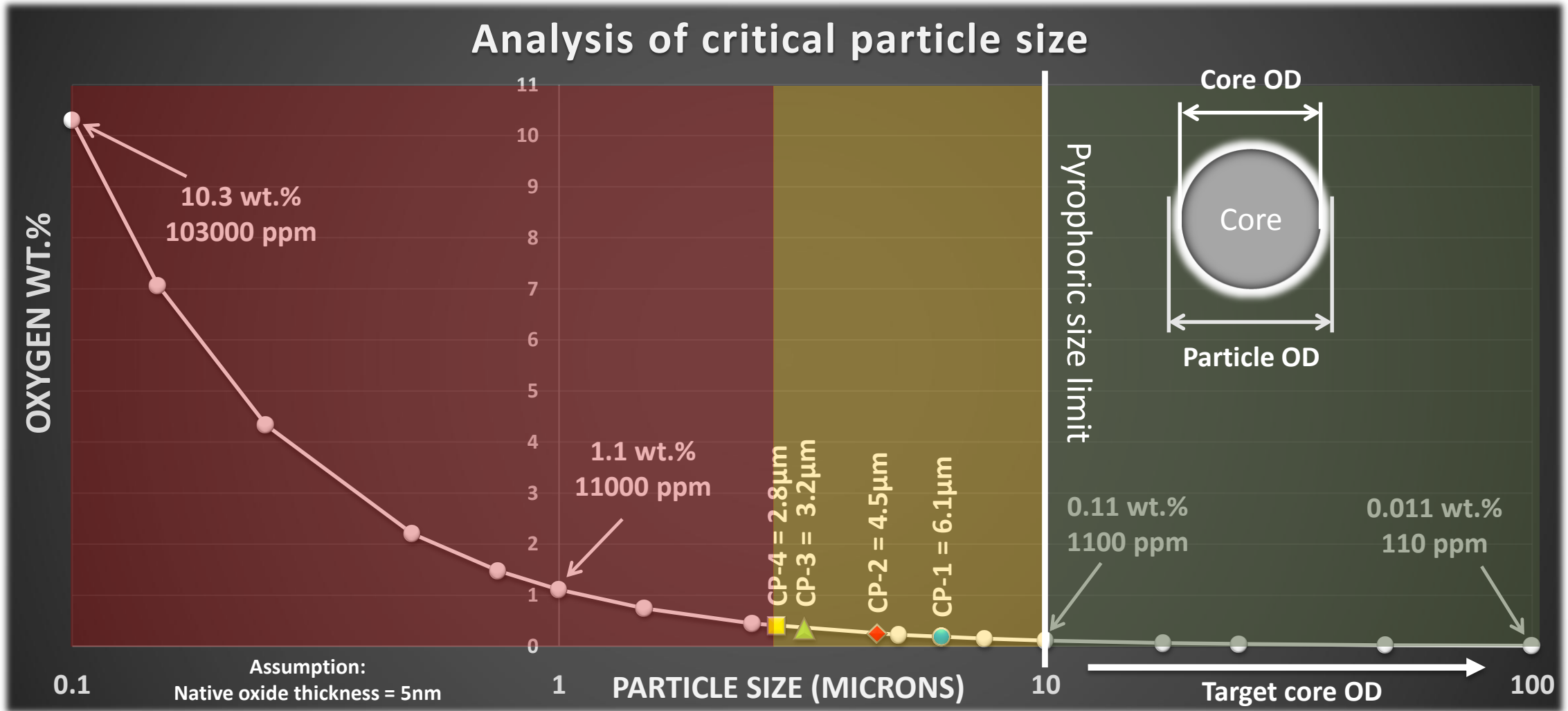
Electrorefined product

- Significant reduction in all cationic impurities with low final values
- Increase in purity from 96.5% feedstock to >99.5% product
- Potential for further purification by process optimisation

Electrolyte

- Gradual build up of impurities; particularly Ca
- Minimal retention of Al and Si
 - Likely due to formation of volatile chlorides
- Residual impurities may be gettered by Ti sponge addition to crucible

A note on oxidation and pyrophoricity





Brief overview

...and the future ■

Comparison of principle titanium extraction processes

	Chinuka Process	Kroll Process	FFC – Cambridge Process
Reaction type	Electrolytic	Chemical	Electrolytic
Operation	Semi-continuous operation	Batch operation	Semi-continuous operation
Feedstock	Broad range of TiO_2	TiCl_4	High-purity TiO_2
Electrolyte	Non-hygroscopic NaCl:KCl eutectic; low oxygen solubility	-	Highly hygroscopic CaCl_2 electrolyte; high oxygen solubility
Operating condition	Operable at voltages well below electrolyte decomposition	-	Typically high cell voltages close to electrolyte decomposition
Post production	Water washing	Vacuum distillation	Water washing
Product type	Ti powder or crystallites	Ti sponge	Ti powder or near-net shape
Scope for development	Emerging technology	Mature technology	Semi-mature technology
Challenges	Eventually requires salt replacement or purification	Requires electrolytic regeneration of Cl_2 and Mg	Involves complex suboxide and titanate/titanite chemistry

Final words and the next steps...

Elevator pitch

- The Chinuka Process is a novel electrochemical method which simultaneously combines electroextraction with electrorefining to produce high purity titanium
- The process offers a number of specific advantages over existing technologies, the most significant of which is the ability to directly treat impure ores

The future

- Continued scale-up of the process with rutile ore feedstock
- Further investigation into the electrolytic performance of ilmenite & blended ores
- Application of the process to non-titanium ores, including niobium (Nb), tantalum (Ta), and the rare earth metals



Question time

...and answers ■

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