In search of low cost titanium: the Fray Farthing Chen (FFC) Cambridge process

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Synopsis

This article explores the Fray Farthing Chen (FFC) Cambridge process, a novel method for the electrochemical deoxidation of metal oxides in molten salt, discovered at the University of Cambridge in 1997. The process was hailed as a highly promising, potentially low cost, novel method for the production of titanium metal direct from its oxides. The article should inform researchers in the field of some of the challenges in the commercialization of a novel, high profile process involving multiple stakeholders. The author, former senior process engineer at British Titanium Plc, the company originally tasked with commercializing titanium production via the FFC Cambridge process, reviews the latest literature and discusses past and present progress in the pursuit of low cost titanium metal via this process. Topics explored include the history of the process, attempts at commercialization, NASA's alternative application, and present status of the process.

Keywords
FFC Cambridge, titanium, molten salt.

Introduction

Titanium offers advantages over many alternative metals in terms of weight, density corrosion, maintenance and lifetime costs. The main barrier to realizing the benefits associated with titanium in numerous applications has been the high cost of raw material and secondary processing, compared to the alternatives, e.g. stainless steel and aluminium.

Present industrial production methods for titanium occur by the reduction of titanium tetrachloride ($TiCl_4$) with magnesium (Kroll process) or sodium (Hunter process). After more than 60 years of research and development, titanium yet holds the promise of a process capable of significantly reducing titanium product cost, ideally by more than 30%.

A process merely delivering a sponge product, aimed at replacing Kroll sponge alone, does not have potential for large reduction in overall titanium cost. Significant cost savings can be achieved only by also reducing the large number of process steps required to process the sponge to mill product, including sponge purification, comminution, electrode forming, vacuum arc re-melting, and hot and cold rolling. Presently, economy of scale in the production of titanium dictates that it is most cost-effective to cast the largest possible size ingot. This, however, leads to significant material waste in downstream processing, contributing to the existence of a large titanium scrap industry.

Titanium powder/granules material can be used in several powder metallurgy processes, e.g. laser forming and powder injection moulding, to directly produce final product in fewer steps. Also, rather than machining intricate components from wrought billet, by creating near-net shape parts, titanium powder metallurgy can decrease processing cost and material wastage. Commercially available titanium powder is, however, costly, as it requires titanium sponge or ingot as starting material. To obtain titanium as a powder requires further processing of the sponge or ingot, e.g. via the plasma rotating electrode process, where a rotating bar of titanium is subjected to gas plasma, the molten droplets are atomized and collected as titanium powder.

The FFC Cambridge process is a metallurgical processing technology developed at the University of Cambridge in 1997, based on the counterintuitive discovery that ceramics like titanium dioxide can be used as electrodes in a molten salt reactor[1]. It has now been demonstrated that oxygen can be separated from most metal oxides by the FFC process, including production of titanium from titanium dioxide, chromium from chromites and silicon metal from silica. The process was hailed as a highly promising, potentially low cost, novel method for the production of titanium metal and several other metals and alloys.

It has been more than a decade since the discovery of the process, and millions of dollars have been invested in the development of the FFC Cambridge process to date. There is, despite numerous apparent benefits, presently no commercial-scale facility employing the process for metal or alloy production. This article examines the FFC process, its relative benefits, the challenges faced in its commercialization, and its present status.

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The basis of this research is the personal experience of the author whilst active as senior process engineer at British Titanium Plc, the now defunct company originally tasked with commercializing titanium production via the FFC Cambridge process. The article also reviews the latest literature, and discusses past and present progress in the pursuit of low cost titanium metal via this process. Topics explored include the history of the process, attempts at commercialization, NASA's alternative application, and present status of the process.

Discussion: the FFC Cambridge process

The invention of the FFC Cambridge process involved three people: Dr George Chen, Prof. Derek Fray and Dr Tom W. Farthing. It resulted, 'completely out of expectation', from a University of Cambridge research programme aimed at removing oxygen from Group IV metals, particularly the alpha case on titanium and alloys by molten salt electrolysis. It was found that on applying a voltage to an insulating metal oxide in a molten alkaline earth chloride, a small amount of reduction takes place in the porous pellet, causing it to become an electronically conducting electrode. The ionization of oxygen then takes place throughout the pellet, with the oxygen anions dissolving in $CaCl_2$, where they diffuse quickly out of the pellet into the melt and eventually discharge at the anode, leaving low oxygen metal at the cathode.

The first patent on the process was filed in 1998 and the invention was first announced in the September 2000 edition of *Nature Magazine*[1], following which the FFC process attracted significant interest and international support for its development and rapid commercialization, including initial financial support from the US Office of Naval Research (ONR) and the Defense Advanced Research Projects Agency (DARPA).

Process description

The process takes place in a molten salt medium, and is limited to operating temperatures above the melting point of the utilized salt, typically being in the range of 800–1100°C. The salt is typically a molten alkali halide, with a preference for $CaCl_2$ due to the high solubility of oxygen (primarily as CaO) in the $CaCl_2$ melt.

Metal oxide reduction via the FFC Cambridge (FFC) process is very simple in that the oxide to be reduced is rendered cathodic in molten alkaline earth chloride, such as molten $CaCl_2$ at 950°C. By applying a voltage below the decomposition potential of the salt (for $CaCl_2$ it is 3 V), it has been found that ionization of oxygen is the dominant cathode reaction, rather than alkaline earth metal deposition. For titanium the suggested overall cathode reaction was given as[2]:

$$TiO_2 + 4e^- \rightarrow Ti + 2O^{2-} \,(in\ CaCl_2)$$

The deoxidation process is driven by the externally applied voltage over an anode (usually carbon) and cathode, comprising the metal oxide to be reduced held in a conductive metal basket. The negative voltage at the cathode drives the release of oxygen ions into the $CaCl_2$ melt, and the oxygen ions react at the carbon anode to evolve CO or CO_2. The overall CaO content is unchanged over the course of the reduction, and the process occurs under the decomposition potential of the salt; hence the process does not consume the electrolyte.

The technique has been applied to reduce a large number of metal oxides to the metals, including titanium, zirconium, chromium, niobium, silicon, tantalum, uranium and nickel. The metal oxide is then directly deoxidized to metal or an alloy, where the starting material was a mixture of metal oxides.

Process benefits

When comparing the FFC process with the industrial processes for titanium production (Table I), it can be seen that there are significant differences, which could lead to significant process advantages.

The FFC process in the production of titanium has been widely claimed to offer the benefits of:

- *An elegant, single stage process*—the Kroll and Hunter processes employ slow, batch wise reduction of aggressive/reactive chemicals to deliver 'titanium sponge', which requires capital and labour intensive product recovery, handling and processing. The batches of titanium sponge are produced over several days in steel vessels, delivering around 10 tons of titanium sponge per vessel. The reactions are highly exothermic, and utilize reactive and hazardous raw materials. When looking at materials handling, the Kroll process requires 380 kg of $TiCl_4$ and more than 100 kg magnesium to produce 100 kg titanium and 380 kg $MgCl_2$ by-product.
  In the FFC process it is possible to simply load a cathode of metal oxide, complete the electrodeoxidation step in a relatively short period, and retrieve a spent cathode of deoxidized metal post reduction. Multiple cathode and anode arrangements can also be simultaneously processed in a single molten salt bath, with the scale of production easily increased. The FFC process requires only 160 kg of TiO_2 to produce 100 kg of titanium.
- *Low environmental impact*—the only significant consumable cost for the FFC process is carbon (consumed at the anode). Some research has been conducted to test anode materials other than carbon, as an 'inert' anode could be used to produce oxygen rather than CO_2, eliminating generation of the greenhouse gas. The FFC process can also process naturally occurring minerals, e.g. rutile (a natural form of TiO_2), whereas the $TiCl_4$ feedstock for the Kroll and Hunter processes requires the carbochlorination of rutile.
  Presently $CaCl_2$ is the preferred molten salt medium. It is a waste product from the chemical industry and whereas it contains very few impurities, it is inexpensively available. The material is also given the same toxicity as sodium chloride so there are no problems in handling or disposal. Salt by-product from the Hunter process is often discarded, and magnesium chloride formed as by-product in the Kroll process is again electrolyzed to produce hazardous chlorine and magnesium for recycle. In comparison, the feedstock and products of the FFC process are non-toxic, and the process does not produce a solid waste.

Table I

Comparison of industrial titanium production processes with FFC process

Process	Feedstock	Reductant	By-products	Duration	Product
Kroll Hunter	$TiCl_4$ $TiCl_4$	Magnesium Sodium	$MgCl_2$ NaCl	Batches, up to 7 days	Sponge Sponge
FFC	TiO_2	Applied current (electrons)	CO, CO_2 (from carbon anode)	Semi-continuous, 8–24 hours	Pellets/powder

- *Direct production of alloys*—through deoxidation of mixtures of oxides it is possible to directly produce alloys via the FFC process, with no need for melting. It is then able to produce 'impossible' alloys which could not previously be made via conventional routes that involve melting the metals, due to the fact that the individual melting and boiling points of the constituent metals differ, or where the metals are immiscible. It could therefore be possible to e.g. produce an alloy of aluminium (boiling point 2467°C) and tungsten (melting point of 3422°C) directly from a mixture of the metal oxides. Some of the earliest attempts at alloy production via the FFC process were aimed at the Ti-6Al-4V alloy, which is extensively used in aerospace, medical, marine, and chemical processing applications.
- *Near-net shape components and low cost powder*—materials losses and scrap rates in aerospace applications are high: the amount of titanium purchased vs. that which ends up in a final part is claimed to be 10:1. It is claimed[5] that the FFC process may improve that ratio to 5:1.

  The FFC process can potentially offer near-net shape parts, by preforming/moulding oxide powder to the intended shape product. A further advantage is that the solid product formed is a porous agglomeration of fine particles, capable of being crushed to produce titanium powder. In Figure 1 is shown preforms (B) produced from a metal oxide (A).
- *Oxygen production/ILMENOX*—in 2004, NASA called for the development of technologies that would allow *in situ* resource utilization (ISRU) of lunar materials. The aim of ISRU technologies are to allow the use of space resources on site to produce useful items, significantly reducing the launch mass, cost, and risk of near and long-term space exploration.

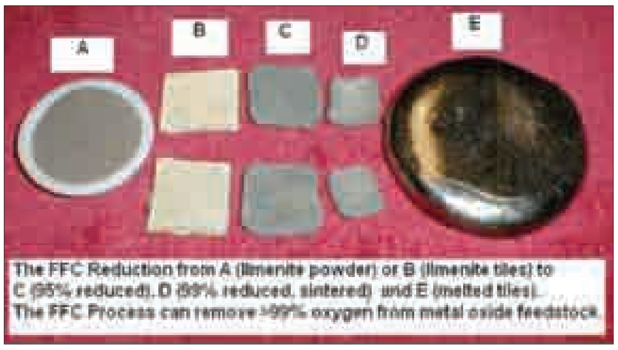
  Oxygen production for rocket propulsion promises by far the greatest cost and mass saving of any off-world *in situ* resource utilization (ISRU). Since the 1960s most work on lunar resource utilization focused on the mineral ilmenite ($FeTiO_3$) as feedstock for *in situ* oxygen production, as samples returned by six Apollo and three Luna missions have shown that ilmenite occurs in high abundance (15 to 20%) in lunar basalt. In conventional ISRU processes oxygen is extracted from ilmenite through a reaction with hydrogen:

$$FeTiO_3 + H_2 \rightarrow Fe + TiO_2 + H_2O$$

This process is unsatisfactory as it extracts only 10% oxygen per weight of ilmenite, requires a feed of hydrogen, and also further electrolysis stages for the separation of products. The titanium dioxide (TiO_2) is left unreduced, robbing the process of 40% oxygen by weight and potentially valuable titanium metal.

The author submitted a proposal suggesting a variation of the FFC process to be developed to extract oxygen from lunar ilmenite. The ILMENOX process could potentially extract >90% of the oxygen present in the $FeTiO_3$ compound. This would allow roughly 32 kg of oxygen to be produced for every 100 kg lunar ilmenite processed, which could then be used as propellant and for human habitation. Liquid oxygen is a primary component of rocket fuel, contributing as much as 85 per cent by weight, and its production outside the earth's gravity well would be very beneficial for extra planetary missions.

NASA allocated funding to the value of $14.3 million for a four year project, aimed at developing an oxygen production technology based on the FFC Cambridge process. The project, dubbed ILMENOX, was continued with some success at both the Cambridge laboratories and at partnering institution, the Florida Institute of Technology.



The FFC Reduction from A (ilmenite powder) or B (ilmenite tiles) to C (95% reduced), D (99% reduced, sintered) and E (melted tiles).
The FFC Process can remove >99% oxygen from metal oxide feedstock

Figure 1—FFC process: from mineral to metal

Process challenges

A number of problems were observed, requiring solution prior to the FFC process being ready for commercial production of titanium metal. These issues included:

- *Current efficiency*—it was found that current efficiencies were not as high as expected, getting progressively worse as the deoxidation reaction neared completion. As the levels of oxygen decreases in the cathode, it is possible that calcium metal, which is also soluble in $CaCl_2$, be produced. Such dissolved calcium leads to a more electronically conductive melt, and measurable reduction in current efficiency.

  There is also a concern that on larger-scale operations, carbon particles from the anode may build up in the cell and cause short-circuiting. A further concern[2] is that CO_2 may dissolve in the melt as carbonate ions (CO_3^{2-}); carbonate ions will react at the anode to deposit carbon both contaminating the product and acting as a parasitic reaction.

  As electricity consumption is a major contributor to the cost of FFC produced metals, current inefficiencies from the above-mentioned issues may lead to high operating costs.
- *Incomplete/partial reduction*—if the Kroll process is not operated with a sufficient stoichiometric excess of reductant (15–20%), partial reduction of $TiCl_4$ to sub-chlorides ($TiCl_2$ and $TiCl_3$) can occur.

  In comparison the FFC process proceeds from TiO_2 to titanium metal via numerous sub-oxides[2] (Ti_4O_7, Ti_3O_3, Ti_3O_5, TiO), and incomplete reduction would leave these sub-oxides at the core of the TiO_2 preform/pellet. Analyses also confirmed the presence of calcium titanate, $CaTiO_3$ and calcium titanite $CaTi_2O_4$ in partially reduced pellets[2].
- *Product purity*—to compete with the existing industrial processes, titanium product from the FFC process must meet the minimum specifications of CP (commercially pure) grade titanium in terms of chemical composition. These specifications determine upper limits for e.g. oxygen, nitrogen, chlorine, carbon and iron present in the titanium product. There are significant challenges in meeting the strict standards required for titanium when utilizing the FFC process.

Interstitial oxygen and nitrogen strongly affect the properties of titanium metal and alloys. Standards are then most often concerned with the levels of oxygen and nitrogen present in the product. When compared to the Kroll and Hunter processes, which start with $TiCl_4$ as raw material and virtually no oxygen present in the system, the FFC process starts with TiO_2 and has to get the oxygen remaining in the material down to less than

250 ppm. This is no small task as oxygen is highly reactive with, and also soluble in, titanium metal.

In the Kroll and Hunter processes significant amounts of iron can be found in the titanium sponge due to contamination from the steel reactor walls. This is lessened in the FFC process which utilizes only a conductive metal cage to hold the material to be deoxidized. Iron, nickel and similar contamination from materials of construction are then expected to be lower in FFC product.

The deoxidized pellets may sinter, trapping chlorides in the microstructure which cannot be leached. Titanium powders with chloride content higher than 50 ppm are known to present problems in downstream sintering, reaching full density when compacted, and during the welding of final products.

Commercial challenges

A number of issues influenced the commercialization of the FFC process. Intellectual property rights to the FFC process are protected by 25 patent families, covering e.g. production of ‘novel alloys’, superconducting and ‘shape-memory’ alloys via the process. The licensing structure was complex and caused some controversy, as per the following summary:

- In 1999 the initial patent was granted[4], with Cambridge University Technical Services (CUTS) owning the head license to the technology and being responsible for stimulating commercialization.
- In 2000 CUTS issued a sub-licence to Qinetiq (formerly UK Defence Evaluation Research Agency) for production of titanium via the FFC process.
- In December 2000, Mr James Hamilton, chairman of South African exploration company, Bushveld Alloys, funded a pilot plant in exchange for the exclusive rights to the FFC process for the production of bulk titanium and titanium alloys. The sub-licence was issued to British Titanium Plc (BTi) by Qinetiq, founded and headed by Mr Hamilton.
- BTi managed to win contracts with the US Office of Naval Research in 2000, and again in 2002 towards research and development of the FFC process for titanium and its alloys.
- In September 2002 the US Defence Advanced Research Agency (DARPA) funded a $12 m project allowing US titanium manufacturer TIMET to purchase a non-exclusive license from BTi and attempt scaling up the process in the US.
- In 2002 Cambridge University spins-out Metalysis (formerly FFC Metals). Metalysis is granted an exclusive world wide licence to the FFC process by CUTS for metals and alloys, excluding titanium above 40% by weight. The company was initially funded by the University of Cambridge Venture Capital Fund to the value of £250,000.
- In 2004 BTi won a $14 m contract with NASA to pursue the in-house developed ILMENOX technology towards production of oxygen from lunar ilmenite simulant.
- In 2005 Metalysis attracted £5 m in venture capital to commercialize the FFC process.
- In April 2005 CUTS transfers all rights/the head license to the FFC Cambridge process to Metalysis.
- In December 2005, BTi receives notice from Qinetiq of termination of its sub-licence to exploit the FFC process as Metalysis had apparently terminated the licensed rights to the FFC process for titanium granted to Qinetiq.
- In February 2006 BTi claimed damages of more than $400 m from QinetiQ and Metalysis. In April 2006 BTi lost a Security for Costs hearing and entered Administration. In April 2008 BTi was liquidated and the case for damages was struck out[6].
- Metalysis has raised >$23 m in venture capital and grant funding to date[6], and is proceeding with development of the FFC process.
- In April 2010 Metalysis claimed[5] to be at the point of commissioning a pilot production cell. The cell is said to represent a capital outlay of single digit millions of dollars and to have the capability to produce titanium in a 4–12 hour cycle at commercial scale (thousands of pounds).

The brief summary above indicates only the activities of the main license holders, excluding developments at other organizations, e.g. Norsk Titanium AS which was formed with the intent to utilize the FFC process for titanium production in Norway, having the support of BTi and researchers at Cambridge University[2]. Norsk Titanium’s connections with Norsk Hydro allowed access to vast experience in molten salts processing (Hydro having magnesium and aluminium production facilities) and more sophisticated laboratory facilities. Experiments were jointly conducted at laboratories in Porsgrunn, and by having improved monitoring and control of the process the team was able to achieve reduction of TiO_2 to titanium in less than 24 hours.

BHP Billiton (BHP) also expressed interest in the FFC process for titanium production, but eventually developed a parallel technology, the so-called Polar process. In 2006 Metalysis acquired the Polar process from BHP in exchange for equity and a seat on the board of Metalysis Titanium Ltd., a company formed as high volume titanium subsidiary of Metalysis[6].

Conclusions

From an optimistic, highly publicized introduction the FFC process has now been the focus of much previous development, numerous scientific studies and attempts at commercialization by various organizations.

The FFC process is versatile and can still offer a wide range of advantages over existing processes, advantages which could positively affect the cost of titanium and titanium products. The study of the issues around the commercialization of the high profile FFC process, hailed as a breakthrough in the production of low cost titanium, can guide decision makers and role players active in the pursuit of novel titanium production processes.

The combination of technical challenges, issues around licensing, and conflict and litigation between stakeholders in the FFC process has negatively affected commercialization efforts. It can also be observed that, despite the relatively large amounts invested in the process, the standard innovation curve involved in the development and commercialization of a new process was followed, including the ‘shake-out’ and consolidation of competing firms.

The article broadly discussed both technical and commercial issues related to process commercialization to date, and as such does not delve deep into specifics. Much literature is still being generated and it is expected that the process will yet form the basis of many future scientific investigations.

There now remains one well funded company tasked with developing the FFC process. Claims of the imminent commissioning of a facility capable of large-scale production of titanium powder via the FFC process have been made. With scale-up often comes yet unknown technical issues, and these will form the basis of future research.

References

1. Chen, G.Z., Fray, D.J., and Farthing, T.W. Direct Electrochemical Reduction of Titanium Dioxide to Titanium in Molten Calcium Chloride. *Nature*, vol. 407, 2000, pp. 361–4.
2. Schwandt, C., Doughty, G.R., and Fray, D.J. The FFC-Cambridge Process for Titanium Metal Winning. *Key Engineering Materials*, vol. 436, 2010, pp. 13–25.
3. Bertolini, M., Shaw, L., England, L., Rao1, K., Deane, J., and Collins. The FFC Cambridge Process for Production of Low Cost Titanium and Titanium Powders. *J. Key Engineering Materials*, vol. 436, 2010, pp. 75–83.
4. Fray, D.J., Farthing, T.W., and Chen, Z. Patent WO9964638 (1999)
5. Bertolini, M. Metalysis Launching Pilot Cell. International Titanium Association Newsletter, April, vol. 1, no. 3, 2010
6. Metalysis Ltd. [Online] Available from: www.metalysis.com [Accessed: 2010-05-20]. 2010.

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