3rd International Round Table on Titanium Production in Molten Salts

Programme & Abstracts

17-19 July 2012
Fitzwilliam College, Cambridge
Programme

**Tuesday 17th July**

11:30 – 12:30  Arrival and Registration

12:30 – 13:45  Lunch

13:50 – 14:00  MSDG’s Chairperson’s welcome

14:00 – 16:30  Technical Session 1  
(Chairperson: Dr Carsten Schwandt)

14:00 – 14:30  Guojing Hu, Qiuyu Wang, Shuqiang Jiao, **Hongmin Zhu**  
The equilibrium between titanium metal and its ions and electrochemical deposition from molten chlorides

14:30 – 15:00  **Geir Martin Haarberg**, Ole S. Kjos, Ana Maria Martinez, and Karen S. Osen  
Titanium Deposition from Molten Chloride Electrolytes by Using Titanium Oxycarbide Anode and Liquid Cathode

15:00 – 15:30  Tea/coffee break

15:30 –16:00  X. Zou¹, X. Lu¹, **Z. Zhou¹,²** C. Li¹ and W. Ding¹  
Molten-Salt Based Extractive Metallurgy Practice with the Use of Solid-Oxide Oxygen-Ion-Conducting Membranes  
¹ *Shanghai Key Laboratory of Modern Metallurgy and Materials Processing, Shanghai University, Shanghai 200072, China*  
² *Institute of Mathematics and Physics, Aberystwyth University, Aberystwyth SY23 3BZ, UK*

16:00  – 16:30  **H. Åsheim**, X. Ning H. Zhu and G.M. Haarberg  
Cathodic Deposition of Titanium in Chloride Melts

16:30 – 17:30  MSDG Committee meeting

18:00 – 19:00  Dinner

**Wednesday 18th July**

08:00 –09:00  Breakfast (for residential attendees only)

09:00 –12:30  Technical Session 2  
(Chairperson: **Professor George Chen**)

09:00 –09:30  **Andrew P. Abbott** and Gero Frisch  
Titanium-based ionic liquids

09:30 –10:00  **Wenyue Zhao**, Bowen Xu, Yue Ma and Shengkai Gong  
The inter-phase selective corrosion of a gamma-TiAl alloy in a molten salt environment at high temperature
10:00 –10:30  **R. F. Watson** and A. H. Jones  
Trials of inert anodes for the electrochemical reduction of TiO₂ powders

10:30 –11:00 Tea/coffee break

11:00 –11:30  **G. Kartal** and S. Timur  
Investigation of growth mechanism and kinetics of titanium borides formed on titanium substrates by electrochemical boriding

11:30 – 12:00 W. Li, X. **B. Jin** and G. Z. Chen  
Cathode Pore-forming: Theoretical and Experimental Studies for the Fast Titanium Production via the FFC Cambridge Process

12:00 – 12:30 General Discussion

12:30 -13:30 Lunch

13:30 –15:30 Technical Session 3

(Chairperson: **Professor Geir Martin Haarberg**)

13:30 – 14:00 **Rohit Bhagat**, Gregory Gibbons, Kartik Rao, David Dye and Richard J. Dashwood  
The Production of Titanium Alloys via the FFC Cambridge Process

14:00 – 14:30 **R. O. Suzuki**, N. Kobayashi, K. Kobayashi, K. Egawa and T. Kikuchi  
Fast Reduction Starting from CaTiO₃

14:30 – 15:00 D. T. L. Alexander, **C. Schwandt**, D. J. Fray  
The electro-deoxidation of dense titanium dioxide precursors in molten calcium chloride giving a new reaction pathway

15:00 –15:30 Tea/coffee break

15:30 –17:30 Cambridge Tour

18:00 – 19:00 Drinks reception

19:00 – 20:30 Banquet

(Host: **Professor Derek Fray**)

**Thursday 19th July**

08:00 –09:00 Breakfast (for residential attendees only)

09:00 –12:30 Technical Session 4

(Chairperson: **Dr Robert Watson**)

09:00 – 09:30 **S. M. Jeong**, E. Y. Choi & J. M. Hur
Electrochemical reduction of metal oxides in LiCl molten salt: from bench scale to laboratory scale

09:30 – 10:00 Daniel Jewell, Michael Kurtanjek, and Derek Fray.
The Chinuka Process: From Ore to Pure

10:00 –10:30 Charles Osarinmwian
Modelling and Scale-up of a Novel Solid Phase Metal Production Process

10:30–11:00 Di Hu and George Z. Chen
Avoidance of in situ Perovskitisation on Electro-Reduction of Solid TiO₂ in Molten CaCl₂: Electro-Co-Reduction with Other Metal Oxides

11:00 –11:30 Tea/coffee break

11:30 – 12:30 General Discussion and close of meeting.
(Chairperson: Professor George Chen)

12:30 -13:30 Lunch
Authors’ Abstracts

Abstracts presented on the following pages are compiled by the MSDG for the sole purpose of distribution amongst attendees of the 3rd International Round table on Titanium Production in Molten Salts are based on the submitted versions from the Authors who are responsible for issues related with the scientific correctness and copyright.
The equilibrium between titanium metal and its ions and electrochemical deposition from molten chlorides

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The equilibrium between titanium metal and its ions Ti(II), Ti(III), and Ti(IV) in molten chloride was examined by analyzing the contents of the various ions. In molten NaCl-KCl melt with the present of titanium metal the balanced ions are Ti(II) and Ti(III). The equilibrium constant of the reaction $3\text{Ti(II)} = \text{Ti} + 2\text{Ti(III)}$ was obtained. The effect of fluoride ion (F⁻) to the equilibrium was also considered. The electrochemical deposition from the chloride melts was performed. Titanium metal with low oxygen content (30ppm) was obtained.
The use of an anode consisting of titanium oxycarbide combined with a liquid cathode is a promising approach to produce pure titanium. This approach was studied in order to overcome problems related to carbon contamination and also possibly to reduce the influence of disproportionation reactions involving various oxidation states of titanium. The electrolyte was molten equimolar NaCl-KCl at 800 - 850 °C. Dissolution of titanium oxycarbide was found to produce dissolved Ti (III) species, which is known to make the deposition of solid titanium very challenging. Preliminary experiments were conducted by using liquid cathodes of Al, Zn, Sn or Bi. Future experiments are planned by using liquid Sn or Bi, which showed promising results.
Molten-Salt Based Extractive Metallurgy Practice with the Use of Solid-Oxide Oxygen-Ion-Conducting Membranes

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Molten-salt based electrochemical extractive metallurgy techniques have attracted great attention of research attribute to their potentials in producing metals and alloys directly from their compounds. In particular, the Fray-Farthing-Chen (FFC) Cambridge process has created a new route of extracting metals and alloys directly from oxides [1]. We have investigated extensively in recent years to enhance the performance of the FFC process by applying solid-oxide oxygen-ion-conducting membranes (SOM) in anode [2] as depicted in Fig. 1 [3]. We have applied successfully the technique in our practice of electrochemical preparation of Ti-Fe alloys [3,4], Ti-Si intermetallics [5-7], Ti5Si3/TiC composites [8] etc. Our experimental work suggested that the use of the SOM could results in the improvement of the current efficiency of electrolysis, and in the meantime, could reduce of the pollution of the molten-salt based electrochemical processes [2-8].

Fig 1. Schematic illustration of the SOM process electrolytic cell used in our experiments.

References
Cathodic Deposition of Titanium in Chloride Melts

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In the present work the possibility of an electrochemical deposition process of titanium from chloride melts is being investigated. Titanium containing salts where prepared by using titanium sponge to reduce titanium tetrachloride in NaCl-KCl.

Electrochemical methods including cyclic voltammetry, chronopotentiometry and square wave voltammetry were employed to investigate the cathodic behavior of Ti²⁺. It was found that titanium deposition in molten chlorides proceeds in a one-step diffusion controlled process and square wave voltammetry demonstrated that the reaction proceeds by the exchange of two electrons [1].

A series of the tests were carried out to investigate the influence of electrokinetic parameters on the titanium deposit morphology. Electrolysis was carried out on a steel cathode with concentrations of 2.5 wt%, 5.0 wt% and 7.6 wt% Ti(II). The grain size and compactness was found to increase with increasing current density, until a certain value. However, a subsequent increase of current density results in the formation of dendrites [2]. The best deposit was found at 0.3 A/cm² with a concentration of 7.6 wt% TiCl₂.

Figure 1: Characterisation of the NaCl–KCl–TiCl₂ system at 750 °C with a TiCl₂ concentration of 0.2 wt%. Glassy carbon was used as working electrode for all the sweeps, while titanium was used both for reference- and counter electrodes; \( A_{GC} = 0.22 \text{ cm}^2 \) [1].

References
Titanium-based ionic liquids

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Handling early transition metal complexes and halides is notoriously difficult due to their extreme reactivity with water and the stability of their oxides. This is a particular issue for the extraction of technologically important metals such as titanium and zirconium through the Kroll process. An alternative high temperature process has been developed for the electrochemical reduction of TiO$_2$ in molten CaCl$_2$. This has undergone scale-up trials although there are some issues associated mostly with the material morphology.

Lower temperature routes have all failed and the only report of the electroreduction of an early transition metal was that by Abbott et al. [1] in aromatic solvents but that only produced a few metallic nuclei after seeding the metal with silver particles.

Ding et al. [2] have used ionic liquids with discrete anions to study the electroreduction of titanium complexes. They found that sub-halides of titanium could be produced but kinetic factors precluded the formation of metallic titanium. In this work we show that eutectic-based ionic liquids based on early transition metals can be easily prepared. Preliminary investigations showed that the addition of butylmethyl imidazolium chloride [C$_4$MIC] to an Early Transition Metal chloride like TiCl$_4$ results in the formation of a system with two liquid phases, the upper phase is pure TiCl$_4$ and the lower phase is an ionic liquid. The lower phase liquid can be made by the addition of 2 mole equivalents of TiCl$_4$ to 1 equivalent of C$_4$MIC. The liquid produced has a relatively high conductivity of c.a. 1-2 mS cm$^{-1}$. The liquid formed between C$_4$MIC with TiCl$_4$ is shown below together with the relative moisture insensitivity of the titanium-based liquid compared to TiCl$_4$. In this presentation the properties of this liquid are presented together with results of attempts to extract titanium from the liquid using both chemical and electrochemical methods.

References
The inter-phase selective corrosion of a gamma-TiAl alloy in a molten salt environment at high temperature

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\( \gamma \)TiAl-based intermetallics have become research focuses presently as a kind of promising candidate materials for the hot components in aero-engine, on account of their lower specific weights, high specific strengths and excellent high-temperature performances [1-3]. However, the hot corrosion process becomes a noticeable problem which might impact the performances of \( \gamma \)TiAl alloys. Owing to the impurities in the fuel and the contaminations from the incoming air, a layer of salt deposits composed of NaCl, Na\(_2\)SO\(_4\) and Na\(_3\)VO\(_4\) will form on the surfaces of components and will cause the hot corrosion of the alloys as a result, which occurs particularly in marine environments [4]. Hot corrosion behavior of Ti-48Al-2Cr-2Nb alloy in a molten salt environment of 75wt. % Na\(_2\)SO\(_4\) and 25wt. % NaCl at 800°C was studied, via oxidation kinetics analyses, scanning electron microscope observations, energy dispersive and diffraction analyses by X-ray, and X-ray photoelectron spectroscopy analyses. The inter-phase selective corrosion, which caused the corrosion pits initiated from lamellar interfaces and the preferential corrosion of \( \alpha_2 \) phases, was observed during the hot corrosion of the alloy. The composition differences between \( \gamma \) and \( \alpha_2 \) phases, as well as the participations of the molten salts in the intermediate corrosion reactions, are the main causes of inter-phase selective corrosion of the alloy. The common controls of thermodynamic and kinetics in corrosion reactions with fluxing and active oxidation process are considered as the essential hot corrosion mechanisms of the alloy. Moreover, microstructure refinement was proved to be an effective way to mitigate the inter-phase selective corrosion of the alloy in molten salts.

\[ \text{SEM cross-section morphology of } \gamma \text{TiAl matrix alloy below corrosion oxide scale after hot corrosion at 800°C for 2h with molten salts} \]

References
Trials of inert anodes for the electrochemical reduction of TiO₂ powders

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Previous work at AWE has demonstrated the electrochemical reduction of TiO₂ powders contained in a woven metal mesh basket with a graphite anode in CaCl₂ – 1wt% CaO. A metallic Ti product could be recovered. However at the end of the process the salt is contaminated with carbon, through reduction of carbonate generated at the anode or erosion of the graphite anode.

Various materials have been reported as being used as alternative anodes for TiO₂ reduction including CaRuO₃. [1] Platinum has been reported to be used successfully as an anode for the reduction of UO₂ in both LiCl and CaCl₂ based electrolytes. [2]

Cyclic voltammetry in CaCl₂ - 1wt% CaO showed the electrochemical window with a platinum anode is about 2.5V at 810°C.

Initial trials with a platinum wire anode showed at -2.5V TiO₂ powder contained in a woven mesh metal basket can be reduced to a titanium metal phase as shown by XRD, Figure 1.

![Figure 1](image1.png)

Figure 1. X-ray diffraction pattern of reduction product of TiO₂, together with reference pattern for TiO₀.₄₂.

Results of further trials containing the oxide powder in a ceramic crucible will also be reported

References

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Investigation of growth mechanism and kinetics of titanium borides formed on titanium substrates by electrochemical boriding

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Titanium and titanium alloys with their exceptional strength-to-weight ratios (even at high temperatures), high stiffness, toughness, and excellent biocompatibility became one of the most important structural materials for a variety of applications. However, these outstanding properties do not translate into good tribological performance as it has been well documented in open literature that titanium and its alloys suffer from high friction, poor wear resistance, and strong tendency to gall and scuff during rolling, rotating, or sliding type tribological applications [1-3]. Boriding seems to be a perfect candidate surface hardening process considering the positive contributions on the working efficiency and improvements in service life [4-6]. In this study, the electrochemical boriding was applied to titanium in a systematic manner and the effects of boriding process parameters on the morphological and chemical state of boride layers were explored. Moreover, kinetic approach was conducted for the boriding of titanium in order to have growth equation of TiB₂ layer and to determine a practical diagram for potential applications. The presence of both TiB and TiB₂ phases were confirmed by the X-ray diffraction method. The cross-sectional examination of borided titanium verified the boride layers consisted of a homogeneously TiB₂ phase on the top and TiB whiskers toward the substrate (Fig.1). The morphology of TiB phase was found to have a strong dependence on boriding temperature and it varied with process temperatures in following order: whiskers structure at around the beta transus temperature (~1173 K), dendritic branches at the temperature ranging from 1273 K to 1373 K, lateral islands at the temperature of 1473 K and above. The micro-indentation studies indicated that the layer on top has hardness values as high as 40 GPa. Methodical studies over a wide range of boriding time (5 min ≤ t ≤ 120 min) and temperature (1173 K ≤ T ≤ 1373 K) confirmed that the rate of the TiB₂ layer formation has a parabolic character. The activation energy (Q) and the pre-exponential factor (K₀) of TiB₂ layer were determined as 189.9kJ/mol and 4.66x10⁻⁷m²s⁻¹, respectively. The specific empirical equations that can be used to estimate the thickness of the TiB₂ layers (d₄₁B₂) was obtained:

\[ d_{\text{TiB}_2} = \frac{682.67}{T} \exp \left( -\frac{22833}{T} \right) \] 1173 K ≤ T ≤ 1373 K; 200 mA/cm²

Figure 1: Typical cross-sectional SEM micrographs of boride layer formed at 1000 °C in 45 min. [200 mA/cm², 90% Na₂B₄O₇ and 10% Na₂CO₃].

References
The present Kroll process for the production of titanium sponge is still regarded as both highly energy and carbon intensive (45–55 kWh and >2kg CO₂ per kg Ti), leading to unaffordable Ti metal and its alloys. The invention of direct electrolysis of the solid TiO₂ cathode to Ti metal in molten CaCl₂ promises (namely, the FFC Cambridge process) an alternative [1], and worldwide researches on this electrolytic process have been carried out in the past decade, but it seems both the electrolysis speed and current efficiency are still unsatisfactory for the industrial scale-up. However, it has been recognized that there is intimate dependency between the current efficiency and the electrolysis speed, indicating the crucial role of the electrolysis speed for the production of Ti via the solid oxide cathode electrolysis [2].

Despite that the detailed mechanism from TiO₂ to Ti has been revealed by many literatures [3-6], the overall mass transfer dynamics for the removal of oxygen from the inner cathode into the bulk electrolyte is still far away from well established. In this presentation, the deoxidation of TiO₂ is assumed to be rate-determined by the liquid diffusion of O²⁻, and then theoretical model has been developed. Beyond the prediction of deoxidation speed, larger porosity preference for TiO₂ cathode has been deduced by the model. Accordingly, the TiO₂ Cathode pore-forming by NH₄CO₃ and CaO additives has been carried out for the experimental tests. The consistency between the theoretical predictions and the experimental results will be reported.

References
The Production of Titanium Alloys via the FFC Cambridge Process

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The Fray-Farthing-Chen (FFC) Cambridge process is a method by which metal oxides can be deoxidised within a CaCl\textsubscript{2} molten salt (typically CaCl\textsubscript{2} - 900°C) to form metals and alloys. The process is currently being commercially utilised, by Metalysi s Ltd, to produce Ti and Ta from their respective oxides. Our research has focussed on co-reducing TiO\textsubscript{2} and two or more oxides to form Ti alloys. This has led to us producing alloys such as, Ti-Mo, Ti-W, Ni-Ti, Ni-Ti-Hf, Ti-6Al-4V, Ti-Y and Ti-6Al-4V-Y.

In 2010 the authors combined this electrochemical process with white beam synchrotron diffraction to analyse the reduction route of TiO\textsubscript{2} to Ti via the FFC Cambridge Process. This novel method of analysing electrochemical reactions has advanced the understanding of the FFC process and elucidated the reactions leading to slower reduction rates and impurities.

This led to a second experiment to understand the reduction behaviour during the reduction of a mixed oxide (TiO\textsubscript{2}, V\textsubscript{2}O\textsubscript{5} and Al\textsubscript{2}O\textsubscript{3}) precursor to form Ti-6Al-4V. The analysis reveals the chemical and electrochemical reactions taking place with reference to the reduction parameters. Mechanisms for carbon contamination and aluminium loss are discussed. Implications for scale-up and commercial production of Ti-6Al-4V alloy via a CaCl\textsubscript{2} melt are discussed.
Fast Reduction Starting from CaTiO$_3$

R. O. Suzuki, N. Kobayashi, K. Kobayashi, K. Egawa and T. Kikuchi

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Calciothermic reduction using electrochemical decomposition of CaO (OS process) was studied by comparing the reduction of CaTiO$_3$ with that of TiO$_2$. CaTiO$_3$ is one of the major intermediate phases during the initial stage of reduction from TiO$_2$. The formation of CaTiO$_3$ is one of the evidences of the presence of Ca and CaO in the electrolysis and reduction. The coarsening and sintering of CaTiO$_3$ particles occur easily and they delay the formation of Ti phase [1]. The slow oxygen diffusion in the Ti layer that adheres to the oxide particles delays further oxygen removal.

Thus, to obtain low oxygen content in the final product, it is first important to reduce the oxides more rapidly at the initial stage to form the smaller particles. For example, it is effective to apply a high current density, and successively to deoxidize the $\alpha$-Ti particles slowly at the final stage to prevent CaO entrapment among the metallic particles. Fig.1 shows the analytical oxygen in the reduced samples, where the current density was varied under this concept. The wide surface area of cathodic carbon crucible could enhance the oxygen removal.

Fig.2 shows the phase equilibria examined at 1173K by mixing small amount of CaCl$_2$ with the oxide powder. The repeated annealing of 5 samples at the compositions (cross marks in Fig.2) clarified that Ca$_4$Ti$_3$O$_{10}$ and Ca$_3$Ti$_2$O$_7$ [2] were hardly found. The tie lines between Ti$_2$O and CaTi$_2$O$_4$ and between Ti$_2$O and CaTiO$_3$ were confirmed. The addition of alkaline chloride significantly enhances the phase formation of CaTi$_2$O$_4$. The intermediate phase formation such as CaTi$_2$O$_4$ is natural in calciothermic reduction in a way from TiO$_2$ to Ti, and it is important to break the sintered oxides particles and to expose their fresh surface to the molten salt.

Fig.1 Time dependency of oxygen residual in the oxide powder. (Ti basket type cathode, reduced at 1173K, 3.0V, in CaCl$_2$-0.5mol%CaO melt).

Fig.2 Phase equilibrium at 1173 K under coexistence of a small amount of CaCl$_2$. The sample compositions are indicated as #1, #2, etc. The reported phase equilibria (dashed lines) [2] were not confirmed.

References
The electro-deoxidation of dense titanium dioxide precursors in molten calcium chloride giving a new reaction pathway

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A study is presented on the electro-deoxidation of TiO$_2$ precursors of low porosity in molten calcium chloride electrolytes. It is shown that by reducing precursor open porosity from standard values of ≥25% to ~11–12%, such that there is insufficient free volume to permit substantial incorporation of calcium, a new reaction pathway for electro-deoxidation is created. Kinetically and microstructurally it is more direct, with an effective pathway of TiO$_2$→Ti$_2$O$_3$→TiO→Ti metal at an inward-moving transformation front. CaTiO$_3$, from limited calcium-incorporation reactions occurring at the beginning of the process, is shunted inwards and eventually reduced to Ti metal. The results indicate that there is greater freedom for precursor design and process optimisation than previously recognised. The practical implications of this finding are also discussed.
Electrochemical reduction of metal oxides in LiCl molten salt: from bench scale to laboratory scale

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Electrochemical reduction technology has been known to be a useful tool for the reduction of metal oxides to their metallic forms.¹⁻³ The electrochemical method in the molten salt such as CaCl₂, LiCl, binary and ternary eutectics has been highly focused on to produce valuable metal products and/or to recycle the spent nuclear fuel in the past 10 years. Our research group has studied the electrochemical reduction of various metal oxides in the LiCl molten salt and made much effort for scale-up of the electrochemical reduction process.

The electrochemical reduction of metal oxides has been carried out by using a basket-type cathode containing metal oxide powder or pellets and a platinum anode at 650 °C. When an electrical potential is applied, the metal oxide is reduced to metal and remains at the cathode. The oxygen ion (O²⁻) produced at the cathode is transported through the salt and discharges at the anode to form O₂ gas. Li₂O is initially added to molten LiCl to speed up the electrochemical reaction and prevent anodic dissolution of platinum. The diffusion of O²⁻ ions from the inside of the oxide fuel to the bulk salt significantly affects the reduction rate and current efficiency during electrolysis.⁴ The cathode and anode reactions are as follows, respectively:

\[ \text{M}_x\text{O}_y + 2y\text{e}^- \rightarrow x\text{M} + y\text{O}^{2-} \text{ (salt phase)} \]
\[ 2\text{O}^{2-} \text{ (salt phase)} \rightarrow \text{O}_2(g) + 4\text{e}^- \]

Based on the bench scale results, a laboratory scale electrolytic cell was designed and installed in Ar glove box (Fig. 1). UO₂ pellets of 20 kg in a batch have been successfully reduced in the lab-scale reactor.

References
The growing needs of an ever developing world have led to an unprecedented demand for high-performance materials. To address this issue, research has mainly focussed on the invention of new materials which offer novel structures or compositions, e.g. CNTs and high-performance alloys. There are occasions, however, when existing materials are available in significant quantities and have established industry, but the cost of extraction limits their wider use; titanium is such an example.

Titanium is the 4th most abundant engineering material in the Earth’s crust, and it exhibits a unique combination of highly desirable properties including its high strength-to-weight ratio, corrosion resistance, refractory nature, biocompatibility, and excellent cryogenic properties. Despite these advantages, the cost of extraction has remained a barrier for all but the most demanding applications, and more than a century has passed in the search for a cheaper extractive process.

Following the publication of the FFC-Cambridge Process [1] in 2000, an intensive worldwide research programme was undertaken to develop novel titanium extraction techniques. A decade on, limited success has been achieved and the Kroll Process remains undefeated. A recent contender has begun to show promise as an alternative route to cheap, large-scale titanium production and is currently under investigation at the University of Cambridge. This method, called the Chinuka Process, is a novel electro-refining method [2-4] which uses a titanium oxycarbide anode to produce a purified titanium deposit on the cathode. A particular advantage is the ability to refine lower grade ores that are prohibitively impure for other titanium extraction processes.

In this paper, results will be presented from the work carried out on the Chinuka Process at the University of Cambridge. Details of process operation, current efficiency, and cathodic purity will be provided, as well as preparation procedures for the oxycarbide. Analysis includes XRD, SEM/EDX, IGFA, ICP, and XRF measurements. Challenges and scale-up will also be discussed.

Figure 2. Schematic of Chinuka Process

References:

Direct electrochemical reduction of solid TiO₂ in molten CaCl₂ was demonstrated more than a decade ago at both laboratory and kilogram pilot scales [1]. While it is now undergoing technical improvement and scaling up for commercialisation, many laboratory investigations have commonly revealed a key intermediate step in the process: formation of various perovskite phases [2-8] due to chemical and electrochemical reactions at the cathode as shown below,

\[
\text{TiO}_2 + \alpha \text{Ca}^{2+} + \beta \text{O}^{2-} + 2(\alpha - \beta) \text{e} \rightleftharpoons \text{Ca}_\alpha\text{TiO}_{2\beta}
\]

where \(1 \geq \alpha \geq \beta \geq 0\). Proposed as “in situ perovskitisation” [5], the above reaction is a chemical reaction for \(\alpha = \beta\), but an electrochemical one for \(\alpha > \beta\). Fig. 1 shows the first reported example of the perovskite phases observed in a porous TiO₂ cathode after partial electro-reduction in molten CaCl₂ [2,3]. The occurrence and consequence of in situ perovskitisation were studied in greater depth by several groups [4-8]. It is now commonly accepted that in situ perovskitisation brings Ca\(^{2+}\) into the solid phase in the cathode, leading to volume expansion and blockage of some of the pores in the cathode, and hence slows down the overall electro-reduction process. The detrimental impact of in situ perovskitisation may be reduced via ex situ or pre-perovskitisation of TiO₂ [5,8], or use of highly porous TiO₂ precursors [9]. In this report, we propose electro-co-reduction of TiO₂ with other transition metal or semi-metal oxides as an alternative and possibly more industrially practical approach to mitigate the impact of in situ perovskitisation. Obviously, this approach will not produce pure titanium metal, but titanium alloys or intermetallics which are in fact more widely applicable, and often higher in technical and market values than pure titanium. Preliminary experimental findings from our own effort will be reported in comparison with relevant publications in the literature.

References

Acknowledgement: We thank the East Midlands Universities Association (EMUA) for a Sport-Related Studentship to D. H., and the EPSRC for partial funding (EP/F026412/1 and EP/J000582/1).
Delegates List

Professor Andrew P. Abbott, University of Leicester, UK.

Miss Rema Abdulaziz, University College London, UK.

Mr Henrik Åsheim, Norwegian University of Science and Technology, Norway.

Dr Robit Bhsgat, University of Warwick, UK.

Mr Leon Brown, University of London, UK.

Professor George Chen, University of Nottingham, UK.

Dr Chanaka De Alwis, UTRS Inc., Butte, MT, USA.

Professor Derek Fray, University of Cambridge, UK.

Professor Geir Martin Haarberg, Norwegian University of Science and Technology, Norway.

Professor Sang Mun Jeong, Chungbuk National University, Republic of Korea.

Dr Daniel Jewell, University of Cambridge, UK.

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Dr, Ole S. Kjos, SINTEF Materials and Chemistry, SINTEF Materials and Chemistry, Norway.

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