Aspects of the Application of Electrochemistry to the Extraction of Titanium and Its Applications

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For over five decades the main route for the extraction of titanium has been the Kroll process. It is regarded as being expensive, labour intensive, reliant on a high quality feedstock, and environmentally unfriendly, but it has thus far not been possible to replace it. As a result the usage of titanium is still restricted to a few high end applications. During the past twenty years several new molten salt based electrochemical approaches have been introduced to meet these challenges, and these may, eventually, lead to novel extraction processes for titanium and other reactive metals. This paper summarises the many interesting concepts that underlie these electrochemical methods, of which some have already advanced to the stage of substantial pilot plants whilst others are still being developed at the laboratory level. The paper also reviews the development of new materials for use as the anode in these processes. Finally, it touches upon the development of processes for the regeneration of oxidised titanium and for the welding of titanium under cathodic protection in cases where protective gas shielding is not possible. [doi:10.2320/matertrans.MK201619]

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1. Introduction

The vast majority of titanium (Ti) is produced by the Kroll process, which was developed in the late 1930s and successfully commercialised in the 1950s\(^1\). In the main it comprises the steps of: carbochlorination of a high purity titanium dioxide (TiO\(_2\)) feedstock to titanium tetrachloride (TiCl\(_4\)); chemical reduction of the TiCl\(_4\) with magnesium (Mg) to Ti metal and magnesium chloride (MgCl\(_2\)) as a by-product; removal of the MgCl\(_2\) and any unreacted Mg by vacuum distillation; and electrolysis of the MgCl\(_2\) in its molten form back to Mg and chlorine for subsequent reuse\(^2\). The Kroll process is obviously a considerable achievement even though it suffers from various disadvantages: the plant has a high capital cost and a significant labour force; the process has a complex multi-step flowchart; it produces a product that requires vacuum melting before use; and its environmental impact is higher than that of aluminium and very much higher than that for steel. This is furthermore coupled with the difficulty of making alloys and powders. All these issues have limited the application of Ti to a few selected areas, such as aircraft, ships and submarines, chemical and desalination plants, medical and sports devices, jewellery, and some others where high value Ti components are the only suitable option. Interestingly, Kroll himself predicted the swift replacement of his chemical process with an electrochemical one, but this has still not happened at the industrial scale.

In recent years several electrochemical processes have been invented which may offer advantages over the Kroll process\(^3\)\(^-\)\(^5\). Processes based on the concept of cathodic reduction of TiO\(_2\) to Ti in molten salts include the OS process (chemical reduction of TiO\(_2\) with cathodically generated calcium)\(^6\), the EMR process (mediated reduction of TiO\(_2\) without direct contact to calcium)\(^7\), the FFC-Cambridge process (electro-oxidation of TiO\(_2\) without calcium formation)\(^8,9\), the SOM process (use of solid electrolyte to transport oxide ions from the molten salt electrolyte to the anode)\(^10\)\(^-\)\(^14\), and the MOE process (direct electrolysis of molten Ti oxides)\(^15\)\(^-\)\(^17\).

The main advantage of these processes is that they avoid the use of TiCl\(_4\). A process based on the concept of cathodic deposition of Ti from molten salts is the Chinuka process (combined electrowinning and electrorefining using a titanium oxycarbide anode)\(^18\). The key benefit here is that this process can use cheaper oxide feedstock with a few percents of iron and other impurities. Overall these methods search for a better and more affordable Ti extraction process, and one whose product can be directly fed to 21st century technologies such as near net shape fabrication and 3D printing.

If a cathodic reaction is being used in the extraction of Ti, there must obviously be an associated anodic reaction. In the OS process, the EML process and the FFC-Cambridge process the anode is presently carbon, which reacts with the oxygen to yield carbon dioxide. The disadvantages of carbon are that it is consumed and generates carbon dioxide. This is an undesirable emission, and also it can dissolve in the molten salt to form carbonate ions that can then react at the cathode to deposit carbon and decrease current efficiency. Consequently, an inert anode would be an advantageous feature of these new processes, and there have been considerable research efforts on this subject.

Once it was realised that the FFC-Cambridge process can reduce TiO\(_2\), as well as many other metal oxides, this also offered a way of removing the oxygen from oxidised Ti components and Ti scrap\(^19\). Furthermore it instigated a method for cathodically protecting Ti while being welded without the use of a protective gas shield.

The present paper will provide an up to date overview of the aspects related to the molten salt electrochemistry of Ti. This includes a brief presentation of new electrochemical processes for Ti winning, a summary of research activities on the development of new anode materials, and some aspects concerning the regeneration and welding of Ti components.
2. Electrochemical Methods of Reducing Titanium Oxides

Over the years there have been numerous attempts at reducing Ti compounds electrochemically, in particular its chlorides. Some promising results have indeed been achieved, especially in the studies by Ginatta, where TiCl$_4$ is fed into molten chloride salts at temperatures in excess of the melting point of Ti such that a liquid cathode product is formed$^{20,21}$. It would seem however that processing costs have as yet been too high and current efficiencies too low for processes of this type to become economic.

A presumably more promising approach is based on the reduction of TiO$_2$ because the oxide is easier to handle than the chloride, can readily be gained from naturally occurring ores such as ilmenite (FeTiO$_3$), and even exists as a rather pure mineral resource in some places on the Earth. Elementary thermodynamics shows that both calcium (Ca) and magnesium (Mg) are able to reduce TiO$_2$ to Ti, forming calcium oxide (CaO) and magnesium oxide (MgO) as the by-products respectively$^{22}$.

The main problem when carrying out the reduction in the solid state is that the TiO$_2$ reactant becomes shielded by the CaO or MgO by-products, this slowing down the reaction or even stalling it. In addition, as solid Ti has the unusual ability to dissolve significant amounts of oxygen, CaO or MgO equilibrium established during the reaction determine thermodynamically the final oxygen content that can be attained in the Ti. This may not be low enough for some applications since residual oxygen renders the metal hard and causes it to undergo more rapid mechanical fatigue.

In order to overcome the above drawbacks, it is advantageous to carry out the reduction in a chloride melt. Particularly the use of Ca as the reductant in molten calcium chloride (CaCl$_2$) improves the process substantially. This is because now the CaO by-product dissolves in the CaCl$_2$ melt and does not block the TiO$_2$ reactant, and also because the CaO content in the CaCl$_2$ can be kept at levels far beneath saturation so that the CaO activity remains below unity and allows for smaller residual oxygen contents in the Ti to be established. In contrast, using Mg in molten magnesium chloride (MgCl$_2$) does not provide these advantages because MgCl$_2$ is not able to dissolve MgO to a significant extent. Overall, the higher thermodynamic driving force in the reduction process and the opportunity of using a chloride melt as the reaction medium, make Ca the preferred reductant despite the fact that it is more expensive than alternative reductants such as Mg.

Okabe and coworkers were the first to use in-situ electrolytically generated Ca in CaCl$_2$ as the reductant in the deoxidation of Ti metal$^{23}$. In this way they were able to achieve exceedingly low dissolved oxygen contents in the Ti.

Ono and Suzuki developed the OS process$^{6}$). In this, TiO$_2$, typically in the form of granules, is placed inside a wire mesh container and this arrangement is positioned inside a CaCl$_2$ melt. The container is made the cathode versus a carbon anode, such that Ca is deposited electrolytically at the cathode and then reduces chemically the TiO$_2$ to Ti. It is assumed that the CaO by-product dissolves in the CaCl$_2$ melt, so that it can be re-electrolysed to release more Ca reductant and ensure the reaction progresses. The gas evolved at the anode is carbon dioxide, provided the CaO content in the melt is sufficiently high, or else it is chlorine. A schematic of the electrolytic cell arrangement is shown in Fig. 1.

Okabe and coworkers then developed the EMR process$^{7}$. By this method, the TiO$_2$ is reduced in a mediated way, i.e., without the Ca reductant being present directly at its surface. In the process, the molten salt is electrolysed in one section of the electrolytic cell to give Ca at an auxiliary nickel cathode, while the gases released at the carbon anode are carbon dioxide and chlorine depending on melt composition. The Ca formed dissolves into the nickel giving a liquid alloy rich in Ca. This alloy is then used in a different section of the same reactor, where the Ca in the alloy ionises to give calcium ions and the electrons move around the external circuit to the TiO$_2$ that is then reduced to Ti. This approach involves Ca at less than unit activity which is beneficial in terms of current efficiency, as discussed later. The cell arrangement is shown in Fig. 2.

Research in Cambridge led to the development of a somewhat different electrolytic process, now known as the FFC-Cambridge process, named after its inventors, Fray, Farthing and Chen, and the place of its invention$^{8,9}$. In this process, the reduction of TiO$_2$, typically in the shape of a disc, is brought about by polarising it cathodically in a bath of molten CaCl$_2$ versus a carbon anode, with the applied potential controlled such that the Ca activity is kept below unity at the cathode and no Ca metal is deposited. Under these conditions, ionisation of the oxygen in the TiO$_2$ occurs. The oxide ions are expelled into the electrolyte and transport to the carbon anode where they are discharged and carbon dioxide is evolved. The set-up is shown in Fig. 3.

The overall reaction at the cathode of an FFC cell is simply the removal of oxygen from it by displacing oxide ions (O$_2^-$) with electrons.

\[
\text{TiO}_2 + 4e^- = \text{Ti} + 2\text{O}^{2-}
\] (3)

It was possible experimentally to force the cathodic reduction
to progress very slowly, by controlling the CaO in the CaCl₂ melt at low levels of around 0.2 mol% and thereby setting up an oxide ion transport limitation across the electrolyte. In this way a current versus time curve could be recorded which, in combination with electron microscopic analyses, clearly reveals the consecutive stages of the overall reduction (4), as shown in Fig. 4.

This proves that the actual reaction sequence in the cathode is far more complex.

\[
\begin{align*}
5\text{TiO}_2 + \text{Ca}^{2+} + 2e^- & = \text{Ti}_4\text{O}_7 + \text{CaTiO}_3 \quad (4) \\
4\text{Ti}_4\text{O}_7 + \text{Ca}^{2+} + 2e^- & = 5\text{Ti}_3\text{O}_5 + \text{CaTiO}_3 \quad (5) \\
3\text{Ti}_3\text{O}_5 + \text{Ca}^{2+} + 2e^- & = 4\text{Ti}_2\text{O}_3 + \text{CaTiO}_3 \quad (6) \\
2\text{Ti}_2\text{O}_3 + \text{Ca}^{2+} + 2e^- & = 3\text{TiO} + \text{CaTiO}_3 \quad (7) \\
\text{CaTiO}_3 + \text{TiO} & = \text{CaTi}_2\text{O}_4 \quad (8) \\
\text{CaTi}_2\text{O}_4 + 2e^- & = 2\text{TiO} + \text{Ca}^{2+} + 2\text{O}^{2-} \quad (9) \\
\text{TiO} + 2e^- & = \text{Ti} + \text{O}^{2-} \quad (10)
\end{align*}
\]

It is interesting to realise that no actual removal of oxygen from the cathode takes place in the first steps of the overall reaction, just a rearrangement of solid phases.

Along with the changes in phase composition, there are also considerable changes in the microstructure (24,25), as seen in Fig. 5. These can affect the mechanical stability of the solid oxide body being reduced, especially at the CaTi₂O₄ stage where coarse elongated crystals are present that render the solid fragile.

The FFC-Cambridge process is a generic approach in that most of the oxides of the elements in the periodic table can be reduced provided these are less stable than CaO. Consequently, over the last one and a half decades the reductions of a whole range of oxides to the respective metals have been reported in the literature. Interestingly, in most cases the reductions seem to follow roughly similar paths as outlined above for TiO₂, with a significant number of phases formed and decomposed intermittently. Detailed investigations revealing the reaction paths have been published for instance for the reductions of niobium oxide (26), chromium oxide (27), zirconi-
um oxide and tantalum oxide.

One very important finding was that alloys and intermetallics can be prepared directly by reducing a mixture of metal oxides. This gives the opportunity for creation of alloys that are difficult to make using co-melting, especially in cases where the boiling point of one element in the alloy is higher than the melting point of the other element. A further advantage is that the alloys are synthesised at temperatures around typically 800 to 900°C and thus do not undergo significant phase changes on cooling, unlike alloys prepared in the molten state. Rather surprisingly, low oxygen Ti alloys have been produced directly from synthetic rutile and processed by conventional and novel consolidation techniques such as isostatic pressing and 3D printing. The FFC-Cambridge process is currently being commercialised by Metalysis Ltd.

One complication in the FFC-Cambridge process, and indeed in all methods relying on the cathodic reduction of TiO$_2$ in CaCl$_2$ melts, is that Ca metal is soluble in molten CaCl$_2$. Consequently, the activity of Ca created at any given cathodic potential leads to an amount of Ca dissolved in the melt. This imparts a degree of electronic conduction in the melt and thereby lowers current efficiency of the reduction process. As this effect increases substantially with more cathodic potentials, it is important not to have too high a potential at the cathode. This cannot be avoided completely in the reduction of TiO$_2$ due to its high stability and very large current efficiencies cannot be reached. However, this is less of a problem for oxides that are less stable than TiO$_2$. A further complication in processes involving CaCl$_2$ arises when a carbon material is used as the anode, as discussed later.

Quebec Iron & Titanium Inc. (QIT) have developed a variation on the FFC-Cambridge process. In this, the metal oxide to be reduced and the metal produced are both in their liquid states. The oxide is typically a Ti based slag, which is placed in between a pool of a molten calcium fluoride based salt and a layer of molten Ti product, and carbon is used as the anode.

Another method based on the cathodic reduction of metal oxides is the SOM process, as advanced by Pal and coworkers for a range of metals including Ti. In this process, the metal oxide is dissolved in a fluoride flux, often a eutectic mixture of calcium fluoride and magnesium fluoride, and is reduced at and deposited onto a solid cathode. Alternatively, oxides that cannot be dissolved in a flux can be reduced in the form of solid bodies using cathode designs more similar to those in the OS process or the FFC-Cambridge process. The oxide ions released during the reduction diffuse in the metal melt electrolyte, transfer into the solid oxide ion conducting electrolyte based upon stabilised zirconia, and emerge on the opposite side of the ceramic membrane. There the oxide ions are oxidised and evolved as molecular oxygen on a pool of oxygen saturated molten silver serving as the anode. A concern might be that the Ti product is likely to be in equilibrium with the oxygen in the electrolytes, thus preventing very low oxygen contents from being established in it. The SOM process is being commercialised by Infinium Inc. in Massachusetts. A schematic of the cell arrangement is shown in Fig. 6.

A further method is the MOE process, as currently developed in the Sadoway group. This process starts from the pure oxide, which is melted and electrolysed, without the use of any solvent, inside a very high temperature electrolytical cell. This approach has been successfully demonstrated for the formation of molten iron metal from molten iron oxide. It is, however, difficult to see how this could work for Ti, as this would be in contact with a molten phase containing oxygen. The MOE process is being commercialised by Boston Electrometallurgical Corporation.

### 3. Anodic Reactions Involving the Evolution of Oxygen

A major complication in the FFC-Cambridge process, and in all other processes using the cathodic reduction in a CaCl$_2$ melt in conjunction with a carbon anode, is caused by the anodic reaction that yields carbon dioxide (CO$_2$).

\[
C + 2O^2^- = CO_2 + 4e^- \]  
(11)

The issue is that, unlike with the cryolite melt in the Hall-Héroult process, there is significant solubility of CO$_2$ in the CaCl$_2$ melt. Due to the presence of oxygen ions in the electrolyte it is likely that the CO$_2$ occurs as carbonate ions (CO$_3^{2-}$). These can diffuse to the cathode where they are reduced such that carbon is deposited and oxide ions are released.

\[
CO_2 + O^2^- = CO_3^{2-} \]  
(12)

\[
CO_3^{2-} + 4e^- = C + 3O^2^- \]  
(13)

These reactions can continue for as long as CO$_2$ is evolved at the anode, causing continuous carbon transfer through the electrolyte and carbon deposition at the cathode.

An alternative reaction path might involve reducing the dissolved CO$_2$ gas or CO$_3^{2-}$ ions with Ca that is also generated at the cathode.

\[
CO_2 + 2Ca = C + 2CaO \]  
(14)

\[
CO_3^{2-} + 2Ca = C + 2CaO + O^2^- \]  
(15)

Again, the net result is the creation of carbon at the cathode from CO$_2$ from the anode. Irrespective of the precise reaction path, the problem always is that the carbon deposit may contaminate the metal product, for example, by entering into pores to form inclu-
sions or by chemically reacting with the metal to form carbides. Moreover, the CO₂ or CO₃²⁻ reduction reactions cause parasitic currents through the electrolyte and thus lower current efficiency of the overall process. Interestingly, the carbon deposits formed via cathodic decomposition of CO₃²⁻ ions are known to be of nanosized particles and tubes and may even find applications in high technology products⁵²–⁵⁷.

Due to these problems an inert, i.e., oxygen evolving, anode is needed with materials properties such as sufficient mechanical and thermal stability, high electronic conductivity, resistance to attack by the electrolyte and oxygen, as well as electrochemical stability. This is a very demanding set of criteria that have never been met in the aluminium industry. However, CaCl₂ should be less corrosive than cryolite, so the task might be simpler.

Doped tin oxide (SnO₂) was considered a possible material for use as an inert anode. SnO₂, doped with antimony oxide and copper oxide to enhance mechanical strength and electronic conductivity, is used successfully in the glass industry as a ceramic anode under conditions of alternating current in CaO and copper oxide to enhance mechanical strength and electronic conductivity. Adding oxides with a lower valency enhances its conductivity. Adding oxides with a lower valency enhances its conductivity. However, incorporating highly electronically conducting titanium carbides is problematic because iridium oxide is unstable above about 1100°C. However, it is very costly which probably precludes it from general metallurgical use. Chromium alloys appear to be stable under anodic conditions for long times, probably offering the best option for oxide melts at present. Unfortunately however, they do not appear to be suitable for CaCl₂ melts as no stable protective film forms⁶⁴.

4. Combination of Electrowinning and Electrorefining

There have been numerous attempts in the past to electrowin Ti from chloride melts, but no such process is viable due to the expensive high purity TiCl₄ feedstock needed and the low current efficiency achieved. However, electrowinning of Ti from oxide feedstock would appear attractive, given that an examination of the cost of TiO₂ as a function of impurities shows that TiO₂ containing 10% of impurities is about an order of magnitude cheaper than TiO₂ of 99.99% purity, and this may offset the cost caused by low current efficiency.

Earlier work in industry and academia had shown that processes using an electronically conducting Ti oxycarbide anode might be feasible⁶⁵–⁷⁵. Oxycarbide of approximate composition Ti₂CO can readily be prepared by reacting TiO₂ with carbon at elevated temperatures in inert atmosphere, and then be used as the anode in a high temperature electrolytic cell with a molten chloride electrolyte. The Chinuka process, developed in Cambridge along with an industrial partner, uses this approach, with low purity oxide as the feedstock and an inexpensive mixture of molten sodium chloride and potassium chloride as the electrolyte, in such a way that it combines electrowinning with electrorefining in the same cell⁷⁶.

In the Chinuka process there is a sequence of ionisation reactions at the anode, in which elements such as calcium, magnesium and aluminium ionise into the molten salt along with the Ti, whereas elements such as silicon, chromium and iron are left behind forming an anode sludge. The driving force of the anodic reaction is enhanced by the concurrent release of carbon oxide gas. At the cathode, Ti deposits in preference to magnesium and calcium that build up in the melt, while the aluminium is removed as a volatile chloride. Current efficiency is relatively high as the valence state of the Ti in solution is between Ti⁴⁺ and Ti²⁺, instead of Ti⁴⁺ as found in processes using TiCl₄. This largely suppresses back reactions with the Ti deposited and is a consequence of the reducing conditions in the preparation of the oxycarbide. The cell arrangement is shown in Fig. 7.

Discussions are ongoing with prospective partners from

![Fig. 7 Schematic of the electrolytic cell used in the Chinuka process.](image-url)

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around the world to commercialise the Chinuka process. There is also considerable interest from the nuclear industry as the process would reduce the number of steps in treating used oxide fuel rods.

5. Other Processes

At the recent 13th World Conference on Titanium, other advances were mentioned but not described in detail\(^5\). These included an electrochemical process that produces Ti by a series of layered membranes by Case Western Reserve University, two processes that avoid the cyclical formation of undesired Ti ions by iMetalx Group and MER Corporation, and an electrochemical process for the production of high quality Ti powder by TIMET.

6. Removal of Alpha Case, Preventing Oxidation, and Welding in Air without Inert Gas

One of the problems with the fabrication and usage of Ti components is the formation of the alpha case when Ti is exposed to an oxidising environment, especially at elevated temperatures. The alpha case is a hard oxygen enriched metallic scale that grows due to the high solubility of oxygen in Ti giving rise to a solid solution of oxygen in Ti. The alpha case often needs to be removed from Ti components because it has inferior mechanical and fatigue properties compared with the pure metal. Conventionally, this is done either chemically by dissolving the scale in hydrofluoric acid based leachant or mechanically by grinding it away. The disadvantages of these treatments are in both cases that there is a slight change in the dimensions of the Ti component and that there are disposal problems of either highly corrosive acids or fine particles. A more suitable treatment would possibly be to regenerate Ti components electrochemically, i.e., by selectively removing the oxygen from the scale. The FFC-Cambridge process is well placed to achieve this. As with the reduction of solid oxides, the Ti artefact is made the cathode in a bath of CaCl\(_2\) and the oxygen is removed from its surface under a calcium fluoride based flux cover and polarising the metal component to be protected versus a suitable anode. Proof of concept for this approach was published in 2001\(^19\).

A better solution would be to prevent the oxidation of Ti components during processing or use in the first place. One way of achieving this is by applying a cover of flux, but commercial fluxes frequently contain fluoroborates and boric acid which should be reduced by Ti, thus bringing oxygen into it. Another way is to use an inert gas such as helium, which is expensive, or argon, which is cheaper but less efficient. Cathodic protection is a method that is applied extensively at ambient temperatures to preclude corrosion of predominantly steel constructions such as ships, pipelines and vessels. This is accomplished by having a moderate cathodic potential at the metal component to be protected versus a suitable anode. Recently this technique has been investigated as a means of prevention of oxidation of Ti\(^76\). Protection was successfully achieved by applying a cathodic potential to Ti metal crucibles, partially filled with molten CaCl\(_2\), against an anode of doped SnO\(_2\) or iridium, as the protected area did not undergo any noticeable oxidation or corrosion after harsh heat treatment. The technique was also successfully applied to protect a molten Ti alloy.

A considerably more exciting application is to use cathodic protection whilst welding Ti components in air. This would be instead of welding under a protective atmosphere provided by either a gas blanket or a gas filled cubicule, as done in established welding technologies. The concept was proven by spot welding Ti-6Al-4V alloy plates with an ytterbium fibre laser under a calcium fluoride based flux cover and polarising the Ti alloy against an iridium inert anode touching the salt flux. Analysing the Ti alloy after the welding experiments, it was found that the oxygen contents of the weld metal were very close to that in the starting material, while the nitrogen contents had increased very slightly\(^77\). The results for oxygen as determined by the hot extraction method are shown in Fig. 8.

7. Conclusions

In the past twenty years several new molten salt electrochemical methods for the cathodic reduction of titanium dioxide have been investigated. A few of these, the OS, FFC-Cambridge, SOM and MOE processes, have managed to gain further funding to advance work to a larger scale and market industrial grade quantities.

In all these processes one of the challenges has been to find an inert anode to avoid carbon dioxide generation and thus overcome the problem of carbon dioxide dissolution in some of the electrolytes. Progress has been made in this direction for both chloride and oxide melts, but research needs to continue.

The Chinuka process, based on the electrowinning of titanium from titanium oxy carbide anodes in molten chlorides, has been advanced aiming to enable the use of cheap impure titanium oxide feedstock. The process is now ready for scaling up.

The application of a cathodic potential to titanium artefacts
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has been shown to be effective in removing the alpha case, stopping oxidation, and allowing the welding of titanium in air without the need of a protective gas.

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