

RECENT IMPROVEMENTS FOR ELECTROWINNING TITANIUM METAL FROM COMPOSITE ANODES

James C. Withers*, François Cardarelli, John Laughlin, Raouf O. Loutfy
jcwitthers@mercorp.com

*Materials & Electrochemical Research (MER) Corporation
7960 S. Kolb Road, Tucson AZ 85706 United States

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1 General Introduction

Nowadays, all the titanium sponge produced worldwide is quite exclusively obtained by the Kroll process invented in the late 1930s and commercialized in the mid 1940s [1]. The Kroll process is basically a batch process that consists to reduce gaseous titanium tetrachloride with molten magnesium inside a steel retort followed by vacuum evaporation or inert gas sweep to remove by-products. Titanium tetrachloride itself is produced from the carbo-chlorination of titania-rich feedstocks such as weathered ilmenite, natural and synthetic rutiles, and titanium slags. The sponge produced is then crushed, hand sorted, compacted into briquettes that are electron-beam welded into electrodes, the electrodes are then vacuum-arc melted into a round ingot, which is finally machined to remove the outer skin [2]. This makes the entire process for preparing titanium metal highly labor intensive and energy demanding with wastage of metal close to 5%.

In the past 50 years, numerous attempts were made to prepare titanium sponge continuously and more economically by an electrochemical process. Among major industrial developments, we can cite, the US Bureau of Mines in 1956 [3], Titanium Metal Corporation (TIMET) in the period 1970-1980s [4], Dow-Howmet in the 1980s [5], and RMI and Elettrochimica Marco Ginatta (EMG) in the late 1980s [6]. All these processes were finally aborted either due to engineering issues or for economical reasons.

More recently, in 1999, following the announcement made by Prof. Derek Fray and co-workers of Cambridge University to be able to electrochemically deoxidize a cathode preform made of titanium dioxide in a molten calcium chloride electrolyte [7] started a new era of intense research and development for producing a low cost titanium metal electrolytically from cost affordable oxides and in a lesser extent also from titanium

tetrachloride. A plethora of electrochemical and metallothermic processes were devised, and a detailed overview of these processes was given in a report conducted and published by EHK Technologies in 2004 [8].

Among them, the MER process starts with cost affordable titania-rich feedstocks and a cheap carbon source to produce a composite of carbon and titanium suboxides which is used as a soluble anode in an electrowinning process for producing titanium metal at the cathode [9, 10, 11].

2 Overview of Electrolytic Processes to Produce Titanium

2.1 Carbothermic Reduction

Any process to produce titanium must begin with a titania-rich ore. There is a plethora of titania-rich feedstocks as a primary source of titanium oxides. These range from cost affordable raw materials like sulfate titanium slags containing about 80 wt.% TiO_2 and that are produced from the smelting of hard-rock ilmenite by QIT Fer & Titane in Canada or Tinfos Titanium & Iron (TTI) in Norway [12]. These are followed by chloride titanium slags ($\text{TiO}_2 > 84$ wt.%) that are produced from the smelting of beach sand ilmenite by Richards Bay Minerals, Namakwa Sands, and TICOR in South Africa. Much richer products containing above 93 wt.% TiO_2 can also be used, such as synthetic rutiles produced in Australia by the Becher process or in India by a modified Benelite process, or even upgraded titania slag (UGS) produced by QIT Fer & Titane in Canada. Finally, chemically pure titanium dioxide coming from either the calciner discharge in the sulfate process or the burner discharge in the chloride process can be used. The selection of the proper feedstock is a compromise between purity and cost, a summary of titania-rich feedstocks are listed in Table 1.

Table 1. Titania-rich feedstocks tested in the MER process.

Titania-rich feedstocks (Producer)	Purity wt.% TiO ₂	Price \$/tonne
Pure anatase (DuPont)	99.9	1780
Upgraded titanium slag (QIT)	94.5	500
Natural rutile (RBM)	95.0	450
Synthetic rutile (Iluka)	93.7	400
Chloride titanium-slag (RBM)	85.8	380
Sulfate titanium slag (QIT)	80.0	350
Beach sand ilmenite (Australia)	56	80-100

The selected oxide feedstock can be carbothermically reduced to a lower oxide which can be utilized in a variety of possible avenues to electrolytically produce titanium metal. Several possible routes to electrowin titanium from a carbothermically reduced feed is shown in Figure 1.

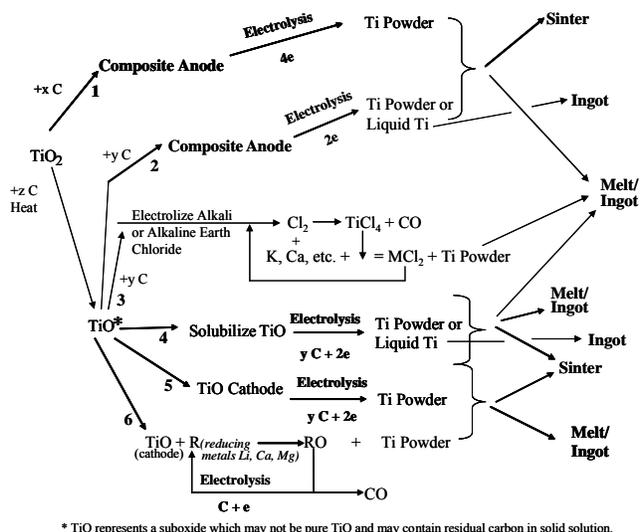
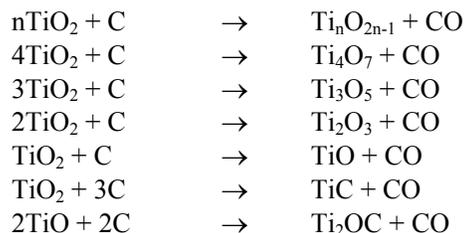


Fig. 1. Possible routes to produce Titanium from a carbothermically reduced suboxide.

Each of these processing routes to electrowin titanium has been investigated at MER. Route 2 has been the processing route that has been sponsored by the Defense Advance Research Project Agency (DARPA) in their Initiative in Titanium which is currently being scaled to 500 lb/day (227 kg/day). The DARPA goal is to produce non-melted titanium ingots/billets for under \$4/lb (\$8.8/kg).

Carbothermic reduction of ore/feeds is typically performed in the absence of air under an inert atmosphere or vacuum in the temperature range of 1200-2100°C [13]. Possible reactions from carbothermic reduction include the following:



Over the years, scientists and engineers at MER have gain considerable expertise controlling accurately the extent of the above chemical reactions to predict exactly the final distribution of phases. The carbothermic reduction process is controllable to produce Andersson-Magnelli's phases (Ti_nO_{2n-1}), anosovite (Ti₃O₅), titanium sesquioxide (Ti₂O₃), hongqiite (TiO), and titanium carbide (TiC) along with some free carbon when needed. It is also possible to produce the phase pure Ti₂OC.

The carbothermic reduction process, depending on the operating parameters removes most of the metallic iron and some other metals that alloy with iron such as Mn, Cr, V etc. Magnetic separation can also further reduce iron levels in the post carbothermic treated feed. Other impurities can be removed in carbothermic reduction processing such as Si, Al and possibly Ca and Mg at higher treatment temperatures and reduced pressure.

The carbothermic reduced feed can be used in route 2 which is the composite anode process being sealed-up in the DARPA Titanium Initiative. The composite anode can be utilized as a granulated anode or in a reconstituted solid anode much like the carbon anodes utilized in electrowinning aluminum. In the solid state, the composite anode depending on the reduced oxide composition with stoichiometric carbon, can exhibit an electrical conductivity superior to high grade graphite in the range of 300 to 800 μΩ.cm. The solid state consolidated anode depending on both the carbothermic processing conditions and the secondary molding and firing temperatures exhibits a density in the range of 2500 to 4000 kg/m³.

2.2 Electrowinning Titanium Metal

As illustrated in Figure 1, there are several processing routes that can be utilized to produce titanium metal from a carbothermic reduced feed. If

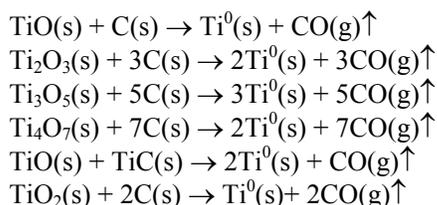
the reduced oxide is free of residual carbon, the oxide can be utilized cathodically as illustrated in routes 5 and 6. The Faradic efficiency is quite low when the reduced oxide is utilized as a cathode wherein the oxygen is extracted cathodically. If an alkali or alkaline earth metal is deposited at the cathode that also contains the reduced oxide cathodically (route 6), the Faradic efficiency is also poor and the diffusion rates of the reducing metal into the reduced titanium oxide and the reduced metal oxide out is also rate limiting. While the reduced titanium oxide can be used cathodically to win titanium metal (routes 4 and 5) the Faradic efficiencies and rate limiting diffusions suggest this processing approach does not have high probability to be scaled into a production process.

When the carbothermic reduced titanium oxide with stoichiometric carbon is used as an anode, titanium ions go into solution from the anode with CO/CO₂ being released at the anode when titanium is being deposited at the cathode. The reaction appears to be:



Depending on the electrolysis temperature, the cathodically produced titanium can be in the solid state or molten when the operating temperature is above approximately 1660°C. Typically low temperature salts that include mixed salts of alkali and alkaline earth chlorides operate in the range of 450-850°C where titanium is solid. If calcium fluoride is used as the operating salt electrolyte with a composite anode the titanium can be produced in a liquid form.

The decomposition potentials of the various carbothermic reduced oxides with stoichiometric carbon to produce CO at the anode are:



The composite anode process provides the flexibility of electrowinning titanium from fused salts that contain titanium ion (Ti²⁺) in the melt or utilizing only titanium cations dissolved from the composite anode. If titanium cations are added to the fused salt melt, TiCl₄ can be reacted with

titanium sponge (TiCl₄ + Ti → 2TiCl₂), or commercially available TiCl₃ can be added followed by using a soluble titanium anode with electrolysis to reduce the TiCl₃ to TiCl₂. If TiCl₂ is used in the salt a concentration of Ti²⁺ in the range of 1 wt.% to saturation depending on the salt composition and operating temperature can be approximately 10 wt%. When TiCl₂ is in the salt the operating potential to deposit titanium without generating TiCl₄ at the composite anode is 2.06 V.

If operation is such that TiCl₄ may be generated at the anode, the TiCl₄ can be returned to the salt to avoid any loss of titanium cations. The return of TiCl₄ to the cathode can improve the titanium deposited at the cathode. To further explore this potential in-situ produced TiCl₄ effect, route 3 was investigated [14]. The composite anode was utilized in a granular state. The composite anode could be utilized within the salt or just above it with a graphite current collector. This processing route permits producing alloys by mixing an alloying composition within the composite anode composition or in the return of the TiCl₄. Of course the TiCl₄ can be produced externally by a conventional carbo-chlorination process.

3 Recent Developments

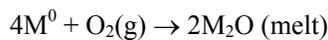
3.1 Dissolved Oxygen Control and Measurements in the Salt

Oxygen contamination of the titanium metal electrodeposited is one of the major issues in electrowinning titanium metal in molten salts. Oxygen contamination of the electrolyte arises from traces of oxygen in the argon stream, possible air leaks and the release of oxygen anions either from the corrosion of wetted ceramic parts or from the oxide layer forming on metal parts. In order to reduce them to a minimum, first argon is purified by using oxygen traps, air leaks are prevented by using vacuum-tight flanges and fittings, while no oxide ceramic parts are used in direct contact with the molten electrolyte, and finally all stainless steel and titanium parts are either electropolished or etched prior to be introduced inside the cell.

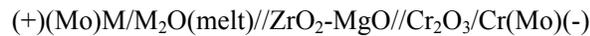
However, even if the potential sources of oxygen contamination are well controlled, it remains important in the MER process to determine the level of oxygen in the melt during and between runs.

For this purpose, a modified commercial oxygen Celox® sensor (Heraeus) used as oxygen probes in iron- and steelmaking to measure the oxygen content of slags was employed satisfactorily.

The probe is a potentiometric sensor, that consists of a galvanic cell established between a bare molybdenum rod or wire immersed into the melt and a primary reference electrode (RE). The primary reference electrode is usually made of a tube of magnesia-stabilized zirconia ($ZrO_2 - 9 \text{ mol\% MgO}$) closed at one end. Magnesia stabilized zirconia is used because it is an excellent oxygen anion exchange membrane that acts as a solid electrolyte and it is resistant to thermal shocks. The zirconia tube is filled with a mixture of pure chromium metal powder (Cr) and chromia (Cr_2O_3) and has a lead made of pure molybdenum metal wire. To prevent loss of materials and contamination, the electrode assemblies is capped with a high alumina ceramic cement. Actually, the same metal must be used for both the leads inside the reference electrode and outside to avoid an additional thermoelectromotive force due to dissimilar metals. In a molten salt electrolyte namely LiCl-KCl in which some oxygen anions are presents, the electrochemical reaction involved are between the alkali-metal and the alkali-metal oxide:



Then the following galvanic cell can be considered:



Therefore, the open-circuit voltage (OCV) or electromotive force (*emf*) of the above galvanic cell is given by the following equation:

$$emf \text{ (V vs. RE)} = (\ln 10 RT / 2F) \log_{10} [(a_{Oref}) / (a_{Omelt})]$$

That can be written in the simplified form:

$$emf \text{ (V vs. RE)} = B(T) - A(T) \log_{10} (a_{Omelt})$$

After calibration and having established calibration plots at various temperature, the probe is used intermittently and it allows to measure dissolved oxygen levels ranging between 50 and 5000 ppm. wt. of oxygen.

3.2 Harvesting/Salt Separation of Titanium Metal

If the titanium is deposited in a quiescent non-agitated fused salt at low temperature and at low current densities approximately below 5 kA/m^2 such as 2.5 kA/m^2 the deposit is a well bonded sponge adhering to the cathode which can be harvested by

removing the cathode. At higher current densities of approximately above 5 kA/m^2 such as 10 kA/m^2 the deposit is powdery whether the salt is agitated or not. Even at the lower current densities powder can be produced using high mass flow over the cathode. This has been achieved using centrifugal pumps of passing the salt at a defined flow over the cathode.

When the titanium is produced as a powder it can settle into a basket or if a pump is used the discharge can be into a filter basket. The titanium powder can then be siphoned from the basket or the basket exchanged. In high volume production a wet cyclone can be used to collect the titanium powder.

Whatever the titanium powder harvesting from the electrolytical cell, the salt must be separated to prevent inclusions in any subsequent component and reducing the chloride content to a level that does not interfere with welding. Water and/or dilute acid washing can be used but can cause high oxygen pick-up and even ignition of fine dried particles. There are environmental issues concerning salt ladened water, and if expensive salts such as LiCl are used they could not be discarded. Currently in the Kroll processing, vacuum evaporation is utilized to remove excess Mg and $MgCl_2$. Vacuum evaporation can also be used to remove electrolytic salts; however diffusion bonding/sintering begins at around 800°C which results in a loosely bonded material after vacuum distillation. If a powder product is required, then the vacuum treated salt separation material must be re-granulated.

4 Conclusions

Carbothermically reduced oxide/ore feeds can produce a purified suboxide without or with residual carbon. The carbothermic reduced titanium oxide can be utilized in several different electrochemical routes to electrowin titanium. The composite anode approach containing stoichiometric carbon with the reduced titanium oxide is being scaled-up to demonstrate 500 lb/day (227 kg/day) of chemically pure titanium. The bench scale product has been produced with oxygen levels below 500 ppm wt. oxygen. The projected cost to produce titanium metal via the composite anode electrolysis route is substantially less than the cost to produce Kroll sponge. It is possible to produce titanium alloys utilizing a carbothermic reduced oxide feed source.

The MER process that relies on electrowinning titanium metal powder in molten salt from a composite anode made from low cost

titanium-rich feedstocks is an innovative technology able to fill the gap existing between the Kroll process and the titanium metal powder manufacture.

5 Acknowledgements

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