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MOLTEN SALTS

BULLETIN

M. GAUNE-ESCARD
Editor

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Recent Advances
in Titanium Metallurgy

Since its early production and manufacture by the Kroll process patented in the 1940s, titanium metallurgy has generated an intensive R&D for exploring alternative methods, most of them based on molten salts routes.

This editorial is 2 fold and is based on documents very recently released in literature as a patent¹ and a scientific article², respectively. The main features of these documents are reported here together with the references of both the full patent and article.

The editor thought that it could be of interest to the readers to be informed concurrently of these major advances.

**A METHOD FOR ELECTROWINNING OF TITANIUM
METAL OR ALLOY FROM TITANIUM OXIDE CONTAINING
COMPOUND IN THE LIQUID STATE ¹**

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**TITANIUM POWDER PRODUCTION
BY PREFORM REDUCTION PROCESS (PRP) ²**
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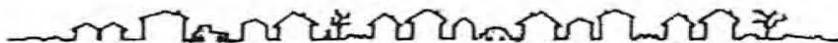
¹ Patent: PCT WO 03/046258 A2 5 June 2003 (05.06.2003),
Applicant: QUEBEC IRON & TITANIUM INC. [CA], Inventor: CARDARELLI François
[CA]

² submitted May 2003, published in J. Alloys Compd., 364, 156-163, 2004

A METHOD FOR ELECTROWINNING OF TITANIUM METAL OR ALLOY FROM TITANIUM OXIDE CONTAINING COMPOUND IN THE LIQUID STATE[†]

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Abstract: This invention relates to a method for electrowinning of titanium metal or titanium alloys from electrically conductive titanium mixed oxide compounds in the liquid state such as molten titania slag, molten ilmenite, molten leucoxene, molten perovskite, molten titanite, molten natural or synthetic rutile or molten titanium dioxide. The method involves providing the conductive titanium oxide compound at temperatures corresponding to the liquid state, pouring the molten material into an electrochemical reactor to form a pool of electrically conductive liquid acting as cathode material, covering the cathode material with a layer of electrolyte, such as molten salts or a solid state ionic conductor, deoxidizing electrochemically the molten cathode by direct current electrolysis. Preferably, the deoxidizing step is performed at high temperature using either a consumable carbon anode or an inert dimensionally stable anode or a gas diffusion anode. During the electrochemical reduction, droplets of liquid titanium metal or titanium alloy are produced at the slag/electrolyte interface and sink by gravity settling to the bottom of the electrochemical reactor forming, after coalescence, a pool of liquid titanium metal or titanium alloy. Meanwhile carbon dioxide or oxygen gas is evolved at the anode. The liquid metal is continuously siphoned or tapped under an inert atmosphere and cast into dense and coherent titanium metal or titanium alloy ingots.

FIELD OF THE INVENTION

This invention relates to a method for the continuous electrowinning of titanium metal or titanium alloys from electrically conductive titanium oxide containing compounds in the liquid state such as molten titania slag, molten ilmenite, molten leucoxene, molten perovskite, molten titanite, and molten natural or synthetic rutile.

[†] abstracted from Patent: PCT
Applicant:
Inventor:

WO 03/046258 A2(05.06.2003)
QUEBEC IRON & TITANIUM INC. [CA]
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BACKGROUND ART

Titanium metal has been produced and manufactured on a commercial scale since the early 1950s for its unique set of properties: (i) high strength-to-weight ratio, (ii) elevated melting point, and (iii) excellent corrosion resistance in various harsh chemical environments¹. Actually, about 55% of titanium metal produced worldwide is used as structural metal in civilian and military aircraft and spacecraft such as jet engines, airframes components, and space and missile applications². Titanium metal is also employed in the chemical process industries (30%), sporting and consumer goods (14%), and in a lesser extend power generation, marine, ordnance, architecture, and medical³. Titanium sponge, the primary metal form during titanium production is still produced industrially worldwide by a process invented by Dr. Wilhelm Justin KROLL⁴ and patented in the 1940s⁵. The Kroll Process consists to the metallothermic reduction of gaseous titanium tetrachloride with pure magnesium metal. However, today potential huge market such as automotive parts are still looking forward to seeing the cost of the primary metal to decrease by 50-70%. Nevertheless, this cost is only maintained high due to the expensive steps used to win the metal. Even if the Kroll's process has been improved since its first industrial introduction it still exhibits several drawbacks: (1) it is performed under strictly batch conditions leading to expensive downtimes, (2) the inefficient contact between reactants leads to slow reaction kinetics, (3) it requires the preparation, purification, and use the volatile and corrosive titanium tetrachloride (TiCl₄) as the dominant feed with its associated health and safety issues, (4) the process can only accept expensive natural rutile or rutile substitutes (e.g., upgraded titania slag, synthetic rutile) as raw materials, (5) the magnesium and chlorine must be recovered from reaction products by electrolysis in molten salts accounting for 6% of the final cost of the sponge, (6) the specification of low residual oxygen and iron content of the final ingot requires expensive and complex refining steps (e.g., vacuum distillation, and/or acid leaching) of the crude titanium sponge in order to remove entrapped inclusions accounting for about 30% of the final cost of the ingot, finally (7) it only produces dendritic crystals or powder requiring extensive reprocessing before usable mill products can be obtained (i.e., remelting, casting, forging) and wastage of 50% is common in fabricating titanium parts.

For all the above reasons, since the early 1970s there is a strong commitment of the titanium industry in synergy with several academic institutes to actively pursue new routes for producing titanium metal. Research and development focus has been directed towards developing a continuous process to produce high-purity and low-cost titanium powder or ingots for metallurgical applications.

Although a plethora of alternative methods have been examined beyond a laboratory stage or have been considered for preparing titanium crystals, sponge, powder, and alloys, none have reached industrial production.

Included in those known processes were: (i) gaseous and plasma reduction, (ii) tetraiodide decomposition, (iii) calcio- and aluminothermic reduction, (iv) disproportionation of TiCl₃ and TiCl₂, (v) carbothermic reduction, and (vi) electrowinning in molten salts. Most were considered by the authoring *National Materials Advisory Board committee (NMAB)*⁶ panel to be unlikely to progress

to production in the near future except electrowinning which seemed to be the most promising alternative route.

Actually, the extraction and preparation of pure metals from ores using an electrolytic process is well known as electrowinning. This relatively straightforward process is based on the electrochemical reduction of metal cations present in a suitable electrolyte by electrons supplied by a negative electrode (i.e., cathode, -), while at the positive electrode (i.e., anode, +) an oxidation reaction occurs (e.g., anode dissolution, gas evolution, etc.). According to the first Faraday's law of electrolysis the mass of electrodeposited metal is a direct function of quantity of electricity passed. Today among the current industrial electrolytic processes several utilize an aqueous electrolyte to electrodeposit metal (e.g., Cu, Zn, Ni, Pb, Au).

Unfortunately, aqueous electrolytes exhibit a narrow electrochemical span and are unsuitable for preparing highly electropositive and reactive metals such as titanium.

Actually, when cathodic (i.e., negative) potentials are applied to the electrode, the competitive process of the electrochemical reduction of protons occurs together with the evolution of hydrogen gas. This main parasitic reaction consumes the major part of the reduction current thereby drastically decreasing the overall current efficiency.

Despite the availability of cathode materials exhibiting a large hydrogen evolution overpotential (e.g., Cd, Hg, Pb), it has heretofore been quite impossible to electrodeposit efficiently such metals despite numerous attempts reported in the literature^{7,8,9,10,11}.

Organic electrolytes were also tested^{12,13,14} but despite their wide decomposition potential limits, organic solvents in which an appropriate supporting electrolyte has been dissolved have not yet been used industrially owing to their poor electrical conductivity which increases ohmic drop between electrode gap, the low solubility of inorganic salts, their elevated cost and toxicity.

By contrast, molten salt based electrolytes were already used industrially since the beginning of the 1900s in the electrolytic preparation of important structural metals (e.g., Al, Mg), and in a lesser extent for the preparation of alkali and alkali-earth metals (e.g., Na, Li, and Be).

Actually, fused inorganic salts exhibit numerous attractive features^{15,16,17} over aqueous electrolytes, these advantages are as follows: (1) they produce ionic liquids having a wide electrochemical span between decomposition limits (i.e., high decomposition potential) allowing the electrodeposition of highly electropositive metals such as titanium. (2) Based on the Arrhenius law, the high temperature required to melt the inorganic salt promotes fast electrochemical reaction kinetics suitable to increase hourly yields. (3) The faradaic efficiencies are usually close to 100%. (4) Due to their ionic state molten salts possess a high electrical ionic conductivity which minimizes the ohmic-drop and induces lower energy consumption. (5) The elevated solubility of electroactive species in the

bath allows to utilize high solute concentrations allowing to operate at high cathodic current densities.

Therefore, it has become clear that the most promising route for electrowinning titanium is to develop a high temperature electrolytic process conducted in molten salt electrolytes. However, despite the numerous attempts performed until today there are still no available electrolytic processes in molten salts for producing titanium metal industrially. In order to reach industrial success the new electrochemical route must solve the major issues of the energy demanding and labor intensive Kroll's process and also overcome the pitfalls that have led to failures until today.

Actually, the electrolytic production of titanium metal has been extensively investigated with the aim of developing a continuous process to replace Kroll's process. Several attempts were made in industry.

Early work was done since 1950 by National Lead Industries, Inc. and in 1956 at the former U.S. Bureau of Mines (USBM) in Boulder City, Nevada. A small pilot was built to investigate the electrowinning of titanium¹⁸. It consisted of a 12-inch cylinder vessel lined with pure iron and containing a molten electrolyte made of a mixture of LiCl-KCl approximately at the eutectic composition with TiCl₄ added. Three equally spaced openings in the cell top accommodated: (i) the replaceable anode assembly, (ii) the titanium tetrachloride feed unit, and (iii) the cathode. Three slide valves combined with air-locks allowed the quick and easy introduction or removal of assemblies without contaminating the cell. The desired solute (i.e., TiCl₂) was produced in-situ either by the chemical reduction of stoichiometric amount of TiCl₄ with titanium metal scrap or by direct electrochemical reduction of TiCl₄ at the cathode. Actually, TiCl₄, a covalent compound, does not ionize and must be converted to an ionic compound such as TiCl₂. The concentration was then increased by operating only the feed cathode and anode and feeding one mole of TiCl₄ per two faradays of charge. In all cases gaseous TiCl₄ was introduced into the bath close to the cathode with a feed nickel tube plated with molybdenum and dipped below the surface level of the melt. In order to avoid the oxidation of the newly formed Ti²⁺ and dragout of the dissolved TiCl₄ with the chlorine evolved at the anode, a porous ceramic diaphragm made of *alundum*® (i.e., 86 wt.% Al₂O₃-12 wt.% SiO₂)¹⁹ surrounded the immersed graphite anode forming distinct anolyte and catholyte compartments. The reported optimum operating conditions identified were: (1) an operating temperature above 500°C to prevent the precipitation of solute, and below 550°C to avoid severe corrosion of the alundum diaphragm, usually 520°C, (2) a solute content comprises between 2 and 4 wt.% TiCl₂, (3) a cathodic current density of 1 to 5 kA.m⁻², while the anodic current density was comprised between 5 and 10 kA.m⁻², (4) a diaphragm current density of 1.5 kA.m⁻². By conducting experiments with the above conditions USBM claimed that high purity titanium was electrowon with a Brinell hardness as low as 68 HB and a current efficiency of 60%. However frequent failures of the diaphragm that became periodically plugged or loaded with titanium crystals proved troublesome. As the titanium content increased, the ceramic diaphragm became conductive and then acted as a bipolar electrode and had to be removed rapidly from the bath. In 1972, the same authors²⁰ built a larger rectangular cell containing 226.8 kg (i.e.,

500 lb.) of bath in order to assess the actual performance of two kind of diaphragm materials: (i) solid materials composite diaphragms, and (ii) loose fill materials composite diaphragms. For solid diaphragms, it was observed that alundum coated nickel screen showed little deterioration but was subject to the same current density limitations as the porous alundum diaphragm. On the other hand, cement coated nickel screens with loose fill material such as alumina was the best material in terms of strength, flexibility, resistance to corrosion, and low replacement of titanium (0.2 to 1.0 wt.%).

In 1968, Priscu²¹ of the *Titanium Metal Corporation* (TIMET) disclosed that a new electrowinning cell was patented²², designed and operated in Henderson, Nevada. This electrolytic cell was a unique pilot based on a non diaphragm basket cathode type. The cell used a suspended central metal basket cathode with sixteen anodes peripheral to the basket. The central basket cathode was a cubic box with the four sides made of perforated steel plates, while the bottom and top were blind plates. Four steel rods were used in the basket to act as cathode collectors while TiCl_4 was fed using a tube positioned at the center of the basket. TiCl_4 was initially fed at a low rate into the center of the basket walls. This porous sidewall deposit served as a diaphragm to keep the reduced TiCl_2 inside the basket while a mechanical system was provided for withdrawing the large cathode deposits into an inert-gasfilled chamber, installing a new cathode, and reclaiming the inert gas for reuse.

The average valence of dissolved titanium cations was maintained very low generally no greater than 2.1 to obtain the electrodeposition of premium-grade titanium metal. TIMET claimed that later models of pilot-plants have produced up to 363 to 408 kg (i.e., 800 to 900 lb.) of titanium metal in one cathode deposit. This semi-works plant produced about 68 tonnes (i.e., 150,000 lb.) of electrolytic titanium sponge but discontinued the operation in 1968 owing of overcapacity for making sponge by Kroll's process.

Later in 1971, Hashimoto et al. have worked extensively on the electrowinning of titanium metal from its oxides or mixed oxides^{23 24 25}. Titanium solute was introduced in a molten fluoride bath, as a solid compound such as TiO_2 , FeTiO_3 , CaTiO_3 , or MgTiO_3 . The melt chemistries tested were CaF_2 , MgF_2 , BaF_2 , NaF and their mixtures. The first electrolysis study was conducted at temperatures above 1600°C with graphite anode and cathode. Only in the cases of the CaF_2 - TiO_2 (1-10% wt.) and CaF_2 - CaTiO_3 (10% wt.) melt systems molten titanium was obtained but largely contaminated by carbon and oxygen (2-4 wt.%). In other cases, fine titanium powder was only obtained. After the preliminary results, they focussed on the electrowinning of titanium from pure TiO_2 carried out in molten salt baths made of CaF_2 , BaF_2 , MgF_2 , CaF_2 - MgF_2 , CaF_2 - NaF , CaF_2 - MgF_2 - NaF , CaF_2 - MgF_2 - NaF , and CaF_2 - MgF_2 - SrF_2 at 1300-1420°. The titanium electrodeposited in CaF_2 and BaF_2 baths was considerably contaminated by carbon owing to graphite electrodes. In NaF -containing fused salts such as CaF_2 - NaF and CaF_2 - MgF_2 - NaF , only fine powdery deposits were obtained due to simultaneous sodium reduction that occurs. In the baths of MgF_2 , CaF_2 - MgF_2 , CaF_2 - MgF_2 - BaF_2 , and CaF_2 - MgF_2 - SrF_2 , dendritic deposits were obtained. They pointed out that best result was obtained in the CaF_2 - MgF_2 bath, but the purity of the deposit was not as high as that of the common grade titanium sponge required by the industry. In the third

article, electrowinning of titanium was carried out in CaF_2 - MgF_2 (50-50 wt.%) molten salt bath at 1020-1030°C in an argon atmosphere by using a completely enclosed cell. In electrowinning from TiO_2 , the form of the electrodeposited metal changed from crystalline to spongelike with an increase in current density, or cell voltage, but when CaTiO_3 was used, deposits were spongelike. Despite the material yield of titanium was superior to 95 wt.% it did not still meet the requirements of commercial sponge.

Later in 1973, the *Dow Chemical Company* in a close working relationship with the *HOWMET group* (i.e., subsidiary of the French *Pechiney Ugine Kuhlmann* (PUK) Group) founded the *D-H Titanium Company* for producing continuously high-purity electrolytic titanium at Howmet's plant in Whiteall, MI²⁶. Cell design, operating procedure, metal quality, proposed production, and economic projections have been described by Cobel et al.²⁷. The technology was based on the cell designed in the previous work done at *Dow Chemical* by Juckniess et al.²⁸. Actually, a major cell improvement in the D-H Titanium design was the fabrication of a metal screen diaphragm that was electroless-plated with cobalt or nickel to give the required electrical and flow characteristics. The cell operated at 520°C under argon atmosphere with LiCl-KCl-TiCl_2 (ca. 2 wt.% TiCl_2) as molten salt electrolyte. TiCl_4 was fed continuously into a pre-reduction cathode compartment where reduction to dichloride TiCl_2 takes place at a separate feed cathode within the cell. Final reduction to metal was continuously done on separate deposition cathodes. The cathodes were periodically removed hot and placed into a stripping machine under inert atmosphere. Metal-working cathodes were individually pulled, stripped, and replaced in the cell, in an argon atmosphere, by a self-positioning and automatically operated mechanical device. A sealed, argon-shielded hopper containing the titanium crystals and entrained electrode was cooled before being opened to discharge its contents. Crystalline metal and dragout salts were crushed to 3/8-inch size and leached in dilute 0.5 wt.% HCl solution. Then the spent solution was neutralized with a mixture of Li_2CO_3 and KOH in a ratio equivalent to that used in the electrolyte. Dragout of electrolyte varied with the titanium crystal sizes to about 1 kg per kg of fine titanium for coarse washed metal. Dragout was dried and passed over a magnetic separator, and metal fines were removed by screening to about 80 mesh (177 μm). They claimed that the sponge produced exhibited both a low residual oxygen, nitrogen, iron and chlorine content, had a Brinell hardness of 60 to 90 HB and excellent melting characteristics. According to Cobel et al.²⁹, the direct current required for electrowinning (17.4 kWh/kg) appears to be only about half that required for the Kroll process. Although titanium sponge of apparently satisfactory purity was claimed to be produced in relatively small pilot-plant cells with a daily titanium capacity of up to 86 kilograms per day, the electrowinning of titanium was far from an industrial scale.

Unfortunately, in December 30th, 1982, according to *American Metal Market*, the expenses for completing the joint program and the economic climate at that time have forced the dissolution of the *D-H Titanium Company*. With the breakup each company (i.e., *Dow* and *Howmet*) *Dow* has continued some research and development work on the electrolytic process but without success while *Howmet* apart having patented some work done in France^{30 31} has later focused in the metals fabrication area.

In 1985, the Italian company *Elettrochimica Marco Ginatta S.p.A.* (EMG) owned by the Italian scientist and businessman Marco Vincenzo Ginatta claimed a new electrowinning process³² inspired from the previous attempts³³. This new upgraded process for the electrolytic preparation of titanium uses always the dissolution and cathodic reduction of titanium tetrachloride in an electrolyte made of alkali or alkaline-earth metal halides and the electrodeposition of the dissolved titanium cations. The process was supported by RMI Titanium, and the company built a pilot plant. Ginatta claimed that the current production capacity of this plant reached 70 tonnes per year in 1985³⁴. Unfortunately, in 1990 RMI closed the plant owing to inability to solve "engineering issues".

Later, in the period 1997-2000 Kawakami et al.³⁵ have proposed an electros slag remelting process. The main idea was to avoid common dendritic electrodeposits by producing the electrodeposited titanium metal in its liquid state. Direct electrowinning of liquid titanium metal was the investigated techniques by using a direct current Electro-Slag Remelting (i.e., DC-ESR) apparatus. A small scale DC-ESR unit of 110 mm inner diameter was operated in d.c. reverse polarity mode, where a graphite rod was used as anode and a steel or a copper base-plate was used as cathode. The used slag was CaO-CaF₂-TiO₂ mixture. The current was approximately 1.5 kA. Under certain experimental conditions, some amount of titanium was electrodeposited in the metal pool. From the view point of heat balance, the sufficient heat was supplied by Joule heating in a molten slag phase. It can be seen from the published results that unfortunately most of the deposit was obtained as TiC and the current efficiency for the reduction was only 1.5%.

In 1999, the process was improved³⁶, the current efficiency for the reduction was up to 18% with a larger distance between the electrodes. Some amount of titanium was electrodeposited on the base-plate though its state changed with the electrolytic condition. Pure titanium metal pieces were obtained in the solidified salt after the run with the bigger electrode distance. It was concluded that the electrowinning of liquid titanium metal by the present process was possible if sufficient heat to form a metal pool can be supplied at the bigger distance between the electrodes. The DC-ESR process was patented in 1988 and reconducted in 2000, and then recently presented at ECS meeting³⁷.

The idea to use a molten pool of titanium was also recently claimed by *Ginatta Torino Technology* (GTT) who patented a new process for electrowinning titanium based on the recovery of the molten metal using a pool of liquid titanium as cathode like for aluminium³⁸.

The main idea of Ginatta is to avoid common dendritic electrodeposits by producing the electrodeposited titanium metal in the liquid state such as for aluminium. Nevertheless, the process which operates at 1750°C still needs to convert the expensive titanium dioxide to the titanium tetrachloride and the dissolution of the feedstock into a molten salt electrolyte made of CaCl₂-CaF₂ and containing calcium metal Ca.

Recently in 2000, based on early results obtained by Fray, Farthing, and Chen^{39, 40} at the Dept. of Materials Science of the *Cambridge University*, early trials were

conducted and patented^{41, 42} at the *Defence Evaluation and Research Agency* (DERA) at Farnborough (Hampshire, U.K.). A new company *British Titanium (BTi)* has been formed to commercialize the newly discovered process⁴³ that the scientific literature has dubbed the *Cambridge's* or *FFC's Process*. The process claims the electrochemical deoxidation of solid titanium dioxide that was originally applied for refining titanium metal by Okabe et al. in 1993^{44, 45, 46}. The inventors have demonstrated at the laboratory scale that the reduction reaction proceeds at 950°C from a cathode made originally of solid TiO₂ while oxidation of oxygen anions occurs at the graphite anode with evolution of carbon dioxide. Pure calcium chloride (CaCl₂) was selected as molten salt electrolyte owing to its high solubility for oxygen and excellent migration transport properties for oxygen anions. According to inventors, the process for the production of pure titanium metal consists of the following sequences of operations. The pure titanium dioxide powder is mixed with an appropriate binder to form a past or slip, and cast into a rectangular shape cathodes using one of the techniques common in the ceramic industry, such as rolling or slip casting. The green cathode will be then fired in an air kiln to initiate sintering in order to produce a solid ceramic material. After sintering the shapes give solid cathodes. Reduction of titanium occurs in an enclosed electrolytic cell with inert gas filling. The cell is designed for continuous operation with cathodes at different stages in their cycles being inserted and removed through an automated air lock. By controlling the cathode potential, oxygen can be removed from titanium dioxide allowing to leave behind a high purity metal which is morphologically similar to the Kroll's sponge. The cell voltage is roughly 3 V, which is just below the decomposition voltage of CaCl₂ (3.25 V at 950°C), avoiding chlorine evolution at the anode but well above the decomposition voltage of TiO₂ (1.85 V at 950°C). Sufficient overpotential is necessary to reduce the oxygen content of the titanium metal. The inventors claim that stoichiometric mixture of other metal oxides with TiO₂ into the original cathode are also concurrently reduced to metal leading to the possibility to produce also titanium alloys although the microstructure is different. The process has been demonstrated in a bench-scale reactor (i.e., 1 kilogram per day). The Cambridge's process claimed that it overcomes several of the issues encountered by its predecessors but however there are several important pitfalls to be overcome in scaling-up the process for a future commercial development. Primarily, it has an extremely low space time yield, i.e., mass of titanium produced per unit time and cathode surface area. This is related to the slow diffusion kinetics of oxygen across the layer of solid titanium metal at the cathode/electrolyte interface. Actually, several hours are required to completely reduce a porous pellet made of sintered TiO₂ and huge cathode surface areas are needed to compensate. Secondly, since the waste CaCl₂ can be only removed from the titanium by water leaching after the completion of the reaction it is strictly a batch process. Finally, it requires expensive preparation of titanium dioxide pellets as feedstock itself produced from tetrachloride and a preliminary preparation to render the feedstock conductive is needed.

Also in 2000, Sharma⁴⁷ proposed the calciothermic reduction of pure titanium dioxide with a zinc-calcium alloys performed in a molten salt mixture of CaCl₂-CaF₂ at 800°C. Titanium powder was later recovered from the Zn-Ti alloys formed by vacuum distillation which is highly energy demanding.

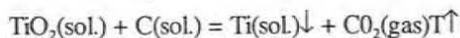
In 2001, Fortin⁴⁸ proposed another process for obtaining titanium metal from ilmenite using a so-called 'shuttle-alloys'. The process which comprises two consecutive steps requires expensive materials and some having environmental issues for an industrial process and is also energy demanding.

In 2001, Pal et al. from Boston University suggested a new way for electrowinning reactive metals including titanium using a solid oxide membrane (SOM) process⁴⁹. The patented method consists to electrolyse a molten salt electrolyte containing the cations of the metal to electrodeposit at the cathode using a porous gas diffusion anode separated from the high temperature melt by a solid ionic membrane capable of transporting the anionic species of the electrolyte to the anode^{50 51}. Nevertheless, this process did not use the electrochemical deoxidation of a cathode and no mention is made to use SOM as a unique electrolyte immersed into a molten titania slag acting as liquid cathode material.

Heretofore, no processes described in the prior art have proven to be satisfactory or gained industrial acceptance. None of the prior art processes directly use inexpensive titanium feedstocks such as crude titania slag for producing electrochemically titanium metal and alloys. Actually, plenty of crude titania slag is produced industrially by the carbothermic reduction of hemo-ilmenite or ilmenite ore concentrate with anthracite coal into an electric arc furnace (EAF) such as those produced industrially by Quebec *Iron & Titanium Inc. (QIT)* in Canada or by *Richards Bay Minerals* in South Africa. Indeed, titania slag exhibits a semiconductive behavior and hence it can be used without any treatment and additives as an electrode material. Its good electronic conductivity ranging from 10 S.m^{-1} for the bulk solid at room temperature until $1.21 \times 10^4 \text{ S.m}^{-1}$ for the melt above its liquidus temperature is related to the sub-stoichiometric titanium oxides it contains. These oxides exhibit the typical Andersson-Magneli crystal structure⁵² having the global chemical formula $\text{Ti}_n\text{O}_{2n-1}$, with n an integer at least equal to 4 (e.g., Ti_4O_7 , Ti_5O_9 , Ti_6O_{11}). Actually, these oxides exhibit in their pure state at room temperature an electrical resistivity sometimes even lower than that of pure graphite (e.g., as low as $630 \mu\Omega\text{cm}$ for Ti_4O_7).

Highly pure form of these titanium oxides were first suggested as electrode material by Hayfield⁵³ from IN and are now produced and commercialized under the trade name *Ebonex*⁵⁴ by the British company *Atraverda Ltd.*⁵⁵

First experimental trials performed at RITT to deoxidize electrochemically solid titania slag with calcium chloride as electrolyte at 950°C indicated that the process works but only produces a thin and brittle layer of titanium-iron alloy at the slag/electrolyte interface. The overall electrochemical reaction corresponds to the carbothermic reduction of titanium dioxide with the following reaction scheme:



The experimental results demonstrated that the electrochemical reaction exhibits both an extraordinarily high specific energy consumption and extremely low

space time yield. These poor performances were attributed mainly to the newly formed titanium metal layer at the slag/electrolyte interface that impedes proper mass transfer by diffusion of oxygen anions. In other words, as soon as a thin layer of solid titanium is produced, the process is "choked" and proceeds little further. Deoxidizing at higher temperatures up to 1350°C was also achieved but despite improved performance the process remained unsatisfactory for a profitable industrial process.

Thus, there remains an important need for an improved deoxidizing process for titanium oxide containing compounds.

SUMMARY OF THE INVENTION

In general terms, the present invention provides an improved deoxidizing process for titanium oxide containing compounds. Thus, the present invention, provides a method for electrowinning of titanium metal or titanium alloys from conductive titanium oxide containing compounds selected from titanium oxides, ferro-titanium oxides, titanium compounds and mixtures thereof. The method comprising the steps of (a) providing the conductive titanium oxide containing compound at 15 temperatures corresponding to the liquid state so as to provide a molten material; (b) pouring the molten material into an electrochemical reactor to form a pool of electrically conductive liquid acting as molten cathode material; (c) covering the molten cathode material with a layer of electrolyte, preferably molten salts or a solid state ionic conductor hence providing an interface between the molten cathode material and the electrolyte; (d) providing at least one anode in said electrolyte, said anode(s) being operatively connected to an electrical current source; (e) deoxidizing electrochemically the molten cathode at the interface with the electrolyte by electrolysis induced by said current source and circulating between the anode and cathode; (f) recovering the resulting deoxidized titanium metal or titanium alloy.

In another related embodiment, the method comprises the steps of:

(a) providing the conductive titanium oxide containing compound at temperatures corresponding to the liquid state so as to provide a molten material to be used as a molten cathode material; (b) providing a molten electrolyte, preferably molten salts or a solid state ionic conductor in an electrochemical reactor; (c) pouring the molten cathode material into said electrolyte and allowing separation based on relative densities with settling of the molten cathode material as a layer under the molten electrolyte, hence providing a clean interface between the molten cathode material and the electrolyte; (d) providing at least one anode in said electrolyte, said anode(s) being operatively connected to an electrical current source; (e) deoxidizing electrochemically the molten cathode at the interface with the electrolyte by electrolysis induced by said current source and circulating between the anode and cathode; (f) recovering the resulting deoxidized titanium metal or titanium alloy.

In another related embodiment, the electrolyte is not molten and is simply part of a gas diffusion anode(s) which is dipped in the molten cathode of titanium oxide containing compounds.

In a preferred embodiment, the method is conducted as part of a continuous process

BRIEF DESCRIPTION OF THE DRAWINGS

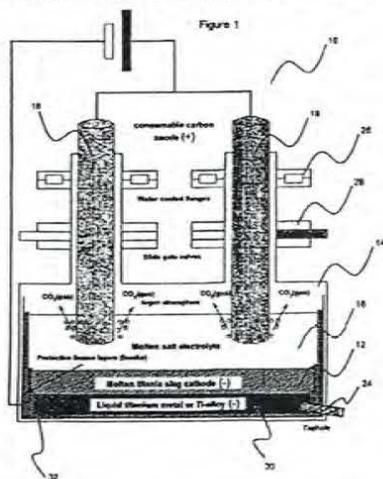


Figure 1 is a schematic illustration of the electrochemical reactor with a molten salt electrolyte and a consumable carbon anode

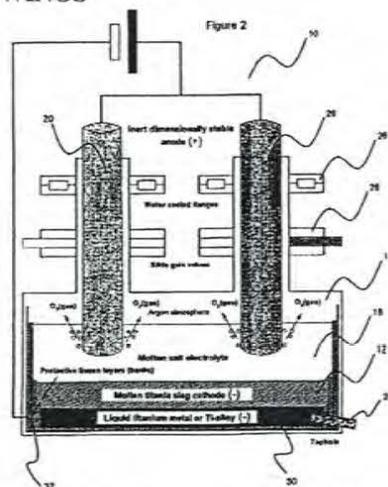


Figure 2 is a schematic illustration of the electrochemical reactor with a molten salt electrolyte and an inert dimensionally stable anode

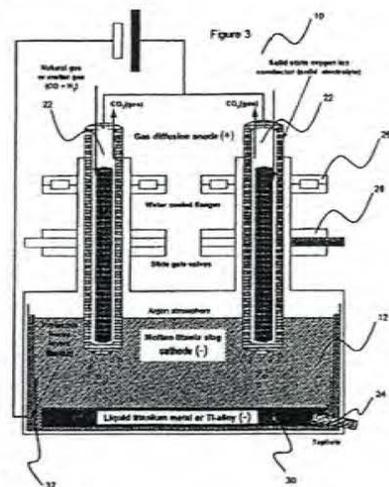


Figure 3 is a schematic illustration of the electrochemical reactor with a solid oxygen anion conductor electrolyte and a gas diffusion anode

A detailed description of preferred embodiments for carrying out the invention, 11 examples and the claims are given in the original patent* (WO 03/046258 A2)

* in which the titanium metal ingots produced exhibited a high purity and other characteristics in accordance with American Society for testing Materials standards 56, 57

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