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CA 2363647 A1 2003/05/22

(21) 2 363 647

(12) DEMANDE DE BREVET CANADIEN CANADIAN PATENT APPLICATION

(13) A1

(22) **Date de dépôt/Filing Date:** 2001/11/22

(41) **Mise à la disp. pub./Open to Public Insp.:** 2003/05/22

(51) **Cl.Int.^{7}/Int.Cl.^{7}** C25C 3/26, C25C 7/00

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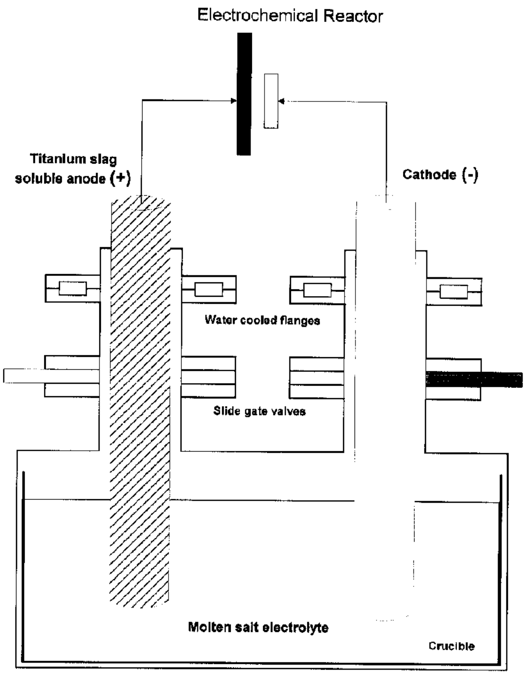
(54) Titre : METHODE D'ELECTROEXTRACTION EN CONTINU DE TITANE METAL PUR A PARTIR DE LAITIER DE TITANE, D'ILMENITE ET D'AUTRES COMPOSES D'OXYDE DE TITANE SEMI-CONDUCTEURS

(54) Title: A METHOD FOR THE CONTINUOUS ELECTROWINNING OF PURE TITANIUM METAL FROM TITANIUM SLAG, ILMENITE AND OTHER SEMICONDUCTIVE TITANIUM OXIDE COMPOUNDS



(57) **Abrégé/Abstract:**

This invention relates to a method for the continuous electrowinning of pure titanium metal from titanium slag and other electrically semiconductive titanium mixed oxides particularly ilmenite, other natural titanium ores or synthetic titanium oxide compounds. In addition, the method relates to the preparation of semiconductive electrodes made of these titanium oxide compounds. The method involves crushing and grinding a mass of crude titanium slag, separating magnetically the major impurities in the ground slag, melting the mass of purified titanium slag, casting the molten purified titanium slag into rectangular slabs or cylindrical rods forming a dense, solid, and homogeneous conductive material, using the dense solidified shapes of titanium slag as electrodes into a continuous electrolytic process conducted into a molten salt electrolyte at elevated temperatures. Extracting by direct current electrolysis the pure titanium metal from the dense cast titanium slag electrodes.

ABSTRACT

This invention relates to a method for the continuous electrowinning of pure titanium metal from titanium slag and other electrically semiconductive titanium mixed oxides particularly ilmenite, other natural titanium ores or synthetic titanium oxide compounds. In addition, the method relates to the preparation of semiconductive electrodes made of these titanium oxide compounds. The method involves crushing and grinding a mass of crude titanium slag, separating magnetically the major impurities in the ground slag, melting the mass of purified titanium slag, casting the molten purified titanium slag into rectangular slabs or cylindrical rods forming a dense, solid, and homogeneous conductive material, using the dense solidified shapes of titanium slag as electrodes into a continuous electrolytic process conducted into a molten salt electrolyte at elevated temperatures. Extracting by direct current electrolysis the pure titanium metal from the dense cast titanium slag electrodes.

A METHOD FOR THE CONTINUOUS ELECTROWINNING OF PURE TITANIUM METAL FROM TITANIUM SLAG, ILMENITE AND OTHER SEMICONDUCTIVE TITANIUM OXIDE COMPOUNDS

TECHNICAL FIELD

This invention relates to a method for the continuous electrowinning of pure titanium metal from titanium slags and other electrically semiconductive titanium mixed oxide compounds particularly ilmenite, other natural titanium ores or synthetic titanium oxides. In addition, the method relates to the preparation of semiconductive electrodes made of these titanium compounds.

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 environments[1]. 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 applications[2]. 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 medical[3]. Titanium sponge which is the primary metal form of titanium is produced industrially by the Kroll's process which is a metallothermic reduction of gaseous titanium tetrachloride with magnesium. Potential huge markets 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 metallothermic process used to win the metal.

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[1] CARDARELLI, F (2001) – *Materials Handbook : A Concise Desktop Reference.* – Springer-Verlag, London, New York, pages 115-135.

[2] GAMBOGI, J. - Titanium and Titanium Dioxide - from - *Mineral Commodity Summaries*.- U.S. Bureau of Mines (1995) p.180.

[3] GAMBOGI, J. - *Annual Report : Titanium-1992* - U.S. Bureau of Mines (1993) p. 1.

Even if the Kroll's process was greatly improved and modernized since its first industrial introduction it still exhibits several drawbacks : (1) it is performed under 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 ($TiCl_4$) as the dominant feed with its associated health and safety issues, (4) the process can only accept expensive rutile or rutile substitutes (e.g., upgraded titanium 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 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 these reasons, since the early 1970s there is a strong commitment of the titanium industry in synergy with several academic institutes for actively researching new routes to produce titanium metal with a focus on developing a continuous process to produce high-purity and low-cost titanium powder 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 the industrial production. Included in those processes were : (i) gaseous and plasma reduction, (ii) tetraiodide decomposition, (iii) calcio- and aluminothermic reduction, (iv) disproportionation of $TiCl_3$ and $TiCl_2$, (v) carbothermic reduction, and (vi) electrowinning in molten salts. Most were considered by the authoring *National Materials Advisory Board committee* (*NMAB*)[4] panel to be unlikely to progress to production in the near future except

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[4] NATIONAL MATERIALS ADVISORY BOARD Committee on Direct Reduction Processes for the Production of

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 known as electrowinning. This 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, -) according to the Faraday's law of electrolysis, while at the positive electrode (i.e., anode, +) an oxidation reaction occurs (e.g., anode dissolution, gas evolution, etc.). Today among the current industrial electrolytic processes several utilize an aqueous electrolyte to electrodeposit the metal (e.g., Cu, Zn, Ni, Pb, Au). Unfortunately, aqueous electrolytes which exhibit a narrow electrochemical span are unsuitable for preparing highly electropositive 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 accompanied with the evolution of hydrogen gas. This main parasitic reaction consumes the major part of the reduction current decreasing drastically the overall current efficiency. Despite the availability of cathode materials exhibiting a large hydrogen evolution overpotential (e.g., Cd, Hg, Pb), it is quite impossible to electrodeposit such metals despite numerous attempts reported in the literature about the electrodeposition of titanium metal from aqueous solutions[5] [6] [7] [8] [9]. Organic electrolytes were also tested[10] [11] [12] but despite their wide decomposition potential limits, organic solvents in which an appropriate

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Titanium Metal. 1974. Report # NMAB-304, National Academy of Sciences, Washington, DC.

[5] KOLTHOFF, M., and THOMAS, J. - *J. Electrochem. Soc.* **9**(1964)1065.

[6] SINHA, N.H., and SWARUP, D. – *Indian Mining J. Spec.* **1**(1975)134.

[7] KUDRYATSEV, V.N., LYAKHOV, B.F., ANUFRIEV, W.G., and PEDAN, K.S. – *Hydrog. Met. Proc. Int. Cong. 2nd.* Pergamon Press, Oxford 1977, page 5.

[8] SOFRONKOV, A.N., PRVII, E.N., PRESNOV, V.N., and SEMIZOROV, N.F. – *Zh. Prikl. Khim.* **51**(1978)607

[9] BRIBIESCA, S.L., CONTRERAS, E.S., and TAVERA, F.J. –Electrowinning of Titanium from Sulfuric Acid Titanium Solutions. – *Proc. Titanium'92*, The Minerals, Metals, and Materials Society 1993, pages 2443-2444.

[10] BIALLOZOR, S., and LISOWSKA, A. – *Electrochim. Acta* **25**(1980)1209.

[11] LISOWSKA, A., and BIALLOZOR, S. – *Electrochim. Acta* **27**(1982)105.

[12] ABBOTT, A.P., BETTLEY, A., and SCHIFFRIN, D.J. – *J. Electroanal. Chem.* **347**(1993)153-164.

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 extend for the preparation of alkali and alkali-earth metals (e.g., Na, Li, and Be). Actually, fused inorganic salts exhibit numerous attractive features[13] [14] 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, the best route for electrowinning titanium is to develop an electrolytic process conducted in molten salt electrolytes. However, despite the numerous attemps performed until today there are still no current 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 expensive and labor intensive Kroll's process and also overcome the pitfalls that have lead to unsuccess until today and abandon of all industrial electrolytic pilot plants.

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[13] DELIMARSKII, Iu.K., and MARKOV, B.F. (1961) - *Electrochemistry of Fused Salts.* - Sigma Press Publishing, New York.

[14] LANTELME, F., INMAN, D., and LOVERING, D.G. (1984) - Electrochemistry-I, in *Molten Salt Techniques*, LOVERING, D.G., GALE, R.J. (Eds.) Vol. 2., Plenum Press, New York, pp. 138-220.

Actually, several attemps were made in the industry to produce primary titanium metal by an electrolytic process. First of all, 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 titanium[15]. It consisted of a 12-inch cylinder vessel lined with pure iron containing the molten electrolyte made of a mixture of LiCl-KCl approximately at the eutectic composition with $TiCl_2$ added. Three equally spaced openings in the cell top accomodated : (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., $TiCl_2$) was produced *in-situ* either by the chemical reduction of stoichiometric amount of $TiCl_4$ with titanium metal scrap or by direct electrochemical reduction of $TiCl_4$ at the cathode. Actually, $TiCl_4$ which is a covalent compound does not ionize and must be converted to a ionic compound such as $TiCl_2$. The concentration was then increased by operating only the feed cathode and anode and feeding one mole of $TiCl_4$ per two faradays of charge. In all cases gaseous $TiCl_4$ 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 Ti^{2+} and dragout of the dissolved $TiCl_4$ with the chlorine evolved at the anode, a porous ceramic diaphragm made of *alundum*® (i.e., 86 wt.% Al_2O_3-12 wt.%SiO_2)[16] surrounded the immersed graphite anode forming distinct anolyte and catholyte compartments. The optimum operating conditions identified were : (1) an operating temperature above 500°C to prevent the precipitation of K_2TiF_6, 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.% $TiCl_2$, (3) a cathodic current density of 1 to 5 $kA.m^{-2}$, while the anodic current density was comprised between 5

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[15] LEONE, O.Q., KNUDSEN, H., and COUCH, D.E. – High-purity titanium electrowon from titanium tetrachloride. – *J.O.M.* **19**(1967)18-23

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 authors[17] build a larger rectangular cell containing 226.8 kg (i.e., 500 lb.) of bath in order to use assess the actual performances 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 showing no deterioration but however it was subject to the same current density limitation as the porous alundum diaphragm. On the other hand, cemented coated nickel screen 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, Priscu[18] of the *Titanium Metal Corporation* (TIMET) has designed and operated a new electrowinning cell[19] 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

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[16] COUCH, D.E., LEONE, O.Q., LANG, R.S., and BLUE, D.D. – Evaluation of diaphragm materials for electrowinning high-purity titanium. *Proc. Extractive Met. Div. Symp., Met. Soc. AIME* Chicago IL December 11-13 1967, pp. 309-323.

[17] LEONE, O.Q, and COUCH, D.E. (1972) – *Use of Composite Diaphragms in the Electrowinning of Titanium.* – Report Investigation #7648, U.S. Dept. of Interior, Bureau of Mines, Washington D.C.

[18] PRISCU, J.C. – *Symp. on Electrometallurgy, Proc. AIME Extractive Metallurgy Div*, Cleveland Ohio, December 1968, page 83.

[19] TIMET - An electrolytic cell for electrolysis of titanium tetrachloride. - *French Pat.* 1,496,806 Aug. 24, 1966.

tube positioned at the center of the basket. $TiCl_4$ initially was 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 for withdrawing the large cathode deposits into an inert-gas-filled 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 until 363 to 408 kg (i.e., 800 to 900 lb.) of titanium metal in one cathode deposit.

Later in 1971, Hashimoto et al. have published a series of three comprehensive articles[20] [21] [22] regarding the electrowinning of titanium from its oxides or mixed oxides. Titanium solute was introduced in a molten fluoride bath, as a solid compound such as TiO_2, $CaTiO_3$, $FeTiO_3$, or $MgTiO_3$. The melts tested were CaF_2, MgF_2, BaF_2, NaF and their mixtures. The first electrolysis study was conducted at temperatures above 1600°C with a graphite anode and cathode. Only in the cases of the CaF_2-TiO_2 (1-10% wt.) and CaF_2-$CaTiO_3$ (10% wt.) systems molten titanium was obtained but largely contaminated by carbon and oxygen (2-4 wt.%). In other cases, fine titanium powder was 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_2, 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

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[20] HASHIMOTO, Y.; URIYA, K.; and KONO, R. - Electrowinning of titanium from its oxides. Part I. Fused salt electrolysis at temperatures above the melting point of the metal. - *Denki Kagaku* **39**(6) (1971)516-522.

[21] HASHIMOTO, Y. - Electrowinning of titanium from its oxides. Part II. Influences of fluoride salt baths on fused-salt electrodeposition of titanium metal from titanium dioxide. - *Denki Kagaku* **39**(12) (1971)938-943.

[22] HASHIMOTO, Y. - Electrowinning of titanium from its oxides. Part III. Electrowinning of titanium from titanium dioxide or calcium titanate in calcium fluoride-magnesium fluoride molten salt baths. - *Denki Kagaku* **40**(1) (1972) 39-44.

sodium reduction. 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 in the industry. In the third article, electrowinning of titanium was carried out in CaF_2-MgF_2 (50-50 wt.%) molten salt baths 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. The hardness of the deposits was influenced by the bath temperature of the last stage of electrolysis and by the duration of electrolysis at the given temperature. The material yield of titanium was superior to 95 wt.% but do not meet the requirements of commercial sponge. Moreover, Hashimoto used a graphite basket to contain the titanium compounds at the anode because it was unable to make a conductive soluble anode.

Later in 1980, the Dow Chemical Company in a close working relationship with the HOWMET group (i.e., subsidiary of the French Pechiney Ugine Kuhlmann Group) founded the D-H Titanium Company for producing continuously high-purity electrolytic titanium at Freeport, Texas. Cell design, operating procedure, metal quality, proposed production, and economic projections have been described by Cobel et al.[23]. The technology utilized was based on the cell designed by the U.S. Bureau of Mines, and on the previous work done at Dow by Juckniess et al[24]. Actually, a alleged 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 with argon blanketed $LiCl$-KCl-$TiCl_2$ (ca. 2 wt.% $TiCl_2$) at 520-600°C molten salt electrolyte. $TiCl_4$ was fed continuously into a pre-reduction cathode compartment

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[23] COBEL, G.; FISHER, J.; and SNYDER, L.E - Electrowinning of titanium from titanium tetrachloride: pilot plant experience and production plant projections 1969-1976. - *Conference: Titanium '80, Science and Technology*, Vol. 3, Kyoto, Japan, 19-22 May 1980 TMS/AIME, Warrendale, Pa.

where reduction to dichloride $TiCl_2$ takes place at a separate feed cathode within the cell. Final reduction to metal is continuously done on separate deposition cathodes which are periodically removed hot into an inert atmosphere stripping machine and then replaced within the cell. 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.[25], 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 excellent 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 the industrial scale. Unfortunately, in December 30th, 1982, according to the *American Metal Market* (AMM), 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

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[24] JUCKNIESS, P.R., and JOHNSON, D.R. – Method for Electrowinning Titanium. – *U.S. Pat.* 4,118,291; October 3 (1978).

[25] MAY COBEL G., FISHER J., and SNYDER L. (1980) - *Electrowinning of Titanium from Titanium Tetrachloride.* - 4th International Conference on Titanium, May 1980, Kyoto, Japan.

apart some works done in France and patented[26][27] have later focussed in the metals fabrication area.

In 1988, the Italian company *Elettrochimica Marco Ginatta S.p.A.* (EMG) owned by the Italian scientist and business man Marco Vincenzo Ginatta[28] applied for patent on a new electrowinning process largely inspired from the three previous pilots of USBM, TIMET, and DH[29]. 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 1985[30]. Unfortunately, in 1990 RMI closed the plant owing to inability to solve "engineering issues". More recenty, the same company, now renamed *Ginatta Torino Technology* (GTT) applied for patent on a new process for electrowinning titanium based on the recovery of the molten metal using a pool cathode like for aluminum. The main idea of Ginatta is to avoid common dendritic electrodeposits by producing the electrodeposited titanium metal in the liquid state such as for aluminum. Marco Ginatta continues to pursue chloride process and has built a pilot in Torino, Italy.

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[26] ARMAND, M. – Process for the Preparation of Titanium by Electrolysis. – *U.S. Pat.* 4,381,976, May 3 (1983).

[27] ARMAND, M. – Novel Apparatus and process for the $TiCl_4$ feed to electrolysis cells for the preparation of titanium. – *U.S. Pat.* 4,396,472, August 2 (1983).

[28] GINATTA, M.V.; ORSELLO, G.; and BERRUTI, R. - A method for the electrolytic production of a polyvalent metal and equipment for carrying out the method. - PCT Int. Appl., 33 pp. WO 8910437 (1990).

[29] GINATTA, M.V.; and ORSELLO, G. - Plant for the electrolytic production of reactive metals in molten salt baths. - Eur. Pat. Appl. EP 210961 Apr. 02, 1987.

[30] DIMARIA, E. – RMI Gets License to Make New Type of Titanium. – *Metalworking News*, February 1st., 1988.

Simultaneously, in the period 1997-2000 Kawakami et al.[31] have proposed an electroslag 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 $CaO-CaF_2-TiO_2$ 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 the Joule heating in molten slag phase. It can be seen from these results that the present process is possible in principle but 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 improved[32], the current efficiency for the reduction was up to 18% with the proper 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 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[33].

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[31] KAWAKAMI, M.; OOISHI, M.; TAKENAKA, T.; and SUZUKI, T. - The possibility of electrowinning of liquid titanium using ESR apparatus. - *Proc. Int. Conf. Molten Slags, Fluxes Salts '97, 5th* (1997) 477-482 Iron and Steel Society, Warrendale, PA.

[32] TAKENAKA, T.; SUZUKI, T.; ISHIKAWA, M.; FUKASAWA, E.; and KAWAKAMI, M. - The new concept for electrowinning process of liquid titanium metal in molten salt. - Electrochemistry **67**(6) (1999) 661-668.

[33] TAKENAKA, T.; ISHIKAWA, M.; and KAWAKAMI, M. - Direct electrowinning of liquid titanium metal by using direct current electro slag remelting apparatus. - *Proc. Electrochem. Soc.* (Molten Salts XII) (2000) 99-41 578-584.

Recently in 2000, based on early results obtained by Fray, Farthing, and Chen[34] [35]at the Dept. of Materials Science of the Cambridge university, and later on early trials that were conducted and patented[36] [37]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 process of refining metallic titanium[38]. The inventors have proposed an entirely novel electrolytic route, that the scientific literature has already called the Fray's or FFC process, the process claims to avoids conversion of the titanium dioxide to the tetrachloride or the dissolution of the feedstock into a molten electrolyte. The inventors have demonstrated at the laboratory scale that the reduction reaction proceeds at 950°C from a cathode made originally of solid TiO_2 while oxidation of oxygen anions occurs at the graphite anode with evolution of carbon dioxide. The molten salt electrolyte selected is made of pure calcium chloride ($CaCl_2$) bath exhibiting both a 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 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

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[34] CHEN, G.Z, FRAY, D.J., and FARTHING, T.W – Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride – *Nature* **407** (2000) 361-364.

[35] FRAY, D.J., FARTHING, T. W., and CHEN, G.Z. – Removal of Oxygen from Metal Oxides and Solids Solutions by Electrolysis in a Fused Salt. – British Pat. Appl. WO 99/64638 16 December 1999.

[36] WARD-CLOSE, C. M., and GODFREY, A.B. – Electrolytic reduction of metal oxides such as titanium dioxide and process applications. – U.S. Pat. Appl. WO01/62996, 20 Feb. 2001.

[37] WARD-CLOSE, C. M., and GODFREY, A.B. – Method of Manufacture for Ferro-Titanium and Other Metal Alloys Electrolytic Production. – U.S. Pat. Appl. WO01/62994, 19 Feb. 2001

[38] *Financial Times* December 21st, 2000, page 12.

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 $CaCl_2$ (3.25 V at 950°C), avoiding chlorine evolution at the anode but well above the decomposition voltage of TiO_2 (1.85 V at 950°C). Sufficient overpotential is necessary to reduce the oxygen content of the titanium metal. The inventors claim[39] that stoichiometric mixture of other metal oxides with TiO_2 into the original cathode are also concurrently reduced to metal leading to the possibility to produce valuable titanium alloys although the microstructure may not be the same. The process has been demonstrated in a bench-scale reactor (i.e., 1 kilogram per day). Whilst there are obvious difficulties to be overcome in scaling-up the vessel, primarily in reducing the diffusion path for oxygen through the metal leading to several hours to completely reduce a porous pellet made of sintered TiO_2, and increase the extremely low energy efficiency. It is a single-stage process, since the waste $CaCl_2$ can be removed of the titanium by water leaching after the completion of the reaction. They claim that operating costs will be somewhat reduced by lower labour requirements, and by the elimination of the vacuum distillation stage. Unfortunately, the specific energy consumption of the process is not provided and the process requires pigment-grade TiO_2 or synthetic TiO_2, such as upgraded titanium slag, though the impurities will report to the finished metal; or on mixtures of oxides.

The Fray's process[40] claimed that it overcomes several of the issues encountered by its predecessors but its poor energy efficiency, its extremely low hourly yield related to the slow diffusion kinetics of oxygen into titanium metal,

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[39] FRAY, D.J., FARTHING, T. W., and CHEN, G.Z. – Removal of Oxygen from Metal Oxides and Solids Solutions by Electrolysis in a Fused Salt. – British Pat. Appl. WO 99/64638 16 December 1999.

[40] CHEN, G.Z, FRAY, D.J., and FARTHING, T.W – Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride – *Nature* **407** (2000) 361-364.

and the mandatory use of a graphite anode are important pifalls for a future commercial development. Actually, the use of a graphite anode leads to an elevated anode overpotential, leading to high cell voltage and thus elevated specific energy consumption. Moreover, the anodic oxidation mechanisms leads to severe corrosion of the graphite with contamination of the melt by floating flakes of graphite leading to short circuits between electrodes. In addition the evolution of gases such as carbon dioxide and chlorine gives the so-called ''anode effect'' at elevated anodic current densities.

Therefore, the present invention would seek to resolve most if not all of the previous issues related to the electrolytic production of the titanium metal by using an anode made of titanium slag such as the Sorelslag® or Richard's Bay slag® which is originally produced at QIT by the reduction of ilmenite with anthracite by smelting into an electric arc furnace (EAF). Actually, titanium slag is mainly composed of sub-stoichiometric titanium oxides with the typical Andersson-Magnelli crystal structure[41] having the global chemical formula TiO_{2-x}, (e.g., Ti_3O_5, Ti_4O_7, and Ti_5O_9). This composition was already confirmed by the work of Desjardins[42]. Hence, these oxides exhibit both a good corrosion resistance and a low electrical resistivity similar to that of pure graphite (i.e., as low as 630 μΩ.cm) and their mechanical and electrical properties can be compared to those of the electrode material named *Ebonex®*[43] and produced commercially by the British company *Atraverda Ltd.*

The major benefits to use a soluble anode made of titanium slag are : (1) the anodic dissolution of the titanium slag feed continuously providing the electrochemical reactor with titanium electroactive species avoiding the tedious

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[41] ANDERSSON, S., COLLEN, B., KUYLENSTIERNA, U., and MAGNELLI, A. *Acta Chem. Scand.* 11(1957)1641.

[42] DESJARDINS, J.F. (1986) – *Study of Insoluble Formation in Richards Bay Slag.* – QIT Internal Report No. R-11-86.

[43] CARDARELLI, F (2001) – *Materials Handbook : A Concise Desktop Reference.* – Springer-Verlag Ltd., London, pages 329-330.

introduction of a solute (i.e., the electrode acts as an electroactive species reservoir) and hence preventing the anodic evolution of chlorine or carbon dioxide. (2) The cell operating voltage is being maintained extremely low resulting in a low specific energy consumption. (3) Finally, the more active impurities (e.g., Si, Ca, Mg) contained in the titanium slag remaining dissolved in the bath while the more noble (e.g., Fe, V, Mn, and Cr) not dissolving and being recovered in the sludge at the bottom of the cell (i.e., electrorefinning). In addition conducting the electrolysis in inorganic fluoride melts which are strong complexing ligands solves the issue of disproportionation of titanium species and stabilizes the high valence states of titanium in the form of the TiF_6^{2-}. Other benefits provided by inorganic salt melts such as fluoride melts that are utilized in this invention are: (1) wide decomposition potentials, (2) low dynamic viscosities, (3) low melting range when used in mixtures with the eutectic composition, (4) elevated ionic conductivities, and (5) capability to dissolve large amount of solute leading to operate at elevated cathodic current densities. Therefore, the soluble titanium slag anode overcomes the poor hourly yield and the low energy efficiency of the prior art FFC process.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic flow sheet of the entire process.

Figure 2 is a schematic illustration of the electrochemical reactor.

Figure 3 is a schematic illustration of the four possible electrode configurations.

MODES OF CARRYING OUT THE INVENTION

Generally speaking, the invention relates to a method for the continuous electrowinning of pure titanium metal from titanium slag and other electrically semiconductive titanium mixed oxide compounds particularly ilmenite, other natural titanium ores or synthetic titanium oxides. In addition, the method relates to the preparation of semiconductive electrodes made of titanium compounds. The method involves comminuting a mass of crude titanium slag, separating magnetically the major impurities, melting the mass of purified titanium slag, casting the molten purified titanium slag into solid shapes such as conductive slabs or rods, using the solidified and conductive titanium slag as electrodes into a continuous electrolytic process conducted into a molten salt electrolyte at elevated temperature. Extracting by electrolysis pure titanium metal from the titanium slag electrodes.

The first step consists in comminuting (i.e., crushing and grinding) the crude titanium slag (i.e., 78-82 wt.% TiO_2) or other semiconductive titanium compounds such as ilmenite to a final particle size comprised preferably between 0.075 mm and 0.42 mm (i.e., 40 and 200 mesh Tyler), but most preferably between 0.105 mm and 0.150 mm (100 and 150 mesh Tyler). The comminution step is necessarily required in order to render easier the removal of inert minerals present in the crude titanium slag (e.g., silicates, sulfides) and facilitate the removal of associated chemical impurities (e.g., Fe, Si, Ca, Mg). The removal of these impurities is suitable for both improving the electrical conductivity of the titanium slag and for enhancing its titanium concentration.

Secondly, the finely ground titanium slag produced undergoes a common magnetic separation step. The strong ferromagnetic phases such as for instance free metallic iron entrapped in the titanium slag during the smelting process and the intimately binded silicate minerals may be efficiently removed using a low magnetic induction of 0.3 tesla and separated with the magnetic fraction which is discarded. Then the remaining materials undergoes a second magnetic separation conducted with a stronger magnetic induction of 1 tesla. The non magnetic fraction that contains all the diamagnetic mineral phases (e.g., silica, silicates, etc.) is also discarded or rerouted. The remaining material consists of a finely purified ground titanium slag (i.e., 85-88 wt.% TiO_2) mainly composed of semiconductive titanium oxide with the Andersson-Magnelli crystal structure (i.e., titanium oxides having the general stoichiometry TiO_{2-x}, such as Ti_3O_5, Ti_4O_7, and Ti_5O_9).

Thirdly, the purified ground titanium slag may be poured into a crucible made of molybdenum, tungsten, niobium or tantalum and melted under an inert argon atmosphere above 1700°C during at least 2 hours. Once totally liquid the molten purified titanium slag is either cast into slabs or rods or let to cool down into the crucible having the desired shape. After complete solidification and careful demoulding the dense, homogeneous and coherent cast titanium slag is ready to be used as a conductive electrode. The typical electrical resistivity of the final electrode material ranges between 600 and 5000 $\mu\Omega$.cm. In order to have an efficient and reliable current collector a metallic a threaded rod insert made of pure molybdenum can be introduced in the mould before casting or the cast titanium slag can be machined at room temperature in order to be easily connected to external busbars. The electrode is then ready to be used in the continuous electrolytic production of titanium metal of the present invention.

The electrolytic cell which is designed for continuous operation may consist of a closed reactor vessel set into a high temperature furnace. The cell has soluble titanium slag anodes and titanium or molybdenum cathodes that can be inserted and removed from the electrochemical reactor at different stages in their cycles being without any entries of air and moisture through airtight locks which are closed by means of large gate valves. The molten electrolyte bath is contained into a large crucible. The material selection for the crucible strongly depends of the melt chemistry and the operating temperature at which the electrolysis must be performed. Hence, pure copper (e.g., electrolytic pure copper), pure iron (e.g., armco® iron), or pure nickel (e.g., nickel 200) are suitable containment materials for operating in molten fluoride baths in the temperature range 700°C-900°C, while pure molybdenum, pure niobium, pure tantalum, or pure tungsten owing to their high melting points are required for operating at temperatures above 1200°C. The electrochemical reactor is closed by means of water cooled flanges, the proper tightness is insured o-ring gaskets made of fluoroelastomers (e.g., Viton®) or annealed ductile metals (e.g., Cu, Au). The components of the apparatus were selected to achieve a vacuum tight cell at elevated temperatures. The inert atmosphere within the cell is performed by an argon stream purified by passing it through a water and oxygen traps (i.e., getter).

The electrolytic bath is made of inorganic salts or their mixtures selected from the group consisting of M_nX_m wherein M = Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and X = F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, BO_3^{2-}, PO_4^{3-}or mixtures thereof, preferably alkali-metals and alkali-earth metals halides, but more preferably alkali-metals and alkali-earth metals fluorides with a final preference for CaF_2, or the following mixtures of salts with the eutectic composition (e.g., CaF_2-MgF_2, CaF_2-BaF_2-LiF, CaF_2-LiF). The solutes that can be used are : TiO_2, TiF_3, or K_2TiF_6.

Before premelting the electrolyte, the electrochemical reactor is purged from background contaminants by high-vacuum pumping (i.e., 0.01 mbar). As the temperature reached the electrolyte's melting point the vacuum circuit was switched to a pure argon stream. Then the electrodes are immersed in the bath. Once thermal equilibrium is reached, the electrolysis is performed under galvanostatic conditions (i.e., at constant current) by imposing a direct current between the soluble titanium slag anode (+) and the metallic titanium cathode (-) by mean of an electric power supply or a rectifier . Usually cathodic and anodic current densities of 20 $kA.m^{-2}$ are imposed with a cell voltage of less than two volts. The electric current is maintained until the desired electric charge has circulated. During electrolysis the concentration of titanium in the melt was maintained constant by the continuous dissolution of the soluble titanium slag anodes. Final reduction to metal is continuously done on separate titanium deposition cathodes which are periodically removed hot into an inert atmosphere, cooled in an argon stream and then replaced within the cell. Note that several electrode configurations (i.e., anode, electrolyte, cathode) were successfully tested and are presented in greater detail in the examples. The electrodeposited titanium metal ingot produced exhibited a high purity (i.e., 99 wt.% Ti) and other characteristics that satisfies the grade EL-110 in accordance with the standard B299-99 from the *American Society for Testing Materials* (ASTM)[44] such as a low residual oxygen, nitrogen, iron and chlorine content, a Brinell hardness of 60 HB. The electrowinning process exhibits a low specific energy consumption of 15 kWh/kg of titanium metal produced.

EXAMPLES

Example 1 : Two large rectangular slabs of soluble titanium slag anodes (+) are immersed into an electrolyte made of the mixture CaF_2-MgF_2-TiO_2 with an eutectic composition while the cathode is a rectangular thick titanium plate positioned between the two anodes for optimizing the current distribution. The electrolysis is performed at the operating temperature of 1000°C with an anodic and cathodic current density of 20 $kA.m^{-2}$ while the cell voltage is about 2V.The electrodeposited titanium metal is recovered continuously as a slab ingot.

Example 2 : A large titanium slag block is machined in order to form a large cavity in the core containing the molten electrolyte made of the mixture CaF_2-BaF_2-TiO_2 with an eutectic composition while the cathode is made of a titanium rod positioned at the center of the hollow soluble titanium slag anode. The electrolysis is performed at the operating temperature of 1400°C with an anodic and cathodic current densities of 20 $kA.m^{-2}$ while the cell voltage is about 1.5V. The electrodeposited titanium metal is recovered continuously as an ingot.

Example 3 : The electrolytic cell consists to a molybdenum crucible connected to the positive pole of the power supply that contains solidified titanium slag at its bottom acting as a soluble anode. The molten pool is covered by the electrolyte made of the mixture CaF_2-LiF-TiO_2 with an eutectic composition while the cathode

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[44] ASTM B299-99 - *Standard Specification for Titanium Sponge.* – American Society for Testing and Materials (ASTM)

is made of a titanium rod immersed into the electrolyte at the center of the cell. The electrolysis is performed at the operating temperature of 1200°C with an anodic and cathodic current densities of 20 $kA.m^{-2}$ while the cell voltage is about 1V. The electrodeposited titanium metal is recovered continuously as an ingot.

Example 4 : The electrolytic cell consists to a molybdenum crucible connected to anodically to the positive pole of the power supply that contains a large pool of molten titanium slag at its bottom acting as a soluble liquid anode. The molten pool is covered by the electrolyte melt made of the of the mixture CaF_2-TiO_2 with eutectic composition while the cathode is made of a large molybdenum cylinder immersed into the electrolyte close to the cell wall. The electrolysis is performed at the operating temperature of 1680°C with an anodic and cathodic current densities of 20 $kA.m^{-2}$ while the cell voltage is about 1V. The electrodeposited liquid titanium metal droplets fall by gravity at the bottom of the electrolytic cell close to the walls and it is recovered continuously around the molten slag pool by continuous tapping under an argon atmosphere.

CLAIMS

1. A method for the continuous electrowinning of pure titanium metal (Ti) from titanium slag and other electrically semiconductive titanium mixed oxides $Ti_xM_yO_z$ particularly ilmenite $FeTiO_3$, other natural titanium ores or synthetic titanium oxide compounds in a molten salt electrolyte M_nX_m or a mixture of these salts.

2. A method according to claim 1, wherein $Ti_xM_yO_z$ is a semiconductor used as a soluble titanium containing anode where M = Ti, Fe, Ca, Mn, Cr.

3. A method according to claim 1, wherein the titanium slag is obtained by the direct reduction of ilmenite with anthracite by smelting into an electrical arc furnace such as the Sorelslag.

4. A method according to the preceding claim, wherein the titanium slag, was ground, purified by magnetic separation, melted and cast into final electrode shapes.

5. A method according to claim 1, wherein the titanium slag can also be used in a molten state both as a pool anode or cathode.

6. A method according to any preceding claim, wherein electrolysis is conducted at a temperature ranging between 600°C and 2000°C, but preferably between 800°C and 1700°C.

7. A method according to any preceding claim, wherein the electrolyte is a molten inorganic salt M_nX_m wherein M = Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and X = F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, BO_3^{2-}, PO_4^{3-}or mixtures thereof, prefereably alkali-metals and alkali-earth metals halides, but more preferably alkali-metals and alkali-earth metals fluorides with a preference for the following pure salt : CaF_2, or mixtures (e.g., CaF_2-MgF_2, CaF_2-BaF_2-LiF, CaF_2-LiF) with an eutectic composition.

8. A method according to any preceding claim, wherein the solutes that can be used are : TiO_2, TiF_3, or M_2TiF_6 wherein M = Li, Na, K.

9. A method according to any preceding claim, wherein the specifications of the titanium metal produced satisfies the grade EL-110 in accordance with standard B299-99 from the *American Society for Testing Materials* (ASTM).

Figure 1 - Electrolytic Process Flow Sheet

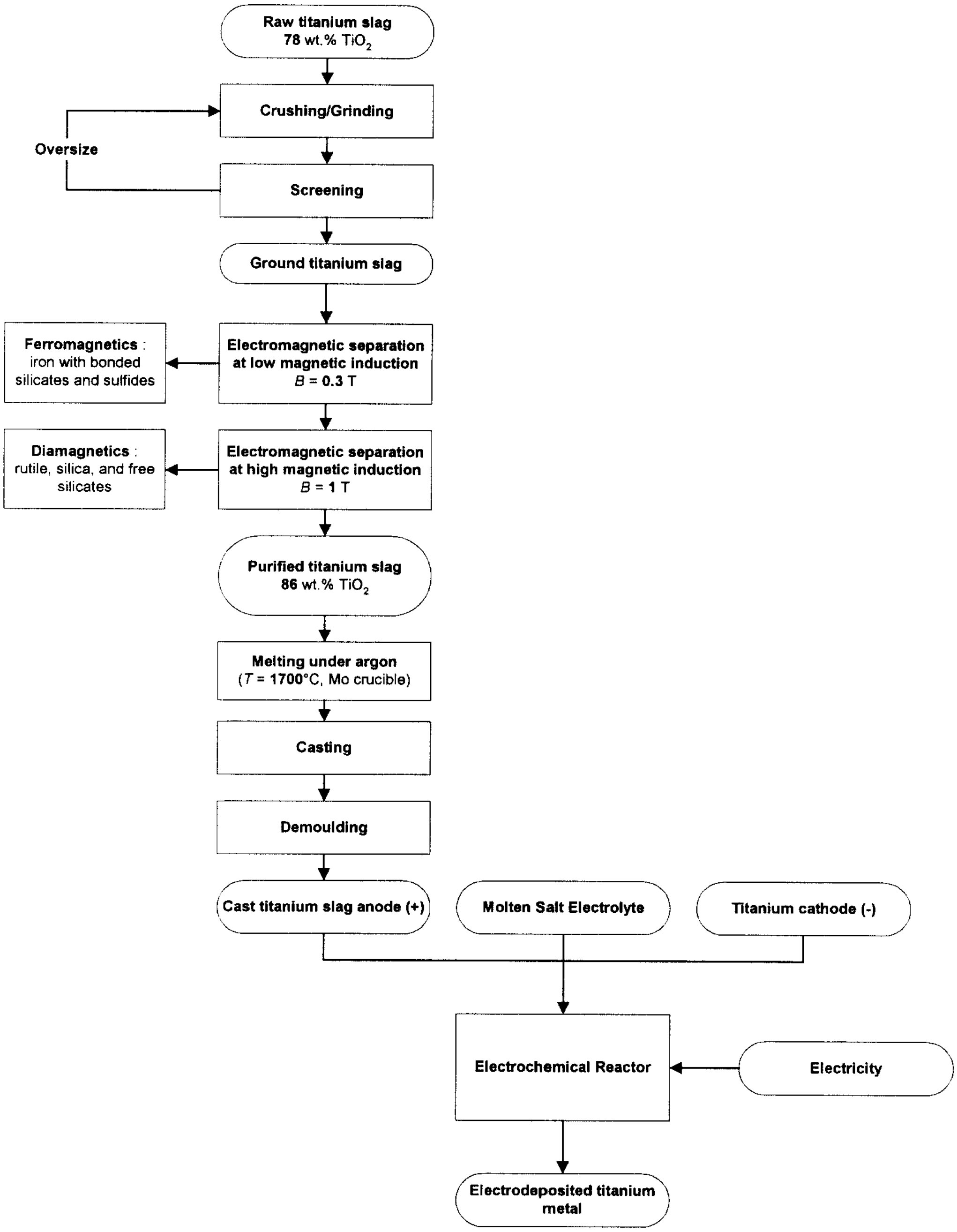

Figure 2 - Electrochemical Reactor

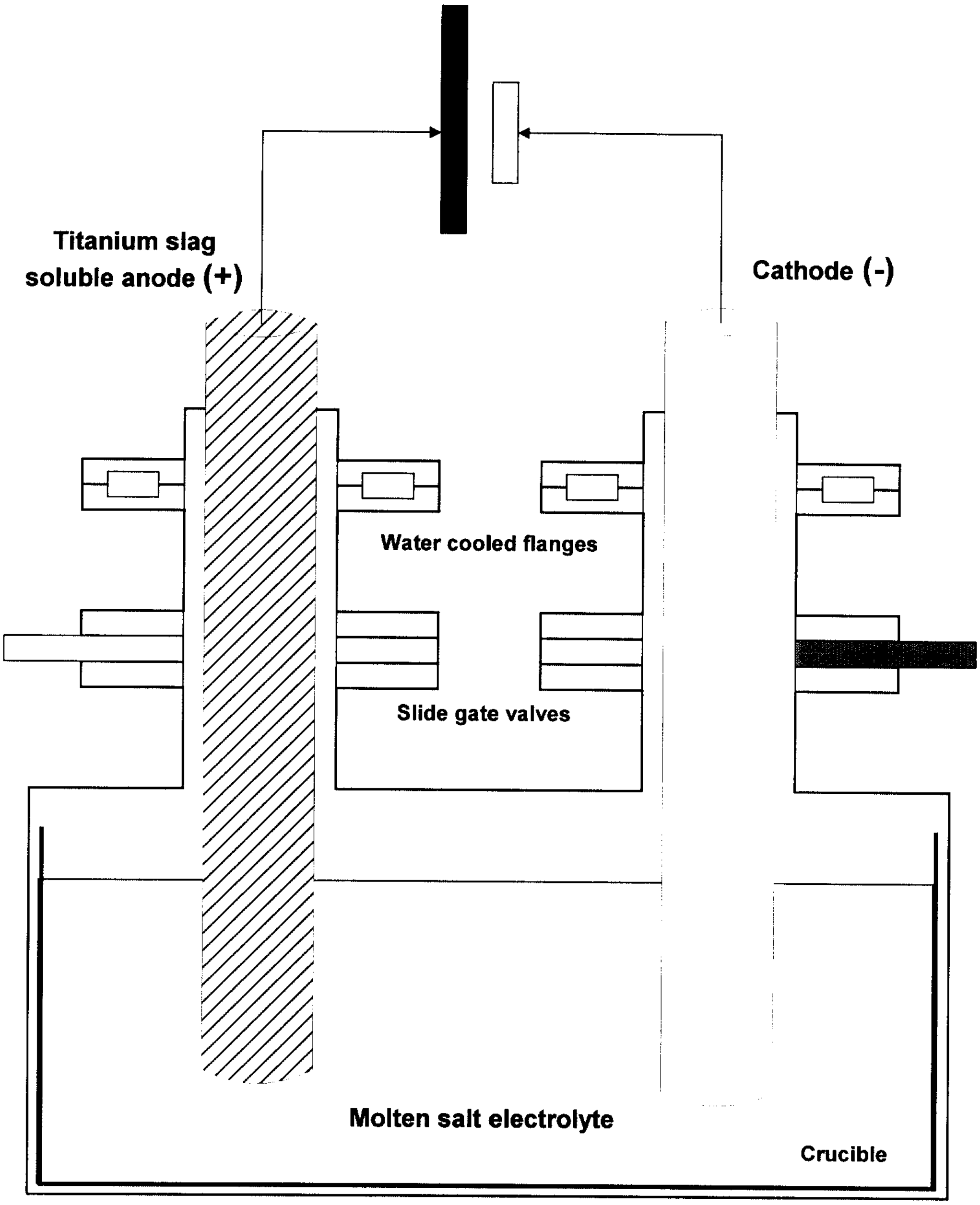

Figure 3 - Electrode Configurations