

# TITANIUM ELECTROWINNING

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## 1 Introduction

With respect to our previous publications, which you will find in the references, [1,2], I would like to discuss about the many advantages and present limitations of the electrolytic processes for titanium production in molten chlorides and at high temperatures.

## 2 The Choice of Titanium Tetrachloride as Raw Material.

Before discussing the merits of the processes, we must first determine, define, the characteristics and the cost of the raw material that we are going to start with.

Looking at the Logo of this Forum, I can see an important point to be addressed, specifically titanium dioxide being the starting compound for the electrolysis.

I assume it to be Purified titanium dioxide and not Rutile (95-97% dioxide).

If this is true I must recall that, for purifying rutile into  $TiO_2$ , the process most used in the world is the Carbochlorination of the ore and separation of the various chlorides: titanium tetrachloride is the product, Fig. 1, [5].

The pigment producers oxidize, in specialized equipments, with additional manufacturing costs, the pure titanium tetrachloride to obtain pigment.

Why don't we use directly pure titanium tetrachloride, which is the purest and the least expensive intermediate titanium compound ?

Further the dioxide feed produces 40 w% wastes, while the chlorine gas instead, is entirely recycled.

Finally we can recall that the most important rules of titanium metallurgy may be summarized as "stay away from oxygen".



Fig. 1. Carbochlorination plant

## 3 The Inadequate Current State of Titanium Electrolysis

It is true that the electrochemistry of titanium is more complex than those of the other industrial metals and this is why titanium has not yet its commercial Electrowinning process.

The current state of the art is not acceptable anymore: 100 years have lapsed since the first documented electrolysis of titanium.

Lets us recall the definition of the Electrowinning of titanium: the metallurgical process for producing metal by electrolysis without the use of any reagent and without the production of any waste.

For the titanium electrochemical systems, a specific electrolyte has not been found yet, that is equivalent to what cryolite is for aluminium. During the past century researchers did experimental work on the electrochemistry of titanium, without having the proper tools for understanding what they were doing. There are no textbooks which give a good treatment of electrode kinetics (dynamic electrochemistry). As of mathematical instruments to calculate and predict the outcome of the experiment, contrary to physics, no one has yet developed quantum mechanical electrochemistry. The ongoing progress of the development work of the high temperature titanium Electrowinning process, depends upon a deeper understanding of the electrochemistry.

The state of the art of Titanium Electrowinning can be summarized as follows:

- the inadequate state of development of the theory of molten salts in fundamental electrochemistry, has retarded the industrial progress in general. Models for electrode/electrolyte systems are still conceived as bidimensional quiescent interfaces at reversible equilibrium conditions in dilute solutions. With current densities of  $1 \text{ A/cm}^2$  there is an exchange of several thousands of atomic layers each second, in molten salts, which are the limits of concentrated solutions, since there is no solvent;
- the insufficient theoretical understanding of the titanium system has slowed the technological development of electrolytic plant engineering. In order to improve the industrial electrolytic process, we need to reach a practical understanding of the physical meaning of the data which describe the operative conditions of the process;

- thermodynamics of irreversible processes, in its present form, is only valid in a region near equilibrium. Since we are very far from equilibrium we must use statistical methods, and the thermodynamic methods are no longer of any use;
- today's still incomplete understanding of the functioning of the aluminium production cell does not aid the understanding of titanium electrolysis. In fact we could not draw useful information from the knowledge of the electrolytic process for producing aluminium since its theoretical formulation is far from a common acceptance, Fig. 3;
- this state of matter is the consequence of the insufficient work performed in fundamental electrochemistry. The formalisms still used in the published literature on the subject are often devoid of a rational base and of a physical significance. In fact, when the metallurgist attempts to interpret the phenomena occurring at a working single electrode, and this is exactly what he is interested in, he gets entangled in matters of principles about thermodynamics of electrically charged species. This state of the science is especially pitiful when we remember how much electrochemistry has contributed to the development of thermodynamics (Nernst Nobel Prize);
- studying the published literature we can see that the electrochemists still have fear of entering deep into the matter, that is to abandon the reversible equilibrium conditions, in which the metallurgists have no interest, and to abandon the two-dimensional interface unrealistic model, for the three-dimensional interphase;
- large amount of work was done in the past for the determination of the values of physicochemical parameters in the absence of live electrochemical processes. Those data are of little use for designing industrial Electrowinning plants;
- there is no reliable reference electrode for electrochemical measurements in medium – high temperature molten salts;
- much work was done using oxides diaphragms ; however the presence of even

small amount of oxygen, coming from the corrosion of the diaphragm, complicates very much the Electrowinning process of titanium.

#### 4 The Limits of Chloride Electrolysis

A fundamental limit of the medium temperature chloride systems is the value of the density of the Catholyte, which is higher than that of the Anolyte (pure NaCl with Cl<sub>2</sub> gas dissolved), because of the Ti ions content and of the lower temperature (larger lines of current) of the catholyte.

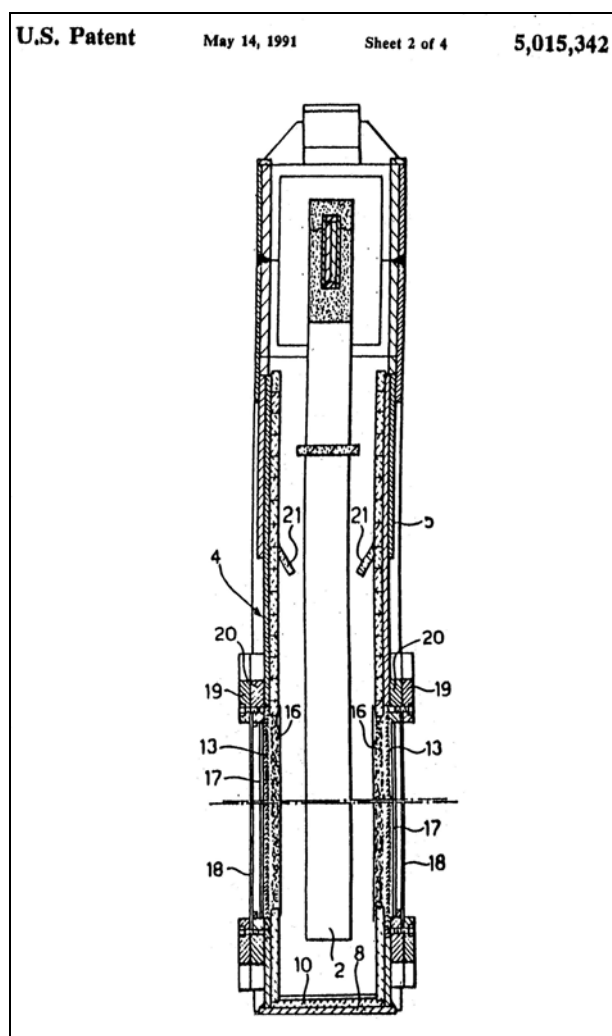


Fig. 2. Intermediate electrode

Anolyte and catholyte are in ionic contact through the Intermediate electrode metallic diaphragm (IE), nanoporous material, Fig. 2, [3] [Nobel Prize in Chemistry 2003]. This

situation generates differences in height of the two liquids that increases with the height of the electrodes.

That produces a labile equilibrium system because of the tendency of the anolyte to seep at the top thru the IE into the catholyte, and of the catholyte at the bottom into the anolyte.

Also large perturbations are produced by the cathodes harvesting and by the immersion of the mother cathodes which lower and rise the level of the catholyte generating pressure differences thru the IE. This effect results in catholyte seepage thru the IE into the anolyte; eventually Ti metal is reduced on the inside of the anodes box (TEB) then going to close-circuit them with the IE.

#### 5 Advantages of High Temperature Electrowinning

Many workers on high temperature electrochemistry are complaining on the lack of reliable experimental data, but very few of them venture to speculate on designing the experiments required to generate those new data.

The importance of making liquid cathodic product cannot be overstated since all industrial metals are produced liquid. And in the case of titanium the physical metallurgical operations of the ingots are expensive, thus the Electrowinning process should give a product with dimensions the closest to the final semi-finished product.

All the advantages of the aluminium electrolysis can be implemented in the titanium cell, in addition to the specific beneficial characteristics of the titanium system.

At above 1700°C titanium forms a liquid cathode with all the process advantages which are:

- complete physical separation between the metal produced and the electrolyte, with no entrapped electrolyte as with solid cathodes, thus no need for product separation steps as vacuum distillation or leaching;

- constant electrode surface area, that permits the maintaining of best steady-state values for the electrochemical process parameters;
- shorter interelectrode distance, thus lower operating voltages, since there is no need for allowing space for irregular crystal growth;
- easier coalescence of micro drops, metal fog, that are liquid, into the liquid cathode surface with horizontal geometry, as compared to chloride systems with suspended solid metal particles on solid cathode with vertical geometry;

Further, titanium Electrowinning has the following specific advantages with respect to aluminium electrolysis:

- raw material feeding is easier with liquid  $\text{TiCl}_4$ , as compared with solid alumina that needs special equipment because of slow rate of dissolution and hard crust formation;
- since titanium metal has a higher melting point than its electrolyte (it is the contrary with aluminium), a solid metal skull that contains the liquid metal cathode is spontaneously formed upon cooling;
- larger difference in density, at their operating temperatures, between the metal and the electrolyte.

### 5.1 Limits of High Temperature Electrolytes

For the stability of the solid electrolyte layers, additions that raise the temperature of primary crystallization are sought. The liquid electrolyte should have one phase.

The characteristics of the electrolyte and its composition are chosen for the high reaction rate with titanium raw material feed, that are conducive to the formation of titanium complex compounds that are promotive to the reduction reaction.

The titanium complex definition should satisfy the requirement that the valence of the titanium present in the electrolyte must be only one, in order to avoid the disproportionation reaction and the simultaneous oxidation-reduction alternate reactions at the electrodes, thus the need for a diaphragm.

The structural stability of the titanium species-carrying compound allows the configuration conducive to cathodic reduction.

The compounds we are experimenting with are producing species analogous to those suggested for the aluminium system Fig. 3. The striking fact is that the majority of the aluminium carrying species, going toward the cathode, are indicated as anions; this observation confirms that the cathodic interphase has a high degree of complexity. Also we have to consider the reactions in the catholyte between the intermediate products of interphase reaction and the electrolyte.

Raman spectra are reporting the presence of  $(\text{TiCl}_6)^{3-}$  and  $(\text{Ti}_2\text{Cl}_9)^{3-}$  in analogy with  $(\text{NbF}_7)^{3-}$ .

The difference of Ti system with respect to Al is that Al does not have a valence higher than  $\text{Al}^{3+}$ . The electrolyte prepared for Ti has the characteristics specific for  $\text{Ti}^{3+}$  as it was done for other systems, as for examples:  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{U}^{4+}$ ,  $\text{Nb}^{4+}$ ,  $\text{Hf}^{2+}$ , which also have higher valence states.

The combined presence of a monovalent alkali metal with a divalent alkaline earth metal has beneficial effect on maintaining Ti in the trivalent state only.

The process rate of the Ti cell is inherently higher than that of the Al cell because, at the higher temperature of operation, all the electrochemical parameters are more favourable, and also because of the need to generate enough heat to maintain the electrolyte temperature.

### 5.2 Operations

Knowledge of the viscosity of the electrolyte is necessary for the study of hydrodynamic processes, the convection in the electrolyte, the transport of gas bubbles from the anodes to the surface of the electrolyte. Surface properties directly influence the electrolytic process, as well as secondary reactions occurring in the cell. The characteristics of the interphase at the electrolyte/solid carbon anode, change with different additions and influence the selective intercalation of constituents of the electrolyte

into the graphite, as well as the separation of carbon particles from the electrolyte.

We need to avoid the formation of high electrical resistance anodic products. The graphite wettability is a function of the

interfacial tension gas/solid, gas/liquid and interphase solid/liquid. The study of the influence of additions on the conductivity of the electrolyte aims to increase the ohmic voltage drop in the electrolyte.

Authors	Method of investigation	Species
Abramov, <i>et al.</i> <sup>13)</sup>	Viscosity, density	Al <sup>3+</sup>
Rolin <sup>9)</sup>	Cryoscopy	AlO <sup>+</sup>
Rolin and Bernard <sup>29)</sup>	Cryoscopy	AlO <sup>+</sup>
Petit and Bourlange <sup>42)</sup>	Cryoscopy	AlO <sup>+</sup>
Boner <sup>43)</sup>	Phase diagram, X-ray analysis	AlO <sub>2</sub> <sup>-</sup>
Rolin <sup>9)</sup>	Cryoscopy	AlO <sub>2</sub> <sup>-</sup>
Foster and Frank <sup>44)</sup>	Activities	AlO <sub>2</sub> <sup>-</sup>
Foster <sup>46)</sup>	X-ray	AlO <sub>2</sub> <sup>-</sup>
Abramov, <i>et al.</i> <sup>13)</sup>	Viscosity, density	AlO <sub>3</sub> <sup>3-</sup>
Belyaev, <i>et al.</i> <sup>48)</sup>	Viscosity, density	AlO <sub>3</sub> <sup>3-</sup>
Rolin and Bernard <sup>29)</sup>	Cryoscopy	Al <sub>2</sub> O <sup>4+</sup>
Fréjacques <sup>47)</sup>	Postulate	Al <sub>2</sub> O <sub>4</sub> <sup>2-</sup>
Boner <sup>43)</sup>	Phase diagram, X-ray analysis	AlOF <sub>2</sub> <sup>-</sup>
Grünert <sup>48)</sup>	Electrolysis	AlOF <sub>3</sub> <sup>2-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	AlOF <sub>3</sub> <sup>2-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	AlOF <sub>5</sub> <sup>4-</sup>
Grünert <sup>48)</sup>	Electrolysis	AlOF <sub>5</sub> <sup>4-</sup>
Førland, <i>et al.</i> <sup>50)</sup>	CO <sub>2</sub> dissolution	AlOF <sub>5</sub> <sup>4-</sup>
Grjothheim, <i>et al.</i> <sup>51)</sup>	Cryoscopy	AlO <sub>x</sub> <sup>1-x</sup> (x = 3,5)
Førland, <i>et al.</i> <sup>50)</sup>	CO <sub>2</sub> dissolution	AlO <sub>2</sub> F <sub>2</sub> <sup>3-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	Al <sub>2</sub> OF <sub>x</sub> <sup>4-x</sup>
Sterten <sup>57)</sup>	Activities	Al <sub>2</sub> OF <sub>6</sub> <sup>2-</sup>
Holm <sup>41)</sup>	Calorimetry	Al <sub>2</sub> OF <sub>6</sub> <sup>2-</sup>
Kvande <sup>59)</sup>	Vapour pressures	Al <sub>2</sub> OF <sub>8</sub> <sup>4-</sup>
Førland <sup>4)</sup>	Theoretical considerations	Al <sub>2</sub> OF <sub>x</sub> <sup>4-x</sup>
Holm <sup>41)</sup>	Calorimetry	Al <sub>2</sub> OF <sub>2x</sub> <sup>4-2x</sup>
Ratkjæ <sup>52)</sup>	Cryoscopy	Al <sub>2</sub> OF <sub>x</sub> <sup>2-x</sup>
Petit and Bourlange <sup>42)</sup>	Cryoscopy	Al <sub>2</sub> O <sub>2</sub> F <sub>2</sub>
Treadwell <sup>53)</sup>	Phase diagram	Al <sub>2</sub> O <sub>2</sub> F <sub>4</sub> <sup>2-</sup>
Sterten <sup>57)</sup>	Activities	Al <sub>2</sub> O <sub>2</sub> F <sub>4</sub> <sup>2-</sup>
Ratkjæ <sup>52)</sup>	Cryoscopy	Al <sub>2</sub> O <sub>2</sub> F <sub>x</sub> <sup>2-x</sup>
Førland, <i>et al.</i> <sup>50)</sup>	CO <sub>2</sub> dissolution	Al <sub>3</sub> O <sub>2</sub> F <sub>14</sub> <sup>9-</sup>
Holm <sup>41)</sup>	Calorimetry	Al <sub>3</sub> O <sub>2</sub> F <sub>2y</sub> <sup>(2y-5)-</sup>
Brynestad, <i>et al.</i> <sup>49)</sup>	Cryoscopy	Al <sub>x</sub> O <sub>z</sub> F <sub>y</sub> <sup>(y+2z-3x)-</sup>

Fig. 3. K. Grjothheim *et al.* Suggested structural entities in molten cryolite-alumina mixtures

The measurements of the specific conductivity isotherms in molten binary mixtures are experimentally difficult mainly due to material problems.

The lowering of the specific conductivity by the addition of bivalent metal fluorides may be interpreted as a consequence of the increased viscosity which is effected by the addition.

This decrease in conductivity is relatively greater in the case of additions containing cations which are able to form complex ions with negative overall charge. This is still a difficult hypothesis for cathodic reactions that produce Ti metal.

Regarding the material of construction for liquid Ti producing electro-winning cell, the engineering solution is the solid electrolyte skin, maintained by external cooling over the container wall. Fig. 4 is a schematic representation of the cell thermal gradient in the electrolyte.

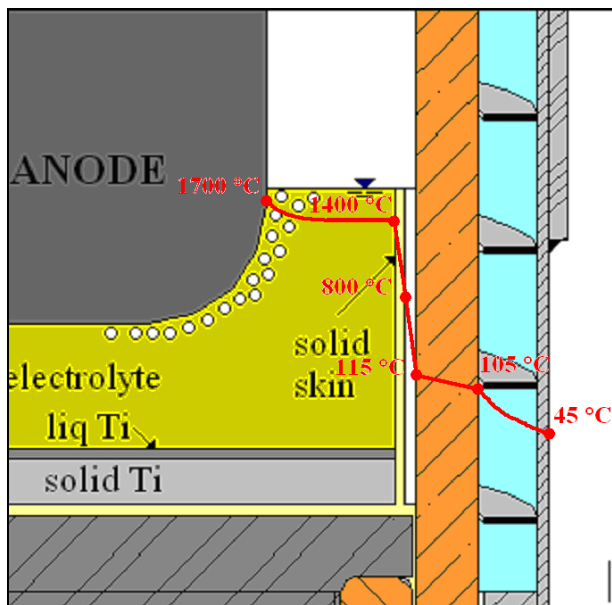


Fig. 4. Thermal regime

Adhering to the copper cell wall, the external side of the electrolyte solid skin, forms a solid Cu/salt irregular interspace physical contact, with high heat transfer resistance, but having good electrical conductivity. The internal side of the solid electrolyte skin, that has a high electronic conductivity, constitutes the electrode side of a cathodic interphase with the liquid electrolyte that has a high ionic conductivity. The study of the electrochemical processes occurring at this interphase is part of

the work in progress. Fig. 5 is a view of the harvested cathode with the electrolyte, of the 250 mm diameter cell.

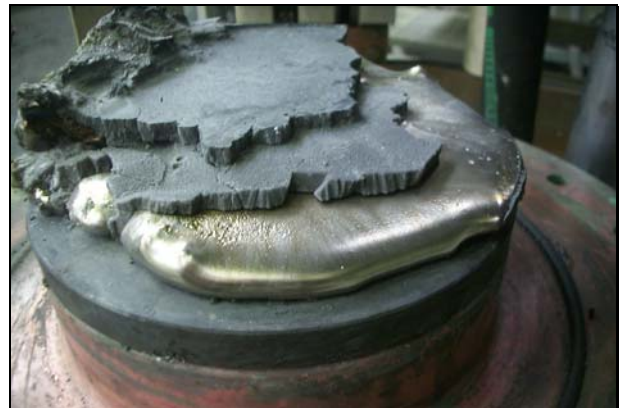


Fig. 5. Titanium cathode and electrolyte

## 6 Innovative Concepts Research

Our studies take into account concepts like the conduction of heat as inseparable from transfer of matter, and the electrolysis is a nonisothermal process. Within the cathodic interphase (the model we have conceived) [4], we are recreating the very reducing environment existing in the Kroll reactor with excess of magnesium metal, where the  $MgCl_2$  by-product drained out, does not contain any lower Ti ionic species, while  $TiCl_4$  is being fed.

The shape of the thermal gradient at the edge, solid-electrolyte/liquid-electrolyte/liquid Ti/solid Ti and mushy zone, Fig. 4, we refer to it as the “Szekely fundamental question” in our studies. At present, suitable wall-flux relationships are not available to represent the transfer process, nor data of surface tension electrolyte/metal. Samples indicating intense turbulent circulation have been obtained. This turbulent flow produces an enhancement in the diffusive transport of the thermal energy; the effective thermal conductivity can be hundred times larger than the molecular value.

Of critical importance to this process are the composition of the electrolyte and the understanding of the Electro-winning process inclusive of the anodic reactions. For  $CaF_2$  based electrolytes we have a high ionic conductivity that sustains high current densities, at the same time reaching a steady state heat balance at  $1700^\circ C$ . We assumed

that different % of the total Joule heat is lost through the cell wall.

The “Interphase Model” [4] is oversimplified with respect to reality and it makes many assumptions, but it allows us to propose some approximate mechanisms.

For the “Simulation of the Electrowinning cell” the real data obtained from the equipments of Fig. 6, are the object of the elaboration.



Fig. 6. Electrowinning cell

## 7 Conclusions

We need to persevere in developing the electrowinning of titanium, in particular the efforts should be directed towards improving the characteristics of the electrolyte and of cell materials.

## 8 References

Detailed references can be found in the following publications:

- [1] Ginatta, M.V., *Titanium Electrowinning*, Ti-2003, Proceedings of the 10<sup>th</sup> World Conference on Titanium, Hamburg 13-18 July 2003, p. 237-244.
- [2] Ginatta, M.V., *Titanium Electrowinning*, M. Gaune-Escard Symposium on Ionic Liquids, Marseille, June 26-28, 2003, p. 157-171.
- [3] Ginatta, M.V., *Selective Transfer of Charged Particles Along Charged Walls*, ECS May 9-13, 2004, San Antonio, Abs.
- [4] Ginatta, M.V., *Multilayer Electrode Interphase*, ECS May 9-13, 2004, San Antonio. Abs.
- [5] Ginatta, M.V., *Economics and production of primary titanium by electrolytic winning*, EPD Congress, Proceedings of the TMS, New Orleans, Feb.11-15, 2001. p. 13-41.