Titanium Electrowinning

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Abstract

To produce primary titanium at a lower cost a most innovative electrolytic cell has been designed, based on over 30 years of development work on the electrolysis of titanium, and it is being tested.

The cell works at high temperature, has a fluoride electrolyte and titanium metal is reduced in the liquid form with all the electrochemical benefits of a liquid cathode, as for example constant electrode area and constant anode-cathode distance.

Under the operational conditions there are no intermediate valence titanium ions in the electrolyte, therefore no need for diaphragms which limit the cell productivity.

The cell is fed with titanium tetrachloride and the dry chlorine gas produced is used in the integrated carbochlorination of titanium oxide raw material purification process, which in turn produces pure titanium tetrachloride feed for the titanium cell.

The fluoride electrowinning cell has many of the industrial advantages of the aluminium cell, plus other favourable characteristics specific of the titanium system, as for example larger difference in density between liquid titanium and the electrolyte, higher melting point for the metal than for the electrolyte. The solidified cathode slab obtained with the fluoride cell is suitable for direct rolling, with large savings in scrap generation, manufacturing costs and avoiding operations where LDI or HDI are introduced into the metal.

In synthesis, one electrolytic pot room replaces the several different plants used for current sponge production.

1 Introduction

Two years have elapsed since my previous presentation [1] on the work in progress at GTT on the high temperature electrowinning of titanium. The equipment depicted in photographs of Figs. 1 and 2 has been designed and built to be performing and instrumented in order to generate large amount of data under different experimental conditions.

The importance of making liquid cathodic product cannot be overstated since all the industrial metals are produced liquid. All the advantages of the aluminum electrolysis are implemented in the titanium cell, in addition to the specific beneficial characteristics of the titanium system. The electrochemistry of titanium is more complex than that of the other industrial metals and this is why titanium has not yet its commercial electrowinning process.

Therefore a new fundamental approach in the electrochemical development work was required and a model of three-dimensional interphase is used for representing the mechanism of the electrolyte-electrode reactions [2-3-4].
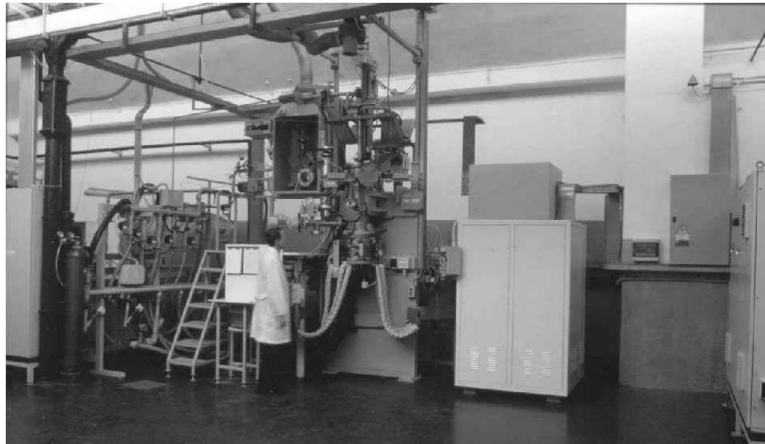
Figure 1. GTT High temperature electrowinning equipment.

Figure 2. GTT High temperature electrowinning cell.

2 Advantages of High Temperature Electrowinning

At above 1700°C titanium forms a liquid cathode with all the process advantages of aluminum electrolysis, 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 interelectrodic distances, thus lower operating voltages, since there is no need for allowing space for irregular crystal growth.
- Easier coalescence of microdrops, metal fog, that are liquid, into the liquid cathode surface with horizontal geometry, as compared with suspended solid metal particles on solid cathode with vertical geometry.

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

- Raw material feeding is easier with liquid $TiCl_4$ with much faster rate of utilization as vapor, as compared with solid alumina that needs special equipment because of slow rate of dissolution and hard crust formation.
- No cathode material problem for holding the liquid metal produced, since titanium has a higher melting point than the electrolyte (it is the contrary with aluminum). 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.
- With $TiCl_4$ feed, insoluble dimensionally stable graphite anodes are used (they have been the dream of aluminum people for many decades) since there is no anode consumption by chlorine evolution, thus no anode manufacturing cost.
- The purity of the titanium produced is higher than that of aluminum since $TiCl_4$ feed is purer than alumina and there is no anode impurity addition.

3   Medium Temperature Chloride Based Electrolyte

Let us summarize the knowledge that was generated by the development work done with electrowinning at temperatures lower than 900°C; that work has confirmed that the chloride system is very complex under that temperature.

The first main problem of the medium and low temperature titanium electrolysis is the multivalence of titanium ions, that is, the simultaneous presence of divalent and trivalent ions in the electrolyte: that is represented by the lines on the left side of the diagram of Fig. 3.

Since in general the conditions for electrolysis are better the greater the percentage of divalent titanium in the electrolyte, it is necessary to have the lowest concentration of trivalent titanium ions, that is to keep below 2.1 the average valence of titanium ions in the electrolytes. This condition requires that a separation between anolyte and catholyte be inserted into the cell in order to avoid the alternating oxidation and reduction of titanium ions which results in very low current efficiencies. The main difficulty for fulfilling that requirement is that, at the same time, we have to permit to chlorine ions to transfer between the catholyte, where they enter with $TiCl_4$ feed, to the anolyte, where they are evolved as chlorine gas from the anode.

The operation of intermediate electrodes satisfies the above requirements for a separation selective for titanium ions, but requires the engineering of complicated plants. This situation defies the original reasons that suggested the selection of low temperature electrolytic systems: simpler materials and design problems with respect to high temperature cells. In fact, Fig. 4 depicts a GTT intermediate electrode/anode assembly (called TA in [5]) which is composed of the central graphite anodes with, at each side, an intermediate electrode (called TEB in [5]).
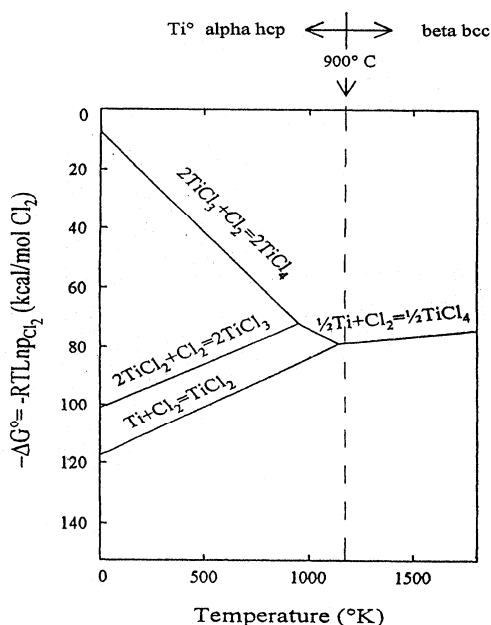

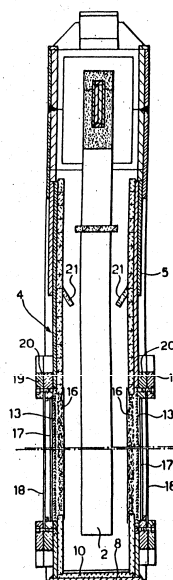**Figure 3.**   The standard free energies of formation of titanium chlorides. [4].

Figure 4.   The GTT intermediate electrode and anode assembly. [5].

The TEB maintains the separation between anolyte and catholyte, by using the "distal panel" deposition-dissolution mechanism.

The second main problem of titanium electrolysis at less than 900°C, is that titanium is produced in the solid state on the cathode, with crystalline morphologies of large surface areas and low bulk densities. The voluminous growth of titanium deposit requires its frequent removal from the electrolyte by means of handling apparatus of the kind depicted in Figs.9-11 of [6]. The stripped deposit entrains some electrolyte among the titanium crystals requiring a subsequent operation for removing the entrapped residual electrolyte. This operation inevitably decreases the purity of the titanium produced, which instead is very pure at the moment of its electrolytic reduction on the cathodes.

The electrochemical characteristics of titanium deposition onto solid cathodes limit the maximum current density at which the electrolysis con operate to low values, with correspondingly low specific plant productivity, with respect to liquid cathodes.

GTT solved many plant engineering problems of cell construction materials and ancillary equipment, however the production of dendritic titanium requires delicate process controls, precise operating procedures and high capital costs per ton of titanium production capacity, with the result that the overall production cost was still too high with respect to the price thresholds that we were given by the large new titanium application manufacturers.

The experimental results produced by GTT pilot plants MX3 (1985-1992) confirmed the calculated thermodynamic data summarized in Fig. 3.

In particular, the solidified anolyte that was removed from the anode/intermediate electrode assembly (TEB) working at regime conditions was always found to be colorless, in the presence of titanium metal crystals inside the assembly, without the slightest amount of Ti^{2+} or Ti^{3+} which would have given a green or purple color to the anolyte.

The reason is that, with the catholyte temperature maintained at 850°C, the operation temperature of the anolyte inside the TEB was always more than 900°C because of the resistance heat generated by the concentration of the lines of current within the TEB assembly. Further, Na° was present on the frontal side of the TEB.

The conclusions that interests us the most for the design of the titanium electrowinning cell are that at higher temperatures we solve the first problem of titanium, that is no more multivalence, no need for diaphragms, and operating at 1700°C we solve the second problem of titanium, that is no more dendritic solid deposit, but titanium reduced in the liquid state, as it is done for all other industrial metals.

Further confirmation of the need to work at higher temperatures comes from analyzing the operating conditions specified by Dr. Kroll for the best yield of his thermochemical process; which is electrochemical in the mechanism (why it does not form a heap of powder sitting on the bottom of the reactor, but it forms a spongy ring layer attached to the reactor steel wall ?) as explained by Dr. Schlechten during his lectures at CSM during the 1970', [7].

In the liquid magnesium chloride, byproduct of the magnesium reduction reaction, drained from the Kroll's reactor in operation, lower valence ions Ti^{2+} and Ti^{3+} are not present: only titanium metal particles are found.

The reason being that the reactor is maintained between 950 and 1050°C, measured on the outside of the bottom, by external cooling, since the $TiCl_4$ reduction reaction is highly exothermic, and by assuming a thermal gradient in the reactor we may conclude that the by produced $MgCl_2$ is always at a temperature of more than 1000°C.

Why Dr. Kroll would not have operated a more intense cooling to just above 720°C, the melting point of $MgCl_2$, greatly extending therefore the life of the reactors and limiting the titanium pick up of Ni and Fe, and also considering the Mg boiling point of 1100°C ?

4 Titanium Tetrachloride for High Temperature Electrolytes

In order to make use of the titanium-chlorine equilibrium over 1000°C, depicted in Fig. 3 where only one valence state titanium ion is present, high temperature halides are selected for the electrolyte to obtain liquid Ti. $TiCl_4$ is safely injected at high temperature in the electrolyte with high reaction rate and efficiency.

Let us summarize the advantages of using $TiCl_4$ as feed:

- For the titanium electrochemical system, a specific electrolyte is not available, that is equivalent to what cryolite is for aluminum, which could allow the feed of titanium oxides to the cell and obtaining titanium metal with an oxygen content within the current trade specification.
- Since titanium ore concentrates, synthetic rutile or slag are only 95-97% pure, a purification process is needed in all cases for removing the 3-5% impurities; in Table 1 are summarized the possible methods for purifying and producing titanium with their results.
- We can use the carbochlorination process to purify titanium raw materials, just as the aluminum industry uses the Bayer alumina refining process.
- Since we have the $TiCl_4$ as the intermediate compound of the chloride purification process, which is currently well developed with very large volumes and high purity, it is cheapest to directly use $TiCl_4$.
- From the electrochemical point of view $TiCl_4$ is the most easily decomposed halogenide and has a high rate of reaction (very high speed to completion) with the reductant in the electrolyte.

Table 1. List of processes for producing primary Titanium from minerals.

Processes for producing primary Titanium from minerals				Product	Defects
Purification Cl_2 +C $TiCl_4$ pure 99,9 %	Thermochemical reduction with Mg, Kroll		Distillation	Sponge	LDI, cost
	Two stages Na reduction		Leaching	Sponge	LDI, cost
	Chemical reduction in fused salts		Leaching	Powder	Impure
	Chemical reduction in liquid Zn		Zn distillat.	Powder	Cost
	Vapour reduction		Leaching	Powder	Impure
	Plasma reduction		Leaching	Powder	Impure
	Electrowinning in chlorides with diafragm		Leaching	Dendrites	Cost
	Electrowinning in chlorides inter. electrode		Leaching	Dendrites	Cost
	Electrowinning at high temperature		-	Metal	-
Chemical reduction Mg, Ca Ti impure	Chlorination to $TiClx$	Thermal decomposit.		Crystals	Cost
	Iodization to TiI_4	Thermal decomposit.		Crystals	Cost
	Bromination to $TiBr_4$	Thermal decomposit.		Crystals	Cost
Chemical reduction Al, Ca, C Ti impure alloy oxy-nitro-carbides	Electrolytic refining			Powder	Cost
Chemical reaction Na_2SiF_6 Na_2TiF_6 purification	Chem. red. with Al in liquid Zn		Zn distillat.	Particles	Cost, byprod
Chemical reaction K_2SiF_6 K_2TiF_6 purification	Chem. Red. with Al in fluorides			Powder	Cost, byprod
Purification H_2SO_4 TiO_2 pure 99,9 %	Thermal reduction Al, Ca, H_2, CO, CaH_2			Particles	Impure
	Electrowinning oxides			Particles	Impure
	Reactions CS_2, H_2S, P to TiS, TiP		Electrolys.	Powder	Impure
	Electrolytic deoxidation of TiO_2 in chlorides			Powder	Suboxides

5 High Temperature Fluoride Based Electrolyte

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

The multilayer cathodic interphase structure is created and maintained to be instrumental to the charge transfer in the titanium ion reduction.

The titanium complex definition 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.

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 Al system [8]. The striking fact is that the majority of the Al carrying species going toward the cathode are indicated as anions; this observation confirms that the cathodic interphase has a high degree of complexity.

Following is an example of an electrolyte composition with reaction with titanium raw material feed which is conducive to the formation of a titanium compound with a structural stability adequate to the metal cathodic reduction.

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

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

$$3\ CaF_2 + KCl + TiCl_4\ =\ TiKCaF_6 + 2\ CaCl_2 + \tfrac{1}{2}\ Cl_2$$
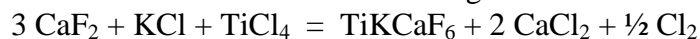
that in the cathodic interphase will rearrange into a dimer Ti_2F_6 which will become the cation Ti_2F^{5+} carrying titanium to the cathode.

Within the cathodic interphase we are recreating the very reducing environment existing in the Kroll reactor with 15% excess of magnesium metal, where the $MgCl_2$ byproduct drained out does not contain any lower titanium ionic species while $TiCl_4$ is being fed.

In the anodic interphase we are building and maintaining a steady state structure similar to that occurring in the aluminum cells at the carbon anodes, but more stable since there is no consumption of carbon. This dimensional stability of the graphite permits the shaping of anodes with non-consumable geometrical configurations that favor the smooth evolution of spherical bubbles.

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

6 Operations

Regarding the material of construction for liquid titanium producing electrowinning cells, the engineering solution is the solid electrolyte skin maintained by external cooling over the container wall. The high temperature electrowinning pilot plant presently in use, (Fig. 1), has

a 250 mm diameter cell assembly,(Fig.2). Fig.5 is a representation of the cell thermal gradient of the electrolyte cake and cathode depicted solid as withdrawn from the cell bottom in Fig. 6.
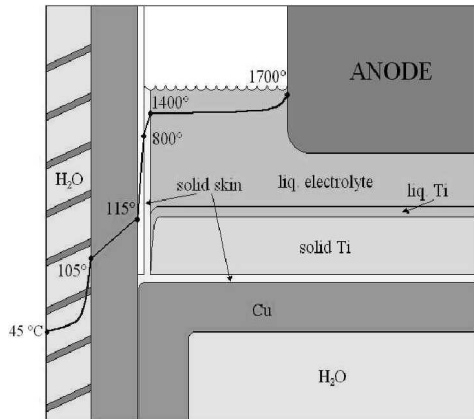

Figure 5. Thermal regime.

Figure 6. Solidified electrolyte and cathode.

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 high electronic conductivity, constitutes the electrode side of a cathodic interphase with the liquid electrolyte that has high ionic conductivity. The study of the electrochemical processes occurring at the transition interphase between the liquid electrolyte and the solid skin that is cathodically connected, is part of the work in progress.

For cold start-up operation an AC, 40 Volt 9 kA, power supply is used, while a DC, 30 Volt 6 kA permits ample selection of operating conditions.

The cell chamber is entirely enclosed gastight with controlled regime pressure. The solid electrolyte addition is through gastight screw feeder. The electrolyte is prepared by melting the salt mixture in an induction furnace.

The cooling system is designed and operated in order to maintain the solid electrolyte skin at the cell wall of a thickness of 1-3 mm, independent from the cathode cooling rate.

The injection of $TiCl_4$ into the fluoride electrolyte at around 1800°C occurs at very high rate and goes to completion; the metering equipment can inject liquid $TiCl_4$ at different rates following the applied current density, namely for 0.1 sec every 2. sec, with the injected volume, 0-2 cm^3/sec, being a function of the back pressure. With a differential manometer we observe the increase in pressure within the $TiCl_4$ feed pipe immersed in the electrolyte during the injection time and the following decrease in pressure during the absorption time. A $TiCl_4$ cold trap on the Cl_2 line checks for correct operations.

The selection of the electrolyte composition takes in account the need that the value of the ionic resistivity of the molten salt at the operation temperature, permits the generation of sufficient Joule heat, with the electrochemical set of operation parameters, in order to supply the energy for the overall reaction $TiCl_4 = Ti° + 2Cl_2$ while maintaining the electrolyte temperature at 1650-1800 °C. For low Volt and low current density regimes, AC is applied to generate the complementary heat, while the electromagnetic movements of the electrolyte and liquid cathode are studied.

With bubbles of Cl_2 evolving, the effective liquid electrolyte cross section is reduced, thereby counterbalancing the high value of ionic conductivity of the electrolyte, and it generates enough heat to counteract the anodic cooling effect.

The raw data acquisition system continuously monitors, collects and elaborates the 12 most important process parameters, as temperature inside the anode, of the electrolyte, of the gas in the chamber, rate of $TiCl_4$ feed, pressure differential, anode-cathode distance, kAh and the electrochemical data. Those primary data drive the automatic controls.

The results include the calculations to further detail the structure of the electrode/electrolyte multilayer interphase, to better design the electrolyte characteristics which destabilizes the titanium complex at the appropriate current density, and to determine the sequential charge transfer which is conducive to the most effective titanium ion cathodic reduction.

The complete simulation of the cathodic interphase is still beyond the capability of modern computers; however, even the above described partial insight is useful to the microscopic treatment of quantum chemical models, and molecular dynamics, in order to generate data needed to better understand the electrowinning processes.

The chemical analytical methods are under development to reach the routine high temperature analysis of the electrolytes and then the in-situ analysis with live electrolysis.

7   Conclusion

Presently we are elaborating the amount of data generated so far, to select the best set of operating conditions and process controls.

We are continuing the development work of high temperature titanium electrowinning as it is the only way to bring the primary titanium metallurgy up to the quality and cost requirements of the industrial potential applications of titanium.

8   References

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