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ECONOMICS AND PRODUCTION OF PRIMARY TITANIUM BY ELECTROLYTIC WINNING

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Abstract

Current world production, 60'000 ton/y, is exceedingly too small for titanium's extraordinary combination of favorable properties; it should be 1,000,000 ton/y (5.5 % of stainless-steel).
Prices that competitively sustain that sales volume are achievable only with electrolytic production, as it is for all other commercial nonferrous metals.
But titanium does not have its commercial electrolytic plants operating yet, because of the titanium producer’s decisions and strategies, scientists works, industrial problems with the chloride system, and lack of consumers and users sponsorship.
Fluoride high temperature process has the advantages of aluminum electrolysis, plus other favorable characteristics specific to titanium and its feed material.
One electrolytic titanium potroom replaces several different plants used for current sponge production.
Production of titanium ingots with zero defects is achieved.
The solidified cathode rectangular slabs are suitable for direct rolling.

Introduction

Warren Buffet stated that the investor must understand the industry before he will invest in. This is the basic difficulty of the titanium industry: it has not been understood yet. It is the duty of the technical people in each specific trade to educate the investors with fairness.

This is the purpose of my paper, which is meant to be a combination of economical and metallurgical considerations, where I wish to examine why it took so long to be ready for the electrolytic production of titanium to be commercial, as compared with all the other nonferrous metals which became industrial commodities after their primitive production processes were replaced by electrolytic plants.

Let us recall Dr. Kroll's [1] prediction mentioned in his 1959 Extractive Metallurgy Division Lecture of AIME [2]: *" It might, however, be fair to say, that titanium will be made competitively by fusion electrolysis within the next 5 to 10 years. "*

But, in his 1960 Sixth Castner Memorial Lecture in Glasgow [3], on the status of the Fusion Electrolysis of Titanium, Dr. Kroll concluded saying: *" The electrochemistry of fused salts has again reached an impasse and we need an electrochemist with practical aptitudes of Castner's* *genius to help us in overcoming the many difficulties of titanium and plurivalent metal electrolysis. "*

Instead all along the following twenty years much work was continued using the same traditional electrolytic cells with diaphragms.

Only J.C. Priscu, who in 1968 at the Extractive Metallurgy Division Symposium on Electrometallurgy [4] presented the Timet's titanium electrowinning cell [5], worked on the most advanced non-diaphragm basket-cathode type.

Prof. Kellogg, at the 1971 AIME Centennial [6] said : *"Titanium sells at the same price as nickel [*which is still today's range*], a much scarcer metal…, despite inexpensive titanium ore… The major problem for the titanium industry will be the development of processes to reduce the cost of converting titanium ore to metal. Design of a continuous process which produces crystalline metal presents formidable difficulties…"*.

During the 1970' I did my Ph.D. thesis on the fundamentals of the electrolysis of titanium at CSM [7] working among other scientists with Dr. Schlechten, who had been Kroll's coworker in the development of titanium and zirconium extractive metallurgy.

In 1983 the National Materials Advisory Board Commission published a report [8] on titanium which conclusions ended with the recommendations: *".. to encourage the pioneer titanium sponge producers to modernize their present plants and to encourage them and others to build more efficient greenfield plants."* Little has been done since.

During the 1980' my company GTT, advanced further the non-diaphragm chloride system [9-10] with a series of four pilot plants [11], one of which in cooperation with RMI [12] between 1988 and 91.

During the 1990' we advanced the fluoride system [13].

This anguishing slow pace of development is really embarrassing, especially as compared to today's rate of innovation of the computer and telecommunication industries.

Reasons for having the electrolytic titanium.

Let us analyze *why* we must have the electrolytic production of titanium and *what* will be our target production volume.

Most users, and recently also the aerospace people, are complaining that the prices of titanium mill products are too high and are demanding significant, *stable*, price reductions. Over the years many potential users of titanium gave us price thresholds, below which they will be able to purchase increasing volumes of titanium products.

Most people agree that the current world titanium production volume is far too small for its extraordinary combination of favorable properties (see the ITA 1999 booklet Titanium Facts [14], which summarizes them well) that sets titanium, for uses and applications, between the aluminum alloys and the stainless steels and copper alloys.

Since the world aluminum production volume is at about 24 million ton/year, the stainless at 18 million ton/year, and copper at 14 million ton/year (2000 data from AIM booklet [32]), I venture to state that the world production of titanium, appropriate to its combination of properties and to its worldwide abundant minerals availability, should be 1 million ton/year, instead of the current 60,000 ton/year. In terms of relative market sizes we would see Steel at 250 BEuro/year, Aluminum 50 BEuro/year and Titanium 10 BEuro/year.

But the price that will competitively sustain that sales volume will be achievable only by a primary production process, which is continuous and automatic, as it is for all the electrolytic processes of the other commercial nonferrous metals.

Some people occasionally keep telling me that primary titanium market will be dominated by the low wages nations. I usually remind them that today, and ever more in the future, the dominant factor is the more efficient production technology environment, as the USA economy has shown during the last 20 years.

Excellent books on the subject of the future of materials have been published by J. Simon [15] who, studying the history of primary materials, saw that their costs have been steadily decreasing since the beginning of their industrialization due to continuous technological improvements both incremental and quantum. Consequently it should not be too adventurous to predict that this behavior will continue in the future, also with the contribution of our work.

Historical comparison with aluminum and stainless steel

Also a look at the history of titanium production shows us how much the electrolytic plant is overdue.

The annual growth rate of the USA domestic titanium mill product shipments from 1951 to 1978 was 12%, in Graph 1 (see J.V.Andrews on 1999 ITA Conference [19]), which is comparable to the introduction stages in the histories of aluminum and stainless steel.

However, titanium annual growth from 1979 to 1998, which should have been its growth stage, has been only 2.5%, while its average price, in real terms, did not change much in Graph 2 (note 1971 equals 1998 [19]).

On the contrary, aluminum production doubled between 1940 and 1950 (from 0.78 to 1.50 million ton/year) while during the same period the price, in constant dollars, halved (from 2.39 to 1.12 $/kg); furthermore between 1950 and 1960 its production tripled with continuing decrease in cost of electrolytic production, while the strong demand resulted in increasing prices which allowed the financial consolidation of the aluminum producers. Between 1964 and 1973 the production increased six fold in Japan (see Y. Oda on 1999 ITA Conference [20]), which is approximately 25% every year.

That growth has occurred because the electrolytic production technology for aluminum was previously developed and the electrolytic aluminum plants were commercial at the time the market growth started.

Modern plants and installed production capacity that exceeds world's demand are the key elements to the stable supply and market price metal products; this has been the historical state of steel and aluminum markets.

Therefore, it is very apparent that at the end of its introduction stage, at the onset of the growth stage of its history, (in the typical “S” growth curve) titanium lacked an adequate primary electrolytic production technology to propel its market growth. Thus the <u>non</u> availability of low cost primary metal has been the factor limiting titanium's growth.

As mentioned in the introduction, the need to replace the thermochemical process has been very evident since the 1960' [2] because it was, already then, technically obsolete being slow, discontinuous, and its cost of production was impossible to reduce.

Also looking to the history of the other metals, produced by electrowinning since many decades, we see a growth pattern similar to that of aluminum, and particularly relevant is stainless steel (also nickel and chromium are produced by electrolysis) in which we see annual rates up to 40 % for Japan (see Oda [20]).

Therefore, the prediction of a titanium world annual production of 1 million ton/year (corresponding to 5.5 % of today stainless steel production) if attained over a period of 10 years, with a series of start ups of new electrowinning plants, will be a 33% growth per year, which can be realistic, on account of the enormous industrial retard of titanium and of the large amount of operational data that are being produced in the last few years.

One example for all; recently the food processing industry has published a comparative study for a dressing-sauce producing plant made of titanium, whose performance is compared with the traditional plant made of 316 stainless steel. After 4.000 hours of operations during a two-year period, the performance of the titanium plant has been not only better but is improving the longer it is working, where instead the 316 is degrading as expected.

Particularly the quality of the titanium surfaces contacting the food material is improving; these surfaces are much more easily cleaned, and the plant consumes less energy (see Amorati [33]).

Current titanium production status

In the last ten years, the cost of production of primary titanium by the present thermochemical plants (Kroll sponge) did not decrease, while all the other industrial metals processes did significantly decrease their costs of production through technological improvements.

There are several reasons for the high cost of current production plants, the main being: they cannot be operated continuously and do not permit the recovery of the large amount of energy released by the exothermic reaction.

No new long term planning investor would invest more in the current obsolete thermochemical technology, while there is a deficit in primary titanium production in USA and no primary titanium is produced in EU.

The amount of sponge needed to support mill products made in the USA far exceeds the domestic production capacity. Imports of titanium raw materials from CIS, Japan and China are critically important even during low market crisis periods [16]. All European requirements are imported.

This situation is generating the extreme cyclicity of titanium market, since during boom times titanium customers tend to purchase much larger quantities that they need for that time period, in order to cover their future production needs, since they have previously experienced long delivery times (up to 80 weeks). This behavior drives the prices to high levels, which momentarily satisfies the producers but, very regrettably, discourages the entering in the market of new users of titanium, especially the large volume new application industries, like the automotive. They will not commit new application development investments in the absence of a modern, reliable, production capacity of titanium, which would guarantee reasonable product availability and fairly stable prices, as they are used with all other metals.

During bust times customers work out their excess inventory and purchase much less titanium, sending the titanium producers into deep financial troubles.

The cost of titanium (*sale price)* is perceived by the general public as high also because of marketing strategies of some manufacturers which are benefiting from titanium glamorous image to set high sale prices to their products, independently of the industrial real costs; for example in a $3,000 titanium bicycle there is probably less than $300 worth of titanium.

However, how do we ascertain the price of titanium at any given time ? There is no official quotation of titanium in commodity exchanges like the LME or Comex as there is for all the other industrial metals. The titanium industry market is structured for spot business on the basis of trading over the phone, fax, e-mail, or long-term agreements which terms are kept confidential. There are some reference prices occasionally published, created by journalits telephoning a number of companies and forming a subjective opinion on prices.

What is generating the extremely long delays in delivery times during boom times ?

Certainly not the upstream chemical metallurgy of titanium minerals, since it is a 5.000.000 ton/ year industry that can easily adjusts for the plus or minus 50.000 ton/year required by the current titanium metal producing industry.

Certainly not the downstream metallurgical manufacturing capacity for sheets, rods and all other semifinished products, since titanium uses the large available excess plant capacity of the stainless-steel industry.

Concluding, the basic problem of titanium industry is precisely resulting solely from the bottleneck constituted by the present obsolete insufficient production technology of primary titanium metal.

Good analyses of the current status of the production and market of titanium have been recently published by M. Cariola [17], and by N. Tunna [18].

Reasons why it took so long

To answer to *why* we are so very much overdue in the commercialization of the electrolytic titanium, we have to consider the following five major reasons.

Producers' decisions and strategies:

- to follow primarily the aerospace market 4-5 year cycles, resulted in a succession of booming periods during which there was no time for waiting for the development of new techniques, where any available process, even if obsolete, was installed to get production for delivery; and of bust periods with little resources available for new technique developments;
- of working on short-medium term programs to develop high quality products in order to achieve high sales prices (over 30$/kg average product price) on low volume production, instead of committing resources on long term-large scale programs in order to decrease the basic costs of ingot production;
- of non-transparent pricing policies: it is not easy to find published data on titanium industry among the large body of news regarding the other commercial metals; this lack of information has been frustrating the investors' interest about titanium.

Scientists' work:

- the inadequate state of development of the theory of molten salts in fundamental electrochemistry has retarded the industrial progress in general. Models for the electrode/electrolyte system are still conceived as bidimensional quiescent interfaces at reversible equilibrium conditions in dilute solutions, even with current densities of 1 A/cm2 where there is an exchange of 2,000 atomic layers each second, and in molten salts which are the limit of concentrated solutions, since there is no solvent;
- the insufficient theoretical understanding of the titanium system has slowed the technological development of the electrolytic plant engineering. In order to improve the industrial electrolytic process, we needed to take decisions which involve changes in physical operating conditions; we needed therefore, to reach a practical understanding of the physical meaning of the data which describe the operative conditions of the process;
- today's still incomplete understanding of the functioning of the aluminum production cell did not aid the understanding of titanium electrolysis. In fact we could not draw useful information from the knowledge of the electrolytic process for producing aluminum since its theoretical formulation is far from a common acceptance;
- this state of the 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 the electrochemistry has contributed to the development of thermodynamics;
- studying the published literature we can see that the electrochemists still have fear to enter deep into the matter, that is to abandon the reversible equilibrium conditions, in which the metallurgist has no interest, and to abandon the two-dimensional interface unrealistic model;

- large amount of work was done in the past (and also today), in the determination of values of physicochemical parameters, in the absence of live electrochemical processes; these data are of little use for designing the industrial electrowinning plants;
- much work was done using oxide diaphragms; however the presence of even small amounts of oxygen, coming from the corrosion of the diaphragms in the electrolyte, complicates very much the electrowinning process of titanium;
- efforts were made to attempt to produce commercially acceptable liquid titanium by direct electrowinning titanium dioxide from 1971 [21] to recently [22], and to electrolyze titanium dioxide at less than 1000 °C in calcium chloride were made from 1955 [23] to recently [24]. Graph n. 3 summarizes the impossibility to both obtain lower cost primary Ti and Ti with low oxygen content as required by the ASTM specifications; the physical significance is that we have to maintain at all times in the electrolyte a very high activity of Ca and at the same time a very low activity of CaO. These operating conditions are impossible to obtain in an industrial production plant.
- currently, very few universities and research centers are working on industrial molten salts electrolysis;
- not enough study was performed on the large amount of experimental results produced by the non-diaphragm full scale electrolytic cells during the pilot plant campaigns of the 1980's, Fig. 1-2-3-4-5-6 ;

Industrial problems with the chloride system:

The diagram in Fig. 7 summarizes the basic data of titanium electrochemistry. The left side is meant to show that below the temperature of 900 °C there is a complex chemistry; however, because of the lower temperature the plant engineering and materials problems are simpler. On the right side, above 900°C we see a simpler chemistry, however the engineering design is more challenging.

- The lower line on the left side of the diagram represent the equilibrium between titanium in solution ready to be extracted by electrowinning, and solid titanium. The medium line, above the previous, represents the equilibrium between titanium in solution ready and titanium intermediate species not ready yet for electrowinning. When the operating conditions, for any reason, drift out of the specified values, the disproportionation occurs, that is, the titanium in solution both goes back to become intermediate species and, simultaneously and irreversibly, goes out of the electrolyte as solid particles. These particles settle as a sludge on the cell bottom, lowering the electrical current efficiency of the process, and requiring their removal because of interference with the electrodes and the electrolyte circulation. To avoid this disproportionation reaction the maintaining of a precise operational control is required as illustrated in Ref. 10. Furthermore, the equilibrium between Ti^{2+} and Ti^{3+} is very easily affected by contaminants in the electrolyte and by materials of construction of the cell especially oxides.
- The medium line of the left side of the diagram in Fig. 7 represents one of the problems of low temperature titanium electrolysis: the multivalence of titanium ions, that is, the simultaneous presence of divalent and trivalent ions in the electrolyte. Since the efficiency of the electrolytic production is greater, the greater the percentage of divalent titanium, it is necessary to have the lowest concentration of trivalent titanium, that is, to keep below 2.1 the average valence of titanium ions in the electrolytes. For this requirement it is necessary to prevent the migration of titanium divalent ions by diffusion into the vicinity of the anodes, where chlorine is evolved, in order to avoid the oxidation of the divalent into the trivalent titanium. That is, a separation between anolyte and catholyte is required to avoid alternating oxidation and reduction of titanium ions resulting in very low electrical current efficiencies. The difficulty is that,

at the same time, we have to permit the chlorine ions transfer between catholyte and anolyte. Here we see why so much work, for so many years, has been done in devising physical diaphragms which were to prevent the passage of small titanium ions and, simultaneously, had to permit the free passage of the relatively much bigger chlorine ions. Even considering titanium-alkali-chlorine ions complexes it has been hopeless.

- The operation of intermediate electrodes satisfies the above requirement for a separation selective for titanium ions but requires the engineering of complicated plants. Fig. 8 depicts a GTT intermediate electrode/anode assembly (called TA in Ref. 10), which is composed of the central graphite anodes with, at each side, an intermediate electrode (called TEB in Ref. 10).
- The TEB maintains the separation between anolyte and catholyte, by using the "distal panel" deposition-dissolution mechanism. Fig. 9 depicts a diagram of the voltage gradient, from the anodes to the cathodes, through the GTT intermediate electrode; the family of dotted lines from the distal side of GTT electrode to the front of the cathode depicts the window of voltages for correct operation of the electrolytic process. The upper line indicates the minimum voltage for preventing titanium ions from diffusing towards the anode, while the lower line indicate the maximum voltage before sodium reduction on the distal side.
- Fig. 10 shows the TEB electrode wire net supporting the microporous distal titanium panel (indicated by the arrow) which is magnified in Fig. 11 to shows the fine titanium structure, cathodically connected, that allows the transit of chlorine ions while reducing and depositing the titanium species. We worked with the Politecnico di Torino on the interpretation of the bipolar electrode mechanism [25].
- Titanium is produced, with the chloride system at less than 1.000 °C, in the solid state on the cathodes, with crystalline morphologies of large surface areas and low bulk densities, Fig. 6. The growth of the titanium deposit requires its frequent removal from the electrolyte by means of handling apparatus of the kind described in Fig. 2-3-4, Ref. 9. 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 limits the maximum current density at which the electrolysis can be operated to low values, with correspondingly low specific plant productivity, with respect to liquid cathodes. Our work with RMI solved many plant engineering problems of cell construction materials and ancillary equipment; however the production of solid dendritic titanium requires delicate process controls, precise operating procedures and high capital cost per ton of titanium production capacity, with the results 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 consumers.

<u>Much more work was done with chlorides than with fluorides</u>:

- because the chloride system was perceived as being easier to work with lower operation temperature, lesser material problems, besides much more data and bibliography were available;
- development programs with chlorides had higher feasibility rating than fluorides, thus larger financing was available for chlorides, which operations of full size prototype cells produced large masses of experimental results;
- prototype work with fluorides obtained comparatively less financing because the investors feared that a higher temperature system would have greater problems.

Customers, titanium end product users, sponsors :

- over the years, only very few companies in the titanium industry have invested in R&D for the development of the low cost primary electrolytic titanium, and within the limits of their financial strength, contributed to further the progress with works which were indispensable to get to the next stage of development; they are listed in Tab. 1.
- the large sale volumes end product potential users, did not participate to this development effort: none is listed in Tab. 1.
- titanium has not had its Sponsor yet, as many other metals did in their development history;
- as mentioned at the beginning of this paper, much of the blame for the present state of the titanium industry is on us, since we did not make the effort to inform the investors about the scrupulous technical development that has been done in the last 20 years on titanium electrowinning. Instead, the investors were left to read the often misleading published literature, with the very sad consequence that the investors readily feel the technical confusion and consequently choose to stay away from titanium altogether.

This state of matter has contributed to make the development of the electrowinning of titanium harder, longer and painful.

Present status of titanium electrowinning

First, why electrolysis and in particular fusion electrolysis, one may ask considering the wide variety of processes available from today metallurgical technologies, as summarized in Tab. 2.

The answer is in the first word of my paper's title: "economics".

I have been producing titanium with different processes for many years and found that the engineering of plant and process operations are most effective with electrowinning.

The main metallurgical reasons for the need to use molten salts electrolysis to produce titanium are:

- the minimum temperature for thermal reduction of the raw materials are too high for an acceptable life of today's available industrial pyrometallurgical equipment materials;
- the formation of by-product compounds hampers the separation of the solid metal powder produced in pyrometallurgical reactors;
- the electrochemical characteristics of titanium are such that it is impossible to produce it in aqueous solutions.

The basic principles of electrochemistry apply to fused salts electrolytic processes, anode and cathode products are analogous to aqueous solution electrolysis, but chemical reaction rates are much greater, therefore the productivity in fused salts is much higher.

The specific conductance of a molten salt is very much greater than that of the same salt in aqueous solution; for instance, KCl at 800°C has a specific conductance which is approximately 22 times grater than that of its molal aqueous solution at 20°C.

Since there is no hydrogen in the molten salts system of our interest, we can apply current densities, which are as much as 500 times greater than the maximum ones applicable in aqueous solutions for the same metal; thus the cell production rate with molten salts is much larger.

In fused salts there is no solvent, in the sense of water in aqueous solutions; the fused salt itself, which is an ionic compound in molten state, may be considered as the limit of a concentrated solution.

The electrochemical potential series of the metal ions depends on the nature of the anion present. The absence of a unique solvent, as water in aqueous solutions, makes it difficult to establish a general electrochemical series to be used as a reference for relative potentials for fused salts. However, have been established a series of potentials for each anionic system: Chlorides, Fluorides, Bromides, and Iodides.

Since the operational temperatures in fused salts electrolysis range roughly between 200°C and 2,000°C the temperature dependence of the ions potential is very marked, and its relative position with respect to other metal ions changes.

Fusion electrolysis is a powerful production technique, which allows freedom of choice of the optimum set of conditions for each metal chemical specification at high rate of production. The history of the improvements of aluminum electrolysis proves that.

The study of the large mass of experimental results produced by works on the electrolysis of titanium in chlorides during the 1980', which were insufficiently analyzed at that time because of the interruptions in the development programs due to the negative periods of titanium market cycles, brought the understanding of the industrial problems of the chloride system as illustrated above.

As an example, during the operations of dismantling of anodes/intermediate electrode assemblies of GTT's MX cells, which were removed because being near the end of their useful life, the solidified anolyte contained was always found to be clear 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 of 850°C, the operation temperature of the anolyte was always more than 900°C because of the resistance heat generated by the concentration of the lines of current within the anode/intermediate electrode assembly.

To confirm the above there is the instance regarding the thermochemical process, in which Ti^{2+} and Ti^{3+} ions are not present in the $MgCl_2$ drained from the Kroll's reactors: only Ti° metal particles are found. The reason being that the thermochemical process operates at above 1,000 °C and as we see in Fig. 7, depicting the diagram of standard free energy of formation of titanium chlorides, above 900°C there is no divalent nor trivalent titanium ions but only Ti^{4+} and Ti°.

From what discussed above, we see how wonderful are the various ionic liquid structures and the energy densities of the titanium system at different temperatures, and if we note that at 888°C solid Ti° transforms from the low temperature alpha close packed hexagonal structure into the high temperature beta body centered cubic, we realize that we begin to understand the titanium system.

The conclusion that interests us the most for the design of the titanium electrowinning cell is that at higher temperatures there is no need for diaphragms any more and there will not be any disproportionation reaction any more.

Consequently, as discussed in my M.Sc. thesis at CSM in 1970 [26], the solution of the industrial problems with the chloride system is the higher temperature fluoride system.

During the 1980' we maintained an ongoing parallel fluoride program that required much work toward getting understandable information of practical usefulness about the processes occurring at the single electrode, under steady state dynamic regimes, at the microscopical level, away from the reversible equilibrium conditions. That work was a development based on my Ph.D. thesis at CSM [7].

During the 1990' we concentrated in the development of the fluoride system [13].

Advantages of higher temperatures

At above 1700°C titanium forms a liquid cathode with all the advantages of aluminum electrolysis, which are:

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

- constant electrode surface area, which permits the maintaining of best steady-state values for the electrochemical process parameters;
- shorter interelectrode distance, thus lower operating voltage, since there is no need for allowing space for irregular crystal growth;
- easier coalescence of microdrops, metal fog, which 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 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 titanium skull that contains the liquid metal cathode is spontaneously formed upon cooling;
- larger difference in density, at the 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 plant cost;
- electricity cost savings are obtained by scheduling the interruption of current supply to the cell, for the removal of the solid titanium slab, during electricity peak hours;
- the impurity content of the solid ingot produced is further reduced by an effect similar to zone refining where impurities have larger solubilities in the liquid than in the solid.

The importance of making liquid product cannot be overstated, as almost all tonnage metal made by molten salt electrolysis is produced as liquid: aluminum, magnesium, sodium, lithium (see Sadoway [27] and Kellogg [6])

Titanium tetrachloride

We favor $TiCl_4$ as raw material in the electrolytic production, for the following reasons:

- 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 a oxygen content within the current trade specifications;
- since titanium ore concentrates, synthetic rutile or slags are only 95-97% pure, a purification process is needed in all cases for removing the 3-5% impurities (Tab. 2); we can use the carbochlorination process to purify titanium raw materials, just as the aluminum industry uses the Bayer alumina refining process;
- oxygen is a very difficult element to deal with in titanium metallurgy; it makes the electrochemistry of titanium exceedingly complicated for industrial processes that want to produce metal within the ASTM specifications; it is very desirable to have oxygen out of the system from the start. Since any kind of purification process is based on the conversion of titanium oxides into some other compound, it is much cheaper to directly use that compound as raw material for producing the metal; it is a technical nightmare even to think of going back to the oxide and having to pay the cost of that additional operation. Graph n. 3 illustrates the difficulties of the thermal reduction of TiOx [34];
- the carbochlorination process is currently well developed and the $TiCl_4$ industry has already very large sale volumes (over 5 million ton oxides/year); it should not be a

problem to install new worldwide $TiCl_4$ production capacity to feed the growing titanium metal needs;

- the chemical purity of commercial $TiCl_4$ is currently very high because the white pigment industry cannot accept coloring impurities, and the metal produced by the thermochemical process can only be less pure than the feed;
- the electrolytic fluoride process has some impurity refining capability and it can accept less pure, less expensive $TiCl_4$, and still produce ASTM metal. Discussions are under way with $TiCl_4$ producers to determine how the carbochlorination plant can be simplified in order to reduce production cost. Some of the elements which are regarded as impurities by the pigment industry, are actually alloying metals for titanium alloys (Al, Fe, Nb, V, Zr);
- the commercial establishment of a second type of $TiCl_4$ of a lower purity and lower cost will be very advantageous in order to reduce the overall cost of titanium electrolytic production, since $TiCl_4$ is the single highest cost item. It is understood that a second brand of $TiCl_4$ could only be obtained by the producers when the volume of the production of electrolytic titanium will be larger;
- aluminum industry has desired for a long time to use $AlCl_3$ since the electrolytic cell operates very well; however, the physicochemical characteristics of $AlCl_3$ and the operating conditions of the chlorination plants have so far, apparently, hindered the commercial use.

Technical objections to fluorides

Over the years there have been objections presented by the investors fearing that the full size prototype plant would have problems related to carbide formation, fluoride inclusion, construction materials, and backreactions.

There will be no titanium carbide formation in large size cells, because using $TiCl_4$ as raw material in fluoride electrolysis, the graphite anode is sheathed, during operation, with layers of chlorine over layers of fluorine which are steadily bound to surface carbon atoms; there is no possibility of physical approach between titanium and carbon species.

For an analogy, in aluminum cells the mechanism of formation of Al_4C_3 requires the three-phase point: C(solid) + Al(liquid) + $O^{=}F^{-}$(electrolyte).

Further, in aluminum cells under cathodic potential on carbon the formation of carbide is kinetically favored, while under anodic potential it has an extremely slow kinetics.

In titanium cells carbon is only and always under anodic potential.

As for chemical reactions, carbon dust from anode spallation only floats on top of the electrolyte and does not enter it; CaF_2 fosters the carbon dust floating.

In analogy with the mechanism of carbochlorination, an electron donor is needed (TiO_2 chlorinates only in the presence of carbon). With liquid titanium, CaF_2 and graphite, but without oxygen in the system, there is no TiC formation (at least TiO_x is needed). In a method for producing TiC commercially from titanium metal, propane with water vapor are used.

Finally, if for any reason TiC is present dissolved in the electrolyte, it undergoes the electrolytic separation with carbon deposition on the anode.

There will be no fluoride inclusions in large size cells, since the electrochemical process occurring at the cathode interphase guarantees the separation between the electrolyte and the liquid metals for any cell dimension.

For an analogy, titanium ingots obtained by electroslag remelting under CaF_2 have a F^- content of about 60 ppm. However, we have to consider that ESR is a fast process, with large mass transfer by high melting rate, due to fusion of the upper metal electrode. A stream of liquid metal drops fall through the liquid slag due to the large difference in specific gravity, and splashes on the liquid upper surface of the solidifying ingot. A small finite amount of entrapment of fluorides is to be expected within this agitated liquid slag/metal ingot interphase.

Further, the large ex-USSR nuclear submarines have a titanium hull, which was fabricated by welding plates 200 mm thick with electroslag welding under CaF_2. Under the severe stress of submarine applications no problem has been reported which could be related to fluoride inclusions.

Titanium electrolysis has a much slower process rate (100 times) than ESR, and the metal arrives at the cathode by ion migration (not by element gravity fall) thus it allows a complete separation of the metal from the electrolyte.

So far, there is no evidence of any effect of the fluoride very low content on the characteristics of titanium. Only the aerospace customers do not allow, at present, secondary phases or compounds, thus we have to go through the certification procedure.

There is no proven technical issue but we must face the fact of life that, like most customers, they prefer to take no chances, thus they tend to resist any change until … we can offer titanium at a lower price.

Regarding the equipment and construction materials for the fluoride system we have designed prototype cells operating airtight with thermal regimes maintaining the solid electrolyte skin, in analogy with aluminum cells and electroslag furnaces, Fig. 12.

External cooling of the structure makes the internal surfaces covered with a layer of solid condensed electrolyte that protects the materials from hot gas corrosion.

Chlorine gas evolution does not consume the graphite permitting thus the anodes to be shaped with geometrical configurations which favor the smooth evolution of small spherical bubbles from the operational electrolyte, as discussed by the group of Prof. Chemla [28]. This mode of operation cannot be used in the electrowinning from titanium oxides since the CO/CO2 producing reaction consumes the carbon changing the anode shape to a geometry which favors the formation of large bubbles which coalesce in big gas volumes that, when separate from the anode, generate perturbations to the process.

The solubilities of the gas and the metal in the electrolyte are very low and the backreaction is not significantly affecting the current efficiency. In fact, anodic molecular gas bubbles do not react with the cathodic liquid metal produced, because it is only the gas atomically dissolved in the electrolyte which reacts only with the metal solubilized within the electrolyte.

During the operations of GTT's MX type electrowinning cells, we always saw, upon opening an anode/intermediate assembly which failed, a titanium metal crystalline mass surrounding the graphite anodes, having channels in the titanium body where anodic gas had been streaming out during the terminal period of electrolysis.

Beck [29] operated an inverted aluminum cell with a copper metal anode at the bottom and a TiB_2 cathode at the top. Bubbles of oxygen evolving from the bottom anode raise through the electrolyte crossing with aluminum metal droplets dripping from the top cathode, while alumina particles remained suspended in the electrolyte. When the produced aluminum is continuously removed the current efficiency is said to be close to 100%.

In the Alcoa horizontal multiple bipolar electrode aluminum cell, chlorine bubbles raise in the center well, generating an uplift of a mixture of electrolyte and small aluminum droplets. The resulting specific energy consumption is 9 kWh/kg Al; the remaining loss in current efficiency is due to shunt currents bypassing the series of bipolar electrodes.

As for electronic conduction of liquid fluorides, in the range of electrolyte compositions used, under operating conditions we did not find appreciable effects; the works of Sadoway [30] exhaustively discuss this subject.

Direct production of slabs

The solidified cathode rectangular slab obtained with the fluoride electrowinning plant is suitable for direct rolling. This is a large saving in manufacturing costs and scrap internal generation over the current thermochemical-metallurgical operations where there is formation of nitrides of titanium during removal of the sponge cake from the retort, and where the alpha-case contamination occurs during high temperature press-forging of cylindrical ingots.

For analogy, it has been reported by the USA Air Force Materials Laboratory [31] that the electroslag remelted titanium slabs are suitable for immediate conversion into plates and sheet products, which have better hot workability, superior toughness properties and slightly better creep strength than VAR material.

The slow mass transfer of the fluoride electrolysis permits the maintaining of a shallow horizontal layer of liquid metal, (not a deep central pool with hyperboloid liquid/solid profile typical of remelted titanium ingots) thus providing the best metallurgical conditions for the solidification; it results in a more vertical freezing pattern and a better soundness of the ingot as compared to usual melting.

The amount and cost of specific inspection techniques requiring labor hours is consequently reduced since there are no LDI nor HDI, because of the characteristics of the electrowinning process.

We hear that although titanium alloys are recognized as having excellent fatigue resistance, there is the belief that in the practical applications it could be the risk that the presence of a defect or an inclusion would start a crack. This fear is eliminated with electrolytic titanium.

Current industry operators remind me that the present commercial titanium slabs contain about 50% low cost scrap. I answer pointing out that, historically, the aerospace industry has been the largest buyer but not the largest consumer of titanium, since about 75% of the metal purchased, after fabrication goes back into the market as scrap. When the titanium sector will became a general industry, the relative importance of aerospace will decrease, so will the availability of low cost scrap, as it has occurred in the aluminum industry history. Furthermore, the presence of high-density inclusions in the scrap is always a threat that often materializes in recalls of defective products with the associated financial losses.

Conclusions

The lower production cost of electrolytic titanium with respect to the thermochemical sponge currently produced, results from the fact that *only one electrolysis potroom replaces* the several *following sections* of the current manufacturing plant:

- electrolytic magnesium potroom;
- liquid magnesium transfer equipment;
- Kroll reactors room;
- vacuum distillation of magnesium chloride and excess magnesium;
- magnesium chloride transfer equipment;
- sponge extraction, cutting, crushing bay;
- sponge visual inspection for low-density inclusions;
- sponge briquetting equipment;
- vacuum consumable electrode welding;
- vacuum arc first melting to cylindrical ingot;
- hot forging of ingot to slab.

During the last twenty years, many technological improvements have been achieved in the downstream physical metallurgy processes of titanium, as well as incremental productivity in fabricating, manufacturing, and in the secondary metallurgy. The rewards for these efforts,

their economical results, will be more than proportionally magnified by the decrease in the cost of primary titanium obtained with the electrolytic production.
That is today for example, the work at an improvement for saving 1 $/kg on the production cost of a titanium product that sales for 30 $/kg does not permit a price reduction which will significantly change the titanium sales volume. Instead saving the same 1 $/kg by the same technical improvement on a titanium product that sales at 10 $/kg generates major increases both in sales volume and in profit.

The *quality characteristics* of titanium alloys produced by electrowinning are:

- extreme cleanliness and microcleanliness ;
- very low content of hydrogen;
- analytically precise content of interstitial and alloying elements,
- complete homogeneity and almost no segregation;
- solidification structure ideal for metallurgical manufacturing.

Since titanium is and will be used in the most demanding and high value applications, we can have an idea of the importance of titanium quality when we think, with all due respect, that the outstanding history of the Concorde has been heavily damaged by the impurity content of titanium fasteners of another aircraft (best wishes to the Concorde to start flying again soon).

Studying the history of the other nonferrous metals, we see that all of them emerged from their initial condition of niche market and became industrial commodities when the electrolytic plants replaced the primitive production processes. In fact, aluminum, magnesium, sodium, lithium and also fluorine gas are produced, since long time, by molten salt electrolysis. Besides, we must recall that copper, zinc, nickel, lead and other industrial metals, as also chlorine gas and soda, are produced by aqueous electrolysis.

Following the introduction of the electrolytic processes, the costs of production of each of these metals have been decreasing, in real terms, every year since.

Why titanium should be the only industrial metal without its commercial electrolytic plants?

I am convinced that it is exactly now, because the titanium industry is starting its recovery from the depth of the last market crisis, that the acceleration of the commercialization of the electrowinning plant will be most effective, in order to solve at the root, once for all, the basic problem of the titanium industry.

Where all that enthusiasm about the "wonder metal" of a few years ago, went?

When I recently heard that we have entered the century of Internet for the communication sector, I realized that it is entirely up to us to make it the century of Titanium for the metals sector, making titanium history to resemble that of aluminum. More along that line of thought, it came to my mind that we are also entering the third millennium in which the epochal transition from iron to titanium will occur, as it has been from wood to iron during the second millennium. No more rusty tanker breakups, or corroded sea oil pipelines, or loss of important building constructions, thus no more second millennium continuous and expensive maintenance works, Fig. 13 , but nice maintenance-free buildings Fig. 14.

If new economy means new products, high technological content, low prices, then electrolytic titanium will be a major driver.

The enormous importance of having modern primary titanium production plants for the future of the titanium market cannot be overstated.

Concluding, I wish to tell you this: often friends are asking me, with their faces full of wisdom, why I am still working and investing in the Titanium Electrowinning, after so many years of efforts and so much capital spent.

Generally I am a bit shy and embarrassed to answer and the conversation develops with deprecating the lack of determination by medium and large metallurgical companies which are recalcitrant to invest in Titanium Electrowinning process to modernize and increase the primary titanium production capacity. Usually the lamentation ends with the easy prediction that as soon as the world demand for titanium picks up, the bottleneck of scarce primary production capacity will make the prices of titanium mill products skyrocket, as it has occurred 5 or 6 times before in the short titanium history, and the work of development of new titanium markets will stop again.

This course of events is even more despicable when we see that the downstream metallurgical operations have vast excess production capacity, and upstream we have a very large titanium tetrachloride industry that can easily adjust to satisfy any primary titanium demand.

Let us hope that the easy prediction of the continuation of the historical pattern for titanium future will be wrong this time.

One of my deep wishes is to be able to produce slabs of titanium at the lowest cost, ready to be efficiently milled, for making welded tubes and structures of low cost desalination plants.

The other dream, being Torino my home, is to be able to contribute with lower cost titanium to the progress of the automotive industry.

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I wish to remember two great personalities in titanium history, whom I had the privilege to learn from: Dr. Albert W. Schlechten of CSM and Mr. John C. Priscu of Timet.

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Glossary

Electrolysis: a chemical process for separating a metal from its compound by the use of electricity only.
Electrolyte: the liquid in which the electrolysis is performed, aqueous solutions or molten salts.
Electrowinning: the metallurgical process for producing metals by electrolysis without the use of any reagent and without the production of any waste.
Cathode: the location in the electrolytic cell where the produced pure metal is collected.
Anode: the location in the electrolytic cell where the element originally combined with the metal in the raw material feed is collected.
Anolyte and catholyte are the portions of electrolyte in the locations of the anodes and of the cathodes respectively.

Table 1

Institutions and companies that contributed relevant work toward the development of the titanium electrowinning process:

United States Bureau of Mines
National Lead
New Jersey Zinc
Horizons
Chicago Development
Sony
Timet
Howmet (D-H)
EMG
GTT