

Why Produce Titanium by EW?

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INTRODUCTION

So many times in the last years I have been asked when the electrolytic production of titanium will be commercial, and why it took so long to be ready as compared with all the other nonferrous metals that became industrial commodities after their primitive production processes were replaced by electrolytic plants. Recall Dr. Kroll's production mentioned in his 1959 Extractive Metallurgy Division Lecture for the American Institute of Mining, Metallurgy, and Petroleum Engineers:¹

"It might, however, be fair to say, that titanium will be made competitively by fusion electrolysis within the next 5 to 10 years."

In his 1960 Sixth Castner Memorial Lecture in Glasgow² on the status of the fusion electrolysis of titanium, Dr. Kroll concluded by 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 polyvalent metal electrolysis."

Instead, much work was still done using cells with diaphragms. Only J.C. Priscu, who presented Timet's titanium electrowinning cell in 1968 at the Extractive Metallurgy Division Symposium on Electrometallurgy,³ worked on the most advanced nondiaphragm basket-cathode type.

During the 1970s, I did my Ph.D. thesis on the fundamentals of the electrolysis of titanium at the Colorado School of Mines,⁴ working with Dr. Schlechten, who had been Kroll's coworker in the development of titanium and zirconium extractive metallurgy. During the 1980s, my company, GTT, further advanced the nondiaphragm chloride system,^{5,6} during the 1990s, we advanced the fluoride system.⁷

PAST DEVELOPMENT OF TITANIUM ELECTROLYSIS

To answer why we are so very much overdue in commercializing electrolytic titanium, we have to consider the following factors in producers' decisions and strategies, scientists' work, industrial problems with the chloride system, the amount of work done with chlorides as opposed to fluorides, and the lack of consumer sponsors.

Producers primarily followed the aerospace market 4-5 year cycles. This resulted in a succession of booming peri-

ods (during which there was no waiting time for the development of new techniques, so any available process, even if obsolete, was installed to get production for delivery) and bust periods with little resources available for new technique developments.

Short-medium term programs were used to develop high-quality products in order to achieve high sales prices (more than \$30/kg average product price) on low volume production, instead of committing resources on long term-large scale programs to decrease the basic costs of ingot production.

The current inadequate state of development of the theory of molten salts in fundamental electrochemistry has retarded the industrial progress.

Today's still incomplete understanding of the aluminum electrolytic process did not aid the understanding of titanium electrolysis.

A large amount of work was done in the determination of values of physicochemical parameters in the absence of live electrochemical processes.

Much work was done using oxide diaphragms. Not enough study was performed on the large amount of experimental results produced by the nondiaphragm full-scale cells during the 1980s.

The multivalence of titanium ions in the electrolyte requires a separation between anolyte and catholyte to avoid alternating oxidation and reduction with very low current efficiency. The operation of any kind of diaphragm needs complicated cells.

To avoid the disproportionate reaction $3Ti^{3+} \rightarrow 2Ti^{2+} + Ti^0$, a precise operational control is required.⁸ The occurrence of this reaction results in the precipitation of solid titanium particles within the electrolyte.

With the chloride system, titanium is produced in the solid state on the cathodes with crystalline morphologies of large surface areas and low bulk densities. The growth of the titanium deposit requires its frequent removal from the electrolyte by means of a handling apparatus of the kind described in Reference 5: 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 produced titanium, 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.

Because the chloride system was perceived as being easier to work at lower operation temperature, fewer material problems, besides much more data and bibliography, were available. Development programs with chlorides had a higher feasibility rating than fluorides; thus, larger financing was available for chlorides. 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.

Over the years, some companies in the titanium industry have invested in R&D for the development of low-cost, primary electrolytic titanium, and all of them, within the limits of their financial strength, contributed to further the progress with works that were indispensable to get to the next stage of development. The large-scale volumes end-product potential users did not participate to this development effort; titanium has not had its sponsor yet.

PRESENT STATUS OF TITANIUM ELECTROWINNING

During the 1990s, our fluoride program had more time for studying the large mass of experimental results produced by the chloride works during the 1980s, which were insufficiently analyzed at that time because of the interruptions in the development programs due to the titanium market cycles. The study of the chloride-system results confirmed what was indicated in Figure 2 of my M.Sc. thesis¹² depicting the diagram of standard free energy of formation of titanium chlorides; it shows that above 500°C there are no more divalent nor trivalent ions in the electrolyte, only Ti^{2+} and Ti^0 .

In short, during the operations of dismantling anodes/intermediate electrode assembly of GTT's MX cells, which were removed near the end of their useful life, the contained solidified anolyte was always found to be clear colorless in the presence of titanium-metal crystals inside the assembly, without the slightest