

ELECTROWINNING OF TITANIUM FROM TITANIUM TETRACHLORIDE:

PILOT PLANT EXPERIENCE AND PRODUCTION PLANT PROJECTIONS

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Introduction

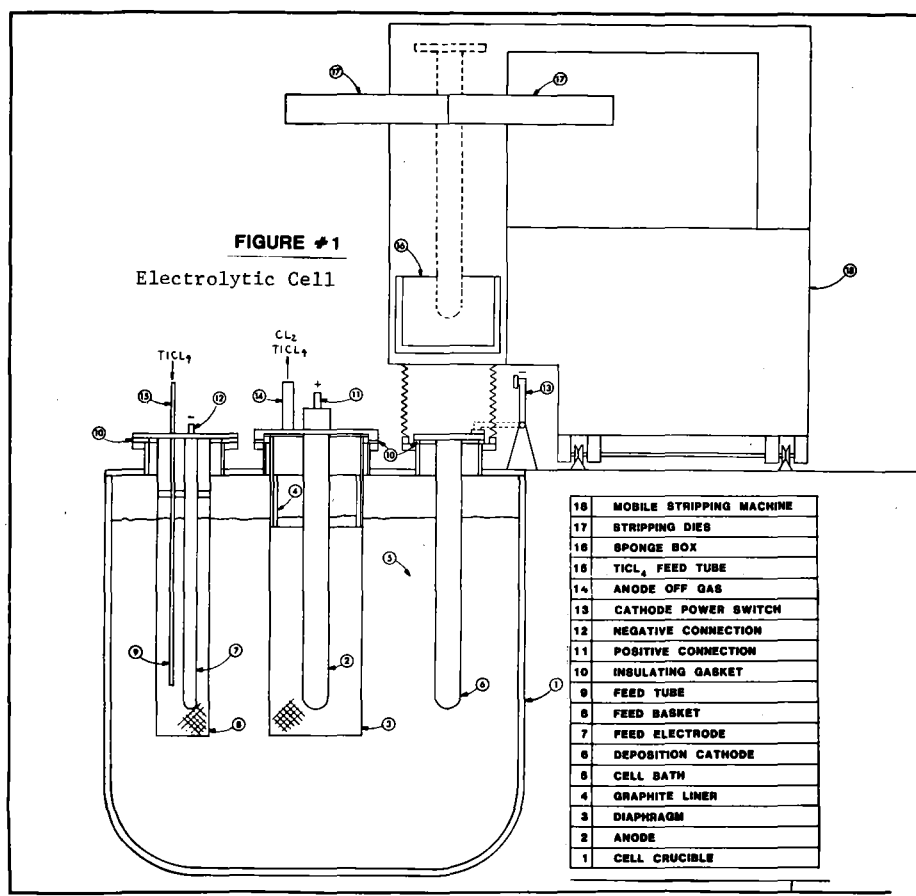
High purity electrolytic titanium is being successfully produced on a pilot plant basis by D-H Titanium Company, a joint venture of The Dow Chemical Company and Howmet Turbine Components Corporation. The technology is an outgrowth of work originating at the U.S. Bureau of Mines, Boulder City, Nevada. [1] The project is aimed at commercialization of this prior bench-scale research. Full-scale prototype components are being operated in a single anode 5,000 AMP cell producing approximately 45 kg./day of metal. Construction of industrial scale multiple anode cells is presently underway that will culminate in operation of a one half to one million kg. per year demonstration plant in 1981.

Previous research in the field has been extensive. Major efforts at prototype scale-up have been conducted by the New Jersey Zinc Co. [2] and Titanium Metals Corporation of America. [3] In both processes the diaphragm, which is required to enable selective oxidation of the chloride ion, was generated in the cell. A substantial fraction of the cathodic current was directed to a screen or perforate plate that divided the cell into anolyte and catholyte areas. As metal deposited restricting the plate openings an efficient semipermeable membrane was set-up which excluded Ti^{+2} , Ti^{+3} interactions at the anode and cathode. High purity titanium was produced by both companies, however, the methods employed had several inherent shortcomings. The operation was discontinuous because the diaphragm periodically became "plugged" or loaded with metal and had to be removed from the cell to harvest the product. This necessitated shorting the cell out of the pot line. Since the diaphragm permeability and effectiveness varies during the cycle the current efficiency was not optimum. Since the voltage drop across the diaphragm increased throughout the cycle the power consumption was relatively high.

The D-H process uses a stable, efficient diaphragm that is electrically isolated from the main current path.

Prototype Equipment

The electrolytic cell is shown schematically in Figure 1. The molten electrolyte is contained in a metallic crucible. Top ports accommodate the $TiCl_4$ feed assemblies, deposition cathode assemblies and the anode/diaphragm assembly. The port to assembly connections are designed to be airtight and provide insulation between the crucible and the electrode.



The diaphragm consists of a reinforced screen electroless plated with cobalt or nickel to give the required electrical and flow characteristics.^[4] It surrounds the cylindrical graphite anode. The diaphragm support housing is protected from chlorine gas attack at the melt level by a graphite liner.

The feed assembly consists of steel electrodes that are electrically connected to and surrounded by a screen basket that has been electroless plated to the required permeability. The feed tube extends into the electrolyte bath a sufficient depth to ensure that all of the TiCl₄ is reduced by TiCl₂ in the electrolyte.^[5]

The cathodes consist of steel round bar stock. The upper sealing flange is designed to open the electrical circuit to the cathode when it is raised into the cathode stripping machine to harvest the metal deposit. The cathode stripping machine which is maintained under an inert gas blanket scrapes the deposit off into a collection cart and returns the cathode into the cell without disturbing the argon atmosphere within the cell.

Procedure

The electrolyte consists of a LiCl/KCl mixture approximately at the eutectic composition with TiCl_2 added. The desired titanium concentration is obtained by first reacting a stoichiometric amount of TiCl_4 with an amount of titanium sponge added to the feed basket calculated to result in several tenths percent titanium. The concentration is then increased by operating only the feed cathodes and anode and feeding one mole of TiCl_4 per two faradays of current.

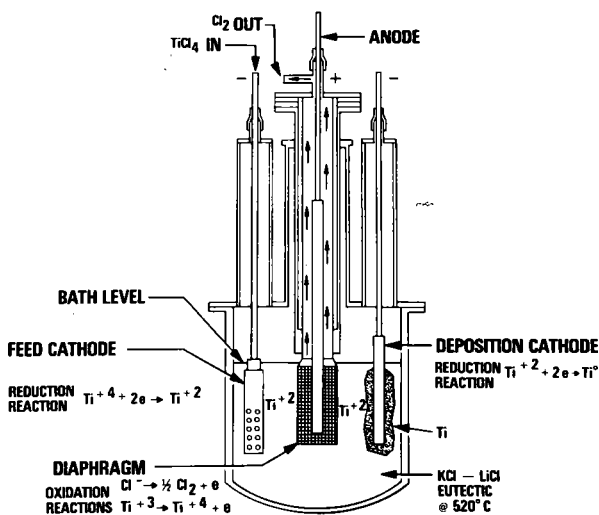
ELECTROLYTIC TITANIUM CELL

FIGURE 2

Current is started to the deposition cathodes and the deposits are removed when a cathode has received about 20,000 AMP hours. The desired electrochemistry is shown in Figure 2. Some electrolyte is removed with the metal deposit and fresh salt is periodically added to the cell to maintain the freeboard and prevent exposing the diaphragm to chlorine. The process flow is shown in Figure 3.

The metal is easily crushed to $-3/8"$ in a saw tooth crusher and the salt is removed using a 0.5% HCl solution in a continuous countercurrent leacher. After a final wash step with deionized water the metal is air dried at 65°C . A small button melt ingot is made from a sample split from the batch and is used for chemical analyses and hardness determination.

The brine solution from the leacher which is near saturation is neutralized with a mixture of LiCO_3 and KOH in a ratio equivalent to the electrolyte composition. This causes any Ti species to precipitate to be removed by a filter. The liquor is then stored for ultimate drying and recycle to the cell.

D-H ELECTROLYTIC TITANIUM PROCESS

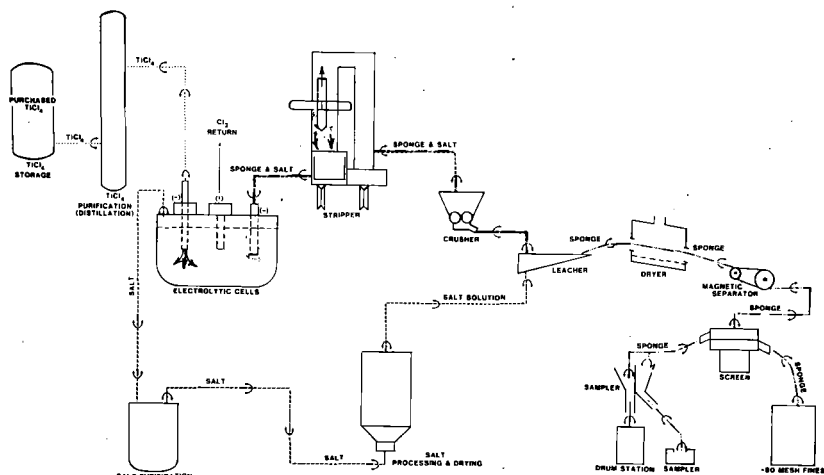


FIGURE 3

The anode gases which are a mixture of TiCl_4 and Cl_2 pass through a packed column where they are contacted with TiCl_4 refrigerated to -12°C . The TiCl_4 recovered at the column bottom is heated to 135°C . to flash the dissolved chlorine back into the column. The TiCl_4 is further purified by a double distillation step and recycled into the cell. The chlorine, which is over 99% pure and suitable for recycle to a chlorination plant is neutralized with NaOH and shipped as bleach.

Results And Discussion

High quality metal has been produced on a continuous basis. Analyses of typical deposits are compared with the standard maximum specifications of sponge produced by other methods in Table 1.

Table 1 Chemical Compositions

Element	D-H Elec. Typ.	Weight Percent		
		Kroll Dist. Max.	Kroll Leached Max.	Hunter Leached Max.
O_2	0.035-0.065	0.10	0.10	0.10
N_2	0.002-0.003	0.015	0.015	0.015
C	0.009-0.011	0.020	0.025	0.020
Fe	0.010-0.020	0.12	0.15	0.05
H_2	0.003-0.005	0.010	0.03	0.05
Cl	0.010-0.035	0.12	0.20	0.20
Bhn	60-90	--	--	--

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The low oxygen, nitrogen and iron contents and resulting low Brinell hardness combined with the low chloride content give a product having great versatility for titanium applications. The low oxygen and nitrogen contents plus the fact that the electrolytic process operates at temperatures below 600°C . give maximum assurance that the crystalline titanium metal can be used for the most critical aerospace structural applications where freedom from the hard, so-called Type I (nitride inclusions) is important or where maximum fracture toughness is a requirement. The low iron content is important in commercially pure titanium chemical industry applications giving maximum assurance of high corrosion resistance. The low chloride content assures "clean" melting characteristics and makes the metal ideal for conversion into powder for use in powder metallurgy applications requiring products free of internal porosity and having good weldability.

It is anticipated that in 1980 D-H Titanium electrolytic sponge will be qualified to be used for critical components of jet engine compressors.

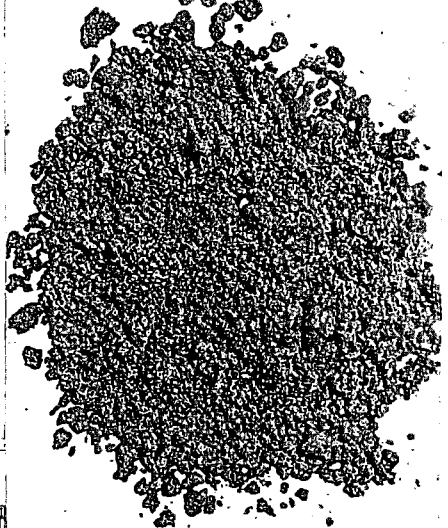
FIGURE #4

Electrolytic Titanium Dendrites



FIGURE #5

Crushed Metal



Typical good quality metal is shown in Figure 4 and 5. The quality of the metal, size of the dendrites and the amount of salt dragged out with the deposit are found to be closely related. The following variables change the morphology of the deposit and result in a fine crystal structure with a high surface area to weight ratio, a high salt drag-out and high oxygen in the leached product: 1) Ti average valence in the electrolyte greater than 2.30 2) Total Ti concentration in the electrolyte less than 1.5% 3) Air contamination of the cell atmosphere.

It is desirable to maintain a low ratio of the weight of salt to weight of metal in the deposit ("drag-out" ratio) since the lower chlorides of titanium in the salt that are removed in the leaching process represent a loss in the titanium yield efficiency. In addition recovery and recycle of the electrolyte is a cost factor in the process. During normal operating conditions drag-out ratios of 0.35 kg. salt/kg. titanium and titanium yield efficiencies of 98% have been demonstrated.

Improvements in diaphragm design and performance are occurring on almost a daily basis. Diaphragms that will operate several weeks with better than 80% titanium current efficiency have been repetitively demonstrated. The titanium current efficiency is calculated assuming a valence of four for the titanium and using the total anode current.

The TiCl_4 feed rate is controlled to maintain the Ti concentration in the electrolyte at the desired level. It is calculated by:

$$\text{lbs. TiCl}_4 \frac{\text{feed}}{\text{hr.}} = \frac{x \text{ amps}}{257 \frac{\text{amps}}{\# \text{Ti}^{+4} / \text{hr.}}} \times \frac{y\% \text{ Ti Cur. Eff.}}{100} + z \text{ lb TiCl}_4 \text{ Rec.} \quad (1)$$

Good cell operation has been demonstrated at temperatures from 520°C. to 600°C. Below 520°C. a stable salt complex, K_2TiCl_6 , forms in the anolyte compartment and tends to plug the chlorine exhaust route. Crucible design strength considerations limit the upper temperature. The electrolyte resistivity, and KWH/lb. Ti, is lower at higher temperatures. The drag-out ratio is slightly improved at higher temperatures because the viscosity of the molten salt is lower.

Electrolyte compositions from 45% to 60% LiCl have been shown to be satisfactory. Higher LiCl concentrations improve the electrolyte resistivity but increase the capital outlay for the initial salt charge.

Good quality metal has been produced from electrolytes with Ti concentration from 1.5% to 3.5% Ti. About 2% is preferred because much below this the deposit crystal structure deteriorates as noted above. The higher the Ti concentration the more Ti is lost as lower chlorides removed in the leaching step.

All of the above variables must be taken into consideration when the diaphragm is manufactured. The electrolyte resistivity and chemical concentration gradients across the diaphragm affect the characteristics required for optimum diaphragm performance.

Production Plant Projections

Table 2 presents some key figures for a conceptual commercial plant having a nominal capacity of 4.5 million kg. of sponge per year.

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Table 2 Key Figures, 4.5 Million Kilograms/Year
Commercial Titanium Plant

No. of Multiple Anode Cells	70
Pot Line Current	22,500 amps
Operating Factor	95%
Titanium Yield Efficiency	98%
Titanium Current Efficiency	80%
Avg. Cell Volts	6.2 volts
DC KWH/kg. of metal	17.4

Economic studies indicate a production facility can operate with product cost, including depreciation, competitive with fully depreciated facilities of conventional technology.

Summary

High purity electrolytic titanium is being produced continuously by the D-H Titanium process. The technology utilized is based on a stable diaphragm type cell having argon blanketed LiCl-KCl-TiCl_2 520-600°C. molten salt electrolyte. TiCl_4 is fed continuously into a pre-reduction cathode compartment where reduction to dichloride takes place. Final reduction to metal is continuously done on separate deposition cathodes which are periodically removed hot into an inert atmosphere stripping machine and then replaced within the cell. The sponge produced is low in oxygen, nitrogen, iron and chlorine and has excellent melting characteristics. It is ideally suited for critical aircraft structural, chemical corrosion resistant and powder metallurgy applications.

Production scale components have been demonstrated and the correct operating parameters ascertained. A full-scale demonstration plant is under construction in Freeport, Texas and will be started up in the fourth quarter of 1980 to confirm the industrial cell design. Assuming this start-up is successful plans are to initiate detailed engineering and construction of a commercial plant employing the D-H Technology in 1981 for a 1984 start-up. Site studies are underway. The plant will be scaled to meet the needs of marketplace and will be very competitive with any current technology plant. The Howmet Titanium Ingot Division will be integrated into the D-H Titanium Company as soon as the decision to commercialize is made.

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