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PRODUCTION OF TITANIUM METAL AT HENDERSON, NEVADA

by R. R. Lloyd

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Titanium has received extensive commercial attention during the ten years since publication of the first U.S. Bureau of Mines report on a practical production process /1. Commercial production of titanium sponge was started by E. I. duPont de Nemours and Company, and by Titanium Metals Corporation of America, shortly after the first Bureau of Mines Pilot Plant was in operation. More recently Cramet, Dow Chemical, and Electro Metallurgical Company, have entered this field on a substantial basis. Formulation and melting of sponge into ingots; rolling, forging, and extruding of ingots into finished mill shapes; and marketing of mill products, are major business ventures of Titanium Metals Corporation of America, Rem-Cru Titanium, Incorporated, Mallory-Sharon Titanium Corporation, and Republic Steel Corporation. Several other companies have entered the titanium metal industry on a more limited basis.

Titanium Metals Corporation was organized to combine the broad chemical industry experience of National Lead Company, for the production of sponge, and the skills of Allegheny Ludlum Steel Corporation in the handling of stainless and other specialty steels, for the production of titanium metal products. It is a wholly owned subsidiary of the two Companies. Until recently, Titanium Metals Corporation was the only integrated producer, from ore to finished mill shapes. It is the only producer operating a Titanium Tetrachloride Plant, a Sponge Production Plant, a captive Magnesium Recovery Plant, and a Melt Shop, in a single location. Ingots produced at Henderson are shipped to Allegheny Ludlum Steel Corporation Mills in Pennsylvania and New York, for fabrication into forgings, sheet, strip, bar, wire, extrusions, and other finished shapes. Bar turnings, sheet clippings, and other mill scrap are returned to Henderson for remelting. The original Henderson plant has been described briefly by P. J. Maddex /2, and R. L. Powell /3. The Henderson facilities started operations in October, 1951, and the original authorized capacity of 3600 tons per year was reached in September, 1954. Planned expansion of the plant to 6000 tons per year was announced on March 21, 1956, and further expansion to 9000 tons per year of sponge and 11,000 tons per year of ingot was announced on August 15, 1956. All of the new capacity is entirely Company financed, and without Government purchase guarantees. The first expansion goal of 6000 tons per year was reached in September, 1956.

Production of titanium sponge at Henderson is based upon the original Kroll process, invented by Dr. W. J. Kroll and developed into a commercially usable process by Frank Wartman of the Federal Bureau of Mines. This basic process has been integrated into the overall flow sheet shown by Slide No. 1 Titanium sponge production and melting are characterized by procedures which are simple in principal, but are relatively complex in operation. The ideal plant site for production and fabrication, would be in a total vacuum. Even helium or argon atmospheres are undesirable for certain operations.

Slide No. 2 shows the basic reaction for chlorination of rutile, or other TiO_2 containing material, into $TiCl_4$. Slide No. 3 is a diagramatic sketch of the equipment used to effect the reaction, and collect the volatile product. Slide No. 4 shows the top of an operating chlorinator.

Crude $TiCl_4$ must be separated from insoluble and soluble impurities. These impurities include dust from the original reaction, compounds of iron, aluminum, magnesium, calcium, zirconium, vanadium, tin, and silicon; as well as chlorine, phosgene, and various other dissolved gases. The flow sheet for purification of crude titanium tetrachloride is shown by Slide No. 5. Chemical treatment with H_2S is for the purpose of reducing certain substances, such as $VOCl_3$, into compounds which can be more readily separated by distillation techniques. Pure $TiCl_4$ is a colorless liquid, resembling carbon tetrachloride, which decomposes in a moist atmosphere to yield HCl and TiO_2. Major engineering problems are involved in pumping, clarifying, distilling, sulfiding, sampling, metering, and storing in a completely enclosed system. A single teaspoonful of $TiCl_4$ could readily drive everyone from this room, so some appreciation of the difficulties of processing and handling can be appreciated. Slide No. 6 shows the distillation columns used for final purification.

The basic chemistry of the Kroll reaction is shown in Slide No. 7, and a schematic diagram of the equipment used at Henderson is shown by Slide No. 8. The reduction is carried out in steel pots in gas fired furnaces, under a helium atmosphere. The furnace operates at a temperature at which magnesium chloride is present as molten salt. A typical installation is shown by Slide No. 9. The molten salt is being tapped for transfer to the Magnesium Recovery Plant. Titanium is produced by the Kroll reaction at a temperature substantially below it's melting point. In the presence of metallic magnesium, however, the sponge like titanium adheres tightly to the pot, and to any other object with which it comes in contact. It must be removed by mechanical means. This is accomplished, after cooling to room temperature, by use of a special boring machine housed in a "dry room". A dry atmosphere is necessary to prevent moisture pick-up by residual $MgCl_2$ in the reactor. Moisture in the reactor "heel" contaminates subsequent batches of titanium with oxygen, resulting in high hardness metal. The crude chips are removed from the controlled atmosphere, reduced by standard crushing techniques, and leached with acid to remove residual magnesium and magnesium chloride. Slide No. 10 shows a view of the Leaching Plant. The leached product is dried, sampled, and blended to give a final sponge of uniform analysis and size distribution.

The magnesium chloride drained from the reactors, is transported molten to the Magnesium Plant, for recovery of both magnesium and chlorine by electrolysis. Electrolysis is effected in units of the original Basic Magnesium, Incorporated plant, which used the Metal Elektron Cell. This cell is designed to use anhydrous magnesium chloride, which is the product of the Kroll reaction. In addition to magnesium, the M.E.L. cell produces an anode gas containing 85 to 100% chlorine. The anode gas is filtered and recycled directly to the Chlorination Plant, without concentration. Magnesium chloride produced in the Reduction Plant, is a very pure grade yielding magnesium low in manganese and other metallic impurities. Slide No. 11 shows a view of a 20,000 ampere electrolysis cell in operation. Each cell building of the original BMI Plant contained 88 cells, and was rated at 15 TPD of magnesium.

Titanium sponge is converted into ingots by compacting and double-melting as a consumable electrode, under a vacuum. Alloying constituents and recycled scrap are melted concurrently with the sponge to give a homogeneous alloy. Slide No. 12 shows the basic principals of melting consumable electrodes into ingots. The crucible is water cooled, and the metal freezes immediately upon contact. This melting procedure is necessary, because no known refractory will hold molten titanium. The system is operated under a vacuum primarily to remove hydrogen, but vacuum melting also removes residual magnesium and other volatile metallic impurities; and helps to stabilize the arc to produce a sound ingot. Melting of titanium in a vacuum was pioneered by Titanium Metals Corporation. This technique has now become fairly standard in the industry, and has received wide publicity during the past year for production of super-alloy steels. The Henderson Plant has the largest vacuum Melt Shop in existence at the present time, using specially constructed furnaces designed by Company engineers. Slide No. 13 shows a furnace installation used for the second melt. The electrodes for use by this furnace are melted into smaller diameter crucibles from compacted sponge electrodes. The double-melt ingots are machined to give a smooth surface, free of porosity and surface contamination, before shipment to the Mills. Slide No. 14 shows three 6000 pound ingots ready for shipment.

Titanium has received wide-spread attention from metallurgists and metal equipment designers, because of its corrosion resistance, high strength at moderately high temperatures, and light weight. The remarkable potentials of titanium as a structural metal combined with inherent difficulties of extraction and fabrication, have resulted in intense technical development on all fronts.

Original problems with sponge quality have now largely disappeared. There is no doubt today, that the Kroll process is capable of producing titanium sponge to meet the requirements of present alloys, as well as those in the development stages. The hydrogen content of Mill products, which has caused concern about the future of the titanium industry, has also been brought under control.

Increased metal production and increased quality of product, has been accompanied by decreased cost of production. During an inflationary period, when labor and raw material costs have steadily increased, the market price of titanium sponge has decreased. This decrease amounted to 10% in 1954, 22% in 1955, and 13% to date in 1956. Market price is now $3.00 per pound, compared with $5.00 per pound in early 1954. All market forecasts indicate a continuing lowering of price, and a continuing increase in production. The current market for titanium is concentrated in the aircraft industry, but with lower costs and increased application know-how, many other uses are economically practical. The chemical industry is a particularly important field, because of the unusual corrosion resistance of the metal.

Nevada is traditionally the "Silver State". Today, however, titanium is much more important to the State's economy. Up-to-date statistics are not available, but it is believed that the dollar value of Titanium Metals Corporation of America operations represent the second largest industrial enterprise in the State. The Henderson Plant employs about 1,100 people at the present time. The major part of the Company's research, development, and plant design, are carried out at the Henderson site. This fact plus an industry based upon rapid technical progress, has resulted in one of the largest concentrations of technical manpower in the State.

The production of titanium metal has reached the status of a stable metallurgical industry, which is expanding at a rapid rate. The future of the industry is bright, but the rapid increase in technology and production requires continuous study of fundamentals, continuous improvements in process, continuous application of quality control techniques, and maintenance of an organization trained in titanium know-how. We believe that the production, fabrication, and application of titanium metal presents a fruitful challenge to engineers, metallurgists, and chemists, who have initiative and imagination.

References

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/3 "Chemical Engineering Aspects of Titanium Metal Production", R. L. Powell, Chemical Engineering Progress; Volume 5, No. 11, pp 578-581, November, 1954.