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Study on Production Methods of Titanium Sponge

[1] S. Sai Harsha, [2] P.V. Chandra Sekhara Rao
[1] MTech Student, [2] Assistant Professor
Corresponding Author Email: [1] saiharsha@gmail.com, [2] chandrasekhararao@rgukt.ac.in

Abstract— Titanium sponge is a porous type of titanium generated during the first stage of the manufacturing process. The titanium sponge is a major raw material used in the production of ingots or slabs during the melting process. It comes in a variety of grades, each with varying degrees of impurities. This paper's main goal is to overview and compare various production methods of titanium sponge individually. And we have tried to discuss the properties, advantages, and disadvantages of those processes, and also mentioned their applications. The various production methods of titanium sponge are divided into batches based on their manufacturing process such as the Kroll process, Hunter process, and Electrolysis process comes under conventional methods, FFC, OS, QIT, etc. are the Electrochemical process.

Index Terms— Electrolysis process, Hunter process, Ingot or slab, Kroll process, Production methods, Titanium sponge

I. INTRODUCTION

Titanium was found as a new and unidentified metallic element by Gregor in England in 1791 and was termed Titanium by Klapproth in Germany many years later (1795) after the Titans of Greek mythology [3]. Titanium metal may be found mainly in the structure of oxide minerals in the crust of the Earth due to its elevated boiling point i.e., 1663°C, large chemical reactivity, and it is one of the most difficult metals to extract [2].

"Titanium is the earth's fourth common structural metal, and its ores occur in a range of oxide forms. The current process for converting these ores to titanium metal consists of three main steps; one is converting from oxide ore to $TiCl_4$, and reducing $TiCl_4$ to metal using sodium, magnesium, or, on a smaller scale, electrolysis, and then purifying the titanium by using vacuum distillation, inert gas sweep, or leaching to remove residual salts and unconsumed reactants. The product produced using these processes is known as titanium sponge, and it has a spongy, open-pore structure. To make ingots that can be processed into mill products, the titanium sponge is combined with alloys, crushed, and softened using one of many methods".[4]

The researchers first attempted to generate titanium from carbothermic reduction and metallothermic reduction of titanium dioxide and are unsuccessful in creating the purity required. From the learnings of these failed investigations, they concluded that oxygen should not be present in the primary material to be used.

The titanium sponge obtained by the Kroll method is usually applied in aircraft (cells and engines), heat exchangers, power, desalination plants, electronic components, and user goods (eyeglass frames and golf clubs), among other uses. [5].

II. CONVENTIONAL METHODS FOR TITANIUM SPONGE EXTRACTION

The Conventional Methods for Titanium Sponge Production involve sodium reduction (Hunting process), magnesium reduction (Kroll process), and salt-fused electrolysis processes. Titanium tetrachloride is used as the first material for all these methods. The titanium part formed during these processes is utilized as a polish or an agglomerated porous mass known as a sponge that, by leaching or vacuum distillation, has been removed from the reduction agent/by-product and then consolidated into the ingots by a softening method.

A. Kroll Process

This process delivers most of the primary titanium metals used by industry around the world today. The Kroll process consists of four processes [5] namely 1. Chlorination and pure cation of titanium ore, 2. Reduction and separation under vacuum, 3. Electrolysis of magnesium chloride, 4. Crushing and sizing of titanium cake. The authors [6] discussed conventional sponge methods and briefly explained the Kroll process and also mentioned some advantages of this process. The procedure entails the reducing of refined $TiCl_4$ in a positive pressure stainless steel refinery of argon gas.

The titanium sponge formation mechanism has been proposed in the Kroll reduction reactor by thermal reduction of TiCl4 magnesium [7] and this research uses reduction tests in a 2000kg titanium sponge reactor prototype to gain a better knowledge of the process parameters of magnesium reduction with $TiCl_4$. In addition, tests in two small size experimental reactors were carried out for investigating the thermal analysis throughout the process as a rate of the $TiCl_4$ input function. During the application of the surgical method, two intriguing occurrences have been noticed.[8]

The Recipe technique was used to evaluate the environmental consequences of titanium sponge manufacturing in China utilizing the Kroll process. They have constructed a life cycle model for the manufacture of Titanium sponges, estimated the Inventory of the life cycle and its environmental consequences connected in conjunction with major methods, and recognized the major variables and springs that generate conservation pressure in this study. Each procedure's entire influence was addressed by the writers. The environmental consequences were also examined before and after new methods and apparatus, such as the cell of multipolar electrolysis and the inverted U-shaped reduction distillation oven [9]. *DUBUC, J. et al., 2003* explained some drawbacks of the Kroll process. [10]

The Kroll technique was used to create two procedures for the manufacturing of sponge, [11]

i. Magnesium Reduced Acid Leach Process (MRAL)
ii. Vacuum Distillation Process (VDP)
   a. VSMPO special metals (Verkhnaya Salda Metallurgical Production Association Russia).

Magnesium Reduced Acid Leach Process (MRAL):

It is one of the Kroll method's procedures for sponge manufacturing. It was created in the 1950s when the titanium industry was just getting started. The authors did not define any of the features or applications of this procedure because it is no longer in use. The primary issue with this method is that it created more acid waste and was less efficient in terms of preserving magnesium values through the reduction phase.[11]

Vacuum Distillation Process

The reference [12] investigated the separation of reduction products by vacuum distillation during the manufacture of titanium sponge. vacuum distillation of thermodynamic analysis, vacuum dissociation reactions $TiCl_2$ and $TiCl_4$ were performed in this work to better understand the distillation process behaviour of magnesiothermic reduction products created in the Kroll process. In their paper, the authors stated that an industrial experiment has shown that a high-quality 0A grade titanium sponge can be obtained using vacuum distillation. This is one of the benefits of this process.

The research paper [11], explained the vacuum distillation technique with TOHO/ Timet process. Parallel to the MRAL method, the Vacuum Distillation Process was created. In this paper, the complete VDP process is explained with the three phases and the flow chart of the process. The authors also explained and compared the merits of the both MRAL and VDP process.

VSMPO Process

In this process, each vessel's top flanges are linked directly with a spacer. The two vessels are vacuumed, the captured repository is placed on top of the support, and the heat is applied to the low-level sponge-containing vessel using the same annular space clearance procedure. Magnesium chloride and magnesium are transported to the top vessel for the distillation process.[5]

B. Hunter Process

This method was initially described by Hunter in the early 1910s and is hence called in honour of his name. In the reduction process, sodium chloride is produced with metallic sodium as a reducing agent. The researchers studied that low-cost titanium is a myth or reality. In this research paper[13], the authors explained the production methods of titanium and a good differentiation between the Kroll and Hunter processes. At the end of this paper, we can find the low-cost and reliable process for the production of titanium.

C. Electrolytic Process

From the study [10], Invented connects to a process for electrodeposition of metallic titanium and titanium alloys from liquid electrically conducted mixed titanium compounds such as fused titania slag, fused ilmenite, fused leucoxene, fused perovskite, fused titanium, synthetic or natural fused rutile or fused titanium dioxide. The electrolytic production of metallic titanium has been extensively studied to develop a continuous process to replace the Kroll process. Various bids have been made in the industry. The first experiment was accomplished in 1950 by *National Lead Industries, Inc.*, and the second attempt was finished in 1956 at the former *United States Bureau of Mines (USBM) in Boulder City, Nevada*.

The reference [14], this paper narrates to a process for electrowinning of uncontaminated titanium metallic from titanium slag continually and another electrical semiconductive titanium mixed oxides, particularly ilmenite, other natural titanium ores, or synthetic titanium oxide compounds. In this paper, the electrolytic process is explained. It was built out of a 12-inch cylindrical container wrinkled with unpolluted iron and contained a melted electrolyte consisting of a combination of LiCI-KCI with $TiCl_2$ added at the eutectic structure. The paper [4]] reviewed and compared the Kroll, hunter, and electrolysis processes. This paper also discussed the production of $TiCl_4$ metal and defines the different types of methods for purifying sponge metal.

The history of the electrolysis process in terms of cost, production, etc. is explained by *Paul. C. turner* [13]. While this process had some merits to implement, it was not adopted commercially. It has been reported that a pilot manufacturing facility depends on two-step electrolysis of $TiCl_4$ in a eutectic mixture of KCl and LiCl has been operating which failed to bring it into commercial titanium sponge production. And he also mentioned the main provocation in the victorious application of the electronic extraction method. [2]

D. Electrochemical Reduction Process

It is possible to directly reduce solid crystalline TiO_2 by using an electrochemical process in which oxygen is ionised, melted in liquefied salt and settled at the anode, exit only pure titanium at the cathode. When compared to previous techniques, the simplicity and speed of this process should consequence in lower manufacturing charges, and the technology would be valid to a widespread range of metal oxides [15]. The Kroll process appears to have reached a stalemate, with no further reductions in the value of titanium metal possible using this process. Several attempts have been made to develop an alternative titanium abstraction technique to manufacture the metal at a lower cost. Wide-ranging research into titanium electrochemical de-oxidation in liquefied calcium chloride electrolytes led to the expansion of electrochemical reducing techniques. [6]

Wang Bixia et al., 2010, explained the effects of the electrochemical reduction products on their microstructure and oxygen content The oxygen content of electrochemically reduced products is also determined[16]

1) FFC Process

The reference [17], reviewed the discussed on the FFC process, the reduction mechanism and its evolution, and its possibilities. The FFC Cambridge procedure for metal oxide reduction was found in 1997 when it was revealed that it was feasible to decrease solid oxide layers on titanium foil by catheterizing the foil in a solution of molten calcium chloride.

The authors [6], mentioned that this method is patented by FRAY, FARTHING, and CHEN of Cambridge University in the United Kingdom, involves removing oxygen from solid titanium dioxide via electrolysis in a melted calcium chloride bath with graphite as the anode. The process begins with the creation of TiO_2 compacts/pellets from oxide powder, which are sintered and used as the cathode.

George Zheng CHEN et al., 2013 [18] the possibilities of the Cambridge FFC, the process of processing ilmenite ore to make Fe-Ti alloys is investigated, as well as its economic potential in the future titanium industry. This study also looked into the one-of-a-kind metal manufacturing technique based on fundamental electrode reaction thermodynamics and processes the complex metal, and electrolyte three-phase interlines (limitations).

2) Ono-Suzuki Process

This process was invented by Kyoto University in Japan, When TiO2 is reduced in melted calcium chloride, it is because the Cao motion is inhibited when it is dissolved in the molten salt, which causes the TiO2 reduction of titanium to occur more frequently. Aside from that, by electrolyzing Calcium oxide in molten calcium oxide, it is possible to regenerate calcium metal. As a result, the setup is made up of two interconnected chambers, one of which is the reduction part and the other is the electrolytic unit, into which the renewed calcium metal is fed to reduce the nonstop fed titanium dioxide granules. According to reports, efforts are underway in Japan to market this approach. [13]

From this experiment, Sponge titanium-containing 1000 ppm oxygen could be produced within 2 hours. from 10g TiO2 powder. Nevertheless, the problems encountered were back reactions because of metallic calcium's solubility in the parasitic then melt responses caused by CO2 gas foam. [16], [19], [20].

E. Armstrong Process

This paper [21] explained the characterization of the Armstrong process of titanium powder. This article presents a systematic investigation of the powder characterization, sintering behavior, and mechanical properties, and powder metallurgy of the Armstrong process, and similarly discussed the sodium problem and the uses and drawbacks of this process residues. The authors examined dust compaction according to which Armstrong's powder deformation mechanism has three stages: rotation of the powder group, decomposition of the powder group to fill more space, and powder deformation to fill the space between particles. Full review on mechanical properties and density, the oxygen content is mentioned. In this article, the clear explanation of the sodium problem in Armstrong CP Ti Powder. The authors [22] studied the result of boron accompaniments on the microstructure and mechanical assets of titanium mixtures manufactured by the Armstrong process. According to the authors of this study, the Armstrong process is a one-of-a-kind method for directly producing commercially pure (CP) titanium and titanium alloy powder from $TiCl4$. EHK Technologies et al.,2004 [23] studied the emerging titanium cost reduction technologies. In this paper, the authors explained all the latest low-cost processes which are under research and also completed processes. All methods are briefly explained with their experimental process and also mentioned their concerns and current status of the experiment. The Armstrong Process termed as this method is built on sodiothermic reduction of $TiCl4$ to create titanium powder and is also called Hunter's continuous process. According to sources, ITP already has a commercial running plant with a capacity of 300tpy. [7]

III. RESULTS AND DISCUSSION

A. Differentiation between Kroll and Hunter Process

The majority of global industries produce the sponge by using the either Kroll method or the hunter's method. So, the basic differences between those two processes are explained in table.1. The Hunter's process is very comparable to the Kroll process, except that magnesium is replaced by sodium. When comparing magnesium recovery to sodium recovery, the Kroll method required just one-third of the energy.

Table.1. Differentiation between the Kroll and Hunter Processes

Kroll Process	Hunter Process
It is a Batch Process	It is a Batch or Continuous Process
This process is 15 to 50% excess magnesium used	This process minor excess of $TiCl_4$ used
The retort walls have a significant amount of iron pollution.	There is little iron contamination from the retort walls.
Griding of the sponge is high	Easy to grind the sponge
Few fines	Up to 10% fines
The majority of the titanium is found in the retort.	Each titanium mole contains four moles of sodium chloride.
Using a sponge leached or a vacuum distillation method	Sponge leached method used

B. Cost and Quality Difference

According to working methodology, the Hunter process and Kroll processes are similar. Even though the processes are comparable, the Hunter method is significantly more costly, and as a result, the Hunter method is now only used to produce a tiny niche market for high-purity powders in specialized applications. In view of quality, all methods give the good BHN but the Electrolytic process is much better than the remaining processes. The cost and qualitative differences for Kroll, Hunter and Electrolysis processes is shown in Table.3.

C. Comparison of all Titanium Sponge Production Methods

The above all processes are titanium sponge extraction processes by using rutile Titanium dioxide in different methodologies, but extracted sponge has different properties. Each process had its applications based on its extraction methodology. All processes had different properties, advantages, disadvantages, and applications. Table.2. differentiates all the processes with these terms.

D. Problems Raised by Using Titanium Sponge

In mechanical alloys with the use of titanium sponge, there are two major issues to consider, one is the poor grindability of titanium sponge and another one is the high chlorine concentration of the sponge and When titanium sponge is manufactured, it has poor grindability as a result of the high strength of the sponge as well as the cold-welding phenomena that occur during the manufacturing process.

One approach to addressing these issues is to type the initial brittle titanium by injecting hydrogen at high temperatures then pressures to produce TiH_2.

Table.2. A Brief Comparison Between the All Methods of Titanium sponge Production

SI.No.	Name of the Process	Description	Advantages	Disadvantages	Properties	Applications	References
1.	The Kroll procedure	Magnesium Reduction of $Ticl_4$	Titanium product with lesser oxygen content, enhanced equipment, and characterization techniques, quality assessment, and size reduction	It is carried out in batches, lead to costly downtimes, Kinetics of slow reactions As a raw material, this technique can only take costly rutile, It exclusively generates dendritic crystals.	Total determined impurities -0.445 Brinell Hardness-122 Change in enthalpy ΔH = +598.8 kJ	The Kroll procedure is a two-step batch procedure that involves Titanium tetrachloride, which is then reduced to through magnesiothermic reduction of titanium tetrachloride to produce Titanium.	[24], [7]

1.1	Magnesium Reduced Acid Leach Process (MRAL)	This technique uses magnesium ingots as the reductant. In the course of the leaching process, NOx emissions were produced as a consequence of the interaction between nitrous acid and Mg	Producing of magnesium remains mandatory for the production of sponge but co-location is not necessary for this process.	More acid wastages and it was inexpensive in the conversion of Mg standards in the reducing process, more sufferers in the decontamination of $TiCl_4$ result in lesser $MgCl_2$ manufacture.	Density- 4.5g/cm^3 Melting point- 1933K Boiling point- 3535K	No more practical applications because it wasn't inexpensive in the conversion of Mg standards in the reducing method	[11]

1.2.	Vacuum Distillation process TOHO timet	VDP is collateral to the MRAL method. The procedure is divided into three stages: reduction, distillation, and cooling.	When using this process, you may get high-quality sponge titanium. The magnesium can be reused in another reduction process.	It is always necessary to have a stoichiometric additional magnesium. In this procedure, some magnesium is lost due to sponge form trapping, and some magnesium is not improved during electrowinning.	The titanium content of the titanium sponge after vacuum distillation is 99.9 percent, and the other impurity content is less than the 0A grade standard.	Vacuum distillation has been used in industrial studies to manufacture high-quality 0 A grade titanium sponge.	[12], [11]
1.2.1	VSMPO special metals (Verkhnaya Salda Metallurgical Production Association, Russia)	The distillation procedure may also be done by directly connecting the distillation vessel to the load retort. In this method, each vessel's top flanges are joined with a spacer	The floor is made of titanium plates for various applications which are simple to clean and avoid sponge contamination.	Stoichiometric excess of magnesium is needed	The titanium content of the titanium sponge after vacuum distillation is 99.9 percent, and the other impurity content is less than the 0A grade standard.	Vacuum distillation can be used in industrial experiments to produce 0A grade titanium sponge.	[11]

2.	Hunter Process	Sodium reduction of TiCl4	Metallic impurities; less expensive to use Mg reduction than Na reduction	A batch procedure that requires a lot of labor, heterogeneous exothermic reactions that result in poor productivity.	Total determined impurities -0.445 Brinell Hardness- 122 Specific gravity-4.50	Titanium oxide is converted to titanium tetrachloride, and titanium is formed by a magnesiothermic decrease of titanium tetrachloride.	[13], [2]
3.	Electrolytic Process	Electrolyte LiCl–KCl graphite as anode and steel as cathode Tio2 feedstuff	Fewer phases, continuous process, no $TiCl_4$ and metal participation , less expensive than thermochemical.	Dendritic products with high redox potential and the ability to handle them	86 wt.% A1203-12 wt.%SiO2 Brinell hardness – 68 Efficiency – 60%	Continuous electrolytic procedures provide a highly refined product. Despite this, no electrolytic procedures are currently using.	[4], [15]

4.	Electrochemical reduction processes	Extensive research into titanium electrochemical de-oxidation in liquefied $CaCl_2$ electrolytes led to the expansion of electrochemical reducing techniques.	Small grain samples may be reduced. Together locked and exposed pores may function as active electrode reaction interfaces, and this is a low-cost extraction approach.	In this, due to the higher grain dimensions being unfavourable to together mass transfer and electron conduction, the models sintered for a long time cannot be entirely reduced within the given time	BHN – 270 Oxygen – 1% Carbon – 0.6%	The technology is appropriate for the creation of alloys that cannot be synthesized using standard procedures.	[15], [16]
4.1.	FFC - Fray Farthing Chen	Pre-formed spongy TiO_2 pellet as the Cathode, sluggish anode for O_2evolution melted $CaCl_2$ state.	Easy, quick, and improved existing effectiveness, the possibility for continued process According to the procedure, be 5 times quicker and 30-40% more cost-efficient than Kroll technology	Slow O_2 diffusion, bit feed, a lengthy time for removing the excess $CaCl_2$ after electrolysis, costly for the TiO_2	Fe - 0.028 Ni - 0.010 Si - 0.021 Cr - 0.035 Al - 0.031	The method's novelty is that alloy production takes happen without melting the component metals. Also suited for preparing alloys, which cannot be synthesized using standard procedures. Most of the metal carbides can be made via the FFC process.	[18], [17]

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4.2.	OS process (Ono-Suzuki process)	TiO_2 Powder cathode graphite rod anode Calcium unwilling and liquefied $CaCl_2$	Shortest TiO_2 Reducing using powder as feedstuff in a one-compartment	Backreaction Owed to the emulsifiable of metal calcium in the melt and sponging reactions because of CO_2 gas bubbles	Change in enthalpy ΔH = +445.1 kJ	This process is described as different because the titanium sponge is advanced in a cell with shape the of granules ranging in size from microns to micrometers.	[25], [20]
5.	Armstrong Process	To produce titanium powder, this technique is based on Hunter's sodio thermic reducing of TiCl4 that is carried out continuously.	Extraordinary compressibility and compaction capabilities, resulting in dense compacts with improved green strength as compared to those formed by unequal powders.	The low apparent density	Oxygen content -2600ppm Yield strength - 909 MPa Ultimate Tensile Strength - 1040 MPa Ductility – 7.3%	A feature of Armstrong powder making it suitable for use in the DPR process is the particle interlocking morphology. It also generates substantial friction between particles, reducing fluidity and apparent flow.	[21], [23],

Table.3. Cost difference and Qualitative between Kroll, hunter, and electrolysis process

Process	Operating cost	Capital cost	Quality, BHN	Residual volatiles	Fine's content
Kroll-Vacuum Distillation	Moderate	High	Good	Low	Low
Kroll – Leach	Moderate	Medium	Good	High	Moderate
Hunter	Moderate	Medium	Good	Moderate	High
Electrolytic	Low	High	Excellent	Moderate	High

IV. CONCLUSION

There is a high demand for titanium sponges all over the globe, as well as the current circumstances, are projected to remain this way for some additional years to come. Kroll and Hunter processes, which are commercialized thermo-chemical chloride processes, are used to manufacture titanium sponge. To generate an intermediate form of $TiCl_4$, these methods need the use of better-quality accepted rutile or improved artificial rutile as feedstock, as well as a chlorination step which is used to manufacture colour grade TiO_2 and titanium metal. Thermochemical methods are very costly and inefficient in terms of energy consumption. Despite this, many of the enhancements made to those processes, such as, have limited potential for major cost savings beyond what is now possible with present technology.

Some progress has been made in the development of electrochemical techniques for the direct reduction of TiO_2 and in-situ electrolysis, both of which have shown promising results. It is necessary to tackle various difficulties, such as redox cycling and feeding as well as kinetics and regulate heat balance, before scaling up the technology for commercial use. Furthermore, other electrochemical companies, such as BHP Billiton, have developed numerous better sulphate methods, which include leaching techniques, to separate metals, use a solvent extraction method., and acid recycling. These processes are extremely promising for commercial applications in the future

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