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Methods Of Titanium Sponge Production

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1. INTRODUCTION

Titanium metal is available in the earth's crust predominantly in the form of oxide minerals. It is one of the 'difficult to extract' metals mainly due to its high melting point (1663^{o}C), high chemical reactivity (reacts/alloys readily with a large number of metallic /non-metallic elements.) and high thermodynamic stability of its oxide, TiO_2. Early attempts to reduce titanium dioxide by conventional means of carbo-thermic, metallo-thermic (by Mg, Al, Si etc) and hydrogen etc have not been successful as the product had always been contaminated with brittle impurities impairing the mechanical properties of the metal. Electrolysis of titanium dioxide in molten fluorides was also tried in vain. Researchers were successful in obtaining pure and ductile metal only when a non-oxygen bearing titanium compound was used as the starting material. Berzellus reduced K_2TiF_6 with sodium (1825), Claire Deville reduced $TiCl_4$ with sodium (1855) which was later improved by Nilson & Patterson (1887) and further modified by Hunter (1910), van Arkel and de Boer tried dissociation of TiI_4 on hot filament and Kroll developed magnesium reduction of $TiCl_4$ (1937) for producing titanium metal of high purity. Electrowinning of titanium by fused salt electrolysis of $TiCl_4$ in molten alkali chloride mixture also yielded titanium with desired purity. Historical developments in titanium extraction metallurgy are discussed in detail in the literature[1-3].

2. CONVENTIONAL TITANIUM EXTRACTION METHODS

Sodium reduction of $TiCl_4$ (Hunter process), magnesium reduction of $TiCl_4$ (Kroll process) and fused salt electrolysis of $TiCl_4$ in alkali chloride mix electrolyte are considered to be conventional methods of titanium extraction (Fig.1), though the fused salt electrolysis process was not commercially adopted. In all these methods titanium tetrachloride is the starting material, the production of which is of commercial importance as the tetrachloride is the intermediate product in the manufacture of pigment grade titanium dioxide. Titanium particulate formed in these methods is harnessed as powder or as agglomerated porous mass known as 'sponge' which is cleared off reductant/by-product by either leaching or by vacuum distillation and subsequently consolidated into ingot by vacuum arc melting process.

The Hunter process was extensively studied and developed by Imperial Chemical Industries, England during early '50s and was used in different variant forms for production of titanium sponge on commercial scale by a few companies. Hazardous sodium handling, tricky reaction temperature control due to narrow operating temperatures, excessive exothermic heat release, non-viability of regeneration of reductant sodium from the by-product sodium chloride etc have been major challenges in the operation of sodium reduction process on commercial scale. Reactive Metals Inc. USA, Nippon Soda, Japan and Deeside Titanium, UK had been successfully using Hunter process for industrial production of titanium sponge till the early 1990s all of which are said to be non-operational henceforth.

The Kroll process of reducing $TiCl_4$ with magnesium metal was pursued vigorously by US Bureau of Mines, Nevada and operated a pilot plant for titanium sponge production by this method during the 1940s. During the period 1951-57 many companies in USA started producing titanium sponge by the Kroll process. The process was also commercialized in Japan and erstwhile USSR during the same period. Since

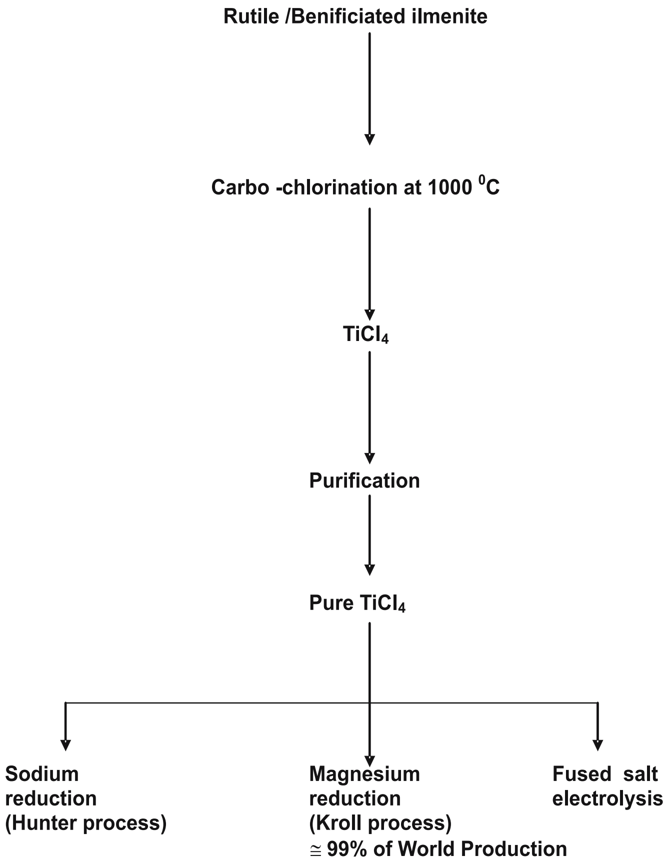


Fig. 1 : Conventional methods of titanium extraction.

then the Kroll process has remained as a major titanium sponge production method till date.

Electrowinning of titanium by fused salt electrolysis of $TiCl_4$ was studied by many investigators as it has its own merits such as viability for semi-continuous operation, no necessity of reductant metal , the cost of which adds on to the cost of titanium sponge production etc. Dow Howmet and Timet of USA spent enormous amount of money and time for the development of electrolytic production of titanium during the '70s and '80s. A pilot plant production based on a two stage electrolysis of $TiCl_4$ in an eutectic mixture of LiCl and KCl reported to have operated which has apparently not been successful for taking it up to commercial production of titanium sponge. M/s Electrochemica Marco Ginatta, Italy have been extensively working on titanium sponge production by electrolysis of $TiCl_4$. Numerous attempts by them for developing the process on a pilot plant scale though have been reported to be continuing[4], commercial implementation of the same has not so far been taken place. The main challenges in the successful application of the electrowinning process are: (i) establishment and continuous maintenance of the diaphragm for effective separation of anolyte and catholyte to avoid recombination of metal and chloride ions and (ii) harvesting and post electrolysis treatment of sponge without impairing its quality.

2.1 Merits of Kroll technology

The Kroll process of magnesiothermic reduction of $TiCl_4$ stood the test of time and has been largely used for commercial production of titanium sponge. The process involves reduction of purified $TiCl_4$ in a stainless steel reactor under a positive pressure of argon gas. It is a batch process and depending on the batch size, required quantity of magnesium metal is taken into the reactor which is heated to a temperature of about 800^oC and titanium tetrachloride is pumped into the reactor though a nozzle on the reactor lid. Titanium tetrachloride with a boiling point of 136^oC vaporizes as it enters the reactor holding liquid magnesium. The gas liquid reaction results in a continuous generation titanium metal particulate which eventually grow into pieces of sponge and settles down on the reactor bottom plate resulting in formation of titanium sponge block towards the end of the reduction. Magnesium chloride, the reaction by-product being heavier than molten magnesium sinks down paving way for continuous interaction of $TiCl_4$ with magnesium metal in the reactor. The reactor wall temperatures are controlled in the range 800-850 for controlling the reaction temperature.

For effective reactor volume utilization, $MgCl_2$ is periodically withdrawn during the reduction process. At the end of the reduction, the reduced mass contains titanium sponge and some amount of Mg and $MgCl_2$ which get entrapped in the pores of sponge. The entrapped Mg/$MgCl_2$ can be removed by leaching or vacuum distillation or inert gas sweep. Vacuum distillation of the reduced mass at about 1000^oC and under a dynamic vacuum of 10^{-3} torr, has been in use by the majority of the sponge producers. In all the integrated titanium sponge plants, magnesium and chlorine are regenerated by fused salt electrolysis of $MgCl_2$ obtained as by-product in the sponge production (Fig.2) which contributes greatly to economy of titanium sponge production.

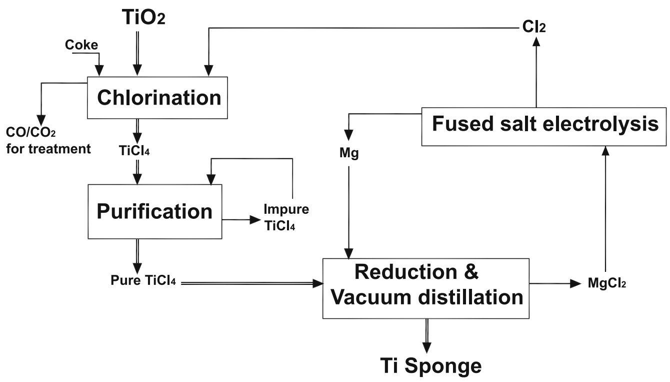


Fig. 2 : Flow sheet of titanium sponge production by Kroll process in an integrated plant

Over the last many years, the Kroll process has been extensively studied and issues and developments related to process chemistry and operation, reaction thermodynamics, reactor material & design, mechanism of sponge formation, sponge structure and morphology, factors affecting the quality of titanium sponge etc have been widely reported[5]. The following are the major advancements in the Kroll process resulting in improved energy savings, quality of the metal and cost effective production of sponge[6]:

- Advent of 'Combination Unit' for carrying out Reduction and Vacuum distillation operations in a single station eliminating intermediate opening of the reactor.
- Enlargement of batch size from 1-2 MT in the beginning to 4-6 MT and even 10 MT batches are also in use at selected producers.
- Computer based process instrumentation and automation
- Evolution of improved equipment and procedures for characterization, quality evaluation and size reduction operations

Eventually the Kroll process has got perfected and emerged as the major method of titanium sponge production. By the advanced Kroll process, it has become possible to produce premium grades of sponge such as low iron (<100 ppm) and low nickel (<20 ppm) sponge and also sponge of 5N purity required for the electronic industry[7].

3. WORLD PRODUCTION OF TITANIUM SPONGE

Commercial production of titanium sponge began in USA, Japan and erstwhile USSR in the early '50s and UK operated commercial sponge production plants in the late '50s. The world titanium sponge production capacity was a few thousand tons in the '50s which went on increasing to 85000 tons by the late '70s and by early '80s it touched 100000 tons. The current world capacity for titanium sponge production is estimated to be over 150000 tons per year. However, the actual level of production had been cyclic with constant ups and downs due to large dependence of metal application in military air crafts which was heavily fluctuating during the cold war period. There are two clearly distinguishing phases of world titanium sponge production scenario (Table 1), one being the drastic fall in metal production/demand with the extinct of former USSR in the early '90s and the other is of dramatic pickup of market due to the recent boom in civilian aerospace sector. The demand supply gap in world market led to soaring of sponge prices. An international market price of 6-7 $/kg prevailing a few years back, sky-rocketed to as high as 28-32 $/kg for premium quality titanium sponge. Many companies world over, attempted to cash in on the all the time high in demand for titanium sponge resulting in expansion of existing facilities or/and creation of new ventures. China, apparently rose to the situation with its capacity of sponge production which was merely 8000 tpy in 2003, touching 30000 tpy as per present estimations presumably to cater to the internal needs of hectic aviation activities[8]. It is interesting to note that the situation in Japan is different with not significant change in its production capacities, as the market in Japan never had been aerospace dependant thanks to the stabilized non-aerospace markets.

4. ALTERNATIVE METHODS OF TITANIUM EXTRACTION

Though titanium stands in 5th place as per the occurrence of metals in the earth's crust, it takes the 15th place in the order of consumption of metals. The reason for this is mainly attributed to higher cost of production of titanium sponge. It is expected that the demand for titanium sponge could be stable provided the non-aerospace market is established which essentially requires considerable lowering of prices. As discussed in the previous sections, the current method of Kroll process of titanium sponge production is matured enough leaving little scope for attempts to bring down the cost of production further. Over the years there have been many R & D attempts to try for an alternative method. The direction of attempts has always been to cut down the steps in the flow sheet of metal production. Thus many attempts had been directing towards producing the metal directly from its oxide, TiO_2 or continuous production of metal/alloy powders resulting in energy savings and increased production rates. A few methods also use a combination of reduction and electrolysis. The following are the recent methods which have seen significant level of development.

(i) The FFC Cambridge Process : This process developed by Fray, Farthing and Chen of Cambridge University, England takes the basis of electro de-oxygenation of titanium dioxide in molten calcium chloride bath which was successfully employed to tackle with the problem of alpha casing on the titanium alloy blades. In this process, titanium oxide granules/pellets are subjected to cathodic treatment at about 950^{o}C using calcium chloride as electrolyte and graphite as anode resulting in removal of oxygen from the oxide making it to combine with carbon to liberate CO/CO_2 at anode. Extensive description of this process is available in the literature[9-11]. British Titanium Co. has taken initiatives for commercializing the process. The process claims to be 5 times faster and 30-40% cost effective compared to the Kroll technology. As per the latest reports, a Consortium led by TIMET is operating a pilot plant based on this method, on a scale of 22 kg of sponge per day at California University, Berkeley, USA.

(ii) The Armstrong Process :This process is based on Hunter's sodiothermic reduction of $TiCl_4$ conducted in a continuous manner to produce titanium powder. In this process[12], titanium tetrachloride is fed into a continuous stream of molten sodium in a tubular titanium reactor resulting in instantaneous formation of titanium powder which is separated from sodium and sodium chloride by washing, filtration and distillation. The process was exclusively studied and developed by International Titanium Powder Inc., Chicago, Illinois,

Table 1
World titanium sponge production capacity

Country	Major producers	Capacity in the year (metric tons)				
		1988	1993	1998	2003	Current(e)
USA	TIMET RTI ATI OREMET	29000	30000	20000	26000	46000
UK/EU	Deeside Titanium	5000	5000	-	-	340 (by QinetiQ)
JAPAN	SUMMITOMO TOHO	26000	29000	26000	22000	30000
Former USSR/ CIS	VSMPO/Avisma, Russia ZTMK, Kazakastan UKTMK, Ukraine	100000	82000	24000	30000	45000
CHINA	Zunyi Ti Industrial Co. Wushun Ti Plant Jinzhou Huashen Ti Industrial Co.	2700	3000	3000	8000	30000

(e) : estimated

Table 2

New Processes of titanium extraction under study

Name/Organization	Process	Product
MER Corporation, USA	Anode Reduction of TiO_2, electrolysis in molten halide mixture to deposit titanium metal on cathode	Powder/flakes
SRI International, USA	Hydrogen reduction of $TiCl_4$ in fluidized bed reactor at 1300°C	Powder
BHP Billiton process	Electrochemical reduction of TiO_2 in calcium chloride bath	Sponge
Idaho Titanium Technologies (ITT)	High temperature plasma reduction of $TiCl_4$ by hydrogen	Fine powder
Millennium Chemical, USA	Not known	Powder
MIR-Chem, Germany	Reaction of TiO_2 with I_2 and decomposition of titanium iodide formed	Powder
CSIR, South Africa	Hydrogen reduction of $TiCl_4$	Sponge
Quebec (Rio Tinto) Iron & Titanium (QIT)	Electrolysis of titania slag in molten fluoride bath	Liquid metal/ingot
Electronically Mediated Reaction (EMR)/ Molten Salt Electrolysis (MSE) Process	Electrolytic reduction of TiO_2 without physical contact of the oxide and calcium using Ca-Ni alloy and $CaCl_2$ electrolyte	Powder
Vartech. Inc., USA	Gaseous reduction of $TiCl_4$	Powder
Idaho Research Foundation, USA	Mechano-chemical reduction of $TiCl_4$	Powder

USA. By using a mixture of metal chlorides, production of titanium alloy powder has already been demonstrated, the product reported to be meeting all the technical specifications. According to reports, a commercial operating facility with a capacity of 300 tpy is already functioning at ITP.

(iii) The OS Process: The Ono-Suzuki process developed by Kyoto University, Japan[13] deals with the calico-thermic reduction of TiO_2 conducted in molten calcium chloride which brings down the activity of CaO as it dissolves in the molten salt thereby thermodynamically favoring the reduction of TiO_2 to titanium.. Further, the reductant, calcium metal is regenerated by electrolysis of calcium oxide in the molten calcium chloride. Thus the set up consists of two connected chambers one being the reduction unit and the other is electrolytic unit from which the regenerated calcium metal is supplied for reducing the continuously fed titanium dioxide granules. Efforts to commercialize this process are reported to be underway in Japan.

There are many other processes that have been pursued for cost effective production of titanium many of which are covered in a recent survey report by EHK technologies and elsewhere[14,15]. Some of the details of these processes are presented in Table 2. As can be seen from the table, it is clear that large scope exists in the titanium extraction metallurgy and the wide range of attempts for evolving a cost effective method brings out competitive spirit prevailing among researchers to produce titanium at a cheaper price.

5. INDIAN SCENE

Initial initiatives by Department of Atomic Energy for developing the titanium extraction metallurgy flow sheet, by taking up laboratory scale studies at Metallurgy Division at BARC in the '60s[16] and pilot plant operations at NFC, Hyderabad during '70s[17] that led to development of understanding for equipment engineering and selection of operating conditions for $TiCl_4$ production, reduction of $TiCl_4$ by magnesium followed by vacuum distillation of reduced mass on 100-300 kg/batch size and handling of titanium sponge for its size reduction and quality evaluation. This had enabled establishment of a technology development/ demonstration plant at DMRL in the year 1985 for further scale up of the activity. Chronological events in the development of technology for titanium sponge production in the country are shown in Table 3.

5.1 Technology development at DMRL

At the DMRL titanium sponge technology demonstration plant, facilities were created for (i) purification of titanium tetrachloride by two stage fractional distillation for removing impurities such as $SiCl_4$, $SnCl_4$, $FeCl_3$, titanium oxy-chloride etc and dissolved gases, so as to produce purified tetrachloride at a rate of 150 kg/h , (ii) magnesio-thermic reduction of $TiCl_4$ in a stainless steel reactor assembly followed by vacuum distillation of reduced mass and (iii) handling of massive sponge cake, it's quality evaluation and size reduction to a finished size of 2-25 mm[18]. In the first phase of technology development program, titanium sponge production in 2000 kg batches by conventional Kroll process involving two separate furnace stations for conducting Reduction and Vacuum distillation , has been extensively experimented and demonstrated.

Subsequently, technology for producing titanium sponge on a batch size of 3000-3500 kg by employing "Combination Unit", the state-of-the-art reactor assembly system wherein reduction & vacuum distillation operations are conducted in a single furnace station without involving the exposure of reduced mass to atmosphere, was taken up. The salient features of the upgraded technology for titanium sponge production are (i) use of a single electrical resistance furnace

Table 3

Stage in the development of technology for titanium sponge production in India

Year	Institute/Lab	Process	Batch size
1953-55	NML	Mg reduction of $TiCl_4$	Bench scale
1960-67	BARC	Mg reduction – vacuum distillation Mg reduction- acid leaching Sodium reduction-leaching	1 kg 1 kg 1 kg
1968-75	BARC	Mg reduction-leaching Mg reduction – vacuum distillation	5 kg 15 kg
1975-79	BARC	Fused salt electrolysis of $TiCl_4$	5 kg
1975-70	NFC	Mg reduction –vacuum distillation Sodium reduction –leaching (single stage) Sodium reduction – leaching (two stage)	100-300 kg 60 kg 120 kg
1985-92	DMRL	Mg reduction – vacuum distillation	2000 kg
1992-98	DMRL	Mg reduction –vacuum distillation trial runs by 'Combined Unit'	3000-3500 kg
2000 onwards	DMRL	Demonstration of titanium sponge production technology by Kroll process in Combination Unit producing aerospace grade sponge	3000-3500 kg

for meeting diverse requirements of air circulation during Reduction for controlling the reaction temperatures and vacuum tightness required during Vacuum distillation, (ii) a cladded (AISI 304/AISI 430) twin stainless steel reactor (to have compatibility with liquid magnesium on the inner surface and for higher oxidation resistance at outer surface) assembly (Fig. 3), one reactor positioned in the furnace for conducting batch operations (Reduction and distillation) and the other in condenser station for collecting the distillates during the vacuum distillation, (iii) a valve-less pressure transfer system for tapping magnesium chloride, the reaction by-product during the reduction process, (iv) a heated inter-connecting pipe which joins the two reactors during the vacuum distillation, (v) a computer based process control and data logging system and (v) custom built presses and tooling for grading, cutting and crushing of titanium sponge into 2-25 mm size. The detailed description of these facilities is presented elsewhere[19].

Painstaking efforts put up over a decade led to improved understanding of the sponge making technology[20-21] and successful operation of the facilities over 15 batch operations. Table 4 lists typical operating conditions of a 3000 kg titanium sponge batch operation at DMRL. A photograph of sponge cake weighing about 3000 kg produced

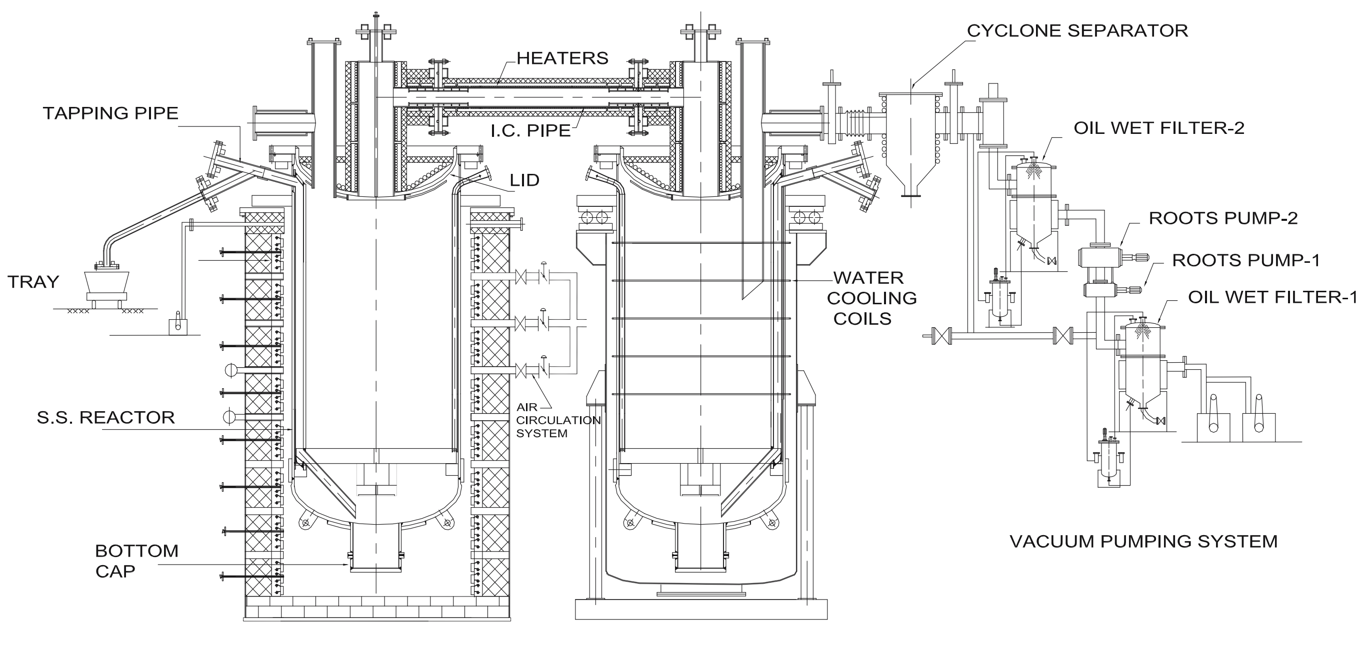


Fig. 3 : Schematic of Combination unit for titanium sponge production (DMRL)

Table 4

Typical operating conditions of a batch operation of titanium sponge production in combined process

REDUCTION	
Temperature	
Reaction Zone	800 - 830°C
In the gas phase	600 - 700°C
Below the reaction Zone	850 - 880°C
$TiCl_4$ feed rate	200 - 230 kg/h.(avs)
Reactor Pressure	0.25 kg/cm^2
Duration	75 - 80 h.
$MgCl_2$ Tapping	
Method	Valveless pressure transfer
Pressure	0.5 - 1.2 kg/cm^2
Average Qty. per tap	800 - 900 kg
VACUUM DISTILLATION	
Temperature	975 - 1000°C
Ultimate vacuum	2-5 x 10-3m bar
Duration	55 - 75 h.

in the demonstration plant is shown in Fig.4. The quality of sponge produced during the technology demonstration has been consistently meeting all the stringent international specifications and that has enhanced our capabilities for evolving a technology package suitable for commercial implementation for producing premium grade titanium sponge from raw titanium tetrachloride[22,23,24].

Fig. 4 : Titanium sponge cake weighing about 3000 kg

5.1.1 Transfer of Technology – Setting up of country's first Commercial titanium sponge plant:

The fact that the country possesses rich reserves of titanium minerals, commercial production of titanium tetrachloride is taking place at M/s Kerala Minerals & Metals Limited, Chavara, Kerala (KMML) and Midhani, Hyderabad has been in the field of ingot melting and manufacture of titanium/ titanium alloy mill products, brings out that the sponge production is only gap in the Indian titanium metallurgy which has been successfully filled by DMRL.

Soaring prices of titanium sponge and crunch in titanium sponge supplies in the international market triggered the necessity of self reliance of this strategically important structural material. Vikram Sarabai Space Centre (VSSC), Department of Space has taken the initiatives for transferring the DMRL titanium sponge production technology for setting of a 500 tpy commercial titanium sponge plant located at KMML and the transfer of technology is being vigorously pursued. As per the progress made so far, it is expected that the commercial plant be operational in the year 2009.

5.1.2 Studies on electrochemical reduction of TiO_2

DMRL has taken up laboratory scale R & D for the development of cost effective method of titanium sponge preparation by electrochemical reduction of TiO_2. The process (Fig.5) involves preparation of titanium dioxide

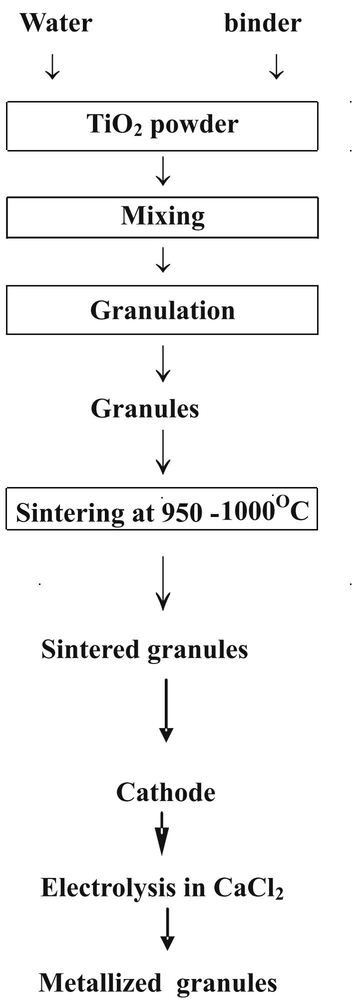
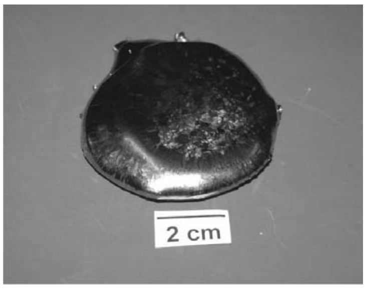


Fig. 5 : Steps in electrochemical reduction of TiO_2

(a)



(b)

Fig. 6 : Titanium sponge produced from electrochemical reduction of TiO_2 and button melted out of the sponge

granules which are sintered at 950°C and then subjected to cathodic de-oxygenation treatment in an experimental setup consisting of a stainless steel reactor heated by an electrical resistance furnace The cathodic treatment involves application of 3.0-3.2 DC voltage between the granules and a graphite anode in molten calcium chloride bath at a temperature of 950-975°C.

After the experiment, the granules are thoroughly washed with water and is followed by washing with acetic acid, dilute HCl, alcohol and acetone. After drying, the granules are characterized for estimating the degree of metallization. Detailed description of the experimental work and results including metallurgical characterization by SEM are presented elsewhere[25,26]. It has been found that in a fully metallized granule the oxygen content is found to be as low as 500 ppm. Fig.6 shows photographs of sponge and a button melted out of sponge produced in the experiments.

The results obtained so far from the experimental work on 200 g scale have been very encouraging with excellent metallization and good yield. There exists a lot of scope for bringing in improvements in the experimental work. Parallely, theoretical work on process mechanism and factors determining the overall kinetics of the process is being pursued while scale up of the activity also is under progress.

6. CONCULSIONS

Titanium sponge is in great demand world over and the situation is expected to prevail for many more years to come. By and large, Kroll technology has been the main method of titanium sponge production. However, a few alternative processes such as electrochemical reduction with promising scope for commercial implementation may emerge as viable methods of sponge production.

In India, setting up of a 500 tpy commercial titanium sponge plant with Kroll technology developed at DMRL, is expected to boost up the internal consumption of the metal in the country in addition to ensuring supplies to the established internal markets.

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