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TITANIUM TECHNOLOGY AND ITS DEVELOPMENT IN INDIA

ABSTRACT

To meet the growing demand for titanium metal and its alloys in a variety of industries, including chemical, power generation, metallurgical etc., the metal industry has kept despite many ups and down, a steady growth in the annual capacity. Over the years, attempts have been made to reduce the product cost and increase the user acceptability. Increasing the production batchsize, reduction of process period, efficient management of energy and adoption of advance process control techniques, in addition to innovations on the basic process technology are some of the measures being pursued.

The paper reviews briefly the titanium in metal production technology. The development of titanium technology in India from the laboratory stage to the demonstration plant scale is discussed.

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1 - INTRODUCTION

Titanium metal industry is about 40 years old; and is limited to only few developed countries. During this period, due to fluctuating demand, the metal industry has faced many ups and downs yet maintained a progressive growth. In recent years, despite high cost of production, the demand for the metal has increased in a variety of industries, particularly chemical, power generation, electrochemical and metallurgical industries (1). It is also predicted that with the standardisation of new titanium alloy a period of fast growth will emerge and 21st century will see titanium as a major structural metal.

Extraction of titanium from its oxide minerals namely ilmenite (beneficiated ilmenite) and rutile through its intermediate product $TiC1_4$ is carried out by Kroll & Hunter processes. Although in their basic concept these metallothermic reduction process have not changed, marked progress on reduced cost of production, improved process and quality control techniques has however been made. From time to time attempts have also been made to develop fused salt electrolysis process to a commercially viable process. Recently Ginatta (2) are reported to have not only developed the process but also have set up plants for the commercial production of the metal.

India is fortunate to have large resources of titanium mainly in the form of ilmenite and rutile along its southern sea coast. Although titanium mineral production and processing industry is quite old in the country, there is no commercial production of titanium sponge. The technology for the large scale production of the metal from its chloride based on Kroll process has however been developed at the Defence Metallurgical Research Laboratory, Hyderabad and efforts to translate this into a commercial production unit are on hand.

The melting of titanium sponge and production of titanium seems like sheets, wires and forging is being carried out at the Mishra Dhatu Nigam Limited, (MIDHANI), Hyderabad having a capacity to produce about 200 TPY of titanium products. Midhani is also planning to set up facilities in collaboration with DMRL to produce titanium welded tubes. A number of companies in the country are also having facilities for the manufacture of a variety of titanium equipment.

The paper concerns the development of titanium metal production technology and its development in India and highlights the activities at DMRL on the production of titanium sponge.

2 - TITANIUM METAL PRODUCTION TECHNOLOGY

By far the two metallothermic reduction processes namely sodium (Hunter) and magnesium reduction (Kroll) processes are practiced for commercial production of titanium sponge.
The electrolytic process long ago predicted by W.J. Kroll as the technique which will ultimately be established for the production of titanium has also been developed. Recent reports indicate that this technique is also being adopted for the production of the metal.

The electrolytic process based on direct reduction of TiO_2 can offer many advantages. Despite many efforts to that end, it was realised that ductile metal could only be achieved through the chloride route. Hence all the electrolysis process so far developed are based on fused salt electrolysis of $TiCl_4$, There are however two distinct schools of development, one which adopts single (stage) cathode concept and the other adopts two cathode concept. It is known that $TiCl_4$ has poor solubility in chloride melt, unlike the lower chlorides which have good solubility in most alkali metal chloride baths. While the lower chlorides, and chlorine are highly corrosive chemicals the metal is very reactive and hence the development of electrolytic reduction of $TiCl_4$ had to meet many challenges:

1) Maintain adequate titanium spices in the melt.
2) Have suitable materials of construction and design to deposit the metal with least redissolution and corrosion problem.
3) Precise control of the reduction voltage to avoid co-deposition of the metals of carrier salts.
4) The use of suitable technique to recover the product with least wastage of carrier salts and the product metal.

Our experience (3) on the electrolysis process although limited, suggests that the process is simple for producing very good quality metal. However, engineering problems like corrosion harvesting of sponge without loss of quality and yield require detailing.

Sodium reduction process is practiced by three or four companies in the world. There are again two schools of development and practice; one adopting single stage reduction and the other two stage reduction. Chemical reduction of $TiCl_4$ with sodium is highly exothermic and to avoid freezing of NaCl (MP 810°C) or volatilisation of sodium (BP 880°C) a close control of temperature is required. The two stage reduction process perhaps facilitates the proper control of temperature and also the process can be carried out if not continuously at least in a semi-continuous fashion. Our own experience (4) with single stage reduction of $TiCl_4$ with sodium suggests that the process also is not difficult to operate. It generates very good quality crystalline metal. The overall yield of the good quality metal is crucial for the process.

Magnesium reduction process which is widely practiced the world over is perhaps the most accepted and yet the less expensive method of producing titanium sponge. The process offers many advantages especially the large productivity per unit and safety in handling and higher yield of high quality metal. There are certain practical differences in the methods adopted by various companies i.e.:

1) Mg reduction followed by vacuum distillation
2) Mg reduction followed by leaching
3) Mg reduction followed by inert gas sweep and leaching
4) Mg reduction and vacuum distillation in one assembly

These modification on the process as well as the innovations on the materials of construction, design of equipment and similar ones on recycle of magnesium and management of heat and material have contributed to greater success and acceptance of magnesium reduction process. The phenomenal rise in the production batch size of 10t has brought down the cost of production of the metal.

In India the magnesium reduction process has been studied in greater detail (5) and a demonstration plant of 100 tpy capacity has recently been set up at the Defence Metallurgical Research Laboratory, Hyderabad. The plant and the other one for the recovery of magnesium from $MgCl_2$ are in operation at DMRL.

During the last four decade titanium process industry has made remarkable progress. We see from the world titanium scene that the developments have distinctly been in the following directions:

1) Persistant efforts to establish the electrolytic process.
2) Reduce the product cost either by the electrolysis process or by modified magnesiothermic reduction process (to reduce process time, energy inputs and precise control of process).

3) Improve the quality of metal by increasing batch size and also by close control of process conditions.

4) Find newer applications for:
   a) the high quality metal (like superconductors, semi conductor)
   b) commercial alloy (like Ti alloys) and
   c) off grade metal (like addition in steels).

3 - INDIAN SCENE

The main constituents of the titanium industry in the country are mining, processing of titanium minerals, beneficiation of ilmenite, pigment oxide production, production of titanium semis and equipment. The Figure 1 shows the structure of titanium industry in the country, the names of the agencies and scale of operations involved. Mining and processing of minerals commenced in the second decade of this century followed by production of TiO_2 pigment by the sulphate route in the 50's. Production of titanium and titanium alloy semis and fabricated components like insoluble anodes for alkali industry, heat exchangers etc. commenced about a decade ago. In recent years, plants for the production of beneficiated ilmenite and pigment oxide by chloride route have come into operation.

It may be seen from the figure that production of titanium sponge on commercial scale is yet to commence in the country. However, efforts have continued for the last two decades. Table 1 shows the mile stones in the development of titanium sponge production technology in the country. it may be seen that all the established routes on the production of titanium sponge have been studied on laboratory scale at Bhabha Atomic Research Centre (Department of Atomic Energy). Pilot plant scale operation have been carried out at the Nuclear Fuel Complex of

Department of Atomic Energy for a comparative study of sodium and magnesium reduction processes. As a consequence of this a demonstration plant has been set up at Defence Metallurgical Research Laboratory (DMRL).

It is hoped that based on the technology developed at DMRL a commercial plant of 1000 tpy capacity will be set up soon in the country.

4 - DMRL PRACTICE

The process flow sheet for the production of titanium sponge at DMRL is shown in Figure 2. It consists of mainly three wings, first purification of $TiCl_4$, second metal production-reduction vacuum distillation and the third sponge handling and metal harvesting.

Fig. 3 shows the purification bay. The raw chloride received in steel drums, is pressure transferred to storage tanks. The chloride is preheated and then passed through two packed columns one to separate dissolved gases and the other for the separation of high boiling components and solids.
The pure chloride vapour is condensed and collected and used for reduction.

Magnesium ingots are pickled for the separation of metal oxide layer. The metal is dried and transferred for reduction to the metal production bay.

Fig. 4 shows the reduction and vacuum distillation bay.
The reduction batch size is 2000 kg electric resistance furnaces are used both for reduction and vacuum distillation.

Fig. 5 shows the sponge harvesting bay. Horizontal and vertical hydraulic presses and jaw crushers are used to crush the sponge cake to 2-12mm size product. Table 2 shows the analysis of $TiCl_4$, Mg used and titanium sponge obtained.

At DMRL we are working simultaneously on two aspects i.e.:

1) use of computer based process control system
2) use of a combination unit

1) A Microprocessor based controller system has been procured and installed recently. it is proposed to operate the chloride purification, reduction and vacuum distillation facilities with the help of this controller. Efforts are being made to commission the unit along with the indegenously available process control field instruments.

2) By confining the reduction and vacuum distillation operation to one unit - called combination unit - many advantages like saving in process time, lesser energy input and improved quality of sponge are expected to be achieved. Fabrication of a furnace and the process equipment for this purpose have been taken up. Plans are on hand to commission this unit.

5 - SUMMARY

India is rich in titanium resources and there exists a basic industry for processing titanium minerals for the production of titanium tetrachloride, titanium and titanium alloy products. Efforts to establish a commercial plant for the production of titanium sponge based on the technology developed at DMRL are being made.

6 - REFERENCES

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Defence Science Journal (India) Vol. 36, NO.2 April 1986.

7 - ACKNOWLEDGEMENTS

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HISTORY OF TITANIUM DEVELOPMENT IN INDIA

1953	Mg REDUCTION — LEACHING	[illegible] SCALE	NML
1967	Mg REDUCTION — VAC. DISTILLATION	[illegible] SCALE	BARC
1972	Mg REDUCTION — VAC. DISTILLATION	[illegible] kg SCALE	BARC
1973	Na REDUCTION — LEACHING	[illegible] kg SCALE	BARC
1975	Mg REDUCTION — VAC. DISTILLATION	400 kg SCALE	NFC
1976	Na REDUCTION — LEACHING	[illegible] kg SCALE	NFC
1978	Na REDUCTION — LEACHING	320 kg SCALE	NFC
1979	ELECTROLYTIC — LEACHING	5 kg SCALE	BARC
1984	Mg REDUCTION — VAC. DISTILLATION	2000 kg SCALE	DMRL

Table 1

ANALYSIS OF TITANIUM TETRACHLORIDE

	RAW CHLORIDE %	PURE CHLORIDE %
$TiCl_4$	99.800 (Min)	99.950 (Min)
$SiCl_4$	0.050 (Max)	0.003 (Max)
$AlCl_3$	0.050 (Max)	0.003 (Max)
$VOCl_3$	0.050 (Max)	0.003 (Max)
DISSOLVED GASES AND HIGH VOLATILES	0.020 (Max)	0.003 (Max)
SOLIDS AND NON-VOLATILES	0.080 (Max)	0.003 (Max)

Table 2.1

ANALYSIS OF MAGNESIUM

ELEMENT	(PPM)
Aluminium	30
Iron	400
Silicon	50
Copper	40
Manganese	60
Tin	50
Magnesium (by difference)	> 99.9

Table 2.2

ELEMENT	Amount Wt% (Max)
NITROGEN	0.015
CARBON	0.020
MAGNESIUM	0.080
CHLORINE	0.120
IRON	0.120
SILICON	0.040
HYDROGEN	0.010
OXYGEN	0.100
HARDNESS BHN	90/95

Table 2.3

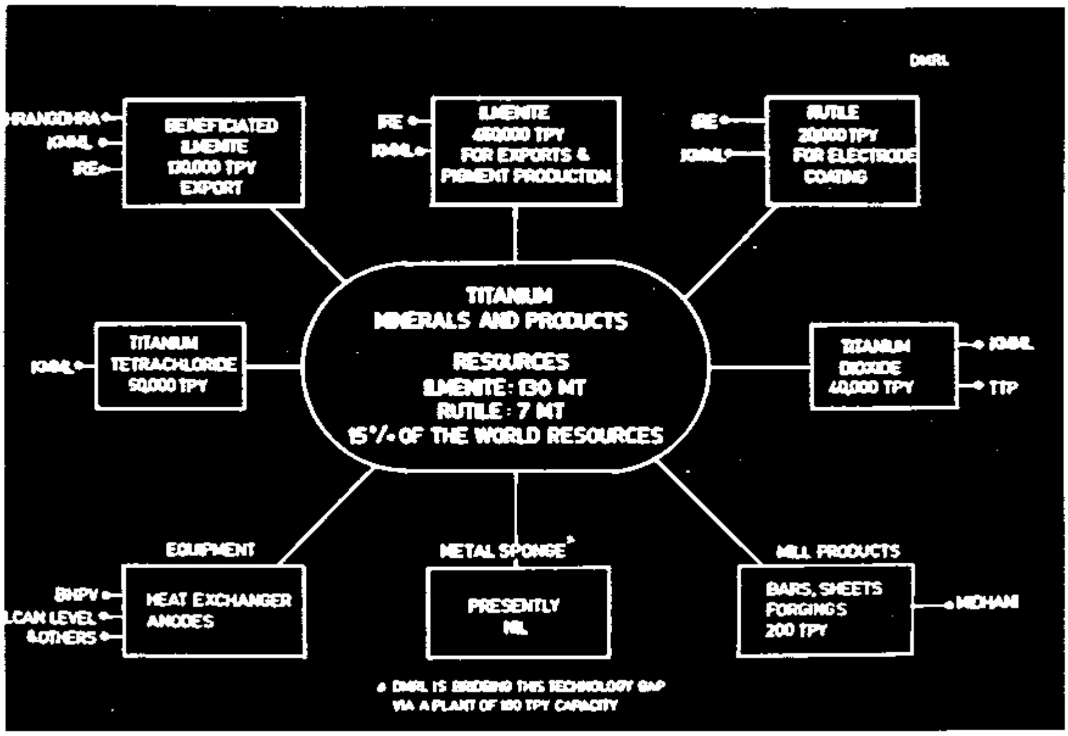
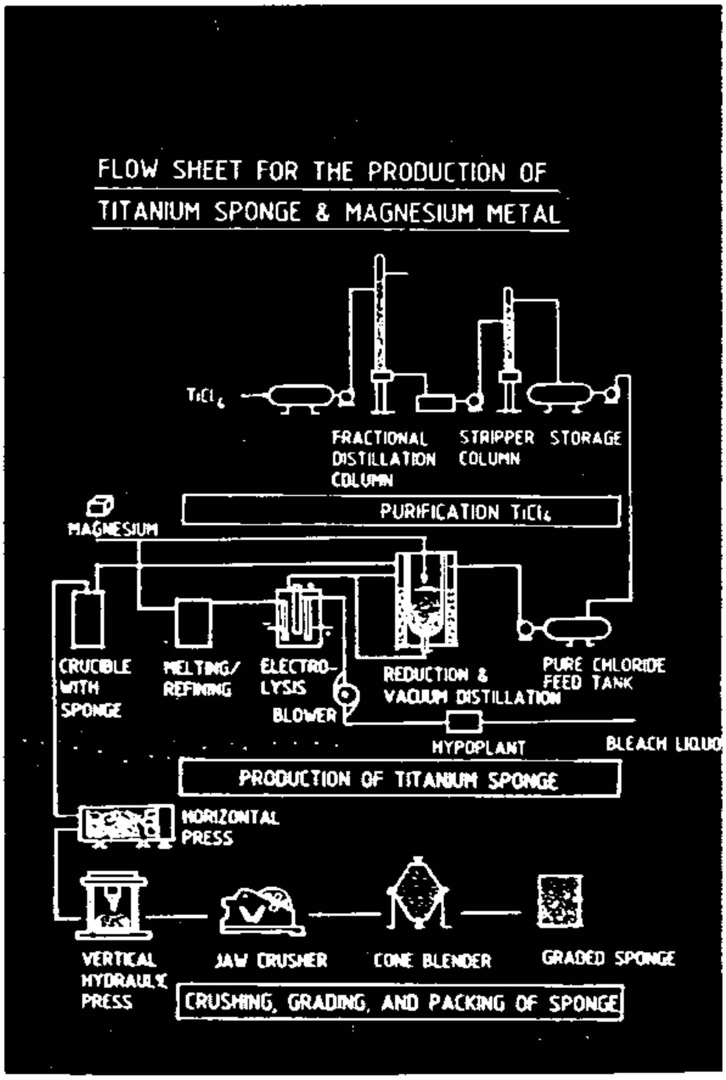

DMRL
HRANGDHRA
KMML
IRE
BENEFICIATED ILMENITE 130,000 TPY EXPORT
IRE
KMML
ILMENITE 450,000 TPY FOR EXPORTS & PIGMENT PRODUCTION
IRE
KMML
RUTILE 20,000 TPY FOR ELECTRODE COATING
KMML
TITANIUM TETRACHLORIDE 50,000 TPY
TITANIUM MINERALS AND PRODUCTS
RESOURCES
ILMENITE : 130 MT
RUTILE : 7 MT
15% OF THE WORLD RESOURCES
TITANIUM DIOXIDE 40,000 TPY
KMML
TTP
EQUIPMENT
BHPV
LCAN LEVEL
& OTHERS
HEAT EXCHANGER ANODES
METAL SPONGE*
PRESENTLY NIL
MILL PRODUCTS
BARS, SHEETS FORGINGS 200 TPY
MIDHANI
* DMRL IS BRIDGING THIS TECHNOLOGY GAP VIA A PLANT OF 100 TPY CAPACITY

Fig. 1

Fig. 2


FLOW SHEET FOR THE PRODUCTION OF TITANIUM SPONGE & MAGNESIUM METAL
TiCl4
FRACTIONAL DISTILLATION COLUMN
STRIPPER COLUMN
STORAGE
PURIFICATION TiCl4
MAGNESIUM
CRUCIBLE WITH SPONGE
MELTING/ REFINING
ELECTRO- LYSIS
BLOWER
REDUCTION & VACUUM DISTILLATION
PURE CHLORIDE FEED TANK
HYPOPLANT
PRODUCTION OF TITANIUM SPONGE
HORIZONTAL PRESS
VERTICAL HYDRAULIC PRESS
JAW CRUSHER
CONE BLENDER
GRADED SPONGE
CRUSHING, GRADING, AND PACKING OF SPONGE

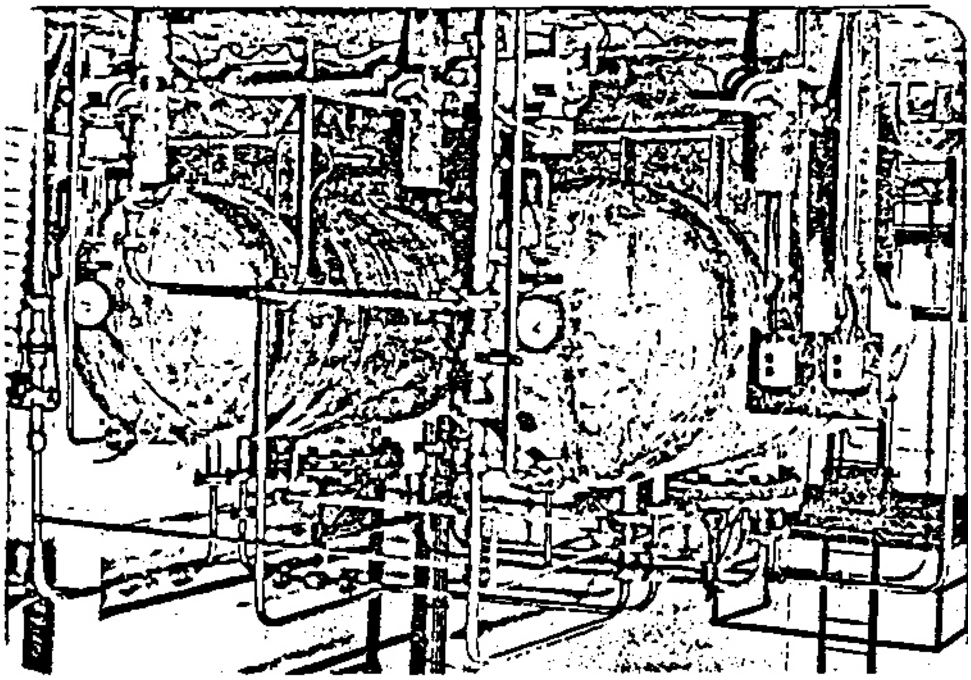


Fig. 3 - Purification bay

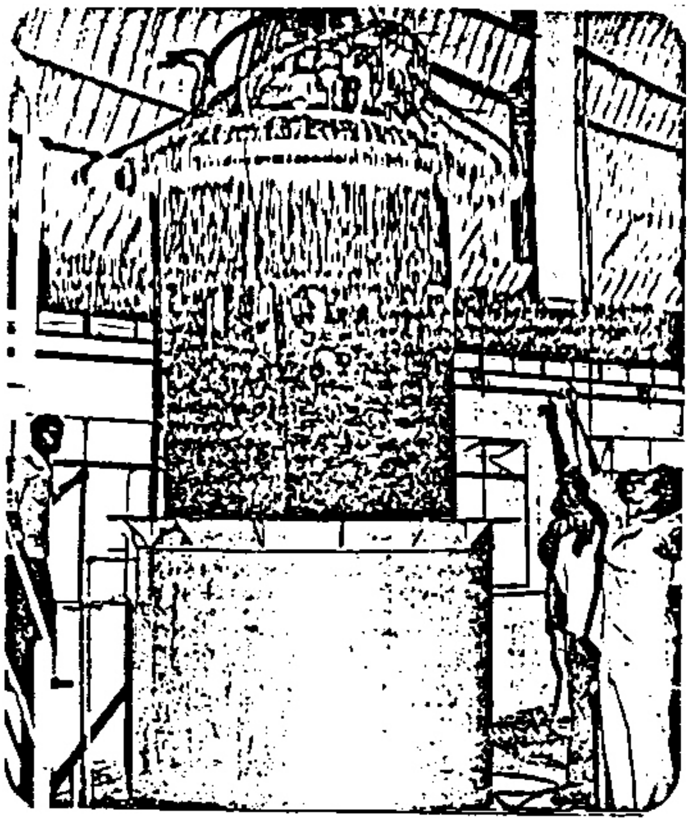


Fig. 4 - Reduction bay

Fig. 5 - Vertical hydraulic presses