High Temperature Materials and Processes, Vol. 9, Nos. 2-4, 1990

Development of Titanium Sponge Production Technology in India

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ABSTRACT

An integrated experimental facility for the production of titanium sponge in 2,000 kg batches has been set up at the Defence Metallurgical Research Laboratory, Hyderabad (DMRL). This paper describes the salient features of the facility and presents some of the experimental results.

INTRODUCTION

Titanium sponge is produced industrially by either the magnesium reduction or the sodium reduction process. The former, also known as the "Kroll Process" after its inventor, Dr. W.J. Kroll, dates back to 1946 and accounts for nearly 80% of the world's sponge production capacity. The sodium reduction process or the "Hunter Process" was invented by Dr. H.E. Hunter as early as 1910 and some producers have also adopted this route /1/. Although these two processes have essentially remained the same since their invention, many technological innovations in process equipment and controls, batch size, energy saving techniques, etc. have resulted in substantial improvements in respect to sponge quality, process efficiency and production cost /2/. Recovery of magnesium from the magnesium chloride by-product in the Kroll process has also formed an integral part of the metal production flow sheet for greater economy.

India is endowed with large reserves of titanium in the form of ilmenite, all along the coast of peninsular India /3/. Commercial plants for the production of (1) ilmenite and rutile from the beach sands, (2) synthetic rutile from ilmenite, (3) titanium tetrachloride from synthetic rutile, (4) pigment grade titanium dioxide both by the sulphate and the chloride routes are already in operation in the country. In addition, facilities for the production of titanium and titanium alloy mill products such as forgings, plates and sheets, rods and wire as well as a wide range of fabricated equipment in titanium have also been created (Fig. 1). However, there is no commercial production of titanium sponge so far in the country, although developmental work on titanium sponge production by all the three commercially viable routes, viz., magnesium reduction, sodium reduction and fused-salt electrolysis, has been in progress since the mid-60s /4,5/. In order to fill the gap in metal production and to establish the titanium sponge production technology in India, DMRL set up a demonstration plant in 1984/1985 and selected the Kroll process to produce the metal in 2,000 kg industrial size batches. In parallel, a demonstration plant for the recovery of magnesium from $MgCl_2$ by the fused salt electrolysis process has also been set up.

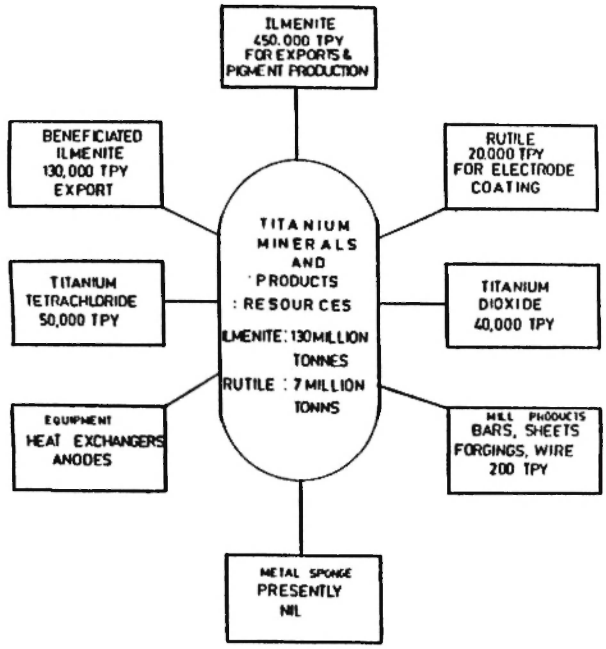

Fig. 1: Indian Ti scene 1987.

Salient features of the facility, its operation and experimental results are presented in the paper.

DMRL FACILITY

The flow sheet for the production of titanium sponge from raw titanium tetrachloride (Fig. 2) consists of the following four major steps:

(1) purification of titanium tetrachloride
(2) reduction and vacuum distillation
(3) sponge handling
(4) magnesium recovery

For carrying out the above operations, the DMRL facility is provided with indigenously designed and fabricated equipment. In addition to process equipment, the plant has installed a power supply and distribution system, ventilation system and other utility systems for process water, cooling water, compressed air, instrument quality air, argon, etc.

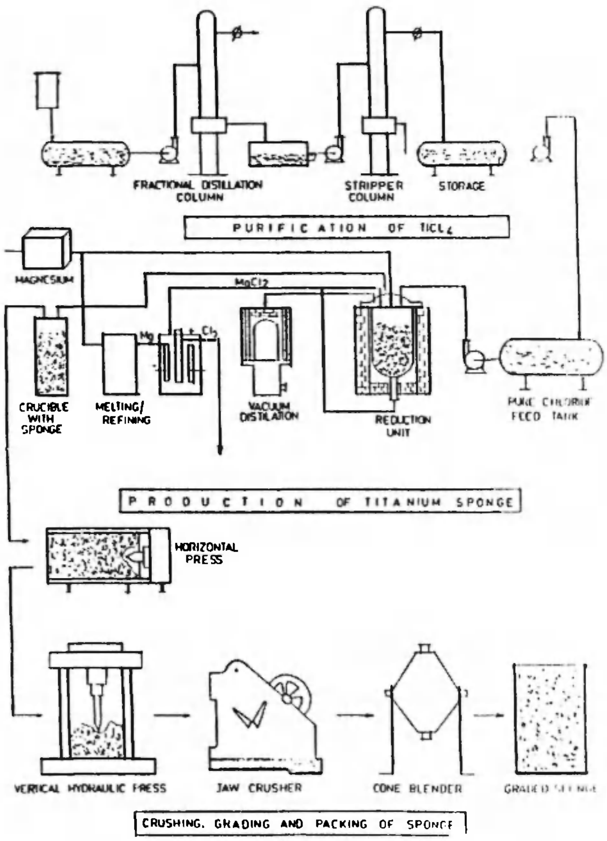

Fig. 2: Flow sheet for Ti sponge.

Purification of Titanium Tetrachloride

The purification section has storage tanks for raw, pure and off-grade titanium tetrachloride, two packed columns (one for fractional distillation and the other for stripping of chloride) for the separation of low and high boiling fractions and other ancillary equipment such as heat exchanges, filters and pumps. All the process equipment and tanks are provided with suitable instruments for the monitoring and control of liquid levels, flow rates, pressures and temperatures. FRP tanks for pickling and washing of magnesium are also housed in this section.

Reduction and Vacuum Distillation

In the metal production section (Fig. 3), equipment for the magnesium reduction of titanium tetrachloride and vacuum distillation of reduced mass is installed. The reduction equipment consists of (1) a pit type electric resistance furnace, (2) a Kroll Reactor with reduction crucible and tapping valve for magnesium chloride removal, (3) a furnace cooling blower for removal of exothermic heat and (4) power supply and process control panels. The vacuum distillation assembly comprises a bell-type vacuum furnace, a stainless steel retort for holding crucible and collecting the distillate, a high vacuum pumping system for the retort and a water-ring type rough vacuum pump for the furnace, with supporting instrumentation and control panels.

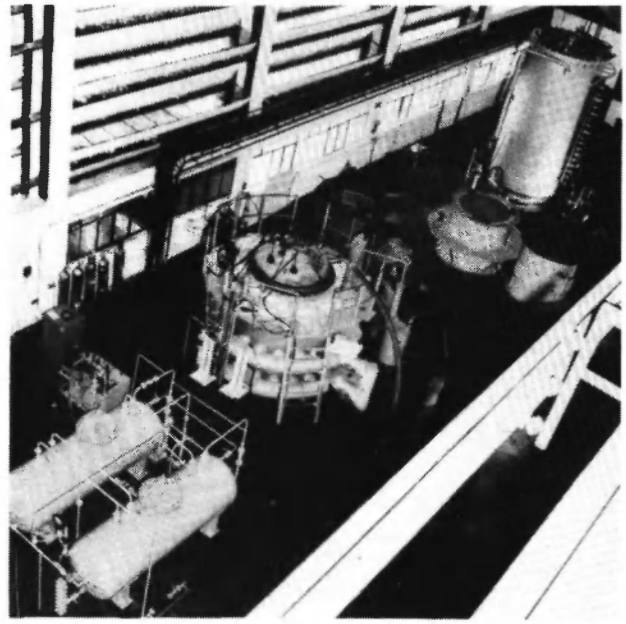

Fig. 3: Sponge production bay.

Sponge Handling

The sponge handling section is equipped with a horizontal hydraulic press, a vertical hydraulic press, a set of two jaw crushers with screens for primary and secondary crushing of sponge and a double cone blender.

Magnesium Recovery

The magnesium plant has two 30,000 amp capacity fused-salt electrolytic cells (Fig. 4) along with a bleach liquor plant for by-product chlorine disposal.

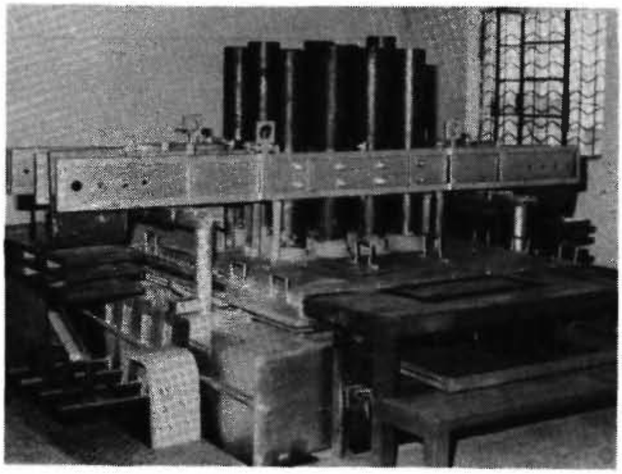

Fig. 4: Mg electrolytic cell.

OPERATIONS

Raw titanium tetrachloride received in 210 L capacity steel drums is first transferred to one of the 25 ton capacity storage tanks in the plant. From the storage tanks the chloride is pumped at a controlled rate, preheated to its boiling point and then admitted to the distillation column. By maintaining a suitable reflux ratio, a product richer in silicon tetrachloride is separated and collected in a separate storage tank. The titanium rich fraction from the reboiler is continuously pumped into the stripping column, and pure titanium tetrachloride is collected from the top of the column. It is cooled to room temperature and stored in 10 ton capacity storage tanks.

About 8 tons of the above chloride required for each batch of reduction is transferred to the feed tanks of the metal production section. A weighed quantity of magnesium ingots, freshly pickled in dilute hydrochloric acid, is charged into the steel reduction crucible placed inside the Kroll Reactor. After bolt down, the reactor assembly is leak tested, placed inside the pit furnace, evacuated and back-filled with argon twice to ensure a good inert atmosphere inside the retort. The assembly is then heated to the reduction temperature of 825-900°C and after a few hours soak at this temperature, titanium chloride is pumped in at a controlled rate. While the reduction is in progress, magnesium chloride is tapped out at scheduled intervals and transferred to the magnesium plant for recovery of magnesium. After completion of reduction, the reduced mass is soaked to facilitate conversion of lower chlorides to titanium and the reactor is tapped for the final time to remove residual magnesium chloride and excess magnesium. The reactor is then cooled to room temperature under a positive pressure of argon.

The reduction crucible with charge is then transferred to the vacuum distillation assembly. Vacuum distillation is carried out for 30 to 40 hrs at above 950°C under a reduced pressure of less than 10^{-3} Torr Hg. During this period, the furnace is also kept under a reduced pressure of 10-20 mm Hg abs. At the end of the vacuum distillation cycle, the furnace is cooled under vacuum to a lower temperature at which temperature the retort is filled with argon (with simultaneous aeration of furnace) for accelerated cooling of the charge. At room temperature a conditioning cycle consisting of gradually replacing the argon in the retort with air for passivating the sponge surface is carried out.

In the sponge handling section, the sponge cake of about 2 tons is extracted from the crucible using the horizontal press. The cake surface is thoroughly cleaned with the help of copper-beryllium chisels and crushed to small size suitable for further cutting and grading on the vertical press. The graded sponge is further crushed and sized to 2-12 mm in the two jaw crushers.

The crushed metal is sampled and analysed as per well laid down procedures, blended to 1 ton lots, packed in 210 L capacity steel drums under argon pressure and supplied to the melt shop of Mishra Dhatu Nigam Limited (MIDHANI) along with certified analysis of the lot.

Electrolysis of magnesium chloride is carried out at 25 KA by feeding magnesium chloride at two hour intervals to the molten salt bath at 720-800°C. The metal is ladded out at frequent intervals. Chlorine gas is withdrawn from the cells and converted to hypo solution.

RESULTS AND DISCUSSION

Experiments to study the effect of various operating parameters on product quality and to establish the optimum production conditions have been carried out.

The nature of formation and the growth of sponge cake (Fig. 5) is strongly influenced by the operating temperature, feed rate of titanium chloride and tapping schedule of magnesium chloride during reduction. Higher reduction temperatures are undesirable from the

Fig. 5: Two ton Ti sponge cake.

point of view of formation of excessive lower chlorides due to the vapour phase reactions between magnesium and chloride. On the other hand, lower temperatures tend to retard the reaction and the reaction does not go to completion. It has also been observed that by increasing the amount of excess magnesium, the feed rate of titanium chloride could be maintained higher almost till the end of reduction. Quantity of magnesium chloride being tapped and the frequency of tapping also seem to influence the reduction reaction quite significantly, and this schedule also needs to be optimised for achieving good results during reduction.

Vacuum distillation above 950°C for a period of 40 hours has been found to be necessary to effect efficient removal of excess magnesium and residual magnesium chloride down to desired levels throughout the height and diameter of the sponge cake.

From the experiments carried out so far, it is seen that the quality of sponge (Table 1) depends on (1) the purity of magnesium and titanium tetrachloride; (2) operating conditions of reduction, vacuum distillation, sponge conditioning, handling and storage and more critically on the reduction process which in turn depends on the efficient management of heat transfer and temperature control.

Yield of magnesium metal and efficiency of the electrolysis are found to be affected by the quality of feed magnesium chloride. The quality of the remelted magnesium metal is found to be acceptable for titanium production.

TABLE 1
Ti SPONGE ANALYSIS

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

FURTHER WORK

With a view to achieving greater reliability and reproducibility of the operating parameters in the critical steps of chloride purification and reduction, a microprocessor based process control system capable of data logging and control of all parameters has recently been installed in the plant. Plans have also been drawn up for installing a combination reduction distillation unit for reducing the process steps, improving the product quality and bringing down the energy requirement. Proposals have also been made to utilise the technology already developed for setting up commercial plants, and at the same time continue the developmental work towards the establishment of a combination reduction-distillation process using the microprocessor based process control system for improving process efficiency and lowering production costs.

CONCLUSION

It may be concluded that:

1. The DMRL technology demonstration plant, a major step towards large-scale production of these metals in India, has provided rich and valuable experience on the production of titanium sponge in 2000 kg batches and magnesium metal in 30 KA cells.

2. The quality of titanium and magnesium produced has met international specifications.
3. Operating conditions to facilitate the establishment of an integrated plant for the production of titanium metal to meet indigenous requirements have been established.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. V.S. Arunachalam, Scientific Adviser to Raksha Mantri, for providing the leadership for setting up the facility. They also express their gratitude to Dr. P. Rama Rao, Director, DMRL, and Shri C.V. Sundaram, Director, Indira Gandhi Centre for Atomic Research, Kalpakkam for their guidance and support. The excellent support provided by the staff of the facility is also gratefully acknowledged.

REFERENCES

1. T. Ikeshima, "Titanium Science & Technology", Proceedings of the Fifth International Conference on Titanium (edited by G. Lutjering, U. Zwicker and W. Bunk), p. 3. Deutsche Gesellschaft für Metallkunde (1985).
2. A.N. Petrunko, "Titanium Science & Technology", Proceedings of the Fifth International Conference on Titanium (edited by G. Lutjering, U. Zwicker and W. Bunk), p. 67. Deutsche Gesellschaft für Metallkunde (1985).
3. Ch. Sridhar Rao and R.B. Subramanyam, "Light Metals Science & Technology", Proceedings of an International Symposium (edited by C. Suryanarayana, P.M. Prasad, S.L. Malhotra and T.R. Anantharaman), p. 171. Trans. Tech. Publications (1985).
4. R.B. Subramanyam and Ch. Sridhar Rao, *Defence Science Journal*, **36**, 105 (1986).
5. A.P. Kulkarni et al., "Titanium '80: Science & Technology", Proceedings of the Fifth International Conference on Titanium (edited by H. Kimura and O. Izumi), p. 1927. TMS AIME, Warrendale, Pa. (1980).