Chapter 4
Titanium Sponge Production and Processing for Aerospace Applications

Ch R.V.S. Nagesh, G.V.S. Brahmendra Kumar, B. Saha and Amol A. Gokhale

Abstract Titanium sponge is widely produced employing the Kroll process of high-temperature reduction of titanium tetrachloride by magnesium. The technological developments over the last few decades have focused on cost/energy savings in addition to introducing sophisticated systems in the manufacturing technology. This chapter concerns Indian efforts to develop 'state-of-the-art' Kroll technology for producing titanium sponge in industrial scale batches. While covering various features of the combined process technology developed at DMRL, the chapter also discusses advanced quality evaluation and sponge processing practice as developed at DMRL and implemented at the KMML sponge plant (which was established with the DMRL technology). Extensive measures that have been implemented to obtain high purity metal and assured quality of the product are discussed.

Keywords Titanium sponge · Extraction metallurgy · Chemical analysis

4.1 Introduction

Titanium and its alloys have excellent engineering properties, including low density (4.5 g/cm^3), good strength, and superior corrosion resistance. High-strength titanium alloys with lower density are attractive materials for aero engine components

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at temperatures up to about 650 °C, and also airframe structural applications requiring higher load densities than aluminium alloys and also higher operating temperature capabilities.

Titanium metal is, however, reactive and poses several problems in high temperature processing operations. Ductility, workability, and other mechanical properties of titanium are highly sensitive to interstitial impurities such as oxygen, nitrogen, carbon, and hydrogen. The corrosion resistance of titanium is also impaired when iron is present beyond specified limits.

Because of the high chemical reactivity of titanium, there are no viable methods of purification for removing the impurity elements. Thus great care needs to be taken during the production of titanium sponge, which is the nascent form of titanium obtained from reduction of titanium tetrachloride by sodium or magnesium, see Sect. 4.2.

Titanium ore is available mostly in the form of the oxide minerals ilmenite ($FeOTiO_2$) and rutile (TiO_2). The titanium dioxide content of ilmenite usually lies in the range of 40–60 wt%, whereas rutile consists of up to 90 wt% TiO_2, the remainder being mostly silica. By employing various physical and chemical methods of beneficiation, ilmenite is processed to increase the TiO_2 content, and this product is referred to as synthetic rutile. Indian reserves of ilmenite are estimated to be 593.5 million tons (12–15 % of world total) and the reserves of rutile are estimated at 31.3 million tons in terms of TiO_2 content [1].

Over 90 % of titanium minerals in the world are processed for the preparation of high purity (pigment grade) titanium dioxide (TiO_2), which has a wide range of applications in cement, textile, paints, pharmaceuticals, and plastics. Both the 'sulphate route' (in which titanium sulfate is the intermediate) and 'chloride route' (in which titanium tetrachloride is the intermediate) are widely used for manufacturing the high-purity TiO_2.

4.2 Established Methods of Titanium Extraction

Early efforts by researchers to produce titanium by metallothermic (Al, Mg, and Ca) and carbothermic reduction of titanium dioxide failed to produce metal of the required purity. From these unsuccessful attempts it was learnt that to prepare pure titanium metal the starting material should be a non-oxygen-bearing compound. There have been several successful attempts:

- In 1910 Hunter succeeded in producing high-purity titanium by sodio-thermic reduction of titanium tetrachloride ($TiCl_4$) in a high-pressure steel vessel.
- In 1925 van Arkel and de Boer produced high purity titanium by dissociation of titanium iodide on a tungsten filament.
- In 1937 Kroll developed the method of magnesio-thermic reduction of $TiCl_4$ in an argon gas atmosphere.

- Fused salt electrolysis of $TiCl_4$ in alkali chloride mixtures was also extensively studied and reported to be a viable method of producing pure titanium metal.

Both the Hunter and Kroll processes were developed to produce titanium on an industrial scale by the late 1940s. While the Hunter process was extensively studied and developed by Imperial Chemical Industries, UK, the Kroll process was developed simultaneously by the US Bureau of Mines, and also in Japan and the former USSR.

Development of the fused salt electrolysis process was taken up by Dow Howmet, USA, and Electrochemica Marco Ginnatta, Italy. However, the process operated only on a pilot plant scale, and has not been implemented in commercial practice.

Historical developments in titanium extraction metallurgy are discussed in great detail in the literature [2–4]. Subsequent developments and new methods of titanium extraction are also summarized and made available in the literature [5–8].

Thus although there are three established methods of titanium extraction, see Fig. 4.1, only two, the Hunter and Kroll processes, are commercially implemented for large-scale production of titanium sponge. The Hunter process involves $TiCl_4$ reduction by sodium; the Kroll process involves $TiCl_4$ reduction by magnesium; and fused salt electrolysis uses $TiCl_4$ (which is obtained from high-temperature chlorination of oxide mineral concentrates) as starting material. In all cases an inert

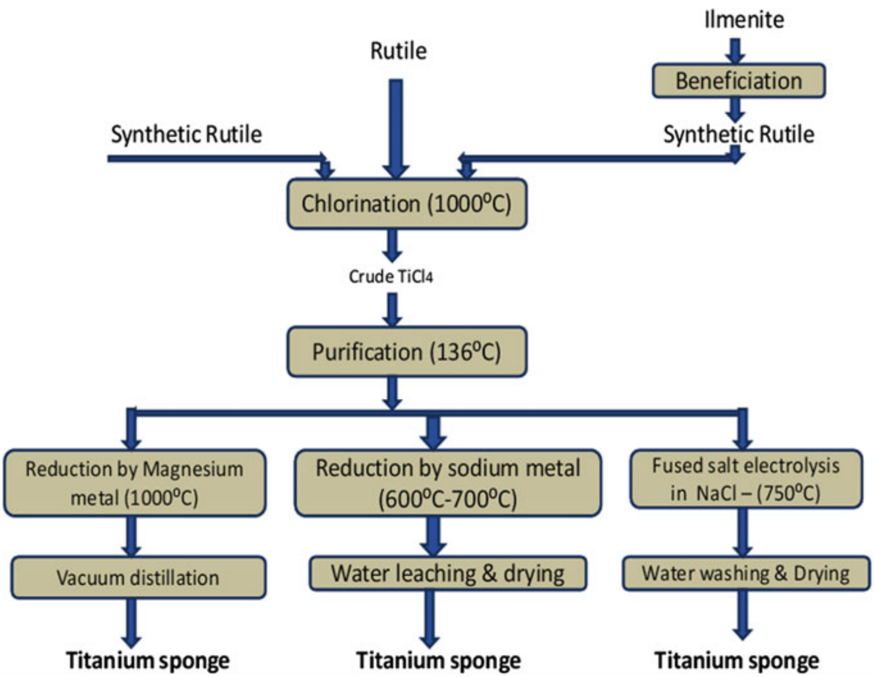

Fig. 4.1 Established methods of titanium sponge production

gas atmosphere is invariably used to protect the quality of the metal throughout the extraction process; and the titanium metal takes the form of a porous agglomerated powder particulate that is referred to as 'titanium sponge.'

4.3 World Production of Titanium Sponge—Recent Developments

Major producers of titanium sponge have been Japan, the US, former USSR countries, the UK and China. Initially, most of the titanium production was for the aerospace industry, especially for military aircraft. The large dependency of titanium sponge production on military applications was mainly responsible for its cyclic demand in the Cold War era. However, subsequently there has been increased usage of titanium in non-aerospace sectors, especially in Japan and Russia.

Figure 4.2 shows that the world production capacity for titanium sponge has risen gradually from around 5000 metric tons (MT) in the beginning, to as high as 300,000 MT at present, although the actual production levels have fluctuated due to the above-mentioned reasons and also global economic recessions and booms in the civil aviation sector [9, 10].

Most of the sodium-based plants that were operating in the UK and Japan were closed in the early 1990s quoting techno-economical difficulties. Hence almost the entire world production is predominantly taking place via the Kroll process (with many engineering advancements and increased batch sizes). The current level of world production of sponge is much lower than the actual capacities (owing to

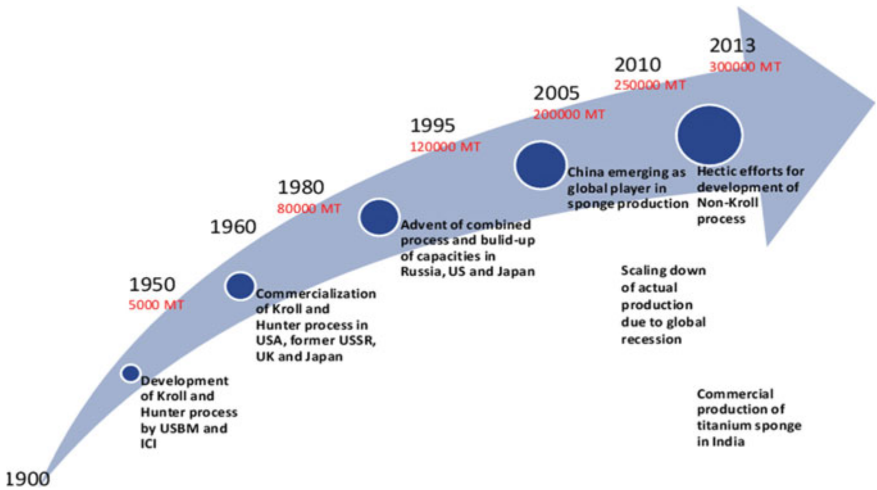

Fig. 4.2 Trends in world titanium sponge production. *MT* = metric tons

economic recession) and placed at about 160,000 MT per year, nearly half of it reportedly taking place in China [11].

There has been much effort to commercialize a non-Kroll process during the last decade or so. Salient among them include the Armstrong process of sodium reduction of $TiCl_4$ in the gas phase to produce titanium powder continuously [6], and electrochemical reduction of TiO_2 (FFC Cambridge process) [12]. It was also reported that a process for titanium hydride production by reduction of $TiCl_4$ by magnesium and hydrogen was tested on a pilot plant scale (ADMA pilot plant) [13].

However, the Kroll technology continues to be the globally most practiced method for the commercial production of titanium sponge. Based on several advancements in the Kroll technology, it has also become possible to produce titanium sponge of 5 N purity for selected electronic applications [14].

4.4 Indian Scenario on Titanium Sponge Production

In India basic research on the preparation of $TiCl_4$ by fluidized bed chlorination of mineral concentrates and production of titanium sponge by the Kroll and Hunter processes were carried out at Bhaba Atomic Research Centre (BARC), Mumbai, in the 1960s [15]. During the 1970s Nuclear Fuel Complex (NFC), Hyderabad, operated a Kroll/Hunter pilot plant facility where titanium sponge production in 100/60 kg batches was studied in detail. Based on this experience it was decided that the Kroll process was suitable for scaling up to industrial production [16].

4.4.1 Development of Kroll Technology at DMRL, Hyderabad

The main technological parameters to be standardized in the Kroll process are (i) control of reaction temperature, since the reduction process is exothermic, by selection of an appropriate $TiCl_4$ feed rate and admission scheme, (ii) tapping the magnesium chloride ($MgCl_2$) reaction by-product for effective utilization of reactor volume, (iii) heating rate, time, and temperature of vacuum distillation of reduced sponge to remove unreacted magnesium and trapped $MgCl_{2,}$ and (iv) grading and size reduction of titanium sponge cake to obtain high-purity sponge in the specified size range.

In the early 1980s the Defence Metallurgical Research Laboratory (DMRL) began industrial scale R&D for the Kroll process. A pilot plant was set up to investigate the sponge production process on a scaled up batch of 2000 kg, and to standardize the technical parameters for production of aeronautical grade sponge [17, 18]. The facilities established for this purpose included the following:

(i) Fractional distillation system comprising a packed-bed distillation column and a stripper column to purify raw $TiCl_4$ and remove impurities such as dissolved gases, $SnCl_4$, $SiCl_4$, and oxy-chlorides.
(ii) Reduction of $TiCl_4$ by magnesium in a stainless steel reactor placed in a multi-zone electrical resistance furnace. The bottom of the reactor has a plug and seat type valve to enable tapping hot $MgCl_2$ during the reduction process.
(iii) A separate reactor assembly to carry out the pyro-vacuum distillation process of the reduced sponge, together with the reaction crucible. The reduced mass is heated to high temperature (950–975 °C) with the help of a resistance furnace, and the distillates are collected in a salt which can be placed below the reaction crucible. The assembly also consists of a water-cooled bottom retort connected to the vacuum pumping system.
(iv) A custom-built horizontal hydraulic press for ejection of titanium sponge cake from the reaction crucible; and various size reduction operations to prepare titanium sponge pieces in the finished size range of 2–25 mm.

In a separate study the magnesiothermic reduction process was extensively studied and explored for improved understanding of the reaction mechanism and sponge formation scheme in the reduction reactor [19].

4.4.2 Development of Combined Process Technology at DMRL, Hyderabad

The quality of titanium sponge produced by the Kroll process depends on many factors such as purity of raw materials, cleanliness and leak tightness of the reactor; interruptions in process operations leading to exposure of reduced sponge to atmospheric air; reactor material; and care taken during handling of the sponge.

Aerospace grade sponge must meet stringent upper limit specifications with respect to O, N, C, Fe, Mg, and chloride. The ***first phase*** developmental work on 2000 kg batches at DMRL suffered from serious setbacks of (i) interruptions in process operations owing to problems in bottom tapping $MgCl_2$ via a valve, (ii) inevitable exposure of reduced sponge to atmospheric air while transferring it to the vacuum distillation assembly, (iii) jamming of connecting pipes with distillates during vacuum distillation, and (iv) unsatisfactory performance of sponge handling systems.

However, the engineering expertise gained from the developmental work immensely helped in understanding the technological requirements and designing improved systems for sponge production in the ***second phase*** of developmental work, i.e. development of a ‘Combined Process Technology’ in 3000–3500 kg batches. This combined process technology has the following advantages:

(i) Low overall energy consumption.
(ii) Highest achievable process efficiency and materials utilization.
(iii) Significant reduction in process cycle time.
(iv) Improved yield and purity of sponge.
(v) Lower capital costs and reduced manpower requirement.
(vi) Safe equipment and operating procedures.

Figure 4.3 shows details of the salient features of the 'Combined Process Equipment' developed at DMRL for sponge production in 3000–3500 kg batches. These features include the following:

(i) Use of a single multi-zone electrical resistance furnace for reduction and vacuum distillation operations at a single station. This meets the requirements of heating in a controlled manner and removing exothermic heat from the reactor at selected sites.
(ii) Two custom engineered identical clad stainless steel retorts (fabricated as per ASME pressure vessel code Section VIII) connected by a heated pipe. One of the two retorts is for sponge production, while the other receives the distillates in the condenser station. This results in improved materials utilization since the condenser retort is subsequently used for sponge production.

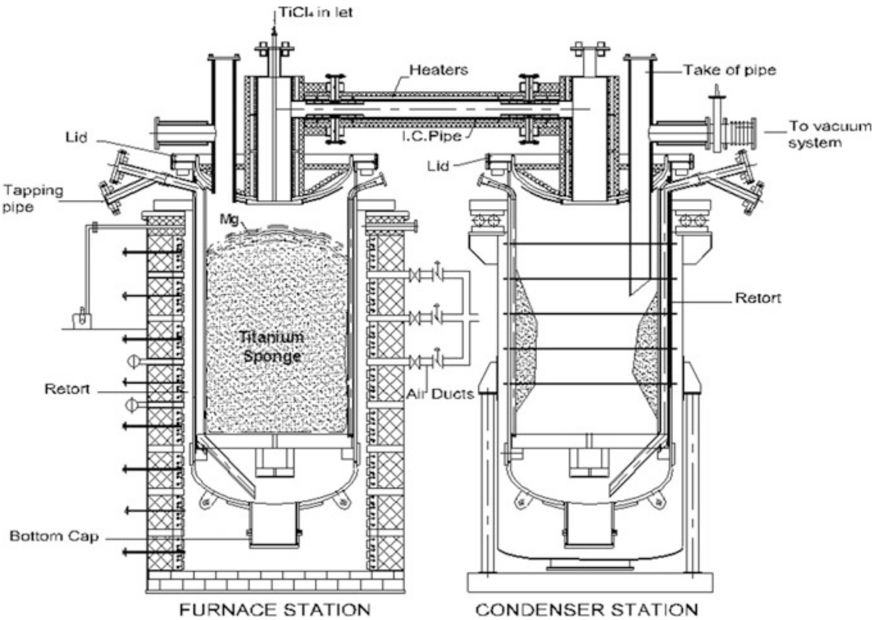

Fig. 4.3 Schematic of Combined Process Equipment developed at DMRL, Hyderabad, India

(iii) A ‘valve-less’ pressure transfer system for tapping hot $MgCl_2$ periodically from the process reactor during the reduction process.
(iv) A set of lightweight ceramic modules embedded with heaters wrapped over the interconnecting pipe to provide heating during the vacuum distillation process.
(v) A high-vacuum pumping system with necessary interlocks for evacuating the reactor assembly.
(vi) Custom-built equipment and tooling for ejection of sponge cake from the reactor and for size reduction operations to prepare homogeneous lots in the required finished sponge pieces of size 2–25 mm.
(vii) A programmable logic controller (PLC) process control and data logging system.

Repeated experimentation and incorporation of several improvements gradually led to standardization [20–22] of all the parameters of the sponge manufacturing process, see Table 4.1, with the process becoming highly reproducible. A photograph of titanium sponge cake (weighing about 3.5 MT) produced at the DMRL technology demonstration plant is shown in Fig. 4.4.

Table 4.1 Standardized operating conditions for producing titanium sponge in 3−3.5 MT batches

$TiCl_4$ purification	Parameters
Column—1	
(a) Top temperature	138 °C
(b) Bottom temperature	139 °C
(c) $TiCl_4$ feed rate	157 kg/h
Column—2	
(a) Temperature	139 °C
(b) Feed rate	150 kg/h
Reduction	
(i) Excess magnesium	60 %
(ii) Reactor pressure	0.5–3.5 psig
(iii) $TiCl_4$ feed rate	180–220 kg/h
(iv) Reaction zone temperature	800–810 °C
(v) Process time (including heating and cooling)	200 h
Vacuum distillation	
(i) Vacuum level	30×10^{-3} torr
(ii) Temperature	975–1000 °C
(iii) High temperature soak	64 h
(iv) Total cycle time	240 h

Fig. 4.4 Titanium sponge cake (weight about 3500 kg) produced at the DMRL technology demonstration plant

4.4.3 Quality Evaluation and Processing of Aerospace Grade Sponge

Titanium sponge obtained by the magnesium reduction and vacuum distillation process takes the shape of a cylindrical cake with loosely held deposits on the top and sides of the cake. The physical characteristics such as porosity and bulk density vary slightly from top to bottom of the cake, with material at the bottom usually being denser.

The quality of the sponge with respect to the impurities O, N, C, Fe, etc. also varies with position in the cake: impurities from the reactor steel wall and bottom contaminate the material at the sides and bottom of the cake, while the top surface material generally contains higher levels of oxygen, magnesium, and chlorides compared to the sponge from core fractions. Hence it becomes essential to isolate the high-purity core fraction from the rest of the material by meticulous sponge grading. At DMRL an elaborate sponge grading practice was evolved for this purpose [23], and cakes are divided into different fractions as shown in Fig. 4.5.

All the fractions are separately cut, crushed, and processed to prepare the finished size of material. The fractions A and B conform to the highest purity and

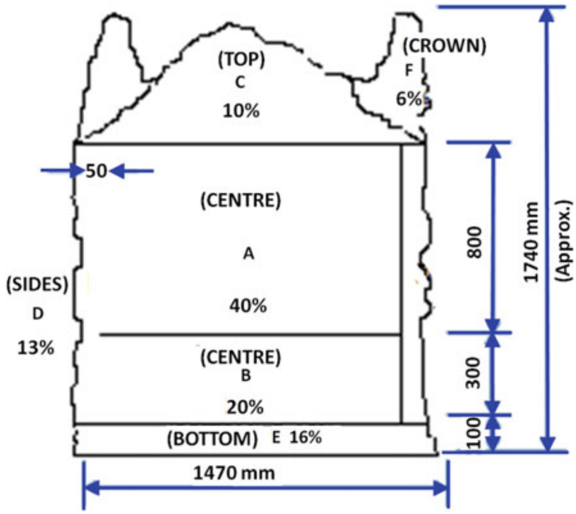

Fig. 4.5 Schematic of quality evaluation and grading of a typical titanium sponge block

meet all the technical requirements/stringent specifications of aerospace grade material.

Depending on the end-use specifications, separate lots of sponge are prepared and stored in argon-filled drums. A typical analysis of a finished sponge lot is presented in Table 4.2, showing that it compares very well with other grades, including ASTM grade MD 120 and the well-known Russian grade TG 90.

Table 4.2 Typical analyses (wt%) of aerospace grade sponge produced at DMRL and comparison with other standards[a]

Element	Midhani specification	CIS TG-90	ASTM MD-120	Showa (japan) S-90	DMRL lot 1 L001/2 k
Fe	0.050	0.060	0.120	0.030	0.018
C	0.015	0.030	0.020	0.020	0.006
O	0.040	0.040	0.100	0.060	0.033
N	0.015	0.020	0.015	0.010	0.003
Mg	0.080	0.080	0.080	0.045	0.004
Chloride	0.100	0.080	0.120	0.080	0.005
Ni	0.050	NS	NS	NS	<0.005
Cr	NS	NS	NS	NS	0.009
H	NS	NS	0.01	0.002	0.0019
Ti (by difference)	99.6	99.6	99.6	99.8	>99.9
Hardness (BHN)	100	80–90	120	90	82

NS Not Specified
[a]Values are upper limits for impurities and hardness

4.4.4 Commercial Production of Titanium Sponge at KMML, Chavara, India

Based on the technology developed at DMRL, a commercial titanium sponge plant with an installed capacity of 500 tons per year (expandable to 1000 tons per year) was established at Kerala Minerals & Metals Limited (KMML), Chavara, Kollam District. This was aided by funding from VSSC, Department of Space, the principal user of titanium and titanium alloys in the country.

Prior to the installation, technical personnel from KMML were given hands-on experience and training at the DMRL demonstration plant on all the activities of titanium sponge production.

The technology was successfully transferred to KMML: complete basic engineering was provided by DMRL, and the detailed engineering was done by DMRL in association with KMML, VSSC, and KITCO (Kerala Industrial & Technical Consultancy Organization), the engineering consultants.

The fully installed equipment was commissioned for (i) $TiCl_4$ purification to produce metal grade tetrachloride from the pigment grade $TiCl_4$; (ii) simultaneous operation of five reduction batches and five vacuum distillation processes on a scale of 3000–3500 kg/batch with related instrumentation; and (iii) ejection of sponge cake, its grading, and size reduction to prepare a generally acceptable finished size range of 2–25 mm. Provision is also made to prepare the finished sponge pieces in the range of 12–25 mm based on user requirements. The plant started production in June 2011 [24].

The first titanium sponge cake produced at the KMML plant is shown in Fig. 4.6. The sponge samples of the batch were analyzed and found to meet all the specifications for aerospace applications.

4.4.5 Quality Assurance Program at KMML Sponge Plant

After commissioning, regular production of titanium sponge has been taking place and efforts are being made to reach the rated production levels. DMRL has been consistently providing technical support, and in association with KMML and the Regional Centre for Military Airworthiness (RCMA, Materials) has drawn up a detailed quality assurance (QA) programme to ensure sponge purity requirements for aerospace/defence use.

The QA programme begins with visual inspection of the ejected sponge cake to remove discoloured material, if any, on the external surface of the cake.

The high-quality (aerospace) fraction of a given cake is then defined from extensive chemical analyses and hardness (BHN values) of buttons prepared from sponge samples. This high-quality fraction of a given cake is treated separately to prepare finished size sponge pieces (12–25 mm).

Fig. 4.6 First titanium sponge cake (weighing about 3 tons) produced in the KMML titanium sponge plant

Different fractions of sponge are also blended together for the preparation of a commercial purity sponge lot weighing about 1.75 MT. This was blended in a double-cone blender of 2 MT capacity.

Under an ongoing evaluation, three randomly chosen batches of sponge cakes have been sampled for an intensive QA programme, as indicated in the flowchart in Fig. 4.7. A typical analysis of one representative sample of a finished sponge lot is presented in Table 4.3. The material comfortably meets aerospace specifications in all respects.

4.4.6 Type Certification of Titanium Sponge—The Approach

Type certification (purity authentification) of titanium sponge is essential for its use in producing aerospace quality alloys. DMRL, RCMA (Materials), and KMML have jointly taken up this type certification of titanium sponge produced at KMML.

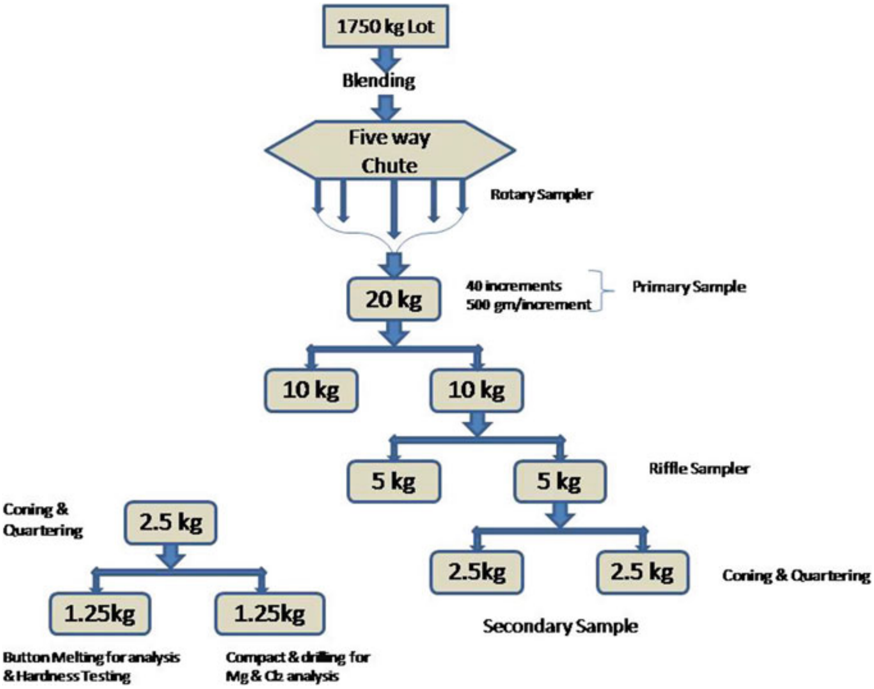

Fig. 4.7 Sampling procedure for the evaluation of finished titanium sponge

Table 4.3 Chemical analysis and hardness of a representative sample from a finished sponge lot of 1.75 MT: ND = detectable

Element	Content (wt%)
Iron (Fe)	0.0023
Oxygen (O)	0.0375
Silicon (Si)	ND
Nickel (Ni)	0.0063
Carbon (C)	0.0033
Chloride (Cl)	0.0243
Nitrogen (N)	<0.0020
Magnesium (Mg)	0.0122
Chromium (Cr)	0.0012
Hydrogen (H)	0.0019
Copper	0.0071
Tin (Sn)	ND
Manganese (Mn)	0.0009
Titanium (by difference)	99.901
Hardness (BHN)	78

As part of the sponge certification activity, the certification agency along with other partners ensured the following:

(i) Capabilities of the firm for producing aeronautical quality sponge.
(ii) Required quality norms followed by KMML in consistently producing a high-purity sponge.
(iii) Availability of skilled and capable manpower with the firm.
(iv) Availability of test facilities at the plant for quality evaluation.
(v) Required procedures are adopted for the maintenance of process records, data logging, etc.
(vi) Calibration of various equipments and instruments, etc., as per the requirement.

A threefold approach was evolved for carrying out the type certification process for titanium sponge, namely

(a) quality checks at required stages of sponge production
(b) implementation of suggested measures related to the quality assurance plan as listed in test schedules, and
(c) sponge quality evaluation based on the stringent international norms.

4.5 Properties of Ti Sponge

During qualification, samples of titanium sponge are tested as per standards for various properties. The physical properties that are looked for include a uniform matte gray color and freedom from foreign particulates such as oxides, nitrides, and other contaminants, which give the sponge other colours/shades.

Also the other requirements to be met are as follows: The size of the finished sponge pieces shall be generally in the range of 12–25 mm. The bulk density of the sponge shall be not more than 1.53 g/cm^3. The hardness of the buttons prepared by inert gas arc/vacuum arc melting of sponge, and tested according to ASTM E 10 (using a 10-mm ball and 1500 kgf load for 30 s) shall not exceed 90 BHN.

The chemical analysis of the sponge samples is carried out by the wet chemical method/spectroscopic method as agreed upon with the airworthiness agencies. The purity of the sponge is expected to meet the specifications as presented in Table 4.4.

Table 4.4 Chemical specification of titanium sponge (wt% basis)

Element	Minimum	Maximum
Titanium	99.74	–
Iron	–	0.05
Oxygen	–	0.04
Silicon	–	0.01
Nickel	–	0.04
Carbon	–	0.015
Chloride	–	0.08
Nitrogen	–	0.02
Magnesium	–	0.04
Chromium	–	0.06
Hydrogen	–	0.01
Water	–	0.02
All others	–	0.05

4.6 Concluding Remarks

Titanium sponge is of strategic importance owing to its usage in manufacturing titanium alloys for aerospace and defence applications. However, the extractive metallurgy of titanium, is complicated and cumbersome, resulting in high material costs and limitations on the use of titanium and its alloys.

Titanium sponge consumption in aerospace alloy manufacture has been increasing owing to growing demand. In view of its chemical reactivity and the sensitivity of titanium alloy properties to the presence of even small amounts of impurity elements, it is necessary to ensure that stringent quality specifications are met. In this chapter we have described successful efforts in the Indian context to develop high-purity titanium sponge for high-end aerospace applications.

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The authors also wish to place on record the outstanding contributions and support by TSP, KMML during the entire programme of type certification of sponge.

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