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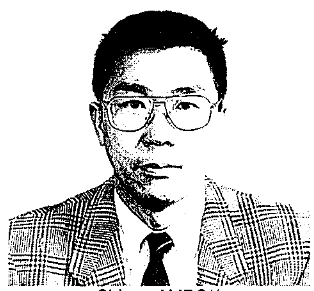
Technology Trend of Titanium Sponge and Ingot Production

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Abstract

Toho Titanium Company has produced Titanium sponge and ingots for more than 40 years and has improved its production technology for cost reduction and quality improvement. Current production technology and trends of R&D are outlined by the description of Toho's production process.

1. Introduction

Toho Titanium Co. Ltd. has a more than 40 years of titanium production history, starting the production of titanium sponge in 1954 and the production of titanium ingots in 1960. During this period, the titanium manufacturing technology has significantly improved to manufacture more titanium products of higher quality and at lower costs.

This article briefly introduces the current production processes and technology trends of titanium sponge and titanium ingots.

2. Titanium Sponge Smelting

All titanium sponge, except an extremely small portion for electronic materials that demand high purity, is manufactured by the Kroll process. The Kroll process involves reducing titanium tetrachloride ($TiCl_4$) with magnesium (Mg) and vacuum distilling the titanium sponge to remove impurities. This production process is schematically illustrated in **Fig. 1**[1].

The Kroll process, being of the batch type, is somewhat low in productivity, but has established itself as a mainstay titanium smelting process due to the advantages of refining titanium tetrachloride by distillation, which enhances the purity of metallic titanium.

In the past, the increase in batch size and the decrease in electric power consumption were important issues. Present goals are toward efficiency enhancement and technology development for further cost reduction and toward quality differentiation for specific applications. High-purity products for electronic materials[2], traditionally said not to be manufactured by the Kroll process, are now also produced by the Kroll process.

2.1 Feedstock ores

Main raw materials for titanium smelting are natural rutile, synthetic rutile (upgraded ilmenite or UGI), and titanium slag. As de-

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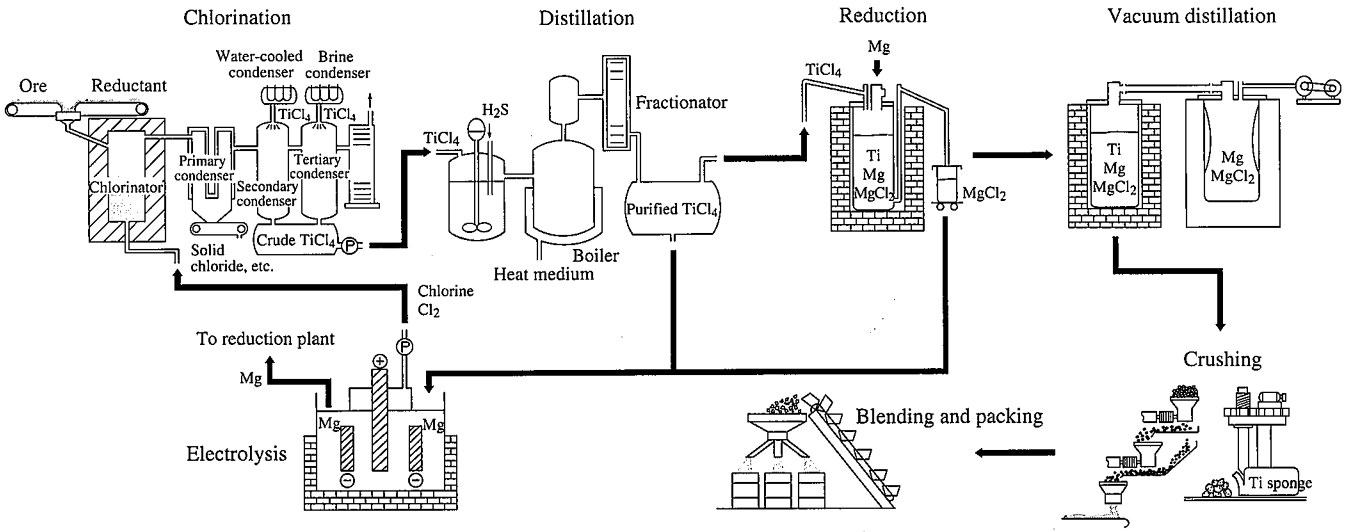

Fig. 1 Titanium sponge production process flow

scribed later, they are charged as raw materials for titanium tetrachloride into a fluidized-bed chlorinator. They look like sand and measure about 100 to 200 μm in average particle size. Representative grades of these raw materials are given in **Table 1**.

Natural rutile has been used as a principal raw material. It is often mined from alluvial deposits. Since its resources are not rich and its price fluctuates greatly, its use percentage for titanium smelting raw material is declining.

Synthetic rutile is upgraded ilmenite whose iron is selectively leached and removed from natural ilmenite ($FeTiO_3$) to a titanium oxide purity of over 90%. It is also produced and consumed in large amounts as raw material for chloride-process pigment titanium dioxide. Recently, synthetic rutile has become a main raw material for titanium metal production.

Titanium slag is produced by melting ilmenite and coke in an electric furnace and by separating and removing reduced iron as pig iron[3)]. Titanium slag is slightly higher in impurities content than natural rutile and synthetic rule, but is stable in price. For these reasons, its use percentage has been increasing year by year.

In actual use, the impurities (such as iron, manganese, arsenic and vanadium) that cause trouble in the titanium tetrachloride production process, as well as price are important. Due to the problem of radioactive elements in wastes, it is also necessary to consider the contents of uranium and thorium.

Table 1 Grade examples of main feedstock ores

Feedstock		Natural rutile	Synthetic rutile	Titanium slag
TiO_2(%)		95 - 97	90 - 96	90 - 96
Impurities	Fe_2O_3 (%)	0.3 - 1.0	2 - 5	2 - 5
	MnO (%)	0.1 - 1.0	0.1 - 2	1 - 2
	CaO (%)	0.02 - 0.1	0.03 - 0.1	0.1 - 0.2
	SiO_2 (%)	0.5 - 2	0.1 - 2	1 - 2
	Al_2O_3 (%)	0.5 - 1.0	0.3 -1.0	1 - 2
	V_2O_5 (%)	0.2 - 0.5	0.1 -0.5	0.5
	SnO_2 (%)	0.02 - 0.1	0.01 - 0.05	< 0.01
	As_2O_3 (%)	0.001	< 0.01	0.001
	U (ppm)	20 - 50	10-30	10 - 20
	Th (ppm)	20 - 70	20-70	10 - 40

2.2 Titanium sponge refining process

2.2.1 $TiCl_4$ production

It is difficult to produce metallic titanium directly from oxide raw materials. The Kroll process produces metallic titanium from $TiCl_4$ as an intermediate.

The $TiCl_4$ is formed by the following reaction (exothermic reaction):

$$TiO_2 + 2Cl + C = TiCl_4 + CO_2/CO$$
$$\Delta H = -176 \text{ kJ/mol at } 1{,}000°C$$

The aforementioned feedstock ores and coke are mixed and continuously fed into the fluidized-bed chlorinator, and are reacted with chlorine gas introduced through the bottom of the chlorinator. Since the temperature of the chlorinator is maintained at or above 1,000°C by the heat of the reaction, the formed $TiCl_4$ is a high-temperature gas. Impurity metals contained in the feedstock ores, such as iron and aluminum, are simultaneously chlorinated, and are carried by the $TiCl_4$ gas into the cooler in the next step.

As the high-temperature $TiCl_4$ gas is cooled in next stages, the impurities like iron chlorides are condensed and removed as solid wastes. The $TiCl_4$ is separated from the noncondensable gases (e.g., CO_2) and recovered as liquid. The liquid $TiCl_4$ (crude $TiCl_4$) still contains many kinds of impurities. Vanadium and aluminum chlorides with their melting point close to that of $TiCl_4$ are chemically treated for separation and removal[4)].

Finally, the $TiCl_4$ is purified in a fractionator (see **Photo 1**) to obtain $TiCl_4$ purified to 4N (99.99%). $TiCl_4$ for the manufacture of high-purity titanium sponge for semiconductor applications is purified further more to a purity of 5N.

2.2.2 Reduction and distillation

The reduction reaction is effected by filling a stainless steel reaction vessel (about 2 m in diameter and about 5 m in length) with argon, charging molten magnesium, and feeding the liquid $TiCl_4$ from above.

$$TiCl_4(L) + 2Mg(L) = Ti(S) + 2MgCl_2(L)$$
$$\Delta H = -387 \text{ kJ/mol at } 800°C$$

The reduction reaction generates a huge amount of heat. The industrial reaction rate is controlled by how to remove this heat.

The by-product $MgCl_2$(L) is intermittently tapped to control the level of the reaction surface. The tapped $MgCl_2$(L) is sent to the elec-

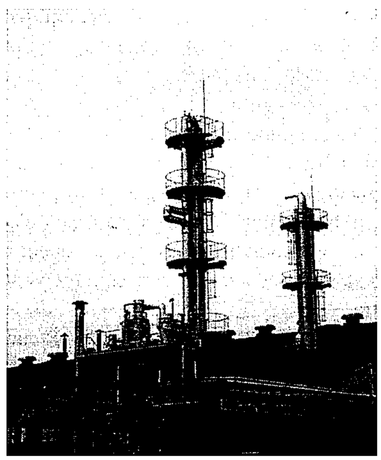

Photo 1 Fractionators (left fractionator used only for ultra-high-purity $TiCl_4$)

trolysis plant where it is regenerated into Mg(L) and Cl_2(G).

The reduction step of an 8-ton batch takes about four days. Productivity can be improved only by increasing the $TiCl_4$ feed rate, but this calls for the solution of such problems as transfer of reaction vessel constituents to formed titanium (quality contamination) and the erosion of the reaction vessel (safety) resulting from the temperature rise with the increase in the amount of heat generation.

After the reduction reaction, the reaction vessel is moved to the next vacuum distillation step.

Vacuum distillation is a step where Mg(L) and $MgCl_2$(L) entrapped in the titanium are vaporized and removed by heating the titanium to about 1,000°C. The titanium obtained after the vacuum distillation is porous and called titanium sponge.

Initially in the vacuum distillation step, heat transfer occurs through Ti(S), Mg(L) and $MgCl_2$(L). As Mg and $MgCl_2$ diminish, the titanium sponge alone must take care of the heat transfer. In addition to the poor thermal conductivity of titanium itself, the presence of pores restricts the heat transfer and the vacuum distillation rate. For this reason, the vacuum distillation step also takes about four days.

After the vacuum distillation step, the titanium sponge is cooled over about four days to room temperature, and is then pushed upward out of the reaction vessel (see **Photo 2**).

Titanium nitride is high in melting point, is not melted during ingot manufacture, and becomes defects in the ingot. Especially, there is a high demand for the titanium for the aircraft industry to be free from nitride inclusions. It is practically impossible to inspect for and remove the nitride inclusions. The quality of titanium for the aircraft industry is thus guaranteed by fixing the reduction and vacuum distillation steps certified by aircraft-related customers and by shipping for aircraft applications only those titanium products that are produced while meeting the specified manufacturing conditions.

Photo 2 Titanium sponge mass with diameter of about 1.7 m and height of about 2.5 m (shown as placed on side)

2.2.3 Crushing and packing

The titanium sponge mass pushed out of the reaction vessel varies in quality from portion to portion. For quality homogenization, the titanium sponge mass is generally crushed to fine particles and mixed. Alternatively, the titanium sponge mass is cut by a guillotine-like press shearing machine into chunks. Then the chunks are crushed to a specified size of 13 mm or less through several cutters and double-roll crushers. About 5 tons of crushed product is charged into a mixer and mixed into a product lot. The lot is appropriately sampled to determine its composition and quality. The product is then packed into drums, the air in the drums is replaced by argon, and the drums are stored until shipment.

2.2.4 $MgCl_2$ electrolysis

Anhydrous magnesium chloride ($MgCl_2$) obtained as by-product in the reduction and vacuum distillation steps of titanium sponge is decomposed into and recovered as metallic magnesium and chlorine gas by the fused-salt electrolytic process. The metallic magnesium and chlorine gas are recycled as a reductant for the reduction step and as raw material for the $TiCl_4$ production step, respectively.

The $MgCl_2$ electrolysis accounts for 60 to 70% of the electric power consumption of the entire titanium smelting process. Electricity is a major component of the titanium smelting cost. The electrolytic cells of Toho Titanium changed from the initial diaphragm type through the diaphragm-less type to the in-house developed bipolar type in 1985[5]. In this course, the electrolysis has been markedly improved with regard to its productivity and power consumption. **Fig. 2** shows the change in power consumption of the electrolysis. The power consumption of today's bipolar electrolytic cells is about 10,000 kWh/ton-Mg and is about a half of that of the conventional electrolytic cells in 1978.

The bipolar electrolytic cell has two or more bipolar electrodes (graphite) arranged between the anode (graphite) and the cathode (iron), and causes electrolytic reactions to occur on the respective anode surfaces. This concept is illustrated in **Fig. 3**. Since the bipolar electrolytic cell has the bipolar electrodes not exposed outside and is basically of the same size as the conventional electrolytic cell, its heat loss (power loss) is the same as that of the conventional electrolytic cell. As a result, a bipolar electrolytic cell with two bipolar

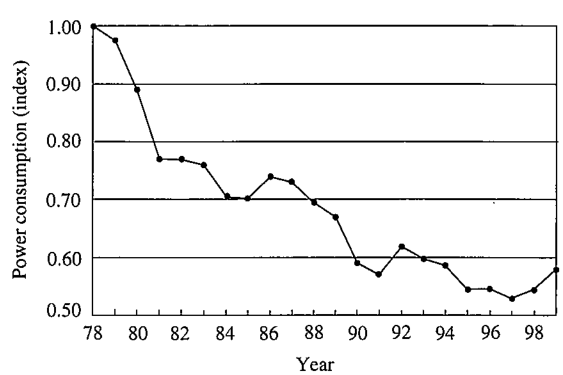

Fig. 2 Change in power consumption in electrolysis

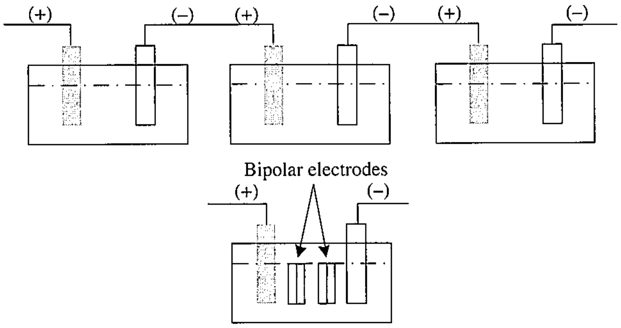

Fig. 3 Concepts of conventional and bipolar electrolytic cells

electrodes installed between the anode and the cathode, for example, is three times higher in productivity and two-thirds lower in the proportion of heat loss in the power consumption as compared with the conventional electrolytic cell.

2.3 New smelting processes

In addition to the Kroll process that reduces titanium with magnesium, the Hunter process[6] that reduces titanium with sodium was commercially applied to smelt titanium sponge. Since the Hunter process was not rationalized as much as the Kroll process, the last Hunter process plant (RMI) was closed in 1993.

The above two processes are of the batch type. There are the following continuous processes:

1) Electro-winning processes[7, 8]
2) High-temperature, high-pressure reduction process[9]
3) Gas-phase reduction processes[10-12]

Studies[13, 14] have been conducted on feedstock ore direct reduction processes that use calcium and aluminum as reductants. These processes are not superior to the Kroll process in cost and quality, and have not reached the stage of commercial production. An electrolytic process[15] and an iodine process[16] are practically applied to produce titanium for limited applications, such as high-purity titanium as raw material for target materials.

With improvement in powder metallurgy technology, demand for powder titanium is increasing. The titanium sponge fines produced by the Hunter process were formerly used as titanium powder for powder metallurgy. With the disappearance of the Hunter process, titanium powders made by the hydrogenation process and atomizing process are now used[17]. Since these processes all use as raw material the Kroll process titanium sponge, there are proposed new processes[18, 19] that directly produce titanium powders by application of electronically mediated reaction (EMR).

In September 2000, the University of Cambridge announced the FFC process (process for direct reduction from titanium oxide) that combines calcium reduction with fused-salt electrolysis[20].

3. Titanium Ingot Melting

Titanium has strong affinity for oxygen and nitrogen, and has a high melting point of 1,670°C. Since conventional refractories thus cannot be used for melting titanium, titanium must be melted in a water-cooled copper crucible in a vacuum or an inert atmosphere. Titanium may be melted by the consumable-electrode vacuum arc remelting (VAR) process, plasma arc remelting process, electron beam remelting process, or electro-slag remelting (ESR) process[21-23]. Here are introduced the vacuum arc remelting (VAR) process and electron beam cold hearth refining (EBCHR) process.

3.1 Vacuum arc remelting (VAR) process

The vacuum arc remelting (VAR) process is easy to operate and low in construction and operating costs, as compared with other melting processes, so that it is now a mainstay titanium ingot melting process in the world. The VAR process ingot production flow is shown in **Fig. 4**.

Titanium sponge, titanium scrap, additives, and master alloy are press formed into a briquette weighing a few tens of kilograms. These briquettes are welded under an inert gas atmosphere to form a primary electrode of a columnar shape. The primary electrode consists of a few tens to a few hundreds of briquettes, depending on the ingot size. The raw materials and additives are equally weighed and mixed in each briquette.

The primary electrode is melted in the VAR furnace shown in **Fig. 5**. The primary electrode of titanium connected to the cathode of the furnace is melted by the direct-current arc produced between the primary electrode and the water-cooled copper crucible connected to the anode of the furnace. The molten titanium is solidified in layers in the water-cooled copper crucible to form an ingot. The ingot is

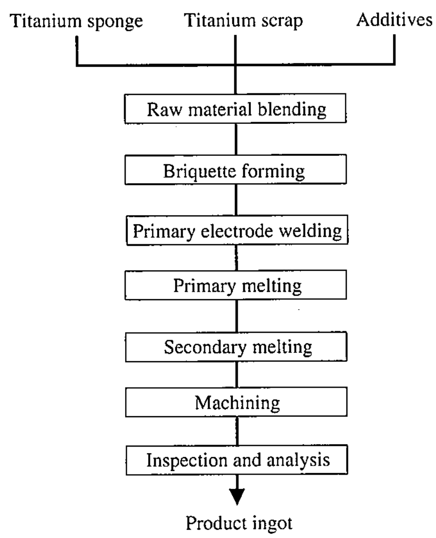

Fig. 4 VAR process flow

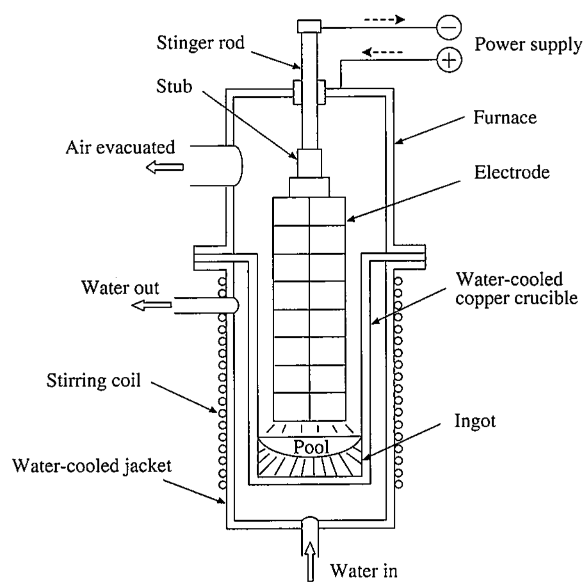

Fig. 5 VAR furnace schematic

melted one or two more times to produce a homogeneous ingot. VAR process ingots generally weigh 4 to 8 tons. Toho Titanium has a VAR furnace capable of producing the world's largest ingots with a diameter of 1,250 mm and weight of 15 tons.

Critical ingot quality requirements are the absence of inclusions, minimization of segregations, and good as-cast surface quality. Inclusions are mainly high-density inclusions (HDIs) due to high-melting point metals like tungsten, and low-density inclusions (LDIs) due to titanium nitride. Both HDIs and LDIs result from high-melting point substances and are melted little in the VAR furnace with a melt temperature of about 1,800°C. The HDIs are caused by the entry of unmolten material particles from cemented carbide machining tools, welding torches made of tungsten, and master alloys. The LDIs are caused chiefly by nitrides formed through air leaks in the titanium sponge production and melting steps. These HDIs and LDIs are very hard and brittle as compared with normal ingot portions, so they cause cracks and surface defects in the forging and rolling steps.

Ingot segregations may be macroscopic chemical segregations or microscopic metallurgical segregations. Each type has an adverse effect on mechanical strength. Briquette homogenization and control of the primary electrode composition gradient[24] and molten pool depth are effective in preventing the segregations. When the melting rate is increased, the cast surface quality improves, but the molten pool depth increases to promote the formation of segregations. The conditions of hot topping, or gradually reducing the electric current in the final stage of melting to homogenize the ingot top and float shrinkage cavities, must be appropriately selected.

3.2 Electron beam cold hearth refining (EBCHR) process

The EBCHR process was developed for the purpose of refining high-melting point metals, such as niobium, tantalum and molybdenum, in the middle of the 1950s. It is now highlighted as melting process for superalloys and titanium. **Fig. 6** schematically illustrates the EBCHR furnace[25]. With EB melting, an electron beam is used as source of heat, and the raw materials are melted in the water-cooled hearth and poured into the water-cooled copper mold to form an ingot. The world's largest EBCHR furnace now in operation for titanium melting has an output of 5.4 MW. Toho Titanium's 2-MW output furnace is Japan's only EBCHR unit for titanium production.

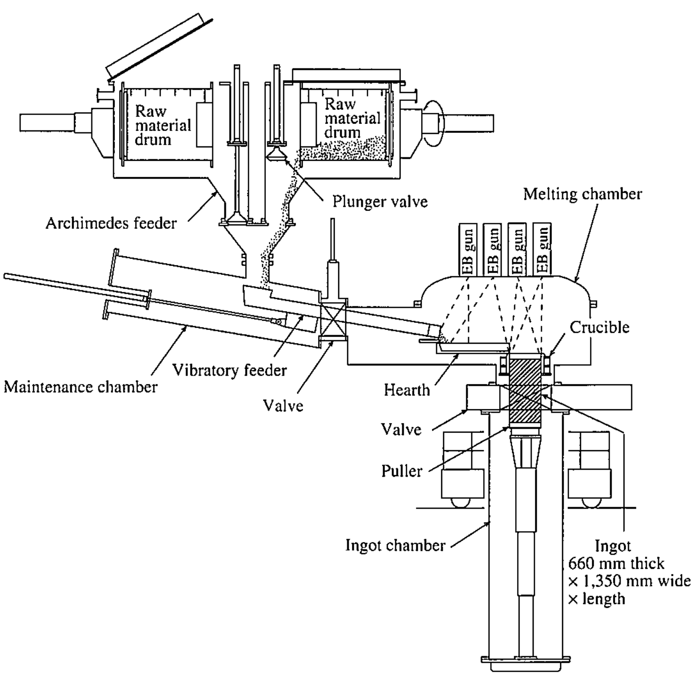

Fig. 6 EBCHR furnace schematic[25]

The EBCHR process has the following characteristics not found in the VAR process:

1) The consumable electrode fabrication step can be eliminated, and scrap can be used in large amounts (up to 100%).
2) HDIs and LDIs can be removed to a high degree.
3) In the case of commercially pure titanium, a homogeneous ingot can be produced by single melting.
4) Square ingots can be made with a resultant expectation of yield improvement in the forging or slabbing step.

When melting a titanium alloy, for example, the high vacuum of the EBCHR process makes it difficult to control aluminum and other components likely to vaporize.

Two melting processes industrially employed for wrought titanium production have been briefly described above. VAR melting is considered to occupy an important position in titanium melting as mature technology. EBCHR melting with a high capability of removing HDIs and LDIs is considered to draw ever increasing attention in critical applications like nuclear reactor and aircraft engine parts as well as from the standpoint of effective scrap utilization.

4. Conclusions

The titanium market is also faced with the worldwide movements that force noncompetitive producers out of business according to the principles of capitalist economy. Enhancing technology so as not to lose in this fierce competition is a serious challenge given to Japan's titanium producers.

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