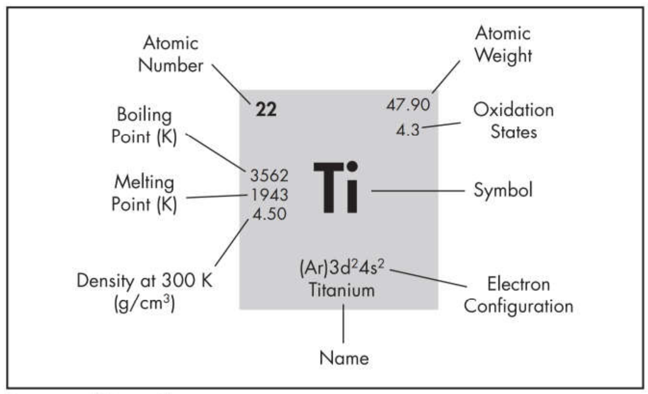
CHAPTER 12.39

Titanium and Titanium Alloys

M. Ashraf Imam and Francis H. (Sam) Froes

The characteristics of titanium are shown in Figure 1. The conventional processing of titanium metal occurs in four major steps: reduction of titanium ore into *sponge*, a porous form; melting of sponge, or sponge plus a master alloy, to form an ingot; primary fabrication, where an ingot is converted into general mill products, such as a billet, bar, plate, sheet, strip, and tube; and secondary fabrication of finished shapes from mill products. An alternate fabrication route is by powder metallurgy (including additive manufacturing), which can have economic advantages compared to the conventional processing route.

Titanium has high passivity; therefore, it exhibits high levels of corrosion resistance to most mineral acids and chlorides. It is also nontoxic and biologically compatible with human tissue and bone, making it an ideal material for medical implant products (Housley 2007; Imam et al. 2010; Froes et al. 1985).



Courtesy of Rector-Elements

Figure 1 Characteristics of titanium

USES

Titanium is used extensively in aerospace applications (both engines and airframes). It is also commonly used in implant components, automobiles (particularly in rotating and reciprocating parts of the internal combustion engine), the oil and gas industries, chemical processing equipment, sporting equipment, and consumer products.

HISTORICAL PRICE

The historical price of titanium sponge is shown in Figure 2. As this sponge is melted to form an ingot and subsequently fabricated to various mill products, the price increases, which is shown in Figure 3.

OCCURRENCE

Titanium occurs in nature in many forms, most notably as ilmenite ($FeTiO_3$) and rutile (tetragonal TiO_2). In the production of titanium metal, only high-grade titanium ores are utilized, such as natural rutile, ilmenite processed to make synthetic rutile, or high-TiO_2 slags. Titanium ores and their processing are discussed in another chapter of this handbook.

PROPERTIES

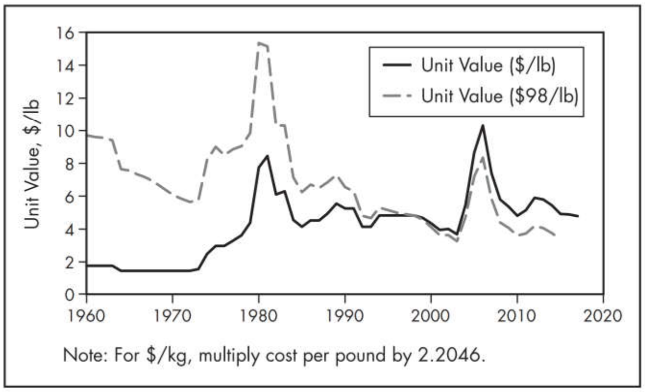
Titanium alloys may be divided into two principal categories: corrosion-resistant and structural (Housley 2007; Imam et al. 2010; Froes et al. 1985). The corrosion-resistant alloys are generally based on a single-phase (alpha) microstructure with dilute additions of solid solution strengthening and alpha-stabilizing elements, such as oxygen (interstitial), palladium, ruthenium, and aluminum (substitutional). These alloys are used in the chemical, energy, paper, and food processing industries to produce highly corrosion-resistant tubing, heat exchangers, valve housings, and containers. The single-phase alpha alloys provide excellent corrosion resistance, good weldability, and easy processing and fabrication, but a relatively low strength.

In markets served by major U.S. titanium producers, corrosion-resistant alloys comprise approximately 25% of the total output; Ti-6Al-4V, 60%; and all other structural alloys, the remaining 15%.

MANUFACTURING

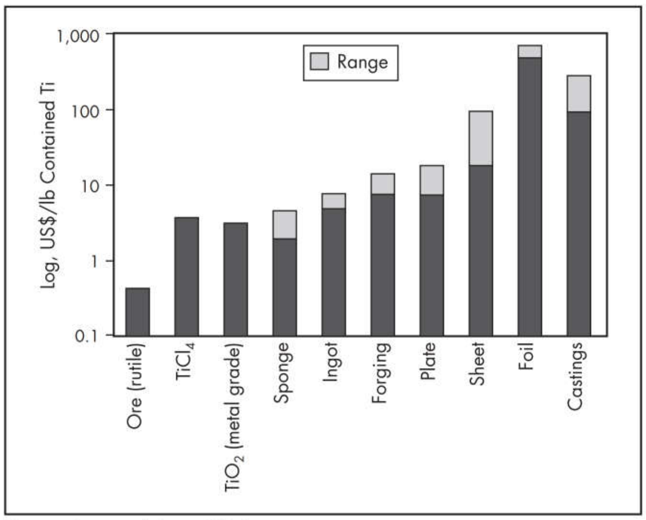
The commercial production of titanium metal, by the Kroll process (Figure 4), involves the chlorination of rutile (TiO_2)

M. Ashraf Imam, Faculty/Research Professor, George Washington University, Washington, D.C., USA
Francis H. (Sam) Froes, Consultant, Tacoma, Washington, USA



Data from USGS 1960–2017

Figure 2 Titanium sponge price



Source: Dutta and Froes 2016

Figure 3 Price of titanium product forms, in 2014 U.S. dollars

in the presence of coke or another form of carbon (Imam et al. 2010; Froes et al. 1985). The resulting titanium tetrachloride ($TiCl_4$; *tickle*) is purified by distillation and chemical treatments and subsequently reduced to titanium sponge using either the Kroll process (Mg) or Hunter process (Na). Titanium tetrachloride for metal production must be of very high purity.

Nearly all sponge is produced by the Kroll magnesium reduction process:

$$TiCl_4(g) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(l)$$
$$\Delta G_{900°C} = -301 \text{ kJ } (-72 \text{ kcal})$$

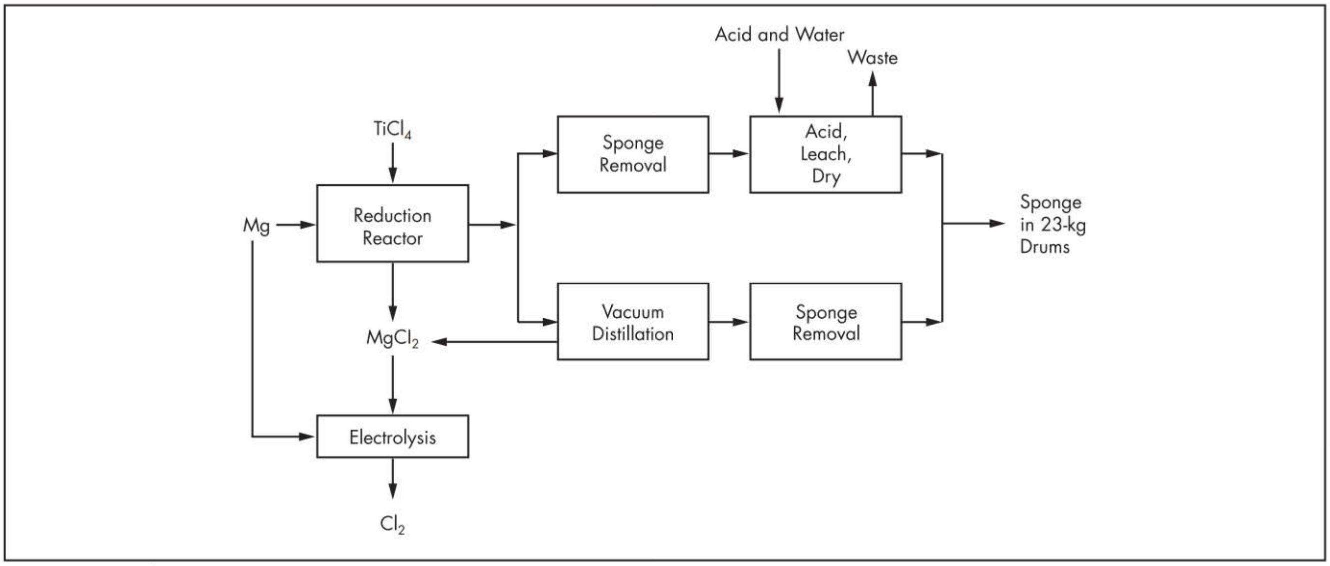
$TiCl_4$ gas (g) is metered into a carbon-steel or 304 stainless-steel reaction vessel that contains liquid (l) magnesium. An excess of 25% magnesium over the stoichiometric amount ensures that the lower chlorides of titanium solids (s) ($TiCl_2$ and $TiCl_3$) are reduced to metal. The highly exothermic reaction [$DH_{900°C}$ = −420 kJ/mol (−100 kcal/mol)] is controlled by the feed rate of $TiCl_4$ at approximately 900°C. The reaction atmosphere is helium or argon. Molten magnesium chloride is tapped from the reactor bottom and recycled using conventional magnesium reduction methods. The production is in batches up to 10 t (metric tons) of titanium. The product, the so-called sponge, is further processed to remove the unreacted titanium chlorides, magnesium, and residual magnesium chlorides. These impurities, which can be as much as 30 wt %, are removed by either acid leaching in dilute nitric and hydrochloric acids at a low energy requirement of approximately 0.3 kW·h/kg of sponge but effluent production of 8 L/kg of sponge; vacuum distillation at 960–1,020°C for as much as 60 hours; or the argon sweep at 1,000°C used by the Oregon Metallurgical Company (Oremet), one of the subsidiaries of Allegheny Technologies Incorporated (ATI). After purification, the sponge is crushed, screened, dried, and placed in airtight, 23-kg drums to await consolidation. The energy required to convert $TiCl_4$ to sponge, which is ready for further processing by the leaching routes, is approximately 37 kW·h/kg of sponge, of which approximately 97% is required for magnesium production. Figure 5 shows the sponge produced by magnesium reduction at ATI Wah Chang (Albany, Oregon, United States).

The sodium-reduction process was employed in Japan, the United States, and England for several years as an alternative to magnesium reduction. The last large production plant was closed in the early 1990s. Although the process was more costly than magnesium reduction, the product contained fewer metallic impurities, that is, iron, chromium, and nickle. Desirable for the electronics and computer industries, high-purity titanium is produced by the Alta Group in Fombell, Pennsylvania (United States), which is a subsidiary of Honeywell Electronic Materials.

Hardness, indicating the degree of purity, is affected both by the interstitial impurities (i.e., oxygen, nitrogen, and carbon) and by the non-interstitial impurity iron. Hardness numbers range from 80 to 150 BHN (Brinell hardness number) units; typical commercial sponge is characterized by 110–120 BHN units. Some developmental processes, such as electrolysis reduction, produce sponge having 60–90 BHN units. Iron impurities in Kroll sponge are difficult to control because of diffusion into the sponge from the reactor wall. In the sodium-reduction process, the sponge is protected from the wall by sodium chloride. The other impurities originate from tetrachloride, residual gases in the reactor, helium or argon impurities, and magnesium or sodium residues.

Sponge Consolidation

Conventionally (the ingot metallurgy approach), the next step is the consolidation of the sponge into ingot. The crushed sponge is blended with alloying elements and cleaned revert (scrap). Consumable electrodes are produced by welding 45–90-kg sponge compactions (electrode compacts) in an inert atmosphere, and then double–vacuum arc remelted (VAR). A portion of the elemental sponge compacts are often replaced with bulk (cleaned) scrap. The ingots are approximately 71–91-cm diameter and long enough to weigh 4.5–9.0 t. The double melt, included in aerospace specifications, is required for thorough mixing of alloying elements, scrap, and titanium sponge, and for improving yields because vaporization of volatiles during the first melt leaves a rough, porous surface. The double melt removes residual volatiles such as Mg, magnesium chloride ($MgCl_2$), Cl_2, and H_2. Triple melts are specified for critical applications such as rotating components in gas turbine engines. The third melt allows more time to dissolve high melting point inclusions that infrequently occur. This is often referred to as *rotating quality titanium*.



Source: Imam et al. 2010
Figure 4 Flow diagram for Kroll titanium sponge production

Source: Imam et al. 2010
Figure 5 Vacuum-distilled titanium sponge

A two-station VAR furnace for double melting has an annual production capacity of approximately 1,400–3,000 t, depending on product mix, that is, the alloy and the number of remelts. The energy requirement is approximately 1.1 kW·h/kg per single melt. Plasma cold hearth melting (also called plasma arc melting [PAM]) and electron beam cold hearth melting (Figure 6) have been employed more recently for both consolidation and final melting. The hearth processes are well suited for utilizing scrap in various shapes and forms and for avoiding the costly electrode fabrication inherent in consumable vacuum arc melting. In addition, these processes can produce cast metal into shapes such as slabs. For many industrial applications, a single hearth melt is acceptable. The hearth process is low cost and can be designed to trap high-density inclusions, such as carbide tool bits, and oxynitride-rich (type I) inclusions in the hearth skull.

Development of New Production and Processing Technologies

One of the problems with the Kroll process is that it is not continuous, as is steel production, but is a slow batch process, making it very expensive. Kroll himself considered a new process to be essential and eventually achievable, predicting in 1959 that an electrolytic process might be possible within 5–10 years. In the 1950s, at least five companies—DuPont, Horizons, Kennecott Copper, Monsanto, and National Research Corporation—invested heavily and futilely in developing new processes. Subsequent attempts by Dow-Howmet, RTI, and other companies led to incremental improvements in the competing processes, but nothing has ever replaced the Kroll process. Besides the metallurgical difficulties, the extreme volatility of the economic market for titanium made heavy investment in experimental technologies difficult.

Although part of the expense of titanium is caused by the batch sponge process, this actually accounts for less than 40% of the final mill product cost. Pressing and/or forging is the next step. These are time-consuming processes, which explain why a replacement for the batch process alone will not sufficiently bring the price down to make the use of titanium commonplace. It also explains the interest in titanium powder metallurgy (PM) technology (Dutta and Froes 2016; Sun et al. 2016) that would lower the final cost by greatly reducing the number of processing steps, opening the metal to a wider range of applications, for example, military land vehicles and artillery, which need to be both lightweight and strong so that they can be airlifted yet can also withstand combat. PM does not require VAR, electron beam melting, or PAM, producing near-net-shape parts directly. Figure 7 demonstrates the advantage of the PM approach using the Armstrong process. There is a significant reduction in processing steps with PM, which will lower the final product cost, compared to the conventional ingot metallurgy technique.

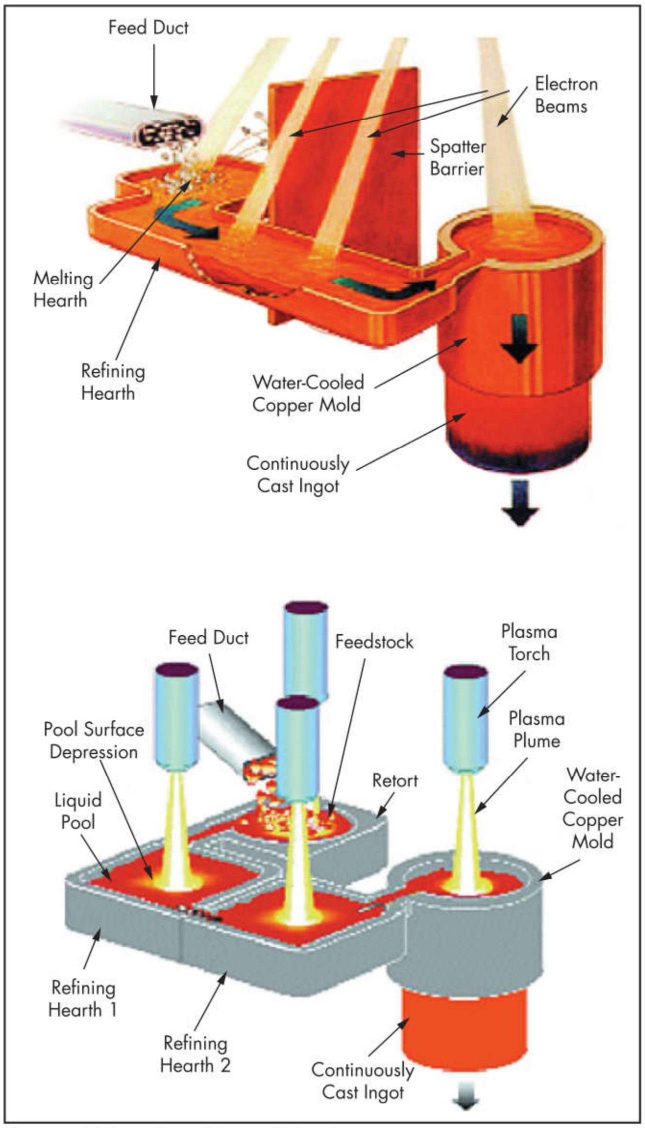


Figure 6 Hearth melting of titanium

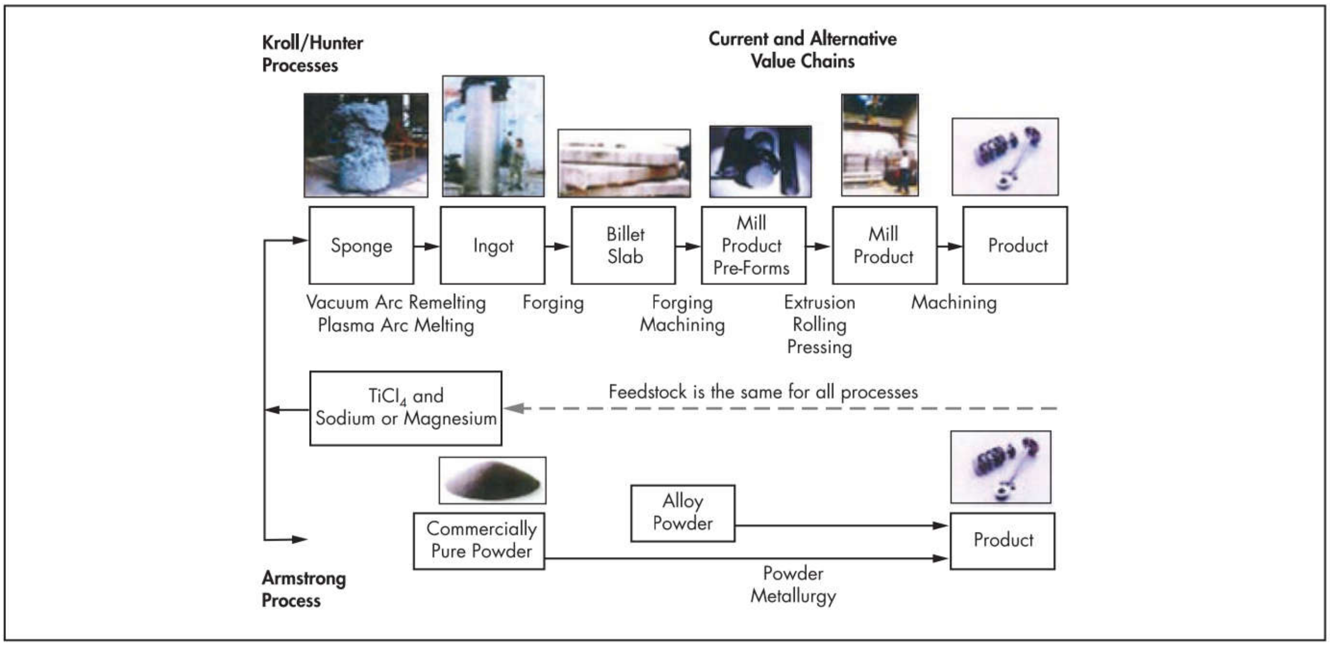
Since the 1990s, research has increased on finding replacements for, or modifications to, the Kroll process, with the greatest concentration being on PM. A non-melt consolidation process being developed by Oak Ridge National Laboratory in Oak Ridge, Tennessee (United States), and industry partners may reduce the energy required and the cost to make titanium parts from powders by up to 50%. The process includes roll compaction for directly fabricating sheets from powder and press and sinter techniques to produce net shape components and extrusions. In Japan, research has concentrated on a high-speed continuous process using subhalide reduction in a titanium container.

Because Australia has some of the largest mineral sand deposits in the world, the Commonwealth Scientific and Industrial Research Organisation has developed a technology for producing, it is claimed, cost-effective commercially pure (CP) titanium using a continuous fluidized bed in which titanium tetrachloride is reacted with magnesium (the TiRO process; Froes 2013). Continuous production of a wide range of alloys including aluminides, Ti-6Al-4V, and many Ti-Al alloys has been demonstrated on a large laboratory scale. The powder produced has been used to fabricate extrusions, thin sheet by continuous roll consolidation, and cold sprayed complex shapes including ball valves and seamless tubing. Commercialization of the process is now in the planning stage with a decision to proceed to the pilot plant stage likely to be taken soon.

In the United Kingdom, scientists at Cambridge University have developed a unique approach that uses titanium as an efficient cathode, made possible by the removal of oxygen from the cathode (Froes 2013). The Fray–Farthing–Chen Cambridge process extracts metals from their solid oxides by molten salt electrolysis (generally with a calcium chloride [$CaCl_2$] electrolyte). Using titanium dioxide as an example, the sequence is as follows: TiO_2 (solid, cathode) → molten salt electrolysis → Ti (cathode) + O_2 (anode). The process is being commercialized by Metalysis, located in South Yorkshire in the United Kingdom.

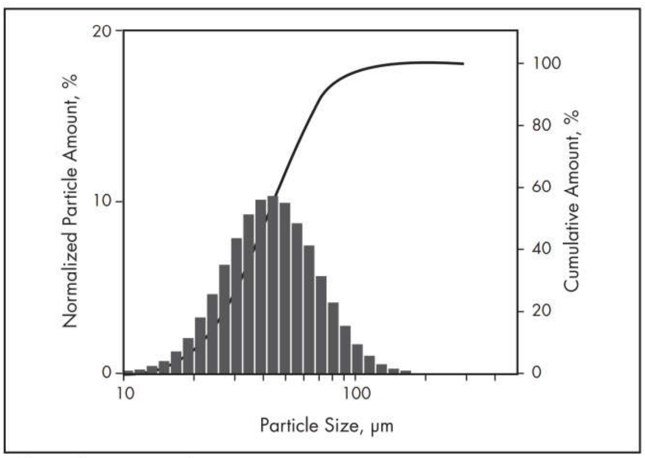
In the United States, several initiatives for industrially scalable methodologies were funded by the Defense Advanced Research Projects Agency (DARPA). In 2003, DARPA listed as the first goal of its Titanium Initiative the "establishment of a U.S.-based, high-volume, low-cost, environmentally benign production capability" (Froes 2013). Its second goal was the development and demonstration of "unique, previously unattainable titanium alloys, microstructures, and properties that enable new high-performance applications" (Froes 2013). Raising the bar significantly higher, DARPA set as its goal the production of high-quality titanium less than US$9/kg for billet with no more than 500 ppm of oxygen. (Generally oxygen in CP titanium is approximately 2,000 ppm.)

One of the projects that received DARPA funding was the Armstrong process as developed by International Titanium Powder (ITP; Froes 2013). In 2008, ITP was acquired by Cristal US (a wholly owned subsidiary of Cristal Global). Cristal Global has extensive experience in the manufacture of titanium tetrachloride and has been supplying the chemical to titanium sponge producers for more than 20 years. The Armstrong process, named after its development director Donald Armstrong (Froes 2013), is continuous and uses molten sodium for reduction of titanium tetrachloride (the Hunter process), which is injected into it as a vapor. Because the sodium exceeds the requirements for the reduction, it cools the reaction products and carries them to separation stages, at which point the excess is removed along with salt. As a result, the powder does not need further purification and can be used in traditional melt-to-billet processes, allowing use of the product in the current value chain. However, the powder is better utilized in direct non-melt consolidation to final end product, eliminating the need to process sponge, thereby reducing supply chain cycle time, energy consumption, manufacturing costs, and environmental impact (Froes 2013). One apparent advantage of the Armstrong process is its ability to produce a range of alloys (including Ti-6Al-4V) as high-quality homogeneous powders suitable for many applications. ITP currently operates a research and design facility and pilot plant in Lockport, Illinois (United States). This site provides limited quantities of materials necessary to successfully complete solid-state consolidation development activities. Additionally, ITP broke ground on a 4-million-t/yr facility in Ottawa, Illinois, in 2010, which was designed to produce both CP titanium and Ti-6Al-4V alloy powder. Independent



Source: Froes 2013

Figure 7 Titanium powder metallurgy technology



Adapted from Sun et al. 2016

Figure 8 Particle size distribution of hydrogen-assisted reduction of TiO_2 with magnesium

research on the process has found that the use of low-grade $TiCl_4$ leads to higher parts density because of the difference in sintering behavior that affects the entrapment of volatiles within the sintered body. This full-scale facility, however, is still not in production in 2017.

Another process is being developed by the Materials and Electrochemical Research Corporation and DuPont. An electrolytic powder process, it uses a composite anode of TiO_2, a reducing agent, and an electrolyte mixed with fused halides (Froes 2013). The titanium is deposited at the cathode. Projections are for titanium production at significantly lower cost than the Kroll process.

A further emerging powder process is being developed by Advanced Materials Products, which also operates under the name ADMA Products (Froes 2013), in which sponge titanium is cooled in a hydrogen atmosphere rather than the conventional inert gas. The hydrogenated sponge is then easily crushed and in the hydrogenated condition can be compacted to a higher density than conventional low-hydrogen sponge. The remnant chloride content of the hydrogenated sponge is reported to be at low levels (helping to avoid porosity and enhance weldability).

Further development of the use of hydrogen-assisted reduction of titanium oxide with magnesium and production of low-cost spherical meltless titanium powder has been conducted by Sun and coworkers (Sun et al. 2016). Figure 8 shows the size distribution of this powder, which features a reduction to <0.2 wt % O_2 at 50% lower cost than with a conventional hydride-dehydride powder.

The hydrided Ti-6Al-4V or blended elemental material is prepared using the following steps:

1. It is ball-milled in a solvent to reduce the particle size to <10 μm.
2. A thermoplastic binder is added to facilitate formation of granules.
3. The product is spray dried with Ar gas to form spherical granules of Ti-6Al-4V hydride.
4. It is thermally debinded, using an inorganic separator to prevent granules sintering together.
5. Finally, the sintered spherical Ti-6Al-4V powder is deoxidized with calcium or magnesium (with an O_2 content tailored in the range 0.08–0.20 wt %).

ECONOMIC ASPECTS

Before 1970, more than 90% of the titanium produced was used for aerospace applications. By 1982, the percentage decreased to approximately 70%–80%. Military use continually decreased from nearly 100% in the early 1950s to 20% in the late 1990s (Housley 2007; Imam et al. 2010; Froes et al. 1985). However, industrial demand for titanium continued to increase through the late 1990s and into the new millennium. Although the destruction of the World Trade Center in New York City on September 11, 2001, had a marked negative effect on the commercial aerospace industry, Boeing and Airbus began to receive orders for their new planes—the 787 Dreamliner and the A380, respectively—both of which contain between 130 and 150 t of titanium components per unit. Also in 2003, the U.S. Air Force's F-22 Raptor went into production. Simultaneously, there was a price surge in titanium. Between 2003 and 2006, the price of titanium more than doubled. However, the recession that began in 2008 reversed the cycle, with cancellations outnumbering orders of new planes. Production of the F-22 came to an end, replaced by production of the F-35 Lightning II.

With the breakup of the former Soviet Union, the internal consumption of titanium was a modest fraction of its former capacity, thus leaving a large capacity available for export. Throughout the 1990s, the Russian company VSMPO-Avisma upgraded their quality standards so that their products could be used in aerospace applications; it completed its transformation by 2000. By 2009, the giant company was exporting 70% of its products, with the remainder supplied to the domestic market, including large contracts with Boeing and Airbus, as well as Safran Aircraft Engines (previously SNECMA), General Electric, Rolls-Royce, and Pratt and Whitney.

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