TITANIUM
Process Technologies

When titanium became available after World War II, many thought that it would become as commonplace as aluminum. That has not happened because titanium remains very expensive, mostly due to the high cost of extraction.

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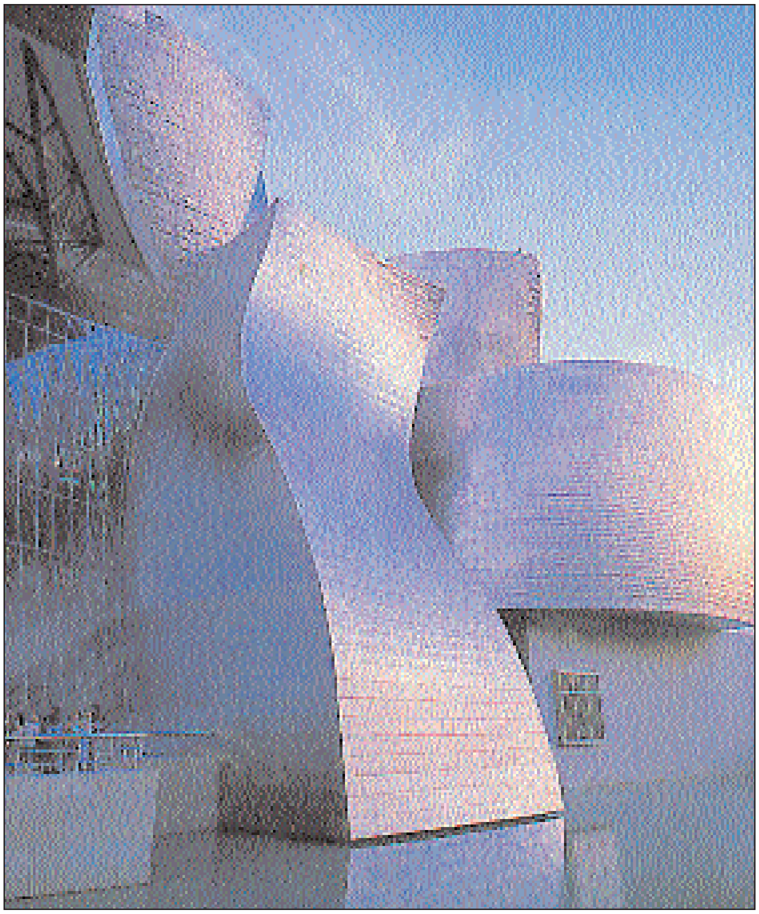

The Guggenheim Museum in Bilbao, Spain, is finished with an ultrathin layer of titanium metal.

Titanium has a unique set of properties: low density, high specific strength, high temperature strength, and exceptional resistance to corrosion. Titanium is the fourth most common structural metal in the earth's crust. Only iron, aluminum, and magnesium are more abundant. More titanium is available than nickel, copper, chromium, lead, tin, and zinc put together. However, the current titanium production system is extremely labor and capital intensive. Titanium is expensive only because the current process for refining the ore to metal is a multi-step, high temperature batch process. This article will first describe current titanium technology, and will then discuss four of the most promising approaches to reduce the cost of titanium. These include the Kroll, Hunter, Cambridge, and Armstrong processes.

Titanium extraction today

Currently all domestic titanium metal production begins with rutile ($\mathrm{TiO_2}$). Rutile (\$0.48/lb Ti) is combined with petroleum coke and chlorinated in a fluid bed reactor at 1000°C (1830°F) to produce $\mathrm{TiCl_4}$ (known as "tickle").

$$\mathrm{TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2}$$

It is possible to start with other less costly materials such as ilmenite or slag, but both of these contain more iron and other impurities. The liquid $\mathrm{TiCl_4}$ is purified and then approximately 90% of the $\mathrm{TiCl_4}$ is oxidized back to $\mathrm{TiO_2}$ for the pigment industry. Titanium metal producers either purchase $\mathrm{TiCl_4}$ from a pigment manufacturer (Oremet, which is now shut down) or produce their own (Titanium Metals Corporation, Timet).

$\mathrm{TiCl_4}$ (\$1.35/lb Ti) is the starting point for all commercial processes and most proposed new routes. The two major reasons for starting with $\mathrm{TiCl_4}$ are its high purity and the fact that titanium is separated from oxygen. Any process that is proposed to eliminate the chlorination step will have to find a way to replace these functions.

Kroll process

Today's Kroll process has changed very little from the one DuPont developed to produce titanium in 1948. Briefly, it involves the following steps. A clean and dry stainless steel retort is pumped down and filled with argon. Then enough magnesium to reduce all the $\mathrm{TiCl_4}$ plus 15% to 30% excess is introduced into the retort. The retort is heated to 800°C to 900°C (1470 to 1650°F), and $\mathrm{TiCl_4}$ is slowly fed into the retort. Magnesium reduces $\mathrm{TiCl_4}$ according to the reaction:

$$\mathrm{TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2}$$

$\mathrm{MgCl_2}$ is periodically tapped off as the reduction proceeds. After several days, depending on the size of the retort, the reaction stops and the retort pressure rises. At this point, approximately 30% of the initial magnesium charge is still unreacted. The titanium metal formed is a porous mass that resembles a sponge.

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The retort now contains titanium metal (sponge), unreacted magnesium, and some $MgCl_2$. These impurities may be removed by either leaching or vacuum distillation. Vacuum distillation removes the unreacted magnesium and $MgCl_2$ by raising the temperature of the retort and applying a vacuum. This removes the more volatile magnesium and $MgCl_2$, leaving behind the titanium sponge. Then the reactor is opened and the titanium is pressed or jack-hammered out. The titanium sponge is sheared to 0.6 cm (0.25 in.) chunks, any alloying metals are added, and perhaps some scrap titanium. It is then melted to produce an ingot. To assure uniformity and remove inclusions, the ingot is remelted once or twice more. The original melt adds approximately $1 per pound and each remelt another $0.50.

From the first, the Kroll process has been criticized as expensive and inefficient. It is a series of batch steps, many of which are labor intensive. However, after more than 50 years and many announced new processes, nothing has replaced it. In fact, the Kroll process has changed very little. The major difference is that the retort size has become larger and the magnesium reduction and vacuum distillation steps are carried out in the same reactor.

The Hunter process is very similar to the Kroll process, except that magnesium is replaced by sodium. Even though the process is similar, the Hunter process is slightly more expensive, and consequently the Hunter process exists today only to supply a small specialty high-purity powder market.

Few theoretical studies have been made of the Kroll process, and consequently much is left to learn about it. Some interesting recent work by Okabe et al. has shown that the Kroll and Hunter reactions can be interpreted as electrochemical reactions. A better understanding would probably lead to incremental improvements in the Kroll process. Possible improvements might include reducing the amount of excess magnesium required, or reduction in the amount of titanium downgraded due to contamination at the walls, or better control of nitride inclusions. It might even be possible to modify the Kroll or Hunter process to make it continuous.

It is unlikely that a revolutionary improvement in the Kroll process would result in a dramatic reduction of the price, but evolutional change resulting in many small improvements could lead to less costly titanium.

Electrolytic processes

In 1953, Kroll predicted that an electrolytic route would produce titanium in 15 years. Electrolytic processes were being developed concurrently with the Kroll and Hunter process. Why is it that after over 50 years of development, no commercial electrolytic titanium plants have yet been built?

The promise of electrolytic processes has always been that they would have the same effect on the price of titanium that the introduction of the Hall-Heroult process had on aluminum. Before Hall-Heroult, aluminum was produced by sodium reduction and was more expensive than gold. Now aluminum costs less than $1.00/lb. However, significant differences between aluminum and titanium make an electrolytic titanium process much more difficult.

For one thing, the melting point of titanium is 1000°C (1800°F) higher than that of aluminum. Thus, all electrolytic processes tried to date have produced solid titanium that results in dendritic structures and a loss of electrolyte due to drag-out. In the electrolytic bath, aluminum has only one stable valence state, but titanium has two. These multiple valence states cause a loss of electron efficiency. But the major problem is that the electrolytic route may not be less expensive than the Kroll process because both begin with $TiCl_4$ ($1.45/lb Ti). Some economic analyses have shown savings over the Kroll process. However, companies that have built pilot scale electrolytic plants (Dow-Howmet, RMI) have not seen these savings in practice.

Electrolytic processes have been the major area of active titanium extraction research. None of these processes has resulted in a commercial production of titanium. In fact, the pattern has been for companies to spend millions of dollars on a pilot plant and then abandon the project.

Part of the problem may be that the development time for a process is longer that the titanium market cycle, and none of the pilot plants have managed to survive a downturn. Another problem may be that the market for titanium has grown so slowly that there has never been a need for a completely new, from-the-ground-up plant. In fact, the number of commercial producers has contracted. In 1958, at least six U.S. companies were in various stages of titanium metal sponge production. Today there is only one, Timet. This is a bit of a cyclic argument, because the slow growth is due, in part, to the consistently high price and cyclic unreliability of the demand. It could also be argued that the commitment to electrolytic extraction has been misplaced, and that the electrolytic route will never be less costly than the Kroll process.

The reality is that titanium can be made electrolytically. The problem has always been one of economics. Marco Ginatta of GTT continues to pursue the chloride process and has built a large pilot plant in Torino, Italy. It is possible that a commercial electrolytic plant may replace the Kroll process someday, but it seems unlikely that any electrolytic process that begins with $TiCl_4$ will dramatically reduce the price of titanium.

The FFC Cambridge process

A second, more radical approach toward electrolytic reduction announced by Derek Fray of Cambridge has created a lot of excitement. In this process, TiO_2 is pressed into pellets and becomes the cathode in a 950°C (1740°F) calcium chloride ($CaCl_2$) bath. A graphite electrode is the anode. When a current is applied, the oxygen is ionized and dissolves into the $CaCl_2$ bath. Because the monovalent oxygen is in solution, the problem of divalent titanium ions is eliminated. This method has produced titanium with only 60 ppm oxygen up to the kilogram scale.

Since this route begins with rutile ($0.48/lb Ti) it appears (on paper) that titanium could be produced at significantly less than the current price. However, rutile is not pure TiO_2. Something must be done to replace the purification achieved through chlorination. Further, one of the reasons for the chloride route is to separate titanium from oxygen. Most previous work in the oxide system has failed to make titanium with low enough oxygen content.

For this process to be successful, it will require not only that the electrolysis of TiO_2 be successful, but also that an inexpensive source of pure TiO_2 be found. It is a long way from the small-scale work to a tonnage commercial process. Still, the potential for a dramatic drop in the cost of titanium makes this process worth investigating.

Titanium powder

The Armstrong process (developed by International Titanium Powder, Chicago, Ill.) can be looked upon as a modification of the Hunter method in which titanium powder is made in a continuous process, rather than the batch method. The Armstrong process produces titanium by the reduction of titanium tetrachloride through reaction with sodium. In this process, $TiCl_4$ vapor is injected into a stream of molten sodium. The sodium flow rate is in excess of the stoichiometric requirements for sodium reduction of $TiCl_4$. The excess sodium cools the reaction products and carries them to separation stages, where the excess sodium and salt are removed. The reaction product is a continuous stream of powder. With simple modifications of the process, it is also possible to make vanadium/aluminum titanium alloys.

ITP has made over 100 runs via this process, and significant quantities of titanium have been produced. The oxygen content has been as low as 0.2%, as analyzed by the Department of Energy's Albany Research Center in Oregon. This matches the standard for grade 2 titanium. Some of the powder has also been melted into buttons for tensile specimens. These also met the standards for strength and ductility of grade 2 titanium.

The advantage of the Armstrong process is that it is a relatively simple continuous process that makes powder. So far, it has not been possible to lower the oxygen content much below 0.2%. This is low enough for some but not all titanium applications. The new, tighter facilities may reduce the oxygen content.

Currently, ITP is building an engineering facility for more experiments. This system will be able to produce approximately 5 kg (11 lb) of titanium per test, and should be online by publication of this article. They are also building a pilot scale plant that can produce 120 kg (265 lb) per test and should be online by late 2001 or early 2002. It is hoped that these new larger and tighter facilities will be able to achieve even lower oxygen content.

The ITP process is close to commercialization. However, a few questions remain to be answered. What will the oxygen content of the product be? How much will it cost to make titanium by the Armstrong process? Because it also begins with $TiCl_4$, the raw material costs are the same as with the Hunter process. However, the ITP process has some advantages over the Hunter process:

- ITP is continuous and operates at low temperature, so capital and labor costs are greatly reduced.
- The product does not require the additional purification needed by sponge produced from the Hunter process.
- The powder is suitable for various applications such as powder metallurgy, spray forming, and other rapid fabrication processes.
- Small diameter, high purity powder is produced directly, with no waste stream.
- Salt is the only by-product and can be broken down into sodium and chlorine and reused in the process.

Well-developed processes are available to convert powder into plate, rod, or more complex shapes such as gears. However, titanium parts today are rarely produced directly from powder. Either the powder must be impure to get the price into an acceptable range (which produces inferior parts); or it must be high-purity, expensive powder to produce high strength parts and as a result, becomes priced out of the market.

High quality parts formed from ITP high purity powder will cost a small percentage of current parts that are either machined or formed from powder. This powder can be used as the feed material for any of several near-net-shaping technologies, such as laser deposition and metal injection molding. ■

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