# TITANIUM METAL: EXTRACTION TO APPLICATION

Joseph Gambogi* and S. J. Gerdemann**

*USGS - National Center, Reston, Virginia 20192
**DOE - Albany Research Center, 1450 Queen Avenue, SW, Albany, Oregon 97321

## Abstract

In 1998, approximately 57,000 tons of titanium metal was consumed in the form of mill products (1). Only about 5% of the 4 million tons of titanium minerals consumed each year is used to produce titanium metal, with the remainder primarily used to produce titanium dioxide pigment. Titanium metal production is primarily based on the direct chlorination of rutile to produce titanium tetrachloride, which is then reduced to metal using the Kroll magnesium reduction process. The use of titanium is tied to its high strength-to-weight ratio and corrosion resistance. Aerospace is the largest application for titanium.

In this paper, we discuss all aspects of the titanium industry from ore deposits through extraction to present and future applications. The methods of both primary (mining of ore, extraction, and purification) and secondary (forming and machining) operations will be analyzed. The chemical and physical properties of titanium metal will be briefly examined. Present and future applications for titanium will be discussed. Finally, the economics of titanium metal production also are analyzed as well as the advantages and disadvantages of various alternative extraction methods.

## Introduction

The titanium metal industry is relatively young. Production of titanium dioxide pigment by the sulfate process began in the 1920's; however, a commercial method for metal extraction was not developed until the 1950's (2). At this time, the U.S. Bureau of Mines (USBM), using the Kroll process (The Kroll process is discussed in detail under the heading "Magnesium Reduction via Kroll Process), was able to produce 91-kilogram (200-pound) batches. Prior to this time, titanium metal was extracted only on noncommercial scales (3, 4).

The Kroll process, as implemented by Dr. Kroll and the USBM (Figure 1), and as practiced today, is a series of batch steps. This, combined with the fact that titanium is a reactive metal that requires special processing, has kept the price of titanium high compared to other metals (Table I). Consequently, titanium is limited to specialized uses, such as aircraft engines and golf clubs, where the performance gains justify the increased cost. Over the years, many different extraction processes have been developed for the production of titanium metal. However, only the Kroll process has been proven to be an economic success.
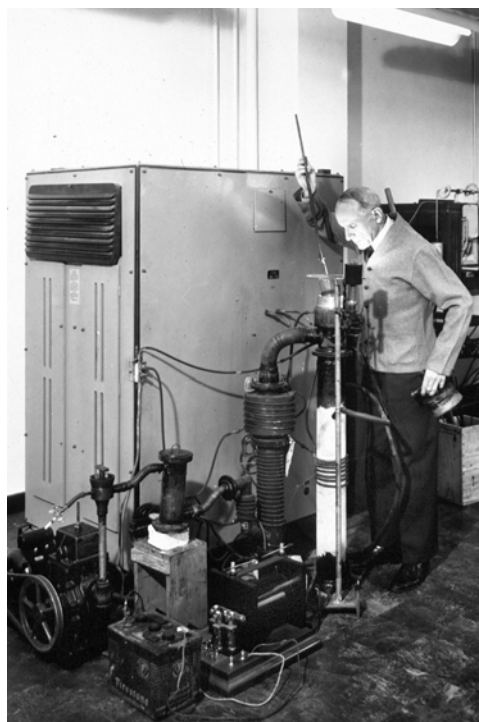


Figure 1: Dr. Kroll at the Albany Research Center.

Table I.-Prices of Selected Metals in 1999 (5, 6)

| Metal | Basis | $/lb | Reference |
|---|---|---|---|
| Iron (Fe) | Hot rolled bar | $0.17 | 6 |
| Lead (Pb) | North American Market | 0.27 | 5 |
| Zinc (Zn) | US Dealer SHG | 0.56 | 5 |
| Aluminum (Al) | US Transaction price | 0.72 | 5 |
| Copper (Cu) | US Producer Cathode | 0.84 | 5 |
| Magnesium (Mg) | US Die Cast Alloy | 1.65 | 5 |
| Nickel (Ni) | LME 15 month | 3.10 | 5 |
| Tin (Sn) | NY Dealer | 2.63 | 5 |
| Titanium (Ti) | US SG Ingot Producer | 5.75 | 5 |

## History

Titanium was discovered in 1790 by Reverend William Gregor, but it was another 86 years before Berzelius reduced potassium fluorotitanate with potassium to produce relatively pure titanium. In 1910, Hunter introduced sodium reduction of titanium tetrachloride ($TiCl_4$). However, the metal was still brittle due to impurities, primarily oxygen. Then, in 1925, Van Arkel produced pure ductile titanium by disproportionating $TiI_4$ (7, 8). During the 1930's, Kroll began experiments that culminated in a 1940 patent for alkaline earth reduction of $TiCl_4$. In 1938, the USBM began a research program to find a method to produce commercial quantities of titanium. By 1941, the USBM was using a small Kroll reactor to produce 100-gram quantities of titanium. By 1948, the USBM was making 91-kilogram (200-pound) batches at a small pilot plant in Boulder City, NV. During that same year, E.I. du Pont de Nemours and Co. (DuPont) began commercial production

of titanium (Table II) (9, 10, 11, 12, 13).

The first uses of titanium were for military aerospace applications, which exploited titanium's high strength-to-weight ratio. Due to strong support from the government, titanium production grew rapidly in the 1950's . By the mid 1950's, several companies were producing titanium and more were considering entering the market. At that time, companies producing titanium sponge included DuPont, Dow Chemical Co., and Union Carbide & Carbon Corp., as well as the precursors of Titanium Metals Corp. (TIMET) and RMI Titanium Co. (RMI). New processes were being explored including electrowinning of titanium.

In 1957, demand was on the rise, mill product production was 5,130 metric tons, and the Air Force was worried about a shortage. Allied Chemical and Dye Corp. and Kennecott Copper Corp. announced plans in 1957 to build a 5,000-ton/yr titanium plant using a new continuous process (9, 14). In 1958, however, demand for titanium decreased dramatically when the United States moved to a missile-based defense rather than airplanes. By 1960, there were only three titanium metal producers: TIMET, RMI, and DuPont. In 1962, DuPont discontinued production of titanium metal. The late 1960's brought an interest in titanium for industrial applications such as in power generation and desalination plants. The early 1970's marked a retrenchment from the growth in demand during the Vietnam war era. In addition, hopes for a titanium-intensive civil supersonic transport (SST) aircraft were ended when the government-sponsored program was canceled. During the mid 1970's, consumption for military uses surged with a peak in the production of the F-14 and F-15 fighter aircraft. During the same period, the energy crisis resulted in a retrenchment of orders from commercial airlines and consequent decrease in titanium consumption by commercial aerospace.

The historic peak in consumption in 1981 and the subsequent collapse were believed to have been accentuated by an overestimation of aircraft orders that did not materialize or were later canceled as the aircraft market deteriorated, leaving some producers with large inventories of titanium metal products to be drawn from during a period of lower demand (9). From 1985 through 1989, titanium metal consumption increased, reflecting renewed strength in the commercial aircraft and other industrial markets. Military aircraft programs, such as the B-1B bomber program, also contributed to the rise in demand during this period. Owing to this increased demand, two of the domestic sponge producers made moderate expansions to their existing capacity during 1988 and 1989.

The early 1990's marked the end of the Cold War and the beginning of sharp cuts in defense spending. Concurrently, commercial aircraft and engine producers were reducing raw material inventory levels, leading to a significant fall in titanium metal demand and prices. Domestic consumption of titanium sponge fell by 42% in 1991. By the mid 1990's, there was an explosion of high-visibility titanium consumer goods followed by a surge in demand from commercial aerospace. Demand for consumer goods was led by titanium golf clubs. There were also titanium eyeglasses, bicycles, backpacking gear, baseball bats, climbing gear, lacrosse sticks, etc. In 1996, production of titanium mill products hit a peak of 62,000 tons (15).

In 1999, there were only 11 plants in the world known to produce titanium sponge. Sponge production capacity exists in China, Japan, Kazakhstan, Russia, and the United States. U.S. producers of titanium sponge include the Alta Group, Allegheny Technologies Inc., and TIMET.

Globally, there are roughly twice as many ingot producers as there are sponge producers. Ingot production is usually integrated with mill processing operations. About 50% of feedstock for titanium ingot is in the form of titanium scrap. A small percentage of scrap is derived from old scrap. Scrap feedstock is derived from "home scrap" generated on site and "purchased scrap"

derived from arrangements with titanium fabricators and scrap processors. Significant ingot production capacity exists in France, Germany, Japan, Russia, the United Kingdom, and the United States. In the United States, ingot is produced by 5 companies in 12 locations (Table III).

Table II.-History of Titanium Production (4)

| | |
|---|---|
| 1790 | Gregor discovers titanium |
| 1920 | First commercial titanium pigment production |
| 1925 | VanArkel produces $TiI_4$ |
| 1930's-1940's | Kroll develops magnesium reduction process |
| 1948 | USBM Kroll process, DuPont begins commercial production |
| 1971 | Research for Supersonic Transport terminated |
| 1975-76 | Military aircraft production peak (F-14 and F-15) |
| 1977-81 | Rapid increase in orders for commercial aircraft |
| 1982-84 | Collapse of the commercial aircraft market |
| 1984-86 | Production of B1-B bombers |
| 1985-89 | Renewed strength in the commercial aircraft market |
| 1988-89 | Increases in U.S. sponge production capacity |
| 1990-94 | Reductions in military and commercial aerospace |
| 1992 | RMI Titanium sodium-reduction sponge plant closed at Ashtabula, OH |
| 1993 | Magnesium-reduction sponge plant commissioned at Henderson, NV |
| 1994-97 | Surge in consumer goods and commercial aerospace orders |
| 1997-98 | Cancellation of commercial aircraft orders |

Numerous companies are involved in the production of titanium cast, forged, mill, and fabricated components. In 1999, the International Titanium Association had 128 member companies. However, it is difficult to quantify all of the companies involved in the fabrication of titanium products. For example, at the mill product level, steel mills often are used to process titanium on a toll basis.

## Titanium Minerals

Although titanium often is considered an exotic element, it is the 9th most abundant element in the earth's crust; only oxygen, silicon, aluminum, iron, magnesium, calcium, sodium, and potassium are higher in abundance. More commonly known metal elements such as zinc, copper, and lead are actually less abundant. The most common titanium-bearing minerals are ilmenite ($FeTiO_2$), rutile ($TiO_2$), anatase ($TiO_2$), arizonite ($Fe_2TiO_5$), perovskite ($CaTiO_2$), leucoxene (altered ilmenite), and sphene ($CaTiSiO_3$), or titanite. Of these, only ilmenite, leucoxene, and rutile have significant commercial importance. For an in-depth examination of titanium mineralogy and geology, please refer to the Geological Society of America Special Paper 259 by Eric Force (16).

On a stochiometric basis, ilmenite contains 53% $TiO_2$ and is by far the most abundant mineral. Unweathered ilmenite often contains less $TiO_2$ than its stochiometric value due to the presence of intergrown iron oxide. However, weathering leaches iron from ilmenite resulting in higher $TiO_2$ content. Thus, the $TiO_2$ content of ilmenite varies considerably. Industry usually classifies ilmenite from below 50% to 70% $TiO_2$. Above 70% $TiO_2$, however, altered ilmenite is usually referred to as leucoxene. Rutile is essentially crystalline $TiO_2$. Commercial concentrates of rutile usually contain about 95% $TiO_2$ (17).

Table III.-U.S. Producers of Castings, Forgings, Ingot, Sponge, and Mill Products

| Company Name | Sponge | Ingot | Cast, forged, or mill products |
|---|---|---|---|
| Allegheny Technologies Inc. | X | X | X |
| Alta Group | X | | |
| Ancotech Inc. | | | X |
| AstroCosmos Metallurgical Inc. | | | X |
| Carlton Forge Works Co. | | | X |
| Coastcast Corp. | | | X |
| Curtis Wright International Extruded Products | | | X |
| Dynamet Inc. | | | X |
| Duriron Co. | | | X |
| G..O.. Carlson | | | X |
| Haynes International Ltd. | | | X |
| Howmet Corp. | | X | X |
| Ladish Co. | | | X |
| Lawrence Aviation Inc. | | X | |
| N F and M International | | | X |
| Precision Cast Parts Corp. | | | X |
| Precision Rolled Products Inc. | | | X |
| RMI Titanium Co. | | X | X |
| Sandvik Special Metals Co. | | | X |
| Selmet REM Products, Inc. | | | X |
| Shultz Steel Co. | | | X |
| Titanium Metals Corp. (TIMET) | X | X | X |
| Viking Metallurgical Corp. | | | X |
| Western Zirconium Inc. | | | X |
| Western Pneumatic Tube Co. | | | X |
| Wyman Gordon Co. | | | X |

## Mineral Reserves, Location, and Types of Deposits

Reserves are classified as deposits capable of yielding economic concentrates under current economic conditions with present technology(18). Titanium ore reserves are widely distributed throughout the world. In 1998, world titanium mineral reserves were estimated to be 370 million tons of contained $TiO_2$. Major ilmenite reserves are located in Australia, South Africa, Norway, and Canada, and major rutile reserves are located in Australia and South Africa (Figures 2 and 3) (19, 20).

Approximate minimum requirements for an economic sand deposit containing titanium minerals include reserves of 300,000 tons to 1 million tons of $TiO_2$ content in rutile or ilmenite; and heavy mineral content in the ore of 1% to 5%, depending on the mix of ilmenite, rutile, and other minerals. Typically, economic placer deposits are 1% $TiO_2$, while hard rock deposits may contain as much as 20% $TiO_2$ (17).

Titanium minerals occur in both placer and hard rock deposits. Ilmenite is a common accessory mineral in most igneous and metamorphic rocks. Rutile is not associated in commercial quantities with hard rock deposits (19, 20).

# World Reserves of Rutile
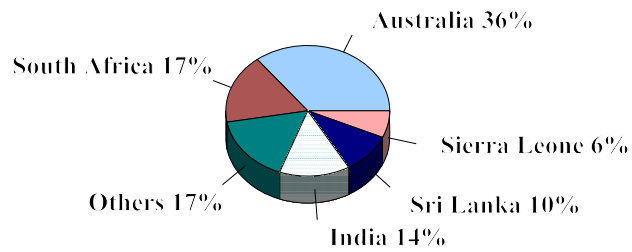### (43 million tons of contained TiO2)

Australia 36%

South Africa 17%

Sierra Leone 6%

Others 17%

Sri Lanka 10%

India 14%

Figure 2:  World Reserves of Rutile (20).

# World Reserves of Ilmenite
### (327 million tons of contained TiO2)

South Africa 19%

Australia 25%

Norway 12%

Others 16%
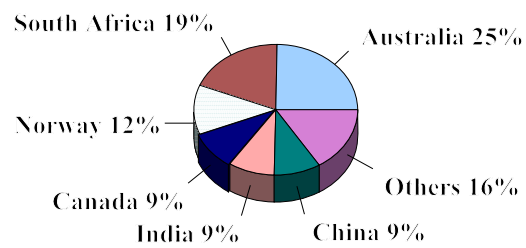
Canada 9%

India 9%

China 9%

Figure 3:  World Reserves of Ilmenite (20).

# Mining

Mining of titanium minerals is usually performed using surface methods. Underground methods are used for the recovery of some hard rock deposits but are uncommon. A dredge (bucket-wheel or cutter head suction) is usually used for the recovery of titanium-mineral placer deposits. In a typical configuration, the sand is pulled ahead of the dredge; initial concentration of heavy minerals takes place using gravity techniques on a floating "wet mill," with tailings deposited near the bank behind the dredge. Thus, the dredge floats in its own lake, which moves as the dredge digs forward and stacks tailings behind it.

Gravity spirals are normally used for wet separation, but pinched-sluice separators of various designs also are used. The Reichert cone concentrator, which operates on the pinched-sluice principle, is sometimes used for large-tonnage operations. Flotation also is used. For stream-type deposits, jigs are sometimes used because they are less sensitive to extreme grain size variation.

The final wet-mill concentrate is dried, usually in a rotary kiln, prior to further treatment. There are numerous configurations used to separate the constituents of the heavy mineral suite using magnetic and high-tension separation circuits. As conductors, ilmenite and rutile usually are removed together by electrostatic separation. The conductor fraction of the dried wet-mill concentrate then is subjected to high-intensity magnetic separation, yielding a final ilmenite product.

The rutile fraction is further cleaned by screening and additional electrostatic separation. Zircon and monazite byproducts are recovered from the nonconductor fraction of the wet-mill concentrate by a combination of gravity, electrostatic, and high-intensity magnetic separation. Recovery rates for titanium minerals from placer deposits are generally about 90% (17).

# Beneficiation

The beneficiation of ilmenite is accomplished by the removal of iron and other impurities in the mineral. Although numerous technologies are used, nearly all are based on either selective leaching or thermal reduction. These processes involve the oxidation, reduction, and leaching of iron oxide contained in ilmenite. Two salient issues these processes face are that they often require higher grades of ilmenite and that they generate iron-base waste. Synthetic rutile is often produced using selective leaching techniques, which may include reduction of iron from a ferric to ferrous state to facilitate leaching (21).

Most commercial operations are based on derivatives of either the Becher or Benilite process. Product purity can exceed 95% $TiO_2$. The most widely used route for the production of synthetic rutile is the Becher process, a thermal reduction method. The Becher process involves roasting highly altered ilmenite with finely ground coal and char in a rotary kiln at 1,100 °C, reducing the iron in the ilmenite to its metallic state. Iron sulfate or sulfur may be added to remove MnO. The reduced ilmenite, taken from the kiln, is cooled, and separated from the unreacted reductants and waste fines using screens and magnetic separation. The reduced ilmenite is added to a mixture of water and ammonium chloride (which acts as a catalyst) through which air is bubbled. Unreacted iron is separated and removed by classifiers and cyclones. Finally, the product is leached with sulfuric acid to remove residual iron and MnO and improve the quality of the product. Currently, this process works most efficiently on ilmenite with $TiO_2$ levels in the range of 60%-63% $TiO_2$. In the Benilite process, ilmenite is prereduced with coke, then leached with hydrochloric acid. After separation and drying, the process yields synthetic rutile of about 92% $TiO_2$ (21, 22).

Titaniferous slag is produced using an energy-intensive pyrometallurgical process. In this process,

an electric arc furnace using a carbon reductant is used to reduce iron oxide contained in ilmenite to its metallic state. During the process, all of the $Fe_2O_3$ and FeO can be reduced to metallic iron. However, the corrosive nature of titanium slag necessitates limiting the reaction to create a frozen layer of slag. Since the reduction of iron is not taken to completion, trace elements such as manganese and magnesium usually remain in the slag. Molten iron is collected from the bottom of the smelter and titanium-rich slag is tapped from above the iron phase. Recently, technology has been developed that involves thermal treatment followed by post-acid leaching to remove magnesium, calcium, and other impurities (22, 23).

## Chlorination

Currently, most $TiCl_4$ is produced by chlorinating rutile in a fluid-bed reactor. Rutile reacts with chlorine and carbon in the form of petroleum coke (used for its low ash and hydrogen content) in a fluidized bed at $1,000°$ C to make $TiCl_4$ and $CO/CO_2$:

$$TiO_2 + 2Cl_2 + C \leftrightarrow TiCl_4 + CO_2 \quad (1)$$
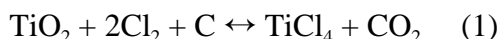
The reaction is fast and exothermic, providing enough heat to be self-sustaining. Conversion of all the reactants is over 95%. Most of the losses are due to fine particles blowing out of the fluid bed. The chlorination step provides limited purification. By controlling the temperature, however, it is possible to prevent silica and zirconia from chlorinating so they remain in the chlorinator residue. Most of the other impurities chlorinate, resulting in a loss of chlorine and an accumulation of impurities that will have to be removed in later steps. $TiCl_4$ leaving the fluid bed is spray-cooled with $TiCl_4$ and then proceeds to purification.

It also is possible to chlorinate ilmenite but the iron in ilmenite chlorinates to $FeCl_3$ or $FeCl_2$, which wastes chlorine and for which there is a limited market. Ilmenite also contains more low-boiling-point impurities like calcium and magnesium that are not readily removed from the fluidized bed reactor. Also, these impurities are liquid at the reaction temperature, thus, they adversely affect the fluidization (7, 24).

At the Zaphorovshe plant in Ukraine, titanium slag and ore are carbochlorinated in a molten salt bath. The chlorination reaction takes place in a bath of molten sodium chloride (NaCl), potassium chloride (KCl), and magnesium chloride ($MgCl_2$) at a temperature of approximately $750°$ C. Carbon and titanium feed material are fed into the bed, and chlorine plus an inert gas is sparged into the molten salt bath. The sparged gases mix in the bath and also provide the chlorine for carbochlorination. Titanium recovery is said to be greater then 80%. This is substantially less than that achieved in a fluid-bed chlorinator. The molten salt technique will tolerate a wider range of impurities, such as magnesium and calcium, which plug fluidized beds, but at the expense of higher titanium losses (25).

## Purification of $TiCl_4$

Purification of the $TiCl_4$ begins in the chlorinator. The highest boiling point chlorides, such as those containing calcium, manganese, sodium and magnesium, remain in the chlorinator. The $TiCl_4$ leaving the chlorinator contains gases (CO and $CO_2$), liquids (soluble metal chlorides such as $VCl_3$, $SiCl_3$, $FeCl_3$ and $AlCl_3$), and solids (fine rutile, petroleum coke, and oxychlorides). All these must be removed before the $TiCl_4$ can be used to make either pigment or metal (26).

$TiCl_4$ leaving the chlorinator is spray condensed with $TiCl_4$, separating the CO and $CO_2$, leaving a liquid that is about 94% $TiCl_4$, 4% solids, and 2% soluble metal chlorides. The solids (carbon,

rutile, sulfur, insoluble metal chlorides and oxychlorides) are allowed to settle out. The boiling point of $VOCl_3$ (127° C) is too close to that of $TiCl_4$ (136° C) to separate by distillation. Therefore, the $VOCl_3$ is reduced to $VOCl_2$ by adding $H_2S$ or oil, and it is allowed to precipitate out. The liquid $TiCl_4$ is fed to a fractional distillation column to remove the low-boiling-point chlorides ($SnCl_4$ and $SiCl_4$) and the higher-boiling $FeCl_3$ and $AlCl_3$ components. The purity of the $TiCl_4$ is determined by the number of plates in the distillation column. By using a high number of plates and by careful monitoring of the Kroll reduction, it is possible to produce titanium of a much higher purity. This material could potentially be used in electronics applications (7, 24).

## Chloride Process

Most of the $TiCl_4$ produced from titanium minerals is oxidized to produce $TiO_2$ for use in the pigment industry. Only about 5% is used to make metal. To produce $TiO_2$ by the chloride process, $TiCl_4$ is fed into a reactor with oxygen. Rutile seed crystals are added to the feed to promote the production of the rutile-grade $TiO_2$. The vigorous reaction occurs at 1200° C. The resulting $TiO_2$ produced is treated with organic and inorganic compounds to enhance surface properties of the pigment (2).

## Sulfate Process

The alternative to the chloride process is the sulfate process. The sulfate process is gradually being replaced by the chloride process, and no metal is produced from sulfate-process $TiO_2$. In the sulfate pigment process, ilmenite or titanium slag is reacted with sulfuric acid. An exothermic reaction occurs yielding the soluble salts, titanyl, ferrous, and ferric sulfates. Ferrous scrap is added to reduce any ferric sulfate to the ferrous state. After passing through a settling tank, the liquid fraction is passed through a crystallization tank. Iron in the form of copperas ($FeSO_4 \cdot H_2O$) is removed by centrifuge. Titanium hydroxide is precipitated by hydrolysis, filtered, and calcined. Compared to the chloride process, the sulfate process is more capital intensive but less energy intensive (2). The sulfate process generates a considerable amount of waste. Sulfate producers have had some success in producing salable products from waste streams such as white gypsum, iron salts, and carbon dioxide (27).

## Magnesium Reduction via Kroll Process

The Kroll process is currently the primary commercial process used to produce titanium metal. The Kroll process in use today is similar to the process that DuPont used to produce titanium in 1948. At the start of a typical run, enough liquid magnesium to reduce all the $TiCl_4$ plus 15% to 30% excess is introduced into an argon-filled retort. The retort is heated to 800° C to 900° C. $TiCl_4$ is slowly fed into the retort over a period of several days. The magnesium reduces $TiCl_4$ according to the reaction:

$$TiCl_4 + 2Mg \leftrightarrow Ti + 2MgCl_2 \quad (2)$$
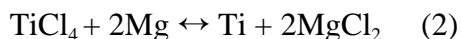
$MgCl_2$ produced is tapped off several times during the reduction. After several days (depending on the retort size), the retort pressure rises, and the reaction stops. At this point, approximately 30% of the initial Mg charge is still unreacted because it is no longer in contact with



Figure 4: Sponge retort at TIMET, Henderson, Nevada.
Source: TIMET.

$TiCl_4$. The retort is opened, and the titanium is pressed or jack hammered out. The titanium metal formed is a porous mass that resembles a sponge (Figure 4). This sponge must undergo further purification to remove any remaining $MgCl_2$ salts and any unreacted magnesium. Sponge near the retort wall is contaminated by iron and/or nickel, and for this reason, must be downgraded. Further downgrading of a batch may be required due to nitride inclusions (28, 29, 30).

### Sodium Reduction via Hunter Process

The Hunter process is very similar to the Kroll process; however, there are some differences caused by the solubility of sodium in NaCl. In the Hunter process, the retort is sealed and filled with molten sodium. Unlike the Kroll process, a slight excess of $TiCl_4$ is used to make sure that no sodium remains in the salt when the reaction is complete. The retort is then heated to the reaction temperature (~900° C) and $TiCl_4$ is slowly fed into the retort, where it reacts with the sodium via the following reaction:

$$TiCl_4 + 4Na \leftrightarrow Ti + 4NaCl \qquad (3)$$

Because the titanium subchlorides and sodium are soluble in sodium chloride (NaCl), it is not practical to drain off the NaCl that is formed during the reduction. At the end of a run, the retort contains a ratio of 4 moles of NaCl for each mole of titanium; for every 1 $cm^3$ of titanium, there are 10.8 $cm^3$ of NaCl. Therefore, the retort for the Hunter process must be considerably larger to produce the same amount of titanium as a Kroll retort. When the reduction is finished, the retort is opened, and the NaCl-titanium mixture is chipped out. The NaCl is leached away from the titanium with hydrochloric acid. A sub-stoichiometric amount of sodium is used so that excess sodium will not be wasted during the leach step. The brine solution is discarded and thus, new sodium must be bought for every run.

The process used by RMI involved a two-stage reduction. In the first stage, $TiCl_4$ and molten Na were reacted in a stirred tank to form $TiCl_2$ at approximately 200° C according to the reaction:

$$TiCl_4 + 2 Na \leftrightarrow TiCl_2 + 2NaCl \qquad (4)$$

The mixture was then fed to a 1,000° C retort containing enough sodium to complete the reaction.

$$TiCl_2 + 2Na \leftrightarrow Ti + 2NaCl \qquad (5)$$

Although the first step was continuous, the second was still a batch process and, thus, the overall process was still a batch process (9, 28).

In 1992, RMI shut down its Hunter process sponge plant. Deeside Titanium in the United Kingdom shut down its Hunter plant in 1993. The only Hunter process in operation today is the Alta Group's plant (340 t/yr) built to satisfy a market for sponge fines. The Alta plant uses a single-stage batch process.

Table IV.-A Comparison of the Kroll and Hunter Processes (31)

| Kroll | Hunter |
|---|---|
| Batch | Batch or continuous followed by batch |
| 15 to 50% excess magnesium | Small excess of $TiCl_4$ |
| Few fines | Up to 10% fines |
| Hard to grind | Easy to grind |
| Substantial iron contamination from retort walls | Little iron contamination from retort walls. |
| Sponge leached or vacuum distilled | Sponge leached |
| Retort contains mostly titanium | Retort contains 4 moles of NaCl for each mole of titanium. |
| 1/3 less energy for magnesium versus sodium recovery | |

Table IV shows a comparison of the Kroll and Hunter process. Recent work by T. H. Okabe, can be used to explain many of the differences between the Hunter and Kroll process. Okabe has suggested that both the Kroll and Hunter reactions are electrochemical reactions. Contact between the reductant (magnesium or sodium) and $TiCl_4$ is not necessary. For the reaction to proceed, it is merely necessary for electrons to be transported from the reductant to the $TiCl_4$. These electrons can travel through a conductor, such as a metal reactor or an electrically conductive molten salt, to reduce $TiCl_4$. This idea can be used to explain much of the difference between the Kroll and the Hunter processes.

In the Hunter process the sodium solubility in the product salt greatly increases the conductivity of the salt. Consequently, electrons can travel through the molten salt and reduction can occur in the salt. Okabe calls this short range Electrically Mediated Reactions (EMR). This means that titanium particles will form in the salt, producing titanium powder (the only Hunter process plant in production today is used to make powder for the electronics industry), and also that any sodium in solution will provide electrons to any available $TiCl_4$. It is possible, therefore, to have virtually 100% utilization of sodium in the Hunter process.

In the Kroll process, magnesium is not soluble in $MgCl_2$, and the salt produced in the Kroll process is much less conductive than the Hunter salt. Therefore, electrons cannot pass through the molten salt as easily and instead pass through the metal reactor. Okabe calls this long range EMR. In a Kroll reduction, the reaction takes place at the reactor wall, which results in the iron contamination from the wall. This also accounts for the fact that 30% excess magnesium is required in the Kroll process. Any magnesium trapped in the sponge cannot transfer electrons to $TiCl_4$ (31, 32).

### Purification via Vacuum Distillation and Leaching

Sponge formed from either the Kroll or Hunter process must undergo further purification to remove salts and any unreacted feed. There are three to ways to remove the chlorides, leaching, vacuum distillation, and helium sweep. Each method has advantages and disadvantages. Table V shows a concise comparison of the acid leaching and vacuum distillation processes for removing sponge salts and contaminants.

Leaching is a simple, continuous process. Sponge is leached with a combination of hydrochloric,

nitric, and citric acids. Leaching removes the excess magnesium and any remaining $MgCl_2$. The problem with leaching is that all the unused magnesium (up to 30%) is lost and the aqueous leach system contaminates the sponge with oxygen. For this reason leaching is no longer used to purify Kroll sponge, but Hunter sponge is still leached.

Vacuum distillation is a batch process involving heating the sponge to 900° C in a vacuum. The chlorides and magnesium volatilize and are condensed in a cold trap. Sometimes vacuum distillation is done in the same reaction retort as the Kroll reduction. This combines two batch steps but more importantly allows the heat from the reduction to be carried into the distillation step.

A third alternative is the helium sweep used by Allegheny Technologies. This technique forces an inert gas (helium) through 1,000° C sponge. The helium is cooled to condense the magnesium and $MgCl_2$, and is then passed back through the sponge. Helium sweep recovers most of the magnesium at the expense of reheating the helium several times. Finally, the sponge is leached with nitric acid (8, 9, 30).

Table V.-A Comparison of the Leaching and Vacuum Distillation Processes

| Leach | Vacuum Distillation |
|---|---|
| High impurity levels | High purity due to low levels of $O_2$, Mg, and $MgCl_2$ |
| High $MgCl_2$ losses | |
| Waste stream disposal considerations | |
| Easy to crush | Hard to crush and grind because of low chloride content |
| | Expensive reactor required |
| | Energy intensive |
| Low capital costs | High capital cost |

## Alternatives to the Kroll or Hunter Process

### Other Metal Reductants

The most promising alternative to magnesium or sodium is aluminum. Aluminum is inexpensive and trivalent. Based on a cost per pound of $0.60 for aluminum and $0.35 for $TiCl_4$, the cost of raw materials for a pound of titanium potentially would be $1.84 for aluminum reduction as opposed to $2.24 for Kroll, a 20% reduction in the cost of raw materials. Unfortunately, aluminum reacts with titanium to make titanium aluminide. Okabe has proposed that because the reduction is an electrochemical reaction, the aluminum could be used as a source of electrons, but it would need to be physically separated from the titanium to prevent the formation of titanium aluminide. Since this route still relies on $TiCl_4$ as a feedstock, the overall cost of titanium would not be significantly reduced by this method.

Other metals that could be used as reductants include lithium, potassium, and calcium. However, these metals are more expensive than magnesium and sodium and offer no apparent advantages.

### Vapor-Phase Reduction

The Albany Research Center (ALRC) have investigated the feasibility of changing the Kroll batch reduction process into a continuous vapor-phase process. The reduction reaction proceeds under conditions in which all reactants are vapors and the only solid product is titanium. An advantage of this route is that the vapor-phase magnesium reduction of $TiCl_4$ proceeds rapidly.

ALRC has conducted studies in which $TiCl_4$ and magnesium vapors were continuously fed into a tube furnace at 1000° C. The magnesium reduced the $TiCl_4$ to produce fine titanium powder and $MgCl_2$. The titanium powder produced was sub-micron size making capture difficult. Most gas/solid separation devices will not efficiently separate submicron particles. Both Tisdale and others and Sohn have tried similar techniques and produced similarly sized particles. Unless the newly formed titanium powder acts as a site for nucleation, gaseous reactions will produce very small particles (33, 34, 35).

Capture of such small particles was possible only because at 1,000° C, magnesium and $MgCl_2$ are liquid. The liquid phase promoted agglomeration of the titanium particles, making it possible to collect most of the titanium powder using a series of cyclones and an electrostatic precipitator. The disadvantage is that the $MgCl_2$ must be separated from the titanium powder. This can be done by vacuum distillation or leaching. Unfortunately, the powder is so small and thus has such a high surface-to-volume ratio that the surface oxide layer raises the oxygen content of leached particles to 2% to 3%. It is estimated that particle must be at least 5 microns before leached titanium will have an acceptable oxygen level.

One possible method to increase the particle size would be to increase the residence time. This could be done either by reycle or by slowing the gas stream. Both methods were tried and neither worked, possibly because when gaseous magnesium reduces gaseous $TiCl_4$, every titanium atom produced also produces two atoms of $MgCl_2$. At 1000° C, the $MgCl_2$ is a liquid that coats the newly formed titanium particle and prevents further growth. Gas-phase reduction will not be a practical route unless the particle size can be increased to the 5-to-10 micron range.

The gas-phase reduction route offers the possibility of a continuous process, but because the raw materials are the same as the Kroll process, this route has limited potential to reduce the cost of titanium. The real advantage of gas-phase reduction is it that is a continuous route to titanium powder. Powder could be used to make near-net-shape (NNS) parts. NNS parts significantly reduces the generation of scrap and processing required to produce a finished part. NNS technology could reduce overall part production costs by 50%.

## Aerosol Reduction

The aerosol process is a continuous, Hunter-based sodium vapor-phase process. The difference between typical Kroll-based vapor-phase processes and the aerosol process, as proposed by Leland, is that reactants are introduced into the reactor through a spray nozzle. Titanium is condensed into a cold-wall induction furnace for consolidation. The advantages of this process are similar to gas-phase reduction except the vapor-phase reduction process makes powder, and this process makes an ingot. The first part of the process, the vapor-phase sodium reduction of $TiCl_4$, has been done successfully. Condensation into a pool that can be withdrawn from a cold-wall induction furnace is still being developed (36).

## Molten Salt

Molten salt approaches attempt to modify the Kroll or Hunter process into a continuous-solution

reaction. The solvent is either the product salt or a mixture of salts, one of which is the product salt. The Albany process attempted to accomplish a Hunter reduction in a continuous stirred tank reactor (CSTR). Santa Fe Alloys, Toho Titanium, and O. Suzuki et al. also have proposed molten salt processes (37,38, 39, 40).

In the Hunter modification explored at the ALRC, the reaction was slowed by diluting the initial reactants, $TiCl_4$ and sodium, with NaCl, in a CSTR. This allowed better control over the reaction product. When titanium particles become too large to be suspended by the stirring action of the CSTR, they fall to the bottom of the CSTR and are removed.

Okura at Toho Titanium has pursued a similar modification of the Kroll process. In this process, $TiCl_4$ is reduced by magnesium in a bath of molten $MgCl_2$ salt. The titanium is drawn off the bottom of the reactor and fed to an induction plasma melter. Toho built a 50-kilogram/hour pilot plant and claims that titanium could be produced at a 30% cost savings using this technology (35).

There is a significant difference between the molten salt versions of the Kroll and Hunter processes. Because magnesium is not soluble in its chloride salt, it floats on top of the $MgCl_2$ and necessitates a two-stage process. Because sodium does dissolve in NaCl, molten salt processes that are Hunter-based require only a single stage.

Molten salt processes are continuous. The powder that is produced is of sufficient size to be useful for powder-metallurgy- (PM) fabrication, thus eliminating melting and fabrication steps that precede semi-finished mill products. The powder also is large enough to be used as feedstock for continuous melters utilizing electron-beam (EB), plasma, or induction. The cost of producing Hunter-based CSTR molten salt powder should be less than the cost of producing Hunter sponge.

Problems include continuous removal and purification of the titanium powder. At ALRC, the problems included reliably feeding $TiCl_4$ and sodium into the CSTR. Toho had problems with removal of the titanium ingot. Because molten salt processes use the same starting material as the Kroll and Hunter processes, there is limited potential for dramatic cost reductions.

**Plasma Reduction**

There are two versions of plasma processes. The first and simplest is based on the idea that at a high enough temperature, $TiCl_4$ molecules will vibrate apart. The challenge is to capture the titanium before it recombines with the chlorine. Work at Idaho National Engineering Laboratory (INEL) and facilities associated with INEL has proceeded along these lines and just recently has begun producing powders in small quantities (41). Powder from this process was sintered at the ALRC, and the titanium produced contained very little chlorine. However, the yield was 6% of high-oxygen titanium. The oxygen was probably introduced during the handling but it also may have increased the yield. An X-ray diffraction analysis of the unsintered powder revealed that it was $TiCl_3$ and $TiCl_2$, not the reported HCl + Ti. Apparently, it was impossible to cool the product fast enough to prevent most of the product from back reacting.

In the second approach, the plasma is used to provide heat and a reductant such as hydrogen and/or sodium is used to remove the chlorine and reduce the $TiCl_4$. This was tried at the Electric Council Research Centre in Great Britain and at Westinghouse Electric Corp. At Westinghouse, the gas was 1 $TiCl_4$: 4 Na : 13.4 $H_2$ : 3.35 Ar. The thermodynamics for this process are favorable, but this process has no advantage over the similar and simpler vapor-phase processes (42, 43, 44, 45).

**Electrolytic Processes**

Electrolytic reduction of $TiCl_4$ is the only process that has ever threatened to replace the Kroll process. Electrolytic processes were being developed concurrently with the Kroll and Hunter process. In 1953, Kroll predicted that titanium would be produced by an electrolytic route in 15 years (12). Electrolytic processes are continuous and produce a highly refined product. Yet today no electrolytic processes are in operation.

In 1825, Hans Christen Orsted produced anhydrous aluminum chloride. Then, in 1827, Friedrich Wohler isolated aluminum by reaction of anhydrous aluminum chloride with potassium. In 1854, Sainte-Claire Deville improved the method by introducing sodium reduction. At this time aluminum was more expensive than gold; a set of aluminum tableware was presented to Napoleon III, and the Washington monument was capped with aluminum. Then, in 1886, Charles Martin Hall of Ohio and Paul L. Heroult of France independently demonstrated an electrolytic process (7, 8). This new process dramatically dropped the price of aluminum so that near the end of 1999, aluminum sold for $0.72/lb (5).

In 1910, Hunter produced titanium by sodium reduction (7). Perhaps Hunter got the idea for sodium reduction of $TiCl_4$ from aluminum processing. Following the example of aluminum, many felt that electrolytic reduction of $TiCl_4$ would produce similar cost reductions for titanium.

In the early 1980's, the D-H Titanium Company (a Dow Chemical and Howmet Corp. venture) built a 100-t/yr electrolytic plant. In the D-H process, $TiCl_4$ was fed into a molten bath of KCl and LiCl at 520° C. After investing millions of dollars, D-H Titanium closed down when the titanium market went through one of its periodic downturns. At about the same time, TIMET piloted its own version of an electrolytic process that employed a NaCl bath at 900° C. Although the D-H process and the TIMET effort apparently fell victim to a downturn in the titanium market, they had trouble controlling back reactions of titanium with chlorine, and, consequently, neither would have produced the kind of dramatic price reduction seen with aluminum (9, 30).

Subsequently, in the early 1990's, RMI built a $40 million pilot plant based on a proprietary electrolytic process developed by Ginatta. It, too, was closed down during a periodic downturn in the titanium market. RMI had been unable to solve "engineering problems" in the process (46).

Both Dow Chemical and RMI also are no longer primary producers of titanium. In both cases, a major investment was made over a period of time, and then the titanium market collapsed. Each company not only dropped the electrolytic process but also ceased all primary production of titanium. These failures may have been precipitated by inadequate development time. The development time for a full-scale electrolytic plant has been longer than the titanium market cycle. Since the RMI plant, the titanium market has not grown enough to justify building a new plant. Given the widely publicized failures of the electrolytic process, it is unlikely that any new attempts to revive electrolytic reduction will be undertaken in the near future.

While electrolytic production of aluminum has been a commercial success, commercial production of electrolytic titanium has yet to come to fruition. There are significant differences between aluminum and titanium, and these differences make electrolytic reduction of titanium a significantly more intransigent problem. Titanium melts at 1660° C, while the melting point of aluminum is only 660° C. The electrolytic cell for aluminum operates at a temperature where aluminum is a liquid, while the titanium cell operates where titanium is a solid. This results in dendritic titanium material and a loss of the electrolyte. Titanium can exist in several stable valence states while aluminum has only one. The multiple valence states allow the ions in solution to move between the electrodes causing a loss of efficiency. $TiCl_4$ is not soluble in the electrolyte while $Al_2O_3$ is soluble. Finally, the potential savings of the electrolytic process are, in fact, not that large because so much of the

cost of titanium is in the cost of $TiCl_4$.

A second, more radical approach toward electrolytic reduction involves reduction of $TiO_2$. This approach, not the chloride route, is really the titanium analog of the Hall-Heroult process for aluminum. The oxide route would require two major developments. An equivalent of the Bayer process (to produce very pure rutile) and then the electrolytic reduction of the purified rutile. The chances for success are questionable because many of the same problems for the chloride process still exist for an electrolytic oxide route. Titanium still exhibits multiple valence states, and the temperature of operation would have to be over 1770° C to keep the titanium molten. Further, one of the reasons for the chloride route is to separate titanium from oxygen. Most of work has failed to make titanium with low enough oxygen content. Still the potential for less expensive titanium makes this route worth investigating (47, 48, 49, 50, 51).

## Non-Chloride Routes

The Kroll process is often criticized as an inefficient series of time-consuming batch steps. In an effort to improve efficiency and reduce the cost of producing titanium, a number of different methods have been investigated. These range from using different reductants in the Kroll or Hunter process to making the Kroll and Hunter processes continuous rather than batch to using a non-chloride route. All have met with limited success.

### Metal Hydride Reduction

In the metal hydride reduction (MHR) process, $CaH_2$ reduces $TiO_2$ at 1,100° C to produce titanium powder, calcium oxide (CaO) and $H_2$:

$$TiO_2 + 2CaH_2 \leftrightarrow Ti + 2CaO + 2H_2 \quad (6)$$
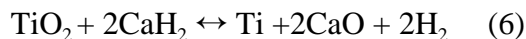
The process begins with very pure $TiO_2$. The $TiO_2$ is reacted with calcium hydride to produce titanium powder and CaO. The CaO is leached away from the titanium powder with an aqueous solution. A large plant was operated in Russia using the MHR process to produce very pure, chloride-free powders. When the Soviet Union broke up and the facility was forced to operate on the basis of market economics, the plant was shut down.

The MHR process has several advantages. Considerable savings are made by eliminating the chloride step, thereby going directly from rutile to titanium. Also, the product is titanium powder that could be used to make NNS parts directly and eliminate most of the post-sponge processing cost of titanium parts. It is questionable, however, whether or not pure enough rutile can be obtained at a reasonable cost and thus attain the savings available from eliminating the $TiCl_4$. Also, calcium is expensive and, in the current process, creates an alkaline leach waste disposal problem.

### Albany Titanium Process

The Albany titanium process has two major advantages over most other processes in that it is a non-chloride process that uses ilmenite. There have been several variations of the Albany process, but all follow the same general outline. In the pyrometallurgical roast version, ilmenite is roasted with $Na_2SiF_6$ to produce $Na_2TiF_6$. The $Na_2TiF_6$ is subsequently reduced with aluminum in a zinc bath. The zinc is removed by vacuum evaporation to produce titanium sponge. This process has several major economic advantages. The starting material (ilmenite) is one-fourth the cost of rutile, the expensive chlorination step is eliminated, and aluminum is an inexpensive reductant compared with either magnesium or sodium.

No matter how "inexpensive" a process is, it will not be economic if the product cannot meet the required specifications. The Albany process has a number of problems. The most obvious problems occur in the zinc-titanium bath, where it was believed that zinc could be vacuum distilled from the bath, leaving pure titanium sponge. It proved impossible to remove all of the zinc from the titanium. The initial step that was expected to produce $Na_2TiF_6$ also had purity problems. Several other approaches that substituted leaching for pyrometallurgical roasting also have not solved the problem.

A multimillion dollar pilot plant that was built to demonstrate the process was closed. No further work has since been undertaken. Given the amount of money already spent on this process and the lack of real progress, the Albany process does not show potential to lower the cost of titanium (28).
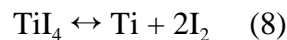
## Van Arkel

The Van Arkel process is based on a thermal decomposition of titanium iodide ($TiI_4$) to produce very pure titanium. This was the process used in 1925 to produce the first relatively pure titanium. And, in fact, is still used today to produce high-purity titanium crystal bar for the electronics industry.

In the Van Arkel process impure titanium reacts with iodine at 200° C to form $TiI_4$:

$$Ti + 2I_2 \leftrightarrow TiI_4 \quad (7)$$
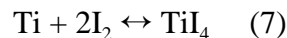
$TiI_4$ is a vapor that diffuses to a filament heated to 1300° C, where it decomposes to produce titanium and iodide gas. The iodide diffuses back to the impure titanium where it again reacts, thus completing the cycle:

$$TiI_4 \leftrightarrow Ti + 2I_2 \quad (8)$$

The Van Arkle process is capable of making very pure titanium but cannot be adapted to a large-scale continuous process. The decomposition of $TiI_4$ to titanium only becomes favorable at low pressures or high temperatures. In addition, deposition rates are slow. In principle, other halides such as bromine or chlorine could be used, but the thermodynamics are even less favorable. To get the same deposition with $TiBr_4$ would require either a lower pressure or a higher temperature. Iodine is expensive, and any losses would make this process noncompetitive with Kroll (52, 53, 54, 55).

## Thermal Decomposition of Halides

It is possible to produce titanium by disproportion reactions. Titanium chloride ($TiCl_2$) will disproportionate according to the following reaction:

$$2TiCl_2 \leftrightarrow Ti + TiCl_4 \quad (9)$$
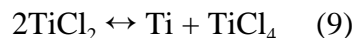
This disproportion can be used to make titanium, but because it is based on a chloride process, it has limited potential to significantly reduce the cost of titanium (3).

## Physical Metallurgy

By far, the operations with the greatest potential to yield major cost savings are fabrication and melting. Post sponge operations can more than double the cost of titanium parts. A technology such as EB hearth melting can cast directly to rectangular slabs. This practice reduces multiple arc-melting steps, initial ingot breakdown, and can readily use scrap feedstocks. Even more appealing

are NNS operations, such as powder metallurgy processes and casting, that eliminate most consolidation, fabrication, scrap, and can lend themselves to high rates of production. Unfortunately, powders and castings are expensive. New processes for powder making and processes for permanent mold casting hold promise for revolutionary advancement, and processes for continuous melting/casting of round bar products are feasible.

Figure 5 shows the proportional cost of each unit operation in the production of a semi-finished slab of titanium alloy plate. Twenty-five percent of the total cost is identifiable with reduction. Because reduction is feasible by several possible routes, and the costs associated with each route are thought to vary widely, new reduction processes represent a fertile field for research. A continuous process to replace standard Kroll or Hunter batch processes, for instance, could reduce the cost of producing titanium by 10% to 15% (28, 56).

## Arc Melting

Vacuum arc reduction (VAR) melting has been the standard, high-volume melting practice that has been used to make ingots since the 1950's. Arc-melted alloy ingots are used as the starting material for subsequent semi-finished fabricated forms such as bar, plate, forgings, sheet, and extrusions. Arc-melted ingots also are used for skull-casting feedstock and some powder-making processes.

VAR melting is a method of sponge or scrap consolidation that is performed in a water-cooled copper crucible to avoid refractory contamination and in a vacuum or an inert atmosphere to preclude atmospheric contamination. It is comparable to stick-arc welding in which an electrode is consumed as the weld progresses. Arc melting requires an electrode that must be fabricated from compacted sponge or clean scrap, along with alloying additions. Electrode fabrication represents a major cost item of arc melting. Melting occurs by striking an arc between the bottom of the copper crucible and the electrode. As the electrode melts, molten metal drops from the electrode to the bottom of the crucible. An ingot is formed from the bottom up, much like filling a glass. The ingot progressively solidifies as the molten metal pool under the arc advances upward from the crucible bottom.

The arc, although relatively stable, causes spitting of the molten electrode metal to the cold crucible wall which, in turn, causes a roughened ingot surface that must be removed, usually by turning the ingot on a large lathe after the ingot is removed from the mold. The removed surface material is downgraded. Inclusions that are contained in the electrode drop into the ingot along with the titanium. Volatile elements, such as magnesium and chloride, are vented to the vacuum system. A single melt is not sufficient for good alloy homogeneity for most applications. First-melt ingots typically are surface conditioned and serve as electrodes for a second melt to improve homogeneity. Some critical aircraft rotary components require a third melt. Arc melting is a batch process that is made more efficient by increasing batch size.

Arc melting is a lengthy and laborious batch process that contributes to the high cost of titanium, and as such, is an impediment to the use of titanium for high-volume, inexpensive applications (56, 57, 58).

## Cold Hearth Melting

EB furnaces consist of a water-cooled copper hearth that is shaped like a rectangular cake pan. One or more EB guns provide point-source heat to the surface of the material in the hearth. Electronic controls move the beam from one point to another very rapidly over the surface in a programable pattern (called rastering) to maintain even heating and consistent melting over the entire hearth.

Loose feed material in the form of scrap or sponge and alloy is fed to one end of the hearth from dual lock hoppers that can be independently charged and evacuated with respect to the furnace chamber vacuum. Molten metal flows over a lip at the opposite end of the hearth into a water-cooled copper mold. The lip of the hearth, as well as the surface of the metal in the mold, is kept molten by rastering the beam over these areas. Removal of the beam from the lip causes the overflowing metal to freeze, and as such, the procedure serves as a valve.

The hearth can be constructed with two or more lips with molds located under each lip. When one mold is filled, the beam can be moved to melt the metal over the second lip to commence filling the second mold. While the second mold is filling, the first can be removed through a lock hopper. Typical hearths are constructed with a dam that is perpendicular to the direction of metal flow. The dam prevents high-density inclusions (HDI) from entering the mold. HDI are present in scrap from tungsten carbide tools used to fabricate titanium components. HDI sink to the bottom of the hearth and must be periodically removed.

EB offers several advantages over VAR. Electrode fabrication is eliminated. Low- and high-density inclusions are removed to produce a higher quality product. Removal of high-density inclusions during melting allows greater usage of scrap. Mixing and dilution in the hearth improves homogeneity. Melting can be halted and resumed nearly at will. EB melting can be made semi-continuous with feed and product lock hoppers. Rectangular, molds eliminate the need for the breakdown forging that is required of round ingots, and rectangular ingots can be made larger than round ingots. Rectangular commercially pure ingots can eliminate the need for initial thermomechanical steps and provide the starting material for sheet rolling and reduce the cost of titanium sheet. Smaller, semi-continuously produced round ingots can be used to make small-diameter bar products. However, power consumption is greater than VAR and high vacuum increases alloy loss. Also, the ingot surfaces require conditioning (56, 57, 58).

## Plasma Cold Hearth Melting

Plasma cold hearth furnaces are similar in design to EB cold hearth furnaces. A plasma gun (or guns) is substituted for the EB torch. The plasma gun is mounted in a ball joint in the furnace chamber roof. The ball joint allows the plasma to be moved over the molten metal in the hearth to maintain even heating in much the same way as the electron beam is rastered.

The advantages of plasma melting are similar to EB melting. In addition, plasma melters produce more stable chemistries than EB melters, and thus, composition control is better. Plasma furnaces can be made for semi-continuous operation. Smaller, semi-continuously-produced round ingots can be used to make small-diameter bar products for suspension springs, valve springs, and valves. Disadvantages are similar to those for EB melting. Power consumption is slightly higher than power consumption for vacuum arc melting, ingot surfaces require conditioning, and consumption of plasma gas is high (57, 58).

## Induction Melting

Induction melting of titanium and other reactive metals is made possible by the design of the water-cooled copper crucible. Conventional cylindrical crucibles within an induction coil are subject to the same eddy currents as the charge within the crucible and will melt as readily as the charge. To avert crucible melting, the induction crucible is segmented along the direction of the centerline of the coil, prohibiting a continuous electrical path. The optimum number of segments varies with a number of factors, but is normally more than 20. Each segment is insulated from its neighbor by a small gap that may be filled with a refractory such as mica. Each segment also is individually water cooled. The segments may be joined at the bottom end, outside of the coil, to a common bosh,

either in a ring arrangement without an internal bottom for producing continuous ingots, or with an internal bottom to make pots full of metal for casting. Molten metal within the crucible appears to levitate from the sides of the crucible and does not form a bridge between the segments.

In the ingot-making version of an induction melter, feed material is dropped into the crucible onto a starter stub that plugs the bottom. As the feed material is melted, additional feed is added. The induction field churns the molten metal and provides excellent mixing. The starter stub and ingot are extracted from the crucible bottom at a rate equal to the feed rate. The ingot exits the crucible hot and solid and is withdrawn into a cooling tube extension to the furnace. Although a variety of feed materials may be used, all must have meet specific compositional requirements because high- and low-density inclusions cannot be removed.

The casting version is similar to the ingot-making version except that a permanent water-cooled bottom forms a pot to contain the metal. Molten metal is melted in the pot and can be retained until ready for pouring. The metal can be superheated by raising furnace power to increase fluidity, which may be necessary to pour thin-wall castings. Inductive mixing imparts homogeneity and allows the close compositional control of alloys such as titanium aluminide. Castings and molds can be removed and additional feed can be added through lock hoppers without breaking vacuum.

Induction melters have a number of advantages including making ingots semi-continuously, when fitted with feed and product lock hoppers. As with EB and plasma melting, electrode fabrication is eliminated, and the melter can accept a wide variety of feedstocks including sponge, powder, and scrap. Mixing and compositional control are excellent, making the induction melter a first choice for alloys such as titanium aluminide. Melting can be halted and resumed at will. Capital costs are low, and power consumption is similar to that in vacuum arc melters. The casting version of the melter can add uniform superheating of the metal to facilitate pouring of thin-wall casting sections. Casting to NNS eliminates waste and the need for fabrication.

There are several drawbacks to induction melting. Ingot cross section may be limited, ingot surface finish is mediocre, and copper crucible life is limited. The casting version of the melter is the best alternative for producing cast parts. The ingot version may be useful for making powders and small-diameter billets (57, 59, 60, 61, 62, 63).

## Permanent-Mold Casting

Permanent-mold casting is practiced successfully with other metals, notably aluminum. Similar to die casting, a metal mold is needed to form a part. The mold can be used over and over but is subject to gradual erosion and wear. Unlike die casting, the casting metal is not injected into the mold, but is normally poured without pressure. The simplest permanent molds consist of two halves that are pressed together to form a cavity in the shape of a part. Metal is poured into the cavity and cooled rapidly due to high heat conductance through the metallic mold. The mold is separated to release the cast part, and prepared for the next cycle. Automotive parts under consideration for titanium application can be made in two-part molds.

Permanent molds, if made durable enough, negate the need for investment casting prerequisites such as wax patterns, investment molds, and mold bakeout, all of which are expensive, hard to control, and labor intensive. Mold/metal reactions are not a factor, and the necessity for removing the alpha-phase layer (alpha-case) formed at the mold interface is eliminated. Spent-mold and etching-acid disposal are eliminated. Multiple-part molds can be stacked to increase the number of parts that are produced at one pour.

The drawbacks to permanent-mold casting are that a Japanese patent protects one version of the permanent mold process, mold wear and life is unknown, part warpage occurs, and the molds cannot be heated to assist metal flow and directional cooling (62, 63).

## Powder Metallurgy

PM allows the use of NNS technology, which reduces waste and thus decreases cost. In addition, the fine grain size possible with powder metallurgy enhances mechanical properties and often allows the formulation of alloys not possible with conventional ingot metallurgy. Titanium powder metallurgy, however, has been limited by the high cost of powder of acceptable size and purity. Titanium and titanium-alloy powders are made by the following processes: Hydride-dehydride, Colt-Titanium, Electron Beam Rotating Disk, Plasma Rotating Electrode Process (PREP). It also is feasible to make powder from scrap. However, even high-quality scrap suffers from high oxygen levels. Katz Metals has licensed a patent from RMI for deoxidizing scrap with calcium and is producing deoxidized chips on a limited basis. Katz's future plans include making powder from deoxidized chips using hydride-crushing-dehydride technology.

Because more than half the cost of a titanium part is incurred during fabrication, NNS technologies could have a substantial impact on the cost of titanium parts. PM is a high-output/low-cost method for producing NNS parts that require little subsequent machining. Dimensions can be tightly controlled, and part stability and reproducibility are excellent. Homogeneity is assured by fine powder dispersal, and mechanical properties are generally nondirectional. If the powder could be made continuously and directly from $TiCl_4$, there would be an associated reduction in cost and energy, as well as economies of scale. Submicron powder would allow lower sintering temperatures and result in a more uniform product piece. Commercial powders are all greater than 100 microns in size. Also, conventional processing can produce titanium nitride inclusions that are of great concern to the titanium producers and aircraft engine manufacturers. Production of submicron powder would eliminate these defects.

PM is a process that can be highly automated. Fine powders are placed in a metallic mold and compacted to form a temporary green part. A small amount of organic binder such as wax or plastic is needed to hold the powders together in this temporary state. In a PM variation, a plastic/powder combination may be injected into a mold to further automate the process. Subsequent heating bakes off the organic binder and sinters and densifies the powders in the part. Heat treating may be done concurrently. However, complete density is seldom achievable. If higher densities are required to achieve mechanical properties, a densification operation , such as hot isostatic pressing (HIP), must be executed to close voids.

PM processes are well developed. The success of PM depends upon a plentiful source of low-cost powder. Low-oxygen titanium powder currently is expensive. HIP may be required for part densification. Die wear is a major cost factor. Protection of powders from oxidation at several stages is expensive, if not impossible, for submicron powders.

## Closed Die Forging

Closed die forging produces parts by deforming semi-finished mill products in a die within large presses that are hammered repeatedly or complete the deformation in one step. More than one die may be required for intricate parts. Although most forged parts generate a significant volume of scrap, some parts, such as valves, can be produced by upending blank rods with little waste in automated presses.

Closed die forging is a conventional process that is used to manufacture many parts. In general, most parts have high integrity and advantageous directional mechanical properties. Forging normally is not a NNS process and usually requires subsequent machining. Titanium forged in air atmosphere produces surface contamination that must be removed. In addition, forging requires expensive semi-finished mill products. Die life is limited, and, capital costs for forge presses are high (28). Table VI shows a summary of the advantages and disadvantages of ingot and post-ingot processing steps.

## Scrap Processing

Titanium scrap is a potentially high-value, usually alloyed waste that competes with sponge as a starting material for melting. Scrap is often too contaminated for recycle to titanium products and must be downgraded for lesser value uses such as an alloying addition for steel. Typically, recycled titanium scrap is highly oxidized and contaminated with cutting oils and other foreign material such as small chips of tool bits that must be removed prior to melting or during melting. Cleaning prior to melting is preferable but not always practicable. The challenge for scrap processors is to economically remove contaminants to make it suitable for melting. This is done by chemical cleaning and sometimes by heating in the presence of calcium or sodium to gather the oxygen. Attempts have been made to convert scrap into brittle titanium hydrides that are easily crushed to make powder. Subsequent heating at low temperature removes the hydrogen but cannot remove oxygen that may contaminate the scrap initially. PM processes have used hydrided powders directly in green compacts. The hydrogen is removed concurrently during sintering.

Companies that produce high volumes of scrap have a constant incentive to reduce scrap generation because it represents cost and inefficiency. Scrap may contain numerous contaminants; the cleaner the scrap, the higher the value. Scrap, such as machine chips, have high oxygen levels (63, 64, 65).

Table VI.-A Summary of Ingot and Post-Ingot Technologies

| Process | Description | Advantages | Disadvantages | References |
|---|---|---|---|---|
| Arc melting (Ingot) | Uses consumable electrode arc heating to melt titanium in copper crucible | In use, low power requirements | Batch, electrode fabrication, multiple melts, poor ingot surface, inclusions not eliminated | 56, 57, 58 |
| EB cold hearth melting (Ingot) | Uses electron beam to melt in flat hearth, Metal overflows to ingot mold | In use, variety of loose feed OK, semi-continuous, inclusions eliminated | High power, alloy control difficult, high capital cost, fair ingot surface | 56, 58 |
| Plasma cold hearth melting (Ingot) | Uses plasma to melt in flat hearth, Metal overflows to ingot mold | In use, variety of loose feed OK, semi-continuous, inclusions eliminated | High capital cost, uses large amount of inert gas, uses more power than arc | 56, 58 |
| Induction melting (Ingot) | Uses induction heating to melt. Bottom withdraw crucible for ingots, casting version tipped to pour | Partially in use, superheat and mixing, variety of loose feed OK, semi-continuous | Inclusions not eliminated, size restrictions | 56, 58, 62, 63 |
| Permanent mold casting (Post Ingot) | Titanium cast in reusable copper mold | In use, no alpha case, near-net shape, no investment materials, eliminates fabrication | Die wear, cast structure, warpage | 64, 66 |
| Powder metallurgy (Post Ingot) | Ti powder pressed to shape, sintered | In use, near-net shape, eliminates melting and fabrication | Depends upon low cost powder, density low, die wear | 65 |
| Processes to promote scrap usage (Post Ingot) | Scrap is treated and consolidated or made into powder | Alloyed scrap saved for use, low cost powder possible | High $O_2$, may contain inclusions, scrap supply not guaranteed | 63, 67, 68 |
| Closed die forging (Post Ingot) | Semi-finished metal is deformed to shape in die by pressing | In use, directional properties, closes voids | Die wear, scrap generated, extensive finishing required | 69 |

## Physical Properties of Titanium and Titanium Alloys

The density of titanium is 4.5 g/cm$^3$, about half that of iron (7.86 g/cm$^3$) and twice that of aluminum (2.7 g/cm$^3$). The yield strength of Ti-6Al-4V alloy is 924 MPa, more than 3 times that of 316 stainless steel and 6061 aluminum. Table VII gives a brief outline of some physical properties of titanium.

Table VII.-Physical Properties of Unalloyed Titanium

| Atomic number | 22 |
|---|---|
| Atomic weight | 47.9 |
| Crystal Structure | α Hexagonal close-pack < 883° C<br>β Body-centered cubic >883° C |
| Density | 4.51 gm/cm3 |
| Melting point | 1667° C |
| Boiling point | 3260° C |
| Yield strength | 241 MPa |
| Tensile strength | 331 MPa |
| Young's modulus of elasticity | 116 x 109 N/m$^2$ |
| Elongation % | 30 |
| Hardness HB | 120 |
| Electrical conductivity | 0.024 |
| Coefficient of thermal expansion | 8.64 x 10$^{-6}$/° C |

Titanium is an allotropic element and it is this fact that is exploited to produce a large number of alloys. At 883° C, pure titanium transforms from hexagonal close-pack (α phase) to body-centered cubic (β phase). The relative amounts of the α and β phase determine the properties of the alloy.

Titanium alloys are usually placed into 3 categories α, α-β, and β depending on the relative amount of each phase. Elements like aluminum and tin stabilize the α phase by increasing the α-β transformation temperature. There are several types of β stabilizers. β isomorphous stabilizers (vanadium, molybdenum, niobium, and tantalum) are soluble in the β phase and thus act to lower the α-β transformation temperature. Manganese, iron, chromium, cobalt, nickel, copper, and silicon form eutectoid systems. Tin and zirconium are soluble in both phases and retard the rate of transformation. The most common alloy, Ti-6Al-4V is an α-β alloy. Interstitial elements oxygen, nitrogen, and carbon often occur as impurities and have a dramatic effect on the strength and ductility. Some alloys with low oxygen, nitrogen, and carbon are labeled extra low interstitial (ELI).

α alloys include Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo. These alloys are non-heat treatable but can be welded. They have lower strength than α-β but reasonably good ductility and can be used for cryogenic applications. α-β alloys such as Ti-6Al-4V, Ti-2.5Al-V, and Ti-6Al-2Sn-2Zr-2Mo-2Cr are heat treatable and have more strength than the pure α alloys. Welding is more of a problem with α-β alloys than with α alloys. β alloys such as Ti-10V-2Fe-3Al and Ti-13V-11Cr-3Al are readily heat treatable, have good formability, are the most difficult to weld of the titanium alloys, and are capable of high strengths and good creep resistance. β alloys also are the heaviest alloys. Generally, as the alloy structure moves from pure α to β, the alloy becomes less sensitive to heat treatment and easier to forge, but more difficult to weld (69, 70).

**Corrosion**

It is an interesting oddity of nature that a metal as reactive as titanium is so resistant to corrosion. The reason for this corrosion resistance is that upon exposure to air a thin and nearly impervious

protective oxide layer immediately forms on the surface.  As long as the protective oxide layer is intact, corrosion will be almost nonexistent.  This is the key to understanding the corrosion properties of titanium.  Thus, in oxidizing environments, titanium is very corrosion resistant, whereas in reducing environments, it is prone to corrosion.  Because the oxide layer forms so quickly, damage to the layer may not cause failure, but if the oxide layer is damaged or removed, the titanium will react with whatever is available.

Titanium is nearly immune to corrosion by sea water, body fluids, oxidizing acids (such as nitric acid) and wet chlorine.  There is sufficient oxygen in water to prevent a breach in the oxide layer. The same is true of methanol.  Pure methanol causes stress corrosion cracking but a small amount of water (as little as 2%) prevents this.  Dry chlorine, however, causes substantial corrosion. Fluoride ions also attack the oxide layer, so even a small amount of HF or other source of fluoride ion will accelerate corrosion.

Reducing acids present more of a problem.  Titanium is resistant to weakly reducing acids such as sulfurous, acetic, and lactic acids.  However, strongly reducing acids, such as hydrochloric, hydrobromic, sulfuric, phosphoric, oxalic, and sulfamic acids, corrode titanium.  It is often possible to prevent corrosion, even in reducing acids, by the addition of inhibitors (small amounts of oxidizing agents or heavy metal ions) (8, 69, 70).

## Applications and Uses

Although aerospace applications dominate the use of titanium metal products, titanium products are used in a variety of applications.  In general titanium is used where there is a need for reduced weight, higher strength, or improved corrosion resistance.  An estimated 65% of titanium is used in aerospace applications while the remaining 35% is divided among armor, automotive, consumer, industrial, medical, and other applications (71).

### Aerospace

Aerospace is by far the largest end use for titanium.  Although titanium may cost 2 to 10 times as much as steel, the performance advantage and weight reduction make it a material of choice for many aerospace applications.  In fact, most commercial and military aircraft have some percentage content of titanium.  Because of their need for higher performance, military aircraft generally have a higher titanium content than commercial aircraft.  For example, the current F-22 is reported to be about 40% titanium by weight.  The percentage of titanium in commercial aircraft has increased over time.  For example, in 1959 the Boeing 707 was just 0.2% titanium while the Boeing 777 in 1993 was about 8% titanium (Table VIII).  Because of availability concerns during the design phase of the Boeing 767, the titanium content of the aircraft was only 1.5% (72).

The driving forces for the use of titanium in aerospace is a focus on weight savings, high strength, volume savings, and compatibility with composite materials.  Aircraft designers take advantage of titanium's high strength-to-weight ratio.  When used as a substitute for steel, titanium may decrease the weight of a component by as much as 40%.  As a substitute for aluminum, titanium may increase the operating temperature, reduce the volume, and improve the compatibility with carbon fiber components.  Material compatibility is important because, when fastened together, materials like aluminum and graphite can create a galvanic potential, resulting in serious corrosion problems. Thermal compatibility with composites is another benefit.

Table VIII.-Examples of Titanium Consumption in Commercial Aircraft (72)

| Year | Boeing Model | Percent Titanium |
|---|---|---|
| 1959 | 707 | 0.20 |
| 1962 | 727 | 0.88 |
| 1967 | 737 | 2.00 |
| 1969 | 747 | 2.10 |
| 1974 | 747-SP | 3.34 |
| 1982 | 767 | 1.50 |
| 1982 | 757 | 4.85 |
| 1993 | 777 | 8.10 |

## Armor

Titanium armor was first developed in the 1950's. The use of titanium in armor applications offers increased ballistic properties and weight reduction compared to steel alloys. New interest in titanium armor has been driven by significant increases in the U.S. Army's ground combat vehicle weight. From 1987 to 1990, vehicle weight has increased by 15% to 20%. Increased weight affects transportability, portable-bridge-crossing ability, and maneuverability. To counteract the negative effects of increased weight, the U.S. Army is upgrading its equipment to incorporate titanium. For example, the Army has successfully replaced the forged aluminum commander's hatch of the M2 Bradley fighting vehicles at a weight savings of 35% and increased ballistic properties. Titanium also is being used as applique armor in the M1 Abrams battle tank. By using the material in this manner, titanium plate can be secured to the vehicle for protection against larger ballistic threats. The army also is looking to incorporate titanium into the frame of the Crusader (a self-propelled 155-mm Howitzer). The prevalent alloy used in titanium armor applications is Ti-6Al-4V (73).

## Automotive

In 1956, shortly after titanium's introduction, General Motors Corp. built a titanium skin for a Firebird 2 concept car. In the early 1980's, the automotive racing industry began using titanium in racing cars. Owing to tremendous competition from other materials, the use of titanium in has progressed slowly. However, use has not been limited to racing cars. The Honda NSX, a limited-production sports car, uses titanium connecting rods made from the α-β alloy Ti-3Al-2.5V to increase performance and eliminate the need for a turbocharger. In Japan, the Toyota Altezza is making use of titanium valves. Titanium also has been used in automotive brake pads since 1995 (74).

The Partnership for a New Generation of Vehicles (PNGV), a domestic auto industry and federal government initiative, has identified a number of ways to move toward achieving 80 miles per gallon fuel efficiency in passenger cars. According to the United States Council for Automotive Research "Titanium is an alternative for lightweight coil suspension springs, exhaust system components, and high performance fasteners as well as some moving engine components, e.g. connecting rods, valves, valve spring retainers. It is the only lightweight metal that can replace stainless steels and heat-treated alloy steels in highly loaded components" (75).

Although high-volume production vehicles are a huge potential market for titanium, material cost competition in the automotive industry is intense. The use of titanium is generally considered cost prohibitive in the current automotive market. In the future, reciprocating engine components currently made of steel are the most likely components to be replaced with titanium to reduce weight, improve engine efficiency, and dampen vibrations. Titanium valve components have been shown to improve fuel efficiency by 4%. Titanium can be used in the suspension to reduce the weight of suspension coils by as much as 70%. Titanium also can improve corrosion resistance and

reduce weight in exhaust systems. The most prevalent alloys used in automotive parts are Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.1Si alloys (76).

## Consumer Goods

Consumer goods include items such as bicycles, golf clubs, and eyeglasses. Over the past decade, titanium use in consumer goods has grown tremendously. The consumer goods market is dominated by the use of Ti-3Al-2.5V alloy.

Titanium bicycles were first introduced in the 1970's using straight gauge 6-4 tubing. Today about 50 companies produce titanium bicycle and wheelchair frames and components using primarily Ti-3Al-2.5V, Ti-6Al-4V, and commercially pure grades of titanium. Although numerous bicycle frames and components are produced each year, the total volume of titanium consumed by the bicycle and wheelchair industry is estimated to be less than 200 tons (77, 78).

The golf industry is the largest consumer of titanium consumer goods. Although prior to 1994 the golf market was nearly nonexistent, by 1997, sales of titanium-metal woods in the United States were 1.72 million clubs. Titanium is used in the golf industry to produce an oversized golf club head that is reported to give a longer drive and improved accuracy over other materials (79).

Lightweight, corrosion resistant, and biocompatible titanium eyeglass frames were first introduced in the early 1980's. Today, millions of eyeglass frames are produced each year from titanium. However, since each frame weighs only 8 to 13 grams each, titanium consumption in this market is limited. Initially, commercially pure grades were used to produce frames. More recently, Ti-3Al-2.5V has become the predominant alloy for eyeglass frames because of its improved cold drawing. β alloys also are used for their good cold workability and because they reduce phase transformation problems (80).

Numerous other consumer goods are produced using titanium. These include camera cases, cooking utensils, gardening tools, scuba tanks, hockey sticks, jewelry, skis, loudspeakers, tennis rackets, and watches.

## Industrial and Marine

Most industrial application make use of titanium's excellent corrosion resistance. Titanium's first use for industrial applications was in sea-water-cooled electrical power generation facilities. Although titanium is a poor thermal conductor, its high strength-to-weight ratio allows for the use of thinner tubing with high-velocity flow rates. Because titanium forms an oxide film, it is nearly immune to attack by sea water at temperatures up to 315° C. At temperatures up to 80° C, titanium is very resistant to crevice corrosion, pitting, and stress corrosion. Consequently, maintenance and life cycle costs can be significantly lower than competing materials such as copper-nickel alloys. Most industrial applications use commercially pure grades of titanium. ASTM Grade 2 titanium is the most widely used type. Other common types include Grades 1, 7, 11, 12, 16, and 17 (81).

Titanium use in the oil and gas industry has grown in recent years and has the potential for significant growth in the coming years. Titanium is used on oil platforms and in riser systems used to transport oil from the sea bed to the platform. In addition, titanium is used in fire suppression and ballast water systems. The chemical process industry uses titanium in specific applications that include condensers, cooling-water systems, heat exchangers, and service water/fire suppression piping systems. Naval ships from Norway, Italy and the United States are incorporating titanium into seawater piping systems and heat exchangers (82).

Titanium has been used for its corrosion resistance as a roofing material for many years. Recently, the exterior of the Guggenheim Museum in Bilbao, Spain was clad in 343,000 square feet of titanium sheets. In Japan, about 10% of titanium consumption is used in construction (82).

## Medical

Titanium has been used in medical applications since the 1950's and is known to be the most biocompatible of all metals. Titanium is extremely resistant to the corrosive environment of the human body. Due to titanium's high dielectric constant, bone and living tissue will bond to titanium. The most common medical use is for hip replacements, and nearly half of all knee replacements are titanium (83).

Table IX.-End Uses of Titanium Alloys (79, 80, 81, 82, 83)

| End Use Sector | Typical Components | Predominant Alloys |
|---|---|---|
| Aerospace | Compressor case, blades, discs, rings for jet engines, wing flap tracks | Ti-6Al-4V |
| Armor | M2 Bradley Fighting Vehicle tank hatch, M1 Abrams Battle Tank turret blow off panels, VSEL towed Howitzer | Ti-6Al-4V |
| Automotive | Valves, valve springs, retainers, and connecting rods | Ti-6Al-4V<br>Ti-3Al-2.5V |
| Consumer Goods | Golf clubs heads, bicycle frames, eyeglass frames, cooking pans | Ti-3Al-2.5V |
| Industrial and Marine<br>  - Power generation<br>  - Nuclear power stations<br>  - Nuclear waste containment<br>  - Chemical processing<br>  - Desalinization<br>  - Chlor-alkali processing<br>  - Flue gas desulfuriztion<br>  - Oil and Gas<br>  - Ships<br>  - Construction | Cryogenic vessels, heat exchanges, condenser tubing, pickling baskets<br>Oil and gas production risers, piping, deep sea cable | Commercially pure CP Grades (1, 2, 7, 11, 12, 16, and 17)<br>Ti-6Al-4V |
| Medical | Prosthesis (hip, knee, shoulder, dental, etc.), heart valves, hearing aids, fixation devices (bone screws, plates, rods, hooks and nails, cables and staples), and surgical instruments (blades, dental drills, forceps, etc.) | CP Grades 5, 23<br>Ti-6Al-4V ELI,<br>Ti-5AL-2.5Fe<br>Ti-6Al-7Nb<br>Ti-13Nb-13Zr<br>Ti-15Mo-3Nb<br>Ti-12Mo-6Zr-2Fe |

**Cost**

Table X shows the approximate cost of raw materials in 1999. The cost of rutile alone, without processing, is \$0.45/lb of contained titanium. Chlorination of a titanium resource to produce $TiCl_4$ increases the raw material cost to \$1.40/lb. Because $TiCl_4$ is a precursor for all practical reduction processes, the cost of $TiCl_4$ is considered to be a fixed cost. The raw material cost of elemental titanium in a final product may vary moderately depending upon what reductant is used in a particular process and what losses are experienced. For the Kroll process, the raw material cost to produce the titanium in sponge is about \$2.24/lb of Ti (28). Even if the cost of labor and overhead

were eliminated, titanium produced by the chloride route would still cost more than copper, aluminum, magnesium or steel. In 1983, Poulsen and Hall estimated the cost for a fully integrated Kroll plant at $2.50/lb for raw materials and $5 to $7/lb when labor and overhead were added (30). In 1999, the price for sponge was approximately $4.25/lb. The Hunter process is similar. Most of the proposed improvements to the Kroll or Hunter processes still use $TiCl_4$ as feedstock. Therefore, as long as titanium is made by chlorinating rutile followed by some form of metallothermic reduction, the price for sponge will remain near its current level.

Table X.-Cost of Titanium and Contained Titanium at Several Stages of Production (28)

| Materials | Cost of material ($/lb) | Cost of contained titanium ($/lb) |
|---|---|---|
| Rutile ($TiO_2$) | 0.25 | 0.45 |
| Ilmenite ($FeTiO_3$) | 0.04 | 0.12 |
| Titaniferous slag (85% $TiO_2$) | 0.17 | 0.33 |
| $TiCl_4$ | 0.35 | 1.40 |
| Magnesium (including and losses) | 0.86 | -- |
| Titanium sponge (Kroll using rutile) | 2.24 | 2.24 |

Fabrication of titanium also is more expensive than steel or aluminum. A typical machined part for an aerospace application may contain only 10% to 50% of the original titanium. The fabrication cost to produce a component from sponge significantly increases the price of a finished part. For example, the published prices for plate and bar are currently about $7.50 and $16.50 per pound, respectively. Precision casting can reduce this cost considerably. Still because titanium is a reactive metal, it must be melted in an inert atmosphere and the crucible must made of something that will not react with molten titanium. PM is another approach that could reduce the cost of titanium parts considerably. If titanium powder could be made for a price similar to that of sponge, then PM could be used to reduce the cost of a titanium part by 50%.

**Conclusions**

The driving force behind the original development of titanium production in the 1930's and 1940's was military aerospace. Today, aerospace applications represent approximately 65% of the titanium market (20). Because of this reliance on the aerospace industry, titanium demand has been cyclic. It is possible to account for every major shift in mill product shipments by looking at the aerospace industry. For titanium to escape these cycles, the non-aerospace use of titanium must expand. To do this, titanium must economically compete with magnesium, aluminum, and stainless steel.
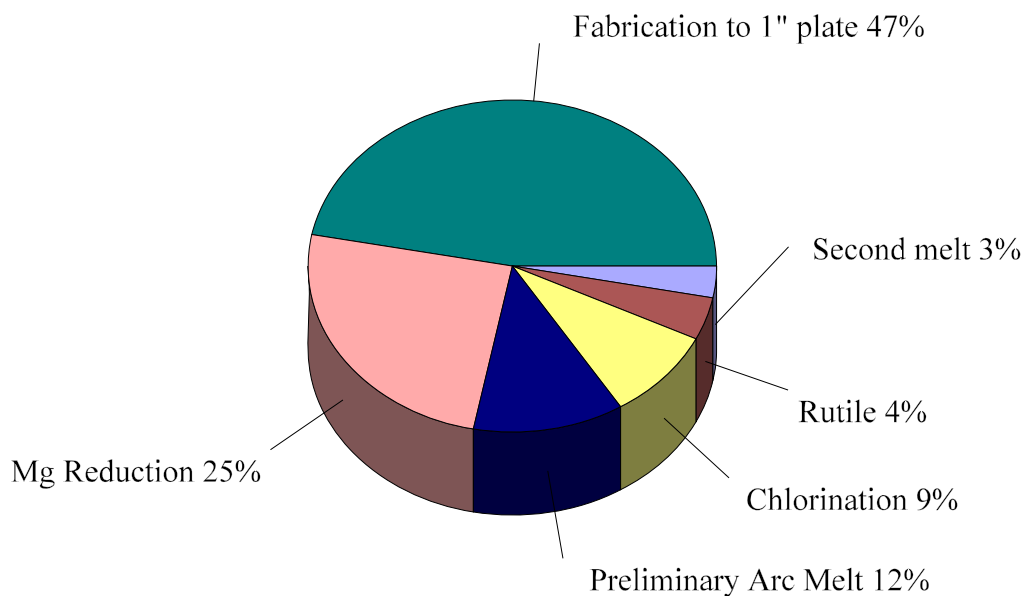
Figure 5: Percentage Breakdown of Costs to Produce Plate.

Recently, some progress on improving the Kroll process has been made through the introduction of vacuum distillation, increasing the batch size, and the use of more efficient magnesium cells (84). Still, the Kroll reduction step remains very similar to the process used by the USBM in 1948. The work by Okabe is one of the few recent studies of the Kroll process. However, more fundamental work might make some improvements in the process such as a means to reduce the portion of sponge that must be downgraded due to vessel contamination at the retort wall or nitride inclusion. Other possible improvements include technologies that will decrease the level of excess magnesium that is required or increase the proportion of sponge fines or the ability to produce higher purity titanium for the electronics industry.

Firoze E. Katrak of Charles River Associates has proposed a 1-10-100 rule to expand the demand for titanium. A $1.00 decrease in the cost of sponge coupled with a 10% reduction in the mill product value-added cost will result in a 100% gain in the volume of the non-aerospace market (85). Given the raw material costs of the Kroll process, it will be difficult, if not impossible, to significantly reduce the price of sponge by the Kroll process. At the same time, NNS technologies such as PM and precision casting may help to reduce the mill product value-added cost.

Although several processes have been put forward as replacements for the Kroll process, none have been successful. For the foreseeable future, the Kroll process will be the method of choice. However, it is apparent there is a need for the development of a new process. The development of

such a process will likely require a significant effort of the type made by the USBM in the 1940's and 1950's. Until a new process is developed, the Kroll process will be the most economical process to produce titanium in the sense that it makes metal at a price acceptable for a limited number of applications.

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