Kirk-Othmer Encyclopedia of Chemical Technology.

TITANIUM AND TITANIUM ALLOYS

1. Introduction

Titanium [7440-32-6], a metal element of Group IVB, has a melting point of 1675°C and an atomic weight of 47.90. Titanium metal has become known as a space-age metal because of its high strength-to-density ratio and inertness to many corrosive environments. Its principal use, however, is as TiO_2 as paint filler (see Paint; Pigments). The whiteness and high refractive index of TiO_2 are unequaled for whitening paints, paper, rubber, plastics, and other materials. A small amount of mineral-grade TiO_2 is used in fluxes and ceramics.

Titanium is the ninth most abundant element in the earth's crust, at approximately 0.62%, and the fourth most abundant structural element. Its elemental abundance is about five times less than iron and 100 times greater than copper, yet for structural applications titanium's annual use is ca 200 times less than copper and 10,000 times less than iron. Metal production began in 1948; its principal use was in military aircraft. Gradually the applications spread to commercial aircraft, the chemical industry, and, more recently, consumer goods.

Commercial production of titanium and titanium alloys in the United States has increased from zero to a peak of more than 27×10^6 kg/yr over the past 50 years (1–9).

The processing and behavior of titanium and its alloys and strongly dependent on the two allotropic forms of titanium (high temperature body-centered cubic, beta phase, and low temperature hexagonal close-packed, alpha phase), with alloying elements generally stabilizing either the alpha phase (Al, O_2, N_2, etc.) or the beta phase (Mo, V, Nb, Fe, H_2, etc.) (10–15).

The catalyst for the remarkable growth in titanium production was the development by Wihelm J. Kroll of a relatively safe, economical method to produce titanium metal in the late 1930s (3). By the late 1940s, the basic mechanical and physical properties, and alloying characteristics of titanium were defined as the commercial importance of the metal was apparent. The first titanium for actual flight was ordered from Remington Arms (later Rem-Cru, and still later, Crucible Steel) by Douglas Aircraft in 1949. Other early entrants to the titanium field included Mallory-Sharon (later RMI) and TMCA (later Timet). In the UK, ICI Metals (later IMI and more recently Timet Europe) began sponge production in 1948, with other involvement from continental Europe a few years later. Recognizing the military potential of titanium, the Soviets began sponge production in 1954. In Japan, sponge production was initiated by Osaka Titanium in 1952, generally to supply other countries.

The work-horse Ti–6Al–4V alloy was introduced in 1954 and the first beta titanium alloy (Ti–13V–11Cr–3Al) was developed by Rem-Cru in the 1950s. This high strength heat-treatable alloy was used extensively on the high speed surveillance aircraft, the SR71. Alloy development in the UK, driven by Rolls-Royce, was concentrated more on elevated temperature alloy for use in engines.

Airframe and engine use of titanium exhibited increasing, but cyclic, use with mill shipments in the U.S. tripling during the 1960s from 4.5×10^6 kg in 1960, with aerospace use accounting for 90% of the market in 1970. This increase resulted mainly from use in nonmilitary engines and the wide-body jets, the Boeing 747, the DC-10 and the L-1011.

Mill product shipments increased in the 1970s in large part due to increased production of the large commercial transports and their high bypass engines. New military airframes featured 20–35% of their structural weight produced from titanium products. Nonaerospace use, took advantage of the corrosion resistance of titanium. The U.S. industry set a new record in 1980–1981 of about 23×10^6 kg, but this figure then dropped because of hedge buying by the aerospace industry. This cyclic nature of the titanium industry will only smooth out if nonaerospace use increases. In Europe, and to a greater extent in Japan, industrial applications exceed 50% of the total use.

Titanium mill shipments in the United States increased steadily during the 1980s with the build up in military hardware, peaking in 1990 at a record 25×10^6 kg (55×10^6 pounds) (3). When “peace broke out”, titanium shipments fell precipitously soon thereafter to about 16×10^6 kg (35×10^6 lb) per year; a level which was suggested at the time to possibly be the true size of the of the titanium market. However, this has proved not to be true. This left a great over-capacity in the U.S.A. and right-sizing by the titanium industry occurred.

During the nineties, a steady growth of titanium shipments occurred in the U.S. (3–9) fueled by increased commercial aerospace orders (the Boeing 777 has almost 10% titanium in its airframe) and for sporting equipment, especially golf clubs. In late 1998, a slowing in commercial aerospace sales occurred in part due to the softening Asian economy. There have also been strategic realignments particularly in the United States. Allegheny Technologies has acquired Oremet-Wah Chang. Timet has acquired IMI Titanium, Cezus and Titanium Hearth Melting. Precision Castparts Corp. is attempting to acquire the forging house Wyman-Gordon. Other companies are also considering realignments.

Further expansion of the titanium market is now very critically dependent on reducing cost for a variety of applications. Addressing this need, lower cost alloys are being introduced into the marketplace which use Al–Fe master alloys to reduce cost rather than the Al–V master alloy needed for alloys such as Ti–6Al–4V. These include the Ti–6Al–1.7Fe–0.1Si (Timetal 62S) and Ti–4.5Fe–6.8Mo–1.5Al (Timetal LCB. low cost betal) alloys (6, 7). Attention is also being given to lower cost processes such as near net shape powder metallurgy (P/M) and permanent mold casting approaches (6–8).

The effect of low cost product from the former USSR, where the peak capacity is estimated to have been four times that of the United States (ie, as much as 90×10^6 kg [200×10^6 lb] of mill products per year) has not yet caused any major problems for U.S. production capacity, but this situation could change as VSMPO in Salda strive to increase exports, particularly to the United States. There is also capacity in China at about the 1.8×10^6 kg/yr of mill products level (mainly from Baoji, with a lesser amount at steel works #5 in Shanghai); by 2010 Chinese titanium mill product levels are expected to reach 5.4×10^6 kg/yr. Ore deposits in the subcontinent of India are extensive but as yet largely untapped.

In the past few years, the requirement to reduce harmful defects (such as Type I, hard, high interstitial [O_2 and N_2] defects), and the possibility of single melting parallel-sided billets which can be rolled directly (hence reducing cost) has resulted in increased present and planned hearth melting facilities using both electron beam and plasma heat sources (6, 7).

2. Occurrence

Titanium mineral occurs in nature as ilmenite, $FeTiO_3$; rutile, tetragonal TiO_2; anatase, tetragonal TiO_2; brookite, rhombic TiO_2; perovskite, $CaTiO_3$; sphene, $CaTiSiO_5$; and geikielite, $MgTiO_3$. Ilmenite is by far the most common, although rutile has been an important source of raw material. Although some deposits of anatase and perovskite are rich enough to be of commercial interest, the abundance and availability of high grade deposits of ilmenite and rutile have postponed the development of these minerals.

The principal titanium mineral, ilmenite, is found in either alluvial sands or hard-rock deposits. After concentrating, the titanium ore color is black. This is the black sand often found concentrated in bands along sandy beaches. The density of this concentrate is ca 4–5 g/cm^3. The concentrate is processed to either pigment-grade TiO_2 or metal. The titanium metal is won from the ore in a physical form called sponge, a name derived from its appearance. The sponge is consolidated to an ingot and further processed to mill products in a manner similar to steel. In metallic form, titanium has a dull silver luster and an appearance similar to stainless steel.

3. Properties

Titanium alloys may be divided into two principal categories: corrosion resistant and structural alloys (4, 11, 12, 15). The corrosion resistant alloys are generally based on a single phase (alpha) with dilute additions of solid solution strengthening and alpha stabilizing elements such as oxygen (interstitial), palladium, ruthenium, and aluminum (substitutional). These alloys are used in the chemical, energy, paper and food processing industries to produce highly corrosion resistant tubings, heat exchangers, valve housings, and containers. The single-phase alpha alloys provide excellent corrosion resistance, good weldability, and easy processing and fabrication, but a relatively low strength.

The beta phase is stabilized by additions such as molybdenum, vanadium, niobium, iron (substitutional), and hydrogen (interstitial). A dispersion of alpha in the beta matrix along with solid solutions strengthening of both the alpha and beta phases leads to higher strength alloys referred to as structural alloys. The structural alloys can be divided into four categories: the near alpha alloys, the alpha + beta alloys, the beta alloys and the titanium aluminide (ordered) intermetallics (based on Ti_xAl where $x = 1$ or 3). With titanium alloys used in structural applications, optimization of mechanical properties is very important, hence processing and microstructure control are critical.

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

3.1. Physical Properties

Titanium in its natural form is a dark gray color; however it is easily anodized to give a very attractive array of colors leading to use in jewelry and various other applications where appearance is important, including use in architecture. The metal and its alloys have a comparatively low density (approximately 60% of the density of steel: 4.508 g/cm^3 at 25°C). Titanium is nonmagnetic and has good heat-transfer characteristics. Its coefficient of thermal expansion is somewhat lower than that of steel, and less than half that of aluminum. The melting point of titanium (1675°C) and its alloys are higher than that of steel, but the maximum use temperature is much lower than would be anticipated based on this characteristic alone. The physical properties of titanium are given in Table 1.

3.2. Mechanical Properties

The mechanical properties of titanium alloys depend not only on the chemistry but are also strongly influenced by the microstructure particularly the distribution and morphology of the alpha phase within the beta matrix; the latter in turn being dependent on the processing. The tensile properties of selected cast and wrought terminal titanium alloys are summarized in Table 2 (14).

As strength increases, fracture toughness decreases, and vice versa. Chemistry, particularly the interstitial content (eg, O_2), influences fracture toughness with high values of K_{lc} associated with low O_2 values; and texture can also have an effect.

The fatigue behavior of titanium alloys can be divided into S-N fatigue (stress versus number of cycles of strain) and fatigue crack growth rate (FCGR or da/dn *v's* ΔK) (13, 14). Within S-N fatigue a further subdivision can be made between low cycle fatigue (LCF) and high cycle fatigue (HCF). For LCF, failure occurs

Table 1. Physical and Mechanical Properties of Elemental Titanium

Property	Value
atomic number	22
atomic weight	47.90
atomic volume, wt/density	10.6
covalent radius, nm	0.132
first ionization energy, MJ/kg-mol[a]	661.5
thermal neutron absorption cross-section, fm^2/atom	560
crystal structure	alpha: close-packed hexagonal ≤1156 K beta: body-centered cubic ≥1156 K
color	dark gray
density, kg/m^3	4510
melting point	1941 ± 285
solidus/liquids, K	1998
boiling point, K	3533
specific heat (at 298 K), J/kg·k[a]	0.518
thermal conductivity, W/(m·K)	21
heat of fusion, kJ/kg[a]	440
heat of vaporization, MJ/kg[a]	9.83
specific gravity	4.5
hardness, HRB	70 to 74
tensile strength, GPa[b]	241
modulus of elasticity, GPa[b]	102.7
Young's modulus of elasticity, GPa[b]	102.7
Poisson's ratio	0.41
coefficient of friction	0.8 at 40 m/min 0.68 at 300 m/min
specific resistance, Ω·m	0.554_{μ}
coefficient of thermal expansion	9.64×10^{-6} K
electrical conductivity	3% IACS (copper 100%)
electrical resistivity, Ω·m	0.478_{μ}
electronegativity, Pauling's	1.5
temperature coefficient of electrical resistance	0.0026/K
magnetic susceptibility	180×10^{-6}
machinability rating	30 (equivalent to 3/4 hard stainless steel)

[a] To convert J to cal, divide by 4.184.

[b] To convert GPa to psi, multiply by 145,000.

in 10^4 cycles or less; in HCF failure occurs at greater than 10^4 cycles. Different uses favor different techniques for determining LCF, specifically strain-controlled and load-controlled tests. Both notch concentration K_t and overall surface condition can strongly influence LCF, with a relatively gentle surface conditioning favoring high values. More severe working of the surface can result in the formation of cracks and degraded LCF behavior. Surface condition can also strongly influence HCF (13, 14).

The FCGR performance generally parallels fracture toughness with a lenticular alpha morphology favoring better behavior. Severe corrosive environments (such as 3.5% NaCl solution) can adversely affect the FCGR by an order of magntidue (13, 14).

Table 2. Compositions, Relative Densities, and Typical Room Temperature Tensile Properties of Selected Wrought Titanium Alloys

Common designations	Al	Sn	Zr	Mo	V	Si	Other	Relative density	Condition^a	0.2% proof stress, MPa	Tensile strength MPa	Elongation %
α-alloys												
CP Ti 99.5% IMI 115, Ti-35A							0	4.51	annealed 675°C	170	240	25
CP Ti 99.0% IMI 155, Ti-35A							0	4.51	annealed 675°C	480	550	15
IMI 260							0.2 Pd	4.51	annealed 675°C	315	425	25
IMI 317	5	2.5						4.46	annealed 900°C	800	860	15
IMI 230							2.5 Cu	4.56	St(α), duplex aged 400 and 475°C	630	790	24
Near-α alloys 8-1-1	8			1	1			4.37	annealed U^b 780°C	980	1060	15
IMI 679	2.25	11	5	1		0.25		4.82	ST (α+β) aged §500°C	990	1100	15
IMI 685	6		5	0.5		0.25		4.49	ST (β) aged 550°C	900	1020	12
6-2-4-2S	6	2	4	2		0.2		4.54	ST (α+β) annealed 590°C	960	1030	15
Ti-11	6	2	1.5	1		0.1	0.35 Bi	4.45	ST (β) aged 700°C	850	940	15
IMI 829	5.5	3.5	3	0.3		0.3	1 Nb	4.61	ST (β) aged 625°C	860	960	15
α/β alloys IMI 318, 6-4	6				4			4.46	annealed 700°C ST (α+β) aged 500°C	925 1100	990 1170	14 10
IMI 550	4	2		4		0.5		4.60	ST (α+β) aged 500°C	1000	1100	14
IMI 680	2.25	11		4		0.2		4.86	ST (α+β) aged 500°C	1190	1310	15
6-6-2	6	2		6			0.7 (Fe, Cu)	4.54	ST (α+β) aged 550°C	1170	1275	10
6-2-4-6	6	2	4	6				4.68	ST (α+β) annealed 590°C	1170	1270	10
IMI 551	4	4		4		0.5		4.62	ST (α+β) aged 500°C	1200	1310	13
Ti-8 Mn							8 Mn	4.72	annealed 700°C	860	945	15
β-alloys 13-11-3	3				13		11 Cr	4.87	ST (β) aged 480°C	1200	1280	8

Table 2. *Continued*

Common designations	Al	Sn	Zr	Mo	V	Si	Other	Relative density	Condition[a]	0.2% proof stress, MPa	Tensile strength MPa	Elongation %
Beta III		4.5	6	11.5				5.07	ST (β) duplex aged	1315	1390	10
8-8-2-3	3			8	8		2 Fe	4.85}	480 and 600°C	1240	1310	8
Transage 129	2	2	11		11			4.81	ST (β) aged 580°C	1280	1400	6
Beta C	3		4	4	8		6 Cr	4.82	ST (β) aged 540°C	1130	1225	10
10-2-3	3				10		2 Fe	4.65	ST (β) aged 580°C	1250	1320	8

[a] ST (α), ST ($\alpha+\beta$), ST (β) correspond to solution treatment in the α, $\alpha+\beta$, and β-phase fields respectively

[b] Annealing treatments normally involve shorter times than aging treatments.

The alpha and near-alpha alloys generally exhibited superior high temperature behavior with Si added for enhanced creep behavior (12).

Titanium alloys have good cryogenic properties, with the alpha alloy Ti–5Al–2.5Sn and the alpha-beta alloy Ti–6Al–4V seeing extensive use.

A number of beta alloys have been developed over the years which exhibit higher strength-toughness combinations than the alpha-beta alloys such as Ti–6Al–4V (13, 14).

3.3. Corrosion Behavior

Titanium's excellent resistance to most environments is the result of its strong affinity for oxygen and tendency to form a stable, tightly adherent, protective surface film (11). This film consists basically of TiO_2 at the metal-environment interface with underlying thin layers of Ti_2O_3 and TiO. It forms naturally and is maintained when the metal and its alloys are exposed to moisture or air. In general, anhydrous conditions such as provided by chorine or methanol as well as uninhibited reducing conditions, should be avoided. The passive film formed in air may not be adequately stable and may not be regenerated if it is damaged during exposure to these environments. Addition of the platinum group metals in general increases the corrosion resistance of titanium alloys even in the presence of chloride ions (Fig. 1).

Although there have been no known service failures related to hot salt stress-corrosion cracking (HSSCC), it is a potential limitation to the long duration exposure of highly stressed titanium alloys at temperatures above about 220°C.

The near immunity of relatively high strength titanium alloys to corrosion fatigue in chloride-containing solutions allows these materials to be used in many hostile environments (eg, body fluids) where other alloys have failed when subjected to cyclic stresses.

The tenacious passive film which forms naturally on titanium and its alloys provides excellent resistance to corrosion including situations in which mechanical impingement with sold particles occurs simultaneously (erosion). For turbine-blade applications where the components are impinged by high velocity water droplets, unalloyed titanium has been shown to have superior resistance compared to conventional blade alloys (eg, austenitic stainless steels and Monel).

It is known that the fatigue behavior of titanium and its alloy is surface condition sensitive; surface damage by fretting can adversely affect the ability of these materials to withstand cyclic stress. For example, fretting corrosion can reduce the fatigue strength, of a titanium alloy, such as Ti–6Al–4V by more than 50%.

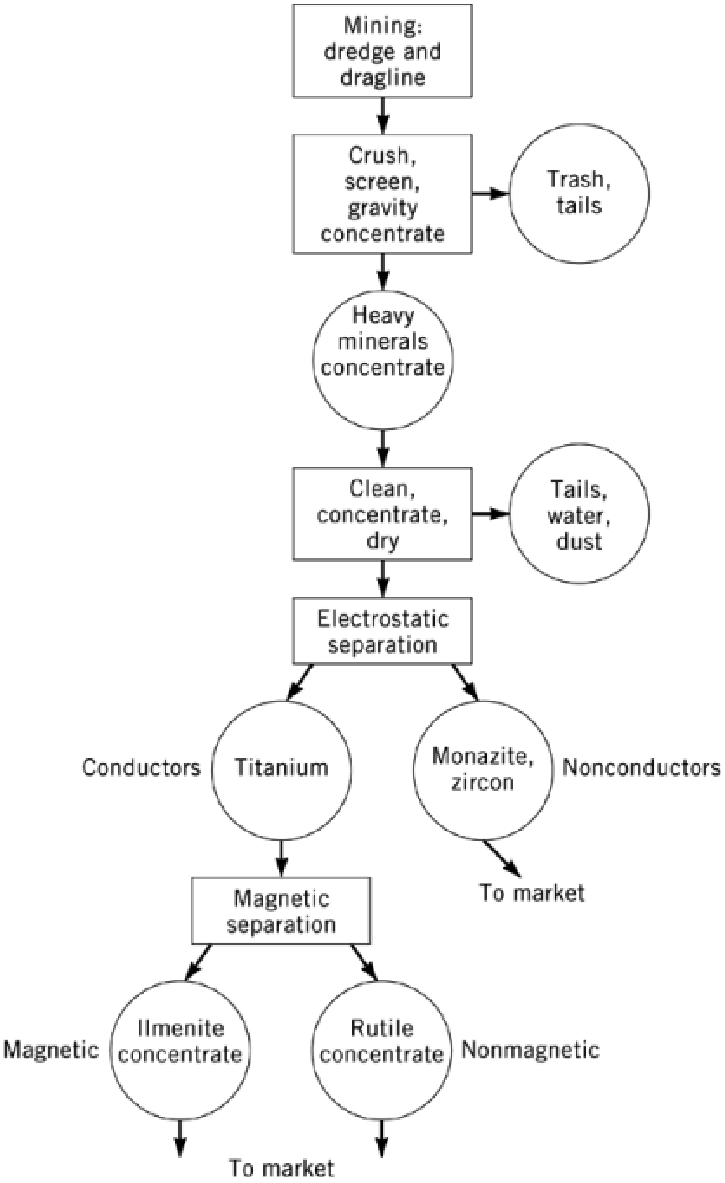

Fig. 1. General corrosion behavior of commercially pure titanium. Each metal or alloy can be used in those environments below its respective solid line.

4. Sources and Supplies

Titanium ore bodies are uniformly distributed throughout the continents of the world (Table 3). They occur either as hard-rock deposits, magnetic in origin, or as secondary placer deposits. Titanium processing from placer deposits is shown in Figure 2. The titanium oxide contained in known deposits of ilmenite is close to 1 billion metric tons, whereas only about 50 million metric tons of titanium oxide in rutile are known to exist. The

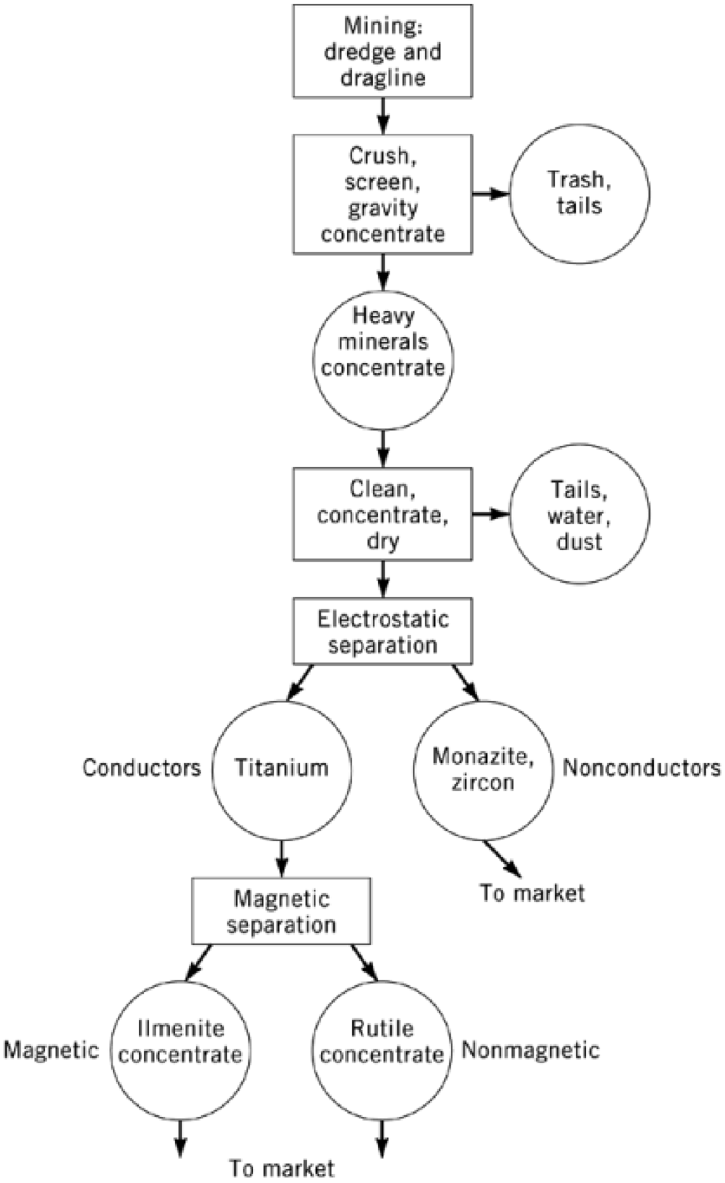

Fig. 2. Typical processes and products of a titanium beach-sand mining and beneficiating operation (17).

largest known reserves of titanium are in Canada and China. However, a significant amount of these reserves may be marginally economical.

Influencing availability is the 1998 contract between Boeing and Timet making the latter company the principal supplier to Boeing's commercial aircraft (18). Timet will supply Boeing with 2,900 tons of titanium products annually, about 70% of Boeing's needs. Timet also has a recent agreement to buy 10,000 t/yr of titanium sponge from Specialty Metals Company, Belgium; this sponge is produced by Ust-Kamenogorsk in Kazakhstan. In a separate long term agreement Toho will become Timet's principal supplier of high grade

Table 3. Ilmenite and Rutile Resources in the World's Major Deposits[a]

	Ilmenite[b], 10^6 t		Rutile[c], 10^6 t		
Country	Economically exploitable	Other[d]	Economically exploitable	Other[d]	% of world Ti resources
Australasia					
Australia	27	3	6.7	0.6	1.5
New Zealand		31			1.1
North America					
Canada	75	541	1.8		22.1
Mexico					0.0
United States	19	77	1.5	5.5	3.9
South America					
Brazil		24			0.9
Europe					
Finland	5				0.2
Italy			6.0	12.0	1.1
Norway	128				4.6
Romania		8		1.7	0.4
CIS	211	118			11.7
Africa					
Mozambique		30		2.0	1.2
South Africa	85	50	5.1	2.4	5.3
Sierra Leone			2.5	23.0	1.6
Tanzania	13				0.5
Madagascar					0.0
Asia					
Bangladesh					0.0
China	216	910	0.2		40.1
India	58	33	4.2	1.8	3.6
Malaysia		10			0.4
Sri Lanka	2		0.3		0.1
Total	*839*	*1,835*	*28.3*	*49.0*	*100.0*

[a] Ref. 6.

[b] Ilmenite includes equivalent titanomagnetite, leucoxene, and perovskite.

[c] Rutile does not include anatase from Brazil.

[d] Marginally economical, economically exploitable, and subeconomic.

sponge. RMI has correspondingly received three long-term contracts, ranging from two to five years, to supply titanium products to Boeing and Northrop-Grumman in the United States and Aerospatiale in France. The contracts add about 550 tons and U.S. $\$100 \times 10^6$ of business to RMI's order books (18).

The major Russian producer VSMPO is running at perhaps 20% of 1989 levels (when in excess of 92×10^6 kg of mill products were produced, much slated for the Alpha class of submarines: 9.2×10^6 kg. A recent development is an exchange of shares with sponge producer Avisma. Further south the Zaporozye titanium sponge works in the Ukraine is to be tendered for privatization. The plant's capacity is 13,000 t/yr with half the capital investment coming from the Swiss group Bearco, who have exclusive right to buy 65% of the production of a number of popular grades.

In 1998 United States sponge consumption rose to an estimated 32,600 tons. Ingot consumption was 45,000 tons and ingot production stood at an estimated 44,000 tons (18). Mill products amounted to 25,900 tons; imports of sponge for domestic consumption reached 13,200 tons. Russia and Kazakhstan accounted for greater than 90% of U.S. sponge imports, sparked by the U.S. government's action in revoking antidumping actions. In 1998 an estimated 65% of the titanium metal used was in aerospace applications with the remaining

Table 4. World Mine Production, Reserves, and Reserve Base; Titanium mineral Concentrates, $\times 10^3$ t[a]

Ore/Country	Mine production		Reserves	Reserve base
	1999	2000[b]		
Ilmenite				
United States	300[c]	300[c]	13,000	59,000
Australia	1,140	1,100	100,000[d]	140,000[d]
Canada[e]	760	760	31,000	36,000
India	204	205	30,000	38,000
Norway[e]	266	270	40,000	40,000
South Africa[e]	935	935	63,000	63,000
Ukraine	225	286	5,900	13,000
other countries	283	259	63,000	98,000
World total (rounded)	*4,100*	*4,000*	*350,000*	*480,000*
Rutile				
United States	[f]	[f]	700	1,800
Australia	181	226	19,000[d]	53,000[d]
India	15	15	6,600	7,700
South Africa	122	122	8,300	8,300
Ukraine	45	45	2,500	2,500
other countries	8	8	7,900	100,000
World total (rounded)	*370*[g]	*410*[g]	*45,000*	*170,000*
World total (ilmenite and rutile, rounded)	*4,500*	*4,500*	*390,000*	*660,000*

[a] Ref. 19.

[b] Estimated.

[c] Includes rutile to avoid revealing company proprietary data.

[d] Derived from data published by the Australian Bureau of Resource Sciences.

[e] Mine production is primarily used to produce titaniferous slag. Reserves and reserve base are limenite.

[f] Included with ilmenite to avoid revealing company proprietary data.

[g] Excludes the United States.

35% uses in the chemical process industry, power generation, ordnance, medical, and other non-aerospace applications. The value of sponge metal consumed was about U.S. $\$316 \times 10^6$ based upon an average selling price of U.S.$9.70/kg.

New scrap metal recycled by the titanium industry was about 31,400 tons in 1998 with the steel industry accounting for the major share (18). The U.S. superalloys industry accounted for an estimated 800 tons of titanium scrap use, with all other industrial sectors accounting for approximately 1,000 tons. Much of the scrap consumed recently in the U.S. has been imported, with the largest suppliers the UK, Japan, Russia, Italy and France. Smaller amounts of scrap originated in Germany and Canada. Old scrap reclaimed was about 300 tons.

In April 1999, the U.S. Defense Logistics Agency (DLA) offered its final negotiated bid solicitation for titanium sponge before converting to a sealed-bid format beginning in May, when 4,540 tons were offered to the market. If all the sponge on offer is not sold, subsequent offerings are scheduled on the second Tuesday of each month. Going to a sealed-bid format should speed the solicitation process for titanium. DLA is authorized to sell 4,500 tons of sponge in 1999 and in each year through 2005. A summary of titanium reserves are given in Table 4 (19).

5. Manufacturing

The commercial production of titanium metal involves the chlorination of rutile (TiO_2) in the presence of coke or other form of carbon (11). The most important chemical reaction involved is the resulting $TiCl_4$ ("tickle") is purified by distillation and chemical treatments and subsequently reduced to titanium sponge using either the Kroll process (mg) or Hunter process (Na).

5.1. Ore-Concentrate Refining

The TiO_2 content of ore concentrates determines further processing steps. High grade ore such as rutile, synthetic rutile, or slag from Richard's Bay is refined to pigment-grade TiO_2 via chlorination. Lower grade ore is processed via the sulfate route. The chlorination process, commercialized by Du Pont in the early 1960s, which produces a better quality pigment, requires less processing energy than the sulfate process (1800 kWh/t compared to 2500 kWh/t), and has less waste discharge (20–22). The sulfate process produces approximately six tons of waste per ton of TiO_2, whereas only one ton of waste is produced through the chloride process (23). However, high grade ore is required for the latter process, ie, TiO_2 content $>70\%$, with $<1\%$ MgO and 0.2% CaO, because ores that have high MgO and CaO can clog the chlorinator. Environmental problems have forced the industry either to shut down sulfate plants or to install expensive pollution-control equipment. Because of the shortage of high grade TiO_2 reserves, the pigment industry must adapt the ore to the chloride process. The trend has been towards ore beneficiation. Ore containing 50–60% TiO_2 content is beneficiated by partial reduction, then leached with sulfuric or hydrochloric acid to yield a concentrate containing $>90\%$ TiO_2, the so-called synthetic rutile (20, 24).

5.2. Sulfate Process

In the sulfate process (Fig. 3), ilmenite ore is treated with sulfuric acid at 150–180°C:

$$5\ H_2O + FeTiO_3 + 2\ H_2SO_4 \longrightarrow FeSO_4{\cdot}7H_2O + TiOSO_4$$

The undissolved solids are removed and the liquid is evaporated under vacuum and cooled. The precipitated $FeSO_4{\cdot}7H_2O$ is filtered and the filtrate concentrated to ca 230 g/L. Heating to 90°C hydrolyzes titanyl sulfate to insoluble titanyl hydroxide.

$$TiOSO_4 + 2\ H_2O \longrightarrow TiO\,(OH)_2 \downarrow + H_2SO_4$$

To ensure the rutile crystal form, seed crystals are added, otherwise anatase is obtained. The precipitate is thoroughly washed using water and sulfuric acid to remove all traces of discoloring elements, eg, iron, chromium, vanadium, and manganese. The $TiO(OH)_2$ is finally calcined at 1000°C to TiO_2 (21).

5.3. Chloride Process

In the chloride process (Fig. 4), a high grade titanium oxide ore is chlorinated in a fluidized-bed reactor in the presence of coke at 925–1010°C:

$$TiO_2 + 2\ C + 2\ Cl_2 \longrightarrow 2\ CO + TiCl_4 \qquad \Delta G_{1300^\circ C} = -125\ \text{kJ}\ (30\ \text{kcal})$$

The volatile chlorides are collected and the unreacted solids and nonvolatile chlorides are discarded. Titanium tetrachloride is separated from the other chlorides by double distillation (25). Vanadium oxychloride, $VOCl_3$,

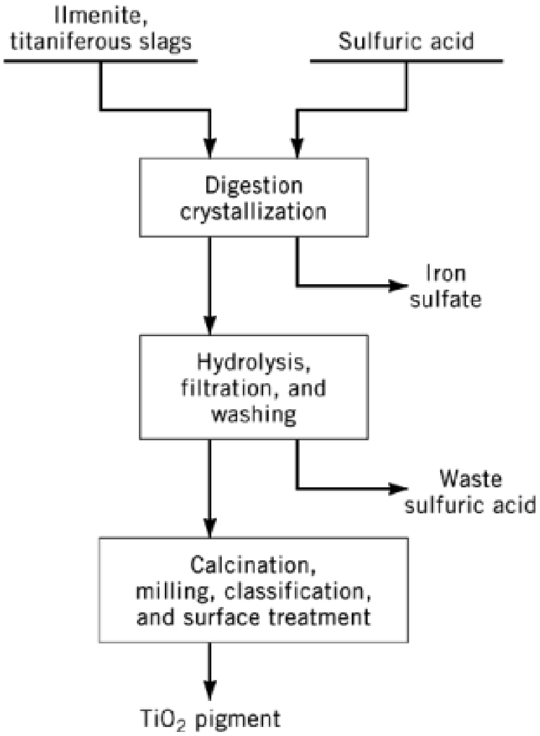

Fig. 3. The sulfate process (20).

which has a boiling point close to $TiCl_4$, is separated by complexing with mineral oil, reducing with H_2S to $VOCl_2$, or complexing with copper. The $TiCl_4$ is finally oxidized at 985°C to TiO_2 and the chlorine gas is recycled (21, 24) (see also Titanium compounds; Pigments, inorganic).

5.4. Tetrachloride-Reduction Process

Titanium tetrachloride for metal production must be of very high purity. The required purity of technical-grade $TiCl_4$ for pigment production is compared with that for metal production in Table 5. Titanium tetrachloride for metal production is prepared by the same process as described above, except that a greater effort is made to remove impurities, especially oxygen- and carbon-containing compounds.

5.5. Magnesium-Reduction (Kroll) Process

In the 1990s, nearly all sponge is produced by the magnesium reduction process (Fig. 5).

$$TiCl_4\,(g) + 2\,Mg\,(l) \longrightarrow Ti\,(s) + 2\,MgCl_2\,(l) \qquad \Delta G_{900^\circ C} = -301\ \text{kJ}\ (-72\ \text{kcal})$$

TiCl4 (g) is metered into a carbon-steel or 304 stainless-steel reaction vessel that contains liquid magnesium. An excess of 25% magnesium over the stoichiometric amount ensures that the lower chlorides of titanium ($TiCl_2$ and $TiCl_3$) are reduced to metal. The highly exothermic reaction ($\Delta H_{900^\circ C} = -420$ kJ/mol(– 100 kcal/mol)) is controlled by the feed rate of $TiCl_4$ at ca 900°C. The reaction atmosphere is helium or argon. Molten magnesium chloride is tapped from the reactor bottom and recycled using conventional magnesium-reduction

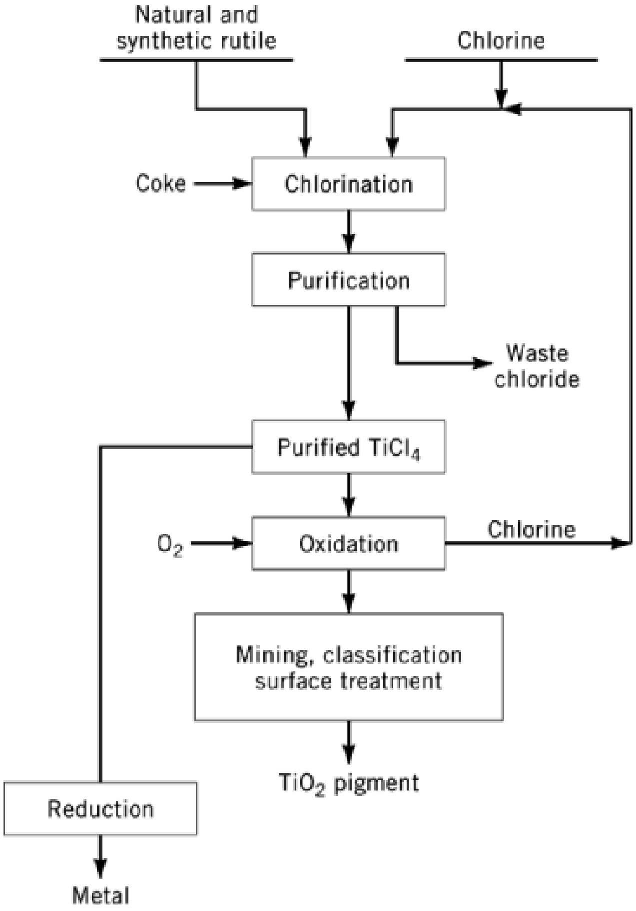

Fig. 4. The chloride process.

methods, including L. G. Farben, Alcan, and USSR VAMI cells. The production is in batches up to 10 metric tons of titanium. The product, the so-called sponge (Fig. 6), is further processed to remove the unreacted titanium chlorides, magnesium, and residual magnesium chlorides. These impurities, which can be as much as 30 wt %, are removed by either acid leaching in dilute nitric and hydrochloric acids at low energy requirement of ca 0.3 kWh/kg of sponge but effluent production of 8 L/kg of sponge; vacuum distillation at 960–1020°C for as much as 60 h; or the argon sweep at 1000°C used by the Oregon Metallurgical Plant. After purification, the sponge is crushed, screened, dried, and placed in air-tight, 23-kg drums to await consolidation. The energy required to convert $TiCl_4$ to sponge, which is ready for further processing by the leaching routes, is ca 37 kWh/kg of sponge (22), of which ca 97% is required for magnesium production. The Japanese have claimed an energy consumption of approaching 15 kWh/kg of sponge using vacuum disillation instead of acid leaching for purification (26). In 1992, Timet installed in Henderson, Nevada, a new facility adjacent to their original acid leach facility, which utilized Japanese vacuum distillation technology from Toho Titanium.

Table 5. Chemical Composition of Titanium Tetrachloride Grades[a], Wt %

Impurity	Technical[b]	Purified[c]
$VOCl_3$	0.33	0.0034
$AlCl_3$	0.02	0.05
$SiCl_4$	0.4	0.006
Si_2OCl_6	0.04	0.003
$FeCl_3$	0.012	0.0029
CCl_3COCl	0.005	0.0002
CS_2	0.01	0.00002
COS	0.009	0.00002
$Si_3O_2Cl_8$	0.007	0.002
$COCl_2$	0.5	0.00002
other[d]	0.175	0.001

[a] Refs. 17 and 24.
[b] Pigment grade.
[c] Sponge grade.
[d] Includes oxychlorides, CO_2, Cl_2, CCl_4, and C_6Cl_6.

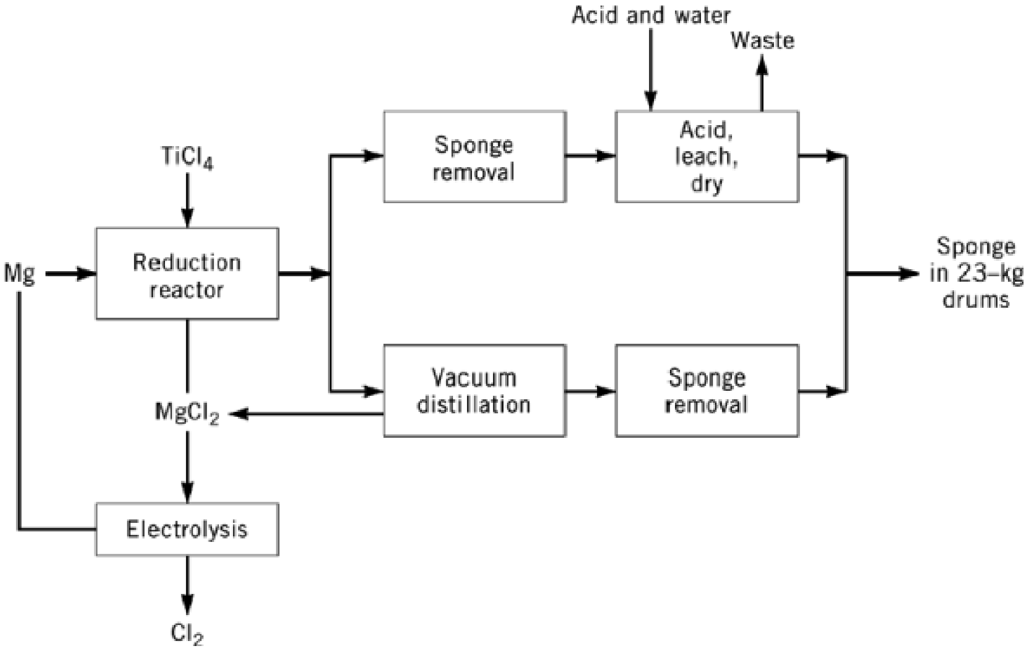

Fig. 5. Flow diagram for titanium sponge production.

5.6. Sodium-Reduction Process

The sodium-reduction process was employed in Japan, United States, and England for several years as an alternative to magnesium reduction. The last large production plant was closed in the early 1990s. Although the process was more costly than magnesium reduction, the product contained less metallic impurities, ie, Fe, Cr, and Ni. This product is desirable for a growing titanium market in the electronics industry. As a result, a small plant having a yearly capacity of 340 metric tons was opened in 1996 by Johnson-Matthey in Salt Lake City.

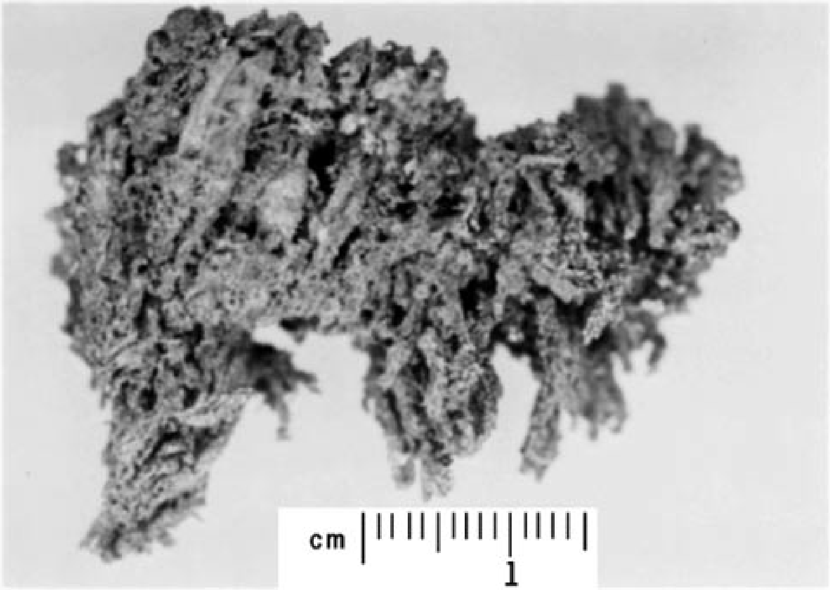

Fig. 6. Vacuum-distilled titanium sponge produced by magnesium reduction at Teledyne Wah Chang (Albany, Oregon).

Comparison of purity of sponge produced by magnesium reduction and acid leach, magnesium reduction and vacuum distillation, and sodium reduction is given in Table 6. Hardness, indicating the degree of purity, is affected both by the interstitial impurities, ie, oxygen, nitrogen, and carbon, and by the noninterstitial impurity, ie, iron. Hardness numbers range from 80 to 150 HB units; typical commercial sponge is characterized by 110–120 HB units. Some developmental processes, eg, electrolysis reduction, produce sponge having 60–90 HB units. Iron impurities in Kroll sponge are difficult to control because of diffusion into the sponge from the reactor wall. In the sodium-reduction process, the sponge is protected from the wall by sodium chloride. The other impurities originate from tetrachloride, residual gases in the reactor, helium or argon impurities, and magnesium or sodium residues.

5.7. Other Reduction Processes

A number of alternating processes have been evaluated for sponge production, including electrolytic, molten salt and plasma processes and while but none of these have yet reached commercial status (11, 27) a promising "reverse electrolytic" approach is at the pilot plant stage (28).

5.8. Sponge Consolidation

The next step is the consolidation of the sponge into ingot. The crushed sponge is blended with alloying elements or other sponge. Consumable electrodes are produced by welding 45–90-kg sponge compactions (electrode compacts) in an inert atmosphere, and then double-vacuum-arc-remelted (VAR). A portion of the elemental sponge compacts are often replaced with bulk scrap. The ingots are ca 71–91-cm dia and long enough to weigh 4.5 to 9.0 t. The double melt, included in aerospace specifications, is required for thorough mixing of alloying elements, scrap, and titanium sponge, and for improving yields because vaporization of volatiles during the first melt leaves a rough, porous surface. The double melt removes residual volatiles such as Mg, $MgCl_2$, Cl_2, and H_2. Triple melts are specified for critical applications such as rotating components in gas turbine engines.

Table 6. Comparison of ASTM Specifications for Titanium Sponge[a], Wt % on a Dry Basis

Property	ASTM B299 69			Electrolytic
	MD 120 type A[b]	ML 120 type B[c]	SL 120 type C[d]	
nitrogen, max	0.015	0.015	0.010	0.003
carbon, max	0.020	0.025	0.020	0.011
sodium, total max			0.190	
magnesium, max	0.08	0.50		
chlorine, max	0.12	0.20	0.20	0.035
iron, max	0.12	0.10	0.05	0.02
silicon, max	0.04	0.04	0.04	
hydrogen, max	0.005	0.03	0.05	0.005
oxygen, max	0.10	0.10	0.10	0.065
all other impurities	0.05	0.05	0.05	
titanium balance, nominal	99.3	99.1	99.3	
Brinell hardness (HB), max	120	120	120	60–90

[a] Refs. 29 and 30.
[b] Type A magnesium reduced and finished by vacuum distillation.
[c] Type B magnesium reduced and finished by acid leaching on inert gas sweep distillation.
[d] Type C sodium reduced and finished by acid leaching.

The third melt allows more time to dissolve high melting point inclusions that infrequently occur. This is often referred to as rotating quality titanium.

A two-station VAR furnace for double melting has an annual production capacity of ca 1400–3000 t, depending on product mix, ie, alloy and number of remelts. The energy requirement is ca 1.1 kWh/kg per single melt. Plasma-hearth melting and electron-beam-hearth melting have been employed more recently for both consolidation and final melting. The hearth processes are well suited for utilizing scrap in various shapes and forms and for avoiding the costly electrode fabrication inherent in consumable vacuum arc melting. In addition, these processes can produce cast metal into shapes such as slabs. For many industrial applications, a single hearth melt is acceptable. The hearth process can be designed to trap high density inclusions such as carbide tool bits and oxynitride-rich (Type I) inclusions in the hearth skull.

6. Alloys

Titanium alloy systems have been extensively studied. A single company evaluated over 3000 compositions in eight years (Rem-Cru sponsored work at Battelle Memorial Institute). Alloy development has been aimed at elevated-temperature aerospace applications, strength for structural applications, biocompatibility, and corrosion resistance. Original effort were in aerospace applications to replace nickel- and cobalt-base alloys in the 250–600°C range. The useful strength and environmental-resistance temperature limit is ca 600°C.

In pure titanium, the crystal structure is close-packed hexagonal (α) up to 882°C and body-centered cubic (β) to the melting point. The addition of alloying elements alters the α–β transformation temperature. Elements that raise the transformation temperature are called α-stabilizers; those that depress the transformation temperature, β-stabilizers; the latter are divided into β-isomorphous and β-eutectoid types. The β-isomorphous elements have limited α-solubility and increasing additions of these elements progressively depresses the transformation temperature. The β-eutectoid elements have restricted β-solubility and form intermetallic compounds by eutectoid decomposition of the β-phase. The binary phase diagram illustrating these three types of alloy systems is shown in Figure 7.

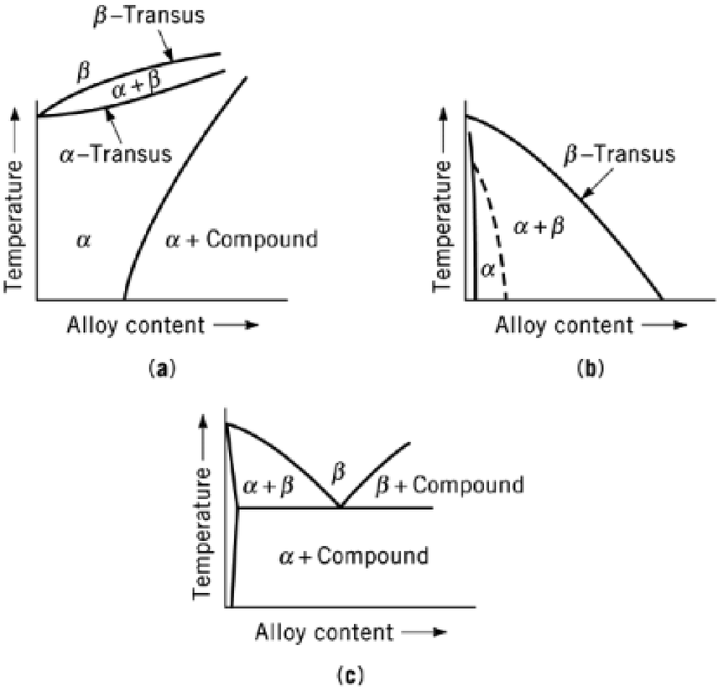

Fig. 7. Effect of alloying elements on the phase diagram of titanium: (**a**) α-stabilized system, (**b**) β-isomorphous system, and (**c**) β-eutectoid system.

The important α-stabilizing alloying elements include aluminum, tin, zirconium, and the interstitial alloying elements, ie, elements that do not occupy lattice positions, oxygen, nitrogen, and carbon. Small quantities of interstitial alloying elements, generally considered to be impurities, are always present, and have a great effect on strength. In sufficient amounts they can embrittle the titanium at room temperature (31). Oxygen is often used as an alloying element, ranging from as low as 500 ppm to as high as 3000 ppm, whereas carbon and nitrogen are maintained at their residual level. Oxygen additions increase strength and serve to identify several commercially pure grades. This strengthening effect diminishes at elevated temperatures. For cryogenic service, low oxygen content (<1300 ppm) is specified because high concentrations of interstitial impurities increase sensitivity to cracking, cold brittleness, and reduce fracture toughness. Alloys having low interstitial content are identified as extra-low interstitial (ELI) after the alloy name. In this context nitrogen has the greatest effect and commercial alloys specify its limit to be less than 0.05 wt %. It may also be present concentrated as high melting point nitride inclusions (TiN), referred to as Type I defects, which are detrimental to critical aerospace structural applications as discussed above. Carbon does not affect strength at concentration above 0.25 wt % because carbides (TiC) are formed. Carbon content is usually specified at 0.08 wt % max (31). The relative effect of these elements on specific room temperature strength is expressed in terms of an oxygen equivalency, O_e (32):

$$\%O_e = \%O + 2\,(\%N) + 0.67\,(\%C)$$

The most important α-stabilizing alloying element is aluminum, which is inexpensive and has an atomic weight less than that of titanium. Hence, aluminum additions slightly lower the density. The mechanical strength of titanium can be increased considerably by aluminum additions. Even though the solubility range

Table 7. β -Eutectoid Elements in Order of Increasing Tendency to Form Compounds[a]

Element	Eutectoid composition, wt %	Eutectoid temperature, °C	Composition for β-retention on quenching, wt %
manganese	20	550	6.5
iron	15	600	4.0
chromium	15	675	8.0
cobalt	9	685	7.0
nickel	7	770	8.0
copper	7	790	13.0
silicon	0.9	860	

[a] Ref. 34.

of aluminum extends to 27 wt %, above 7.5 wt % the alloy becomes too difficult to fabricate and is embrittled. The embrittlement is caused by a coherently ordered phase based on Ti_3Al [12635-69-7]. Other α-stabilizing elements also cause phase ordering. An empirical relationship (33) that describes the compositional ranges where ordering does not occur is

$$\left[\text{wt \% Al}\right] + \left[\text{wt \% Sn}\right]/3 + \left[\text{wt \% ZR}\right]/6 + 10\left[\text{wt \% O}\right] = / <9$$

The important β-stabilizing alloying elements are the bcc elements vanadium, molybdenum, tantalum, and niobium of the β-isomorphous type and manganese, iron, chromium, cobalt, nickel, copper, and silicon of the β-eutectoid type. The β-eutectoid elements, arranged in order of increasing tendency to form compounds, are shown in Table 7. The elements copper, silicon, nickel, and cobalt are termed active eutectoid formers because of a rapid decomposition of β to α and a compound. The other elements in Table 7 are sluggish in their eutectoid reactions and thus it is possible to avoid compound formation by careful control of heat treatment and composition. The relative β-stabilizing effects of these elements can be expressed in the form of a molybdenum equivalency, Mo_e (10):

$$\begin{gathered}\%\ Mo_e = \left[\%\ Mo\right] + \left[\%\ Nb\right]/3.6 + \left[\%\ Ta\right]/5 + \left[\%\ W\right]/2.5 + \left[\%\ V\right]/1.5 \\ +1.25\left[\%\ Cr\right] + 1.25\left[\%\ Ni\right] + 1.7\left[\%\ Mn\right] + 1.7\left[\%\ Co\right] + 2.5\left[\%\ Fe\right]\end{gathered}$$

Alloys of the β-type respond to heat treatment, are characterized by higher density than pure titanium, and are more easily fabricated. The purpose of alloying to promote the β-phase is either to form an all-β-phase alloy having commercially useful qualities, to form alloys that have duplex α- and β-structure to enhance heat-treatment response, ie, changing the α and β volume ratio, or to use β-eutectoid elements for intermetallic hardening. The most important commercial β-alloying element is vanadium.

7. Processing

7.1. Ingot

The titanium for ingot production may be either titanium sponge or reclaimed scrap. In either case, stringent specifications must be met for control of ingot composition. Modern melting techniques remove volatile substances from sponge, so that ingot of high quality can be produced regardless of which method is used for the sponge production. However for critical aerospace use, especially in engines, melting must be carried out to eliminate virtually all of the various types of defects. This has led to development of melting techniques in which the time–temperature for which the metal is molten is increased (eg, electron beam and plasma hearth techniques) compared to conventional vacuum-arc consumable-electrode methods (6, 7).

Recycling of titanium scrap (revert) is an important facet of cost-effective production of titanium product. The revert which is recycled includes cut sheet, reject castings, machine turning and chips.

7.2. Castings

Castings are an attractive approach to the fabrication of titanium components since this technique allows production of relatively low cost parts (12). Basically a near-net shape is produced by allowing molten titanium to solidify in a graphite, ceramic, or metal mold. Use of a ceramic mold, generally produced by the lost-wax process, allows production of large, relatively high integrity, complex shapes. The metal mold process is capable of less complex and smaller parts, but cost can be only 50% of the ceramic- mold process. Enhanced mechanical properties in combination with increased size and shape-making capabilities, have resulted in greatly increased use of titanium castings in both engine and airframe applications. The shipment of titanium castings has increased by a factor of three over the past fifteen years to a level of about 400×10^3 kg/yr.

7.3. Powder Metallurgy

A Number of powder metallurgy (P/M) approaches have been evaluated for the titanium system including the blended elemental (BE) and pre alloyed (PA) techniques (11, 35, 36).

Using a press-and-sinter technique the BE approach allows fabrication of low cost components from elemental and/or master alloy additions. However, because of the porosity resulting from this method, a result of the inherent salt from the Kroll or Hunter processes, generally initiation related properties such as S-N fatigue are inferior to cast and wrought product.

The PA approach yields mechanical properties at least equivalent to those of ingot product. However, a marginal cost advantage in combination with a fear of the P/M approach by design engineers (a result of concerns with contaminants in superalloy powder parts) has resulted in few applications.

Recently, two new titanium P/M approaches have received attention: powder injection molding (PIM) by which small (up to about 0.5 kg) complex parts can be produced in a cost-effective fashion (32), and laser fabrication techniques in which a powder is melted in the laser and allowed to solidify to build up a near-net shape structure (Fig. 8) (38).

7.4. Joining

Adhesive bonding, brazing, mechanical fastening and diffusion bonding are all used routinely and successfully to join titanium and its alloys (11, 12). Welding of various types, including tungsten inert gas (TIG), electron beam and plasma is also used very successfully with titanium and its alloys. In all types of welds, contamination by interstitial impurities such as oxygen and nitrogen must be minimized to maintain useful ductility in the weldment. Thus, welding must be done under strict environmental controls to avoid pickup of interstitials that can embrittle the weld metal.

7.5. Wrought Products

This section addresses the primary processing of wrought (ingot) product to mill products. The following section will then be concerned with forming of these mill products to final components. Mill products include billet, bar plate, sheet, strip, foil, extrusions, tubing and wire. Besides the reduction of section size, and shaping, the

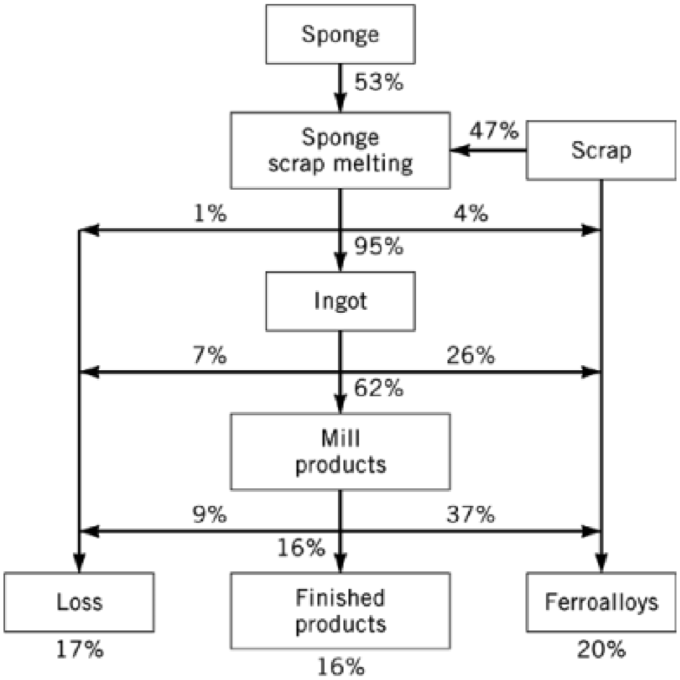

Fig. 8. Typical Lasformed^{SM} and machined parts.

other objective of primary processing is control (generally refinement) of the microstructure to optimize final mechanical property combinations. In many cases titanium is processed on the same equipment used for steel, with appropriate special auxiliary equipment.

Billet product from an ingot starts above the beta transus temperature. This temperature is that above which only the elevated temperature allotriomorphic form of titanium, the body centered cubic beta phase, exists. It then proceeds at progressively decreasing temperatures. In some cases the beta grain size is reduced by a recrystallization treatment well above the beta transus temperature, however elimination of grain boundary alpha and refinement of the transgranular alpha necessitate working below the beta transus temperature.

Bar, plate, sheet and foil products are produced on a relatively routine basis. Generally the processing is done hot, although the very high ductility of the metastable beta allows finishing of strip and foil by cold rolling.

Forging is a very common method for producing titanium alloy components. It allows both control of the shape and manipulation of the microstructure and hence mechanical properties. Generally titanium alloys are considerably more difficult to forge than aluminum alloys and alloy steels, particularly when processing at temperatures below the beta transus is desirable.

Extrusions, tubing and wire titanium products are also produced routinely with the same caveats regarding microstructural control as for the product forms discussed above.

Wrought products (mill products) are fabricated to desired configurations with the same concerns regarding microstructural control as discussed in the previous section. Examples of forming of wrought product include isothermal/hot forging, sheet metal forming, foil production, rod and wire and superplastic forming/diffusion bonding.

Isothermal and hot forging are special forging operations in which the die temperatures are close to the metal temperature, ie, much higher than in conventional forging. This reduces chill effects and allows close to net shape production. Strain rates are much lower than normal, contributing to the near-net shape capability. The metastable beta alloys, with a low beta transus temperature, are particularly amenable to the isothermal forging process.

Sheet metal forming is conducted either hot, which generally allows larger, more precise amounts of deformation, or cold, which is lower cost. Hot forming of titanium alloys is conducted in the range 595–815°C with increased formability and reduced spring back. Formability increases with increasing temperature but at the higher temperatures contamination can become a problem; sometimes necessitating an inert atmosphere or a coating. Beta alloys are easier to cold form than alpha and alpha–beta alloys. The high degree of spring back exhibited by titanium alloys sometimes requires hot sizing after cold forming. This reduces internal stresses and restores compressive yield strength.

Superplastic forming/diffusion bonding makes use of the fact that fine grained material can deform extremely large amounts, especially at very low strain rates (0.0001 to 0.01 s). Superplastic forming (SPF) is the propensity of sheet material to sustain very large amounts of deformation without unstable deformation (tensile necking); for example fine grained ($<10\ \mu$m) Ti–6Al–4V can be deformed $>1000\%$ in tension at 927°C. Diffusion bonding (DB) is a solid state bonding process in which a combination of pressure and temperature allow production of a metallurgically sound bond. Superplastic forming is now used routinely as a commercial sheet metal fabrication process for reduced cost, and complex shapes; generally using gas pressure. The combined SPF/DB process has seen less use than initially anticipated, predominantly because of problems in inspecting the integrity of the bond region.

7.6. Machining

Most titanium parts are still produced by conventional means involving extensive machining and well-defined procedures for various types of machining operations include turning, end milling, drilling, reaming, tapping, sawing, and grinding. In many instances considerable amounts of machining are required for the production of complex components from mill products such as forgings, plate and bar, ie, a high buy-to-fly-ratio. The machining of unalloyed titanium is similar to 1/4–1/2 hard austenitic stainless steel. High quality sharp tools, carbides for high productivity and high speed tool steels for more difficult operations, are required for titanium. This in combination with slow speeds, heavy feeds and the correct cutting fluids generally results in good machining behavior for titanium. Cutting fluids recommended are oil-water emulsions and water soluble waxes at high cutting speeds, low viscosity sulphurized oils and chlorinated oils at low speeds; in all cases the cutting fluids should be removed after machining, especially before heat treatment, to avoid potential stress-corrosion cracking problems.

8. Economic Aspects

Titanium raw-material utilization can be broken down as illustrated in Fig. 9. About 4% of the titanium mined is used as metal, 94% is used as pigment-grade TiO_2 and 2% as ore-grade rutile for fluxes and ceramics. In 1995, the estimated U.S. TiO_2 pigment production was valued at $\$2.6 \times 10^9$ and was produced by five companies at 11 plants in nine states. About 47% was used in paint, 18% in plastics, 24% in paper, and 18% in other miscellaneous applications (16, 39).

In 1995, titanium sponge was produced in two plants in the United States. The value of the domestic and imported sponge was about $\$180 \times 10^6$, assuming a selling price of \$1.80 kg (\$4/lb). Ingot was produced by the two sponge producers and nine other firms in seven states. About 30 companies produce mill products, forgings, and castings. The mill products manufactured in the U.S. had a value of about $\$400 \times 10^6$, assuming an average selling price of 4.10 kg/lb (\$9/lb). Approximately 65% was consumed in aerospace applications; the remainder was used in chemical process industry, power generation, marine, ordinance, and consumer applications.

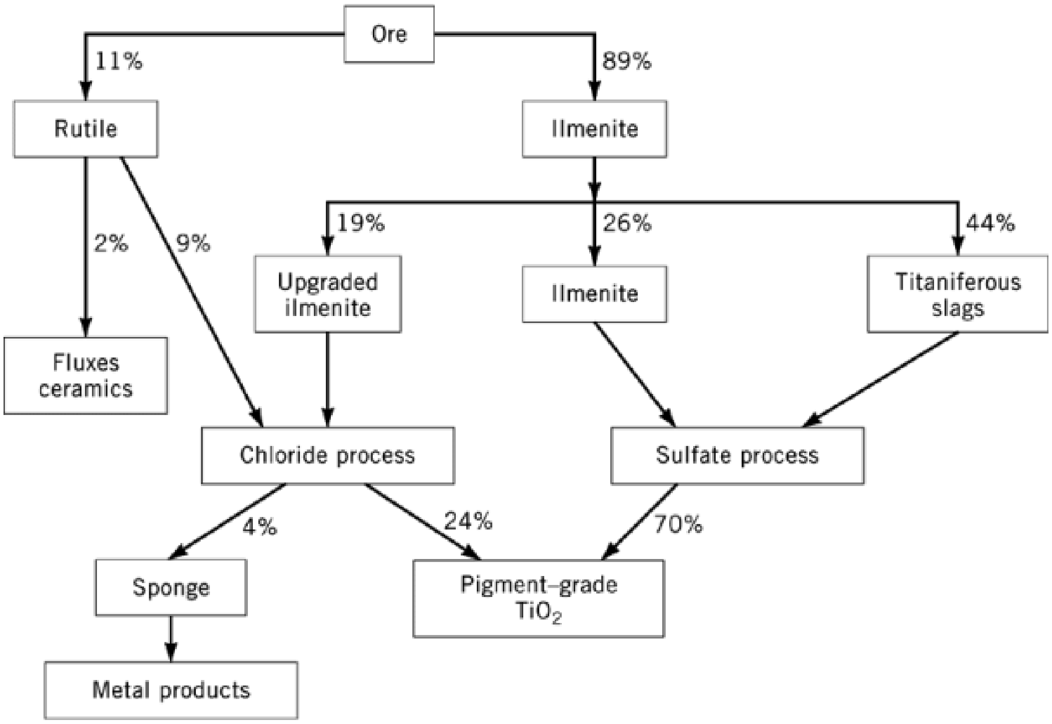

Fig. 9. U.S. titanium raw material utilization (3, 6).

The principal world producers of pigment-grade TiO_2 are the United States Western Europe, and Japan Table 8. The growth rate from 1960 to 1973 was approximately 8% annually. Consumption decreased sharply after the 1973 oil crisis, from 2×10^6 to 1.5×10^6 t. The demand has since recovered and growth rates of 5–8% were reported in the early 1990s. Global growth is expected to be between 3 and 4% annually, with Latin America and the Asia-Pacific areas experiencing slightly higher growth rates (40).

The principal sponge producers are U.S., Japan, and the CIS countries of Russia and Kazakhstan (see Table 8). U.S. metal demand has been greater than sponge production, which has been supplemented by imports, primarily from Japan, Russia, Kazakhstan, and, to a lesser extent, China. Imports supply approximately 25–40% of the U.S. demand. The U.S. does not supply its own demands because of the closing of capacity in the weak markets of the early 1990s and the reluctance to add capacity for peak demand period with a high cost of facilitization ($22/kg of annual capacity). The price history of titanium sponge is given in Table 9.

Before 1970 more than 90% of the titanium produced was used for aerospace, which fell to approximately 70–80% by 1982. Military use has continually decreased from nearly 100% in the early 1950s to 20% in the late 1990s (41). In contrast to the U.S., aerospace uses in Western Europe and Japan account for only 40–50% of the demand (5). The CIS's consumption of titanium metal prior to the breakup was about one-half of the world consumption. In the 1980s, considerable amounts were used for submarine construction. Since the breakup of the former Soviet Union, the internal consumption of titanium in the CIS is believed to be a modest fraction of its former capacity, thus leaving a large capacity available for export. The world production facilities for titanium metal and extraction are given in Table 10.

Table 8. World Sponge and Pigment Capacities[a]

Country	Sponge, 10^3 t	Pigment, 10^3 t
United States	29.5	1330
Australia		150
Belgium		80
Canada		74
China	7	40
Finland		80
France		230
Germany		350
Italy		80
Japan	25.8	320
Kazakstan	35	1
Russia	35	20
Spain		65
Ukraine		120
United Kingdom		275
other countries		585
Total	*132.3*	*3800*

[a] Ref. 40.

Table 9. Price History of Titanium Sponge

Year	$/kg
1948–1955	11.02
1964–1975	2.91
1981	16.86
1982	12.20
1991–1994	8.80
1996	11.00
1999	8.00–12.00[a]

[a] Average values, lower number, standard grade, higher number premium increased purity grade.

9. Grade, Specifications, and Quality Control

The titanium grades most commonly used have compositional specifications tabulated by ASTM. The ASTM specification number is given in Table 11 for the commercially important alloys. Military specifications are found under MIL-T-9046 and MIL-T-9047, and aerospace material specifications for bar, sheet, tubing, and wire under specification numbers 4900-4980. Every large aircraft company has its own set of alloy specifications.

The alloy name in the U.S. can include a company name or trademark in conjunction with the composition for alloyed titanium or the strength, ie, ultimate tensile strength for Timet and yield strength for other U.S. producers, for unalloyed titanium. The common alloys and specifications are shown in Table 11.

Because titanium alloys are used in a variety of applications, several different material and quality standards are specified. Among these are ASTM, ASME, Aerospace Materials Specification (AMS), U.S. military, and a number of proprietary sources. The correct chemistry is basic to obtaining mechanical and other properties required for a given application. Minor elements controlled by specification include carbon, iron, hydrogen, nitrogen, and oxygen. In addition, control of thermomechanical processing and subsequent heat treatment is vital to obtaining desired properties. For extremely critical applications, such as rotating parts in aircraft

Table 10. Principal Titanium Metal Producers

			Ingot	
Region	Company	Sponge, 10^3 t	Vacuum arc, 10^3 t	Cold hearth, 10^3 t
United States	RMI Titanium Co.	0	16.4	0
	Timet	10	12.7	0
	Oremet-Wah Chang[a]	5.5	8.2	0
	Wyman-Gordon	0	1.8	
	Howmet	0	2.3	0
	Allvac	0	2.7	
	Lawrence Aviation	0	1.4	0
	Axel Johnson	0	0	
	Titanium Hearth Technologies	0	0	
	Alta Titanium (Johnson-Matthey)	0.3	0	
Total		*15.8*	*45.5*	*14.3*
Japan	Suimitomo Sitix Corp.	15	5	0
	Toho Titanium	11	6.4	0
	Daido	0	0.5	0
	Kobe	0	7.3	0
	Sumitomo	0	3.7	0
Total		*26*	*22.9*	*0*
Europe	IMI (England)	0	5.5	0
	Deutsche Titan (Germany)	0	1.4	0
	Cezus (France)	0	1.4	0
Total		*0*	*8.3*	*0*
CIS	Ust Kamen (Kazakhstan)	36.4	0	0
	Avisma (Russia)	25.9	0	0
	VSMPO (Russia)	0	100	0
	Vils (Russia)	0	5	0
Total		*62.3*	*105*	*0*
China	Metals Ministry	2.7	3.6	0
Total world		*106.8*	*185.3*	*14.3*

[a] Now part of allegheny technologies.

[b] Plasma.

[c] Electron beam.

gas turbines, raw materials, melting parameters, chemistry, thermomechanical processing, heat treatment, testing, and finishing operations must all be carefully and closely controlled at each step to ensure that required characteristics are present in the products supplied.

Both for corrosion resistant use, and particularly for structural applications, properties are strongly dependent on chemistry and microstructure; the latter in turn is determined by the processing. Hence quality control of chemistry, and processing (deformation temperatures and amounts, annealing temperatures, times, and cooling rates) are very important for titanium alloys. Further details can be found in references (11–15).

10. Analytical Methods

Analytical methods for titanium and titanium alloys are covered in the ASTM procedures: *E-120 Chemical methods for analysis of Ti and its alloys*; *E-1409 Oxygen analysis in Ti*; *E-1447 Hydrogen analysis in Ti*; *E-1937 Nitrogen analysis in Ti*; and *E-1941 Carbon analysis in refractory metals*. References 42 and 43 are two recent papers in this area.

Table 11. Common Name and Typical Specifications for Titanium Alloys

Nominal composition, wt %	Common name	UNS	AMS	ASTM	Military
α-*Alloys*					
99.5Ti	Ti	R50250	4591E	1	9046J
99.2Ti	Ti	R50400	4902E	2	9046J
99.1Ti	Ti	R50550	4900J	3	9046J
99.0Ti	Ti	R50700	4901L	4	9046J
99.8 Ti	Ti–0.2 Pd	R52400 and R52250		7 and 11	
Ti–5Al–2.5Sn	Ti-5-2.5	R54520	4926H	6	9047J
Ti–5.8Al–4Sn–3.5Zr–0.7Nb–0.5Mo–0.35Si	IMI 834				
Ti–8Al–1Mo–1V	Ti–811	R54810	4972C		9047G
Ti–6Al–2.7Sn–4Zr–0.4Mo–0.45Si	TiMetal 1100				
α–β-*Alloys*					
Ti–3Al–2.5V	Ti-3-2.5	R56320	4943D	9	9047G
Ti–6Al–2Sn–4Zr–2Mo–0.1Si	Ti-6242S	R54620	4976C		9047G
Ti–6Al–4V	Ti-6-4	R56400	4911F	5	9046G
Ti–4Al–4Mo–2Sn–0.5Si	Ti-550				
Ti–6Al–26V–2Sn	Ti-662	R56620	4918F		9046J
Ti–6Al–2Sn–2Zr–2Mo–2Cr–0.1Si	Ti-6-2222S				
Ti–6Al–2Sn–4Zr–6Mo–2Cr–0.1Si	Ti-6246	R56260	4981B		9047G
Ti–4.5Al–3V–2Mo–2Fe	SP700	4899			
Ti–5Al–2Sn–2Zr–4Mo–4Cr	Ti-17	R58650	4955		
β-*Alloys*					
Ti–10V–2Fe–3Al	Ti-10-2-3		4984		
Ti–15V–3Cr–3Al–3Sn	Ti-15-3		4914		
Ti–3Al–8V–6Cr–4Mo–4Zr	Beta C	R58640	4957	19	9046J
Ti–3Al–2.8Nb–15Mo–0.2Si	TiMetal21S	R58210			
Intermetallics					
Ti_3Al	Alpha 2				
TiAl	Gamma				

11. Recycling and Environmental Concerns

Because of the high cost of production of primary titanium, every effort is made to recycle “revert” in ingots and castings after appropriate cleaning to remove impurities.

The environmental concerns regarding production of titanium include the following. The Discussion is not exhaustive and is not intended to reflect any order of importance or a recommended procedure.

There are residuals that contain heavy metals in the chlorination of rutile to $TiCl_4$ which present a disposal problem. There is a potential for leaking Cl_2 or $TiCl_4$ but this is rare if systems are maintained. Transport of $TiCl_4$ to sponge producers that have no $TiCl_4$ production is done by rail and this is a concern as is the shipment of Cl_2 which is generated but not consumed. These hazards are all carefully addresses and the Ti metals industry contribute no more than a small fraction of either of these materials shipped around the country.

Sponge production is leached or washed and there is a concern with the effluent from these operations.

Stripping of primary melt electrodes of even vacuum distilled sponge containing melts frequently caused smoking (burning of magnesium deposits on the surface) and this is a concern with respect to air quality, but is dealt with in various ways in the industry to either contain the burning or to passivate the magnesium with low pressure O_2 prior to stripping the ingot from the crucible. The industry does not consider that this is a problem any more.

Magnesium or Sodium plants that support sponge plants always have a potential for leaking of Cl_2 gas. This is minimized for reasons including the fact that Cl_2 is too expensive to let it escape.

Pickling is intrinsic to most titanium mill operations, especially those that make flat products. The acid baths build up dissolved metal ion content and disposal of this liquor is a significant problem especially since they contain fluorine ions. This is so significant that the industry is looking very seriously at ways to minimize or even eliminate HF pickling where possible, even if it means some additional cost to produce the metal.

There is always the potential for Titanium fires in the sponge plant and/or chip plant as well as in powder metallurgy operations. This is more of a safety than an environmental problem.

Contact of molten Titanium with water has occurred in the industry, most recently in the Oremet Wah-Chang plant in Albany, Oregon, with an extremely violent explosion resulting.

12. Health and Safety Factors

The titanium industry is extremely concerned over environmental, health and safety issues relating to all aspects of the production of titanium. In fact, under the auspices of the Trade Organization “The International Titanium Association” (ITA) there is a safety committee which acts in an advisory role to the world-wide titanium industry. Recently the chair of this committee published an article of general interest in this area (44).

Titanium and its corrosion products are nontoxic. A safety problem does exist with titanium powders, grindings, turnings, and some corrosion products that are pyrophoric. Powders can ignite at about 2500°C and should be handled in small quantities at room temperature in electrically grounded, nonsparking equipment made from materials, such as monel, aluminum, and stainless steel. Grindings and turnings should be stored in a closed container and not left on the floor. Smoking must be prohibited in areas where titanium is ground or turned. If a fire occurs, it must be extinguished with a Class-D extinguisher, specially used against metal fires. Dry common salt can also be used to smother a fire. Water or other liquids must not be used as they could react with the titanium and release hydrogen. The larger the surface area, the more pyrophoric the titanium powder. When titanium equipment is being worked on, all flammable and corrosive products must be removed and the area well ventilated. A pyrophoric corrosion product has been observed in environments of dry Cl2 gas and in red-fuming nitric acid. The concerns mentioned above also apply to the transportation of finely divided powder, grindings or turnings, however there are no such concerns with solid titanium.

The thermal cutting of Ti-6Al-4V produces vanadium pentoxide, which has established threshold limits. Ventilation requirements can be minimized if cutting is done directly over water. Experience has shown that simple dilution via venting to the atmosphere is sufficient. The same situation exits for welding.

Pyrophoric reactions with fine machine turnings or grinding dust can occur. Being aware of this and maintaining good housekeeping should eliminate this problem without the use of special equipment.

Titanium is one of the least toxic meterials and is essentially benign to the human body, which in combination with excellent mechanical properties has led to use in medical implants such as hip joints and knees.

13. Uses

Titanium alloy markets and product requirements can be described by three major market segments: jet engines, airframes, and industrial applications, as shown in Table 12 (5). The first two of these segments are related to the broad aerospace market which dominates the use of titanium in the U.S. and consumes

Table 12. Market and Product Requirements Titanium Alloys[a]

Market segment	Market share		Product requirements
	United States	Europe	
	United States	Europe	
jet engines	42%	37%	elevated temp. tensile strength creep strength elevated temp. stability fatigue strength fracture toughness
airframes	36%	33%	high tensile strength fatigue strength fracture toughness fabricable
industrial	20%	30%	corrosion resistance
			adequate strength fabricable cost competitive

[a] Total 1990 consumption: U.S. 23.6×10^6 kg; Europe, 9.1×10^6 kg.

about equal amounts for engines and airframes. These two applications are based primarily on the high specific strength (strength-to-density ratio) of titanium. The third, and smallest, market segment in the U.S. comprises industrial applications, based on the excellent corrosion resistance of titanium towards salt and other aggressive environments. As indicated in Table 12, the specified market segments have similar proportions in both the U.S. and Europe, although the total U.S. market is about 2.5 times that of Europe based on 1990 data. In Japan, a majority of the titanium is for nonaerospace use. The titanium capacity of the former Soviet Union was estimated to be about 90×10^6 kg/yr. This capacity could totally change the Western World marketplace with low cost products.

The product requirements for titanium alloys in each market segment are based on the specific needs for the particular application. For example, jet engine requirements are focused primarily on high-temperature tensile and creep strength as well as thermal stability at elevated temperatures. Second tier property considerations are fatigue strength and fracture toughness. Airframe applications require high tensile strength combined with good fatigue strength and fracture toughness. Ease of fabrication of components is also an important consideration. Industrial applications demand good corrosion resistance in a variety of media as a prime consideration as well as adequate strength, fabricability and competitive cost, relative to other types of corrosion-resistant alloys.

Jet engine applications include discs and fan blades (Fig. 10). Air frame components produced from titanium vary from small parts to large main landing-gear support beams, the aft section of fuselages and truck beam forgings.

Traditional non-aerospace applications cover tubing in heat transfer equipment (Fig. 11) and medical prosthesis devices. They also include watches, sporting goods, boats, and roofs of buildings.

The high cost of titanium alloy often limits use. For example, Table 13 compares the amount of titanium slated for use in three U.S. Air Force systems, expressed as airframe weight percentage, with early design figures shown for comparison (11). Thus much work has concentrated on reducing component cost while maintaining acceptable mechanical property levels; approaches including near net shape techniques and lower cost alloy formulation.

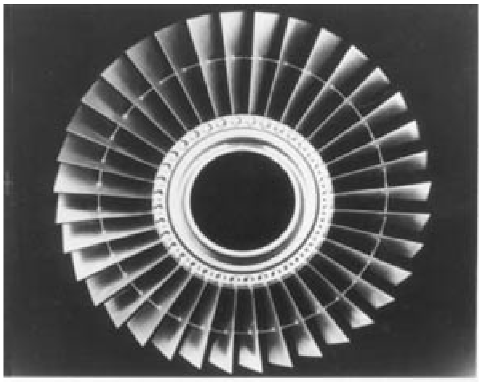

Fig. 10. Fan disc used on the CF6-80C2 engine. Disc diameter 838 mm, with blades 2438 mm, Courtesy GE Aircraft Engines.

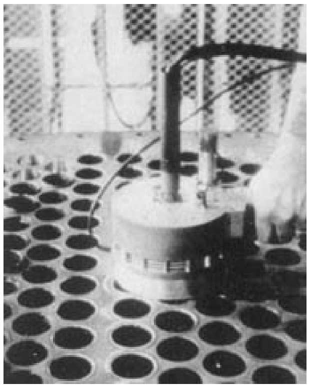

Fig. 11. Titanium tubing in heat transfer equipment. Courtesy of RMI Titanium Company.

Table 13. Airframe Weight Percentage of Titanium

System	Early design	Final concept
C5 (cargo)	24	3
B1 (bomber)	42	22
F15 (fighter)	50	34

An area for expansion for titanium is in automobiles with about 16×10^6 cars and light trucks produced in the U.S. above each year. Thus just 1.8 kg of titanium per vehicle could more than double titanium yearly consumption in the U.S.; albeit with a dramatic effect on the titanium infrastructure. However, wide-spread use in large volume production automobiles will require a cost-effective product.

A recent development has been the use of titanium in golf clubs, particularly metal “woods” (9).

The current world titanium marketplace in shown in Figure 12 (12).

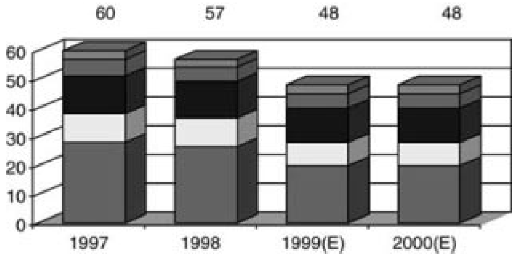

Fig. 12. Total titanium shipments by producing regions, × 10^3 t.■ North America,;□ Europe;■ Japan;■ Russia;■ China.

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