

# CHAPTER 6

## TITANIUM AND ITS ALLOYS

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<b>6.1 INTRODUCTION</b>	<b>91</b>	6.5.2 Drawing	100
<b>6.2 ALLOYS</b>	<b>92</b>	6.5.3 Bending	104
6.2.1 Aerospace Alloys	94	6.5.4 Cutting and Grinding	104
6.2.2 Nonaerospace Alloys	95	6.5.5 Welding	104
6.2.3 Other Alloys	96	<b>6.6 SPECIFICATIONS, STANDARDS, AND QUALITY CONTROL</b>	<b>105</b>
<b>6.3 PHYSICAL PROPERTIES</b>	<b>96</b>	<b>6.7 HEALTH AND SAFETY FACTORS</b>	<b>107</b>
<b>6.4 CORROSION RESISTANCE</b>	<b>97</b>	<b>6.8 USES</b>	<b>107</b>
<b>6.5 FABRICATION</b>	<b>98</b>		
6.5.1 Boiler Code	98		

### 6.1 INTRODUCTION

Titanium was first identified as a constituent of the earth's crust in the late 1700s. In 1790, William Gregor, an English clergyman and mineralogist, discovered a black magnetic sand (ilmenite), which he called menaccanite after his local parish. In 1795, a German chemist found that a Hungarian mineral, rutile, was the oxide of a new element he called titan, after the mythical Titans of ancient Greece. In the early 1900s, a sulfate purification process was developed to commercially obtain high-purity  $TiO_2$  for the pigment industry, and titanium pigment became available in both the United States and Europe. During this period, titanium was also used as an alloying element in irons and steels. In 1910, 99.5% pure titanium metal was produced at General Electric from titanium tetrachloride and sodium in an evacuated steel container. Since the metal did not have the desired properties, further work was discouraged. However, this reaction formed the basis for the commercial sodium reduction process. In the 1920s, ductile titanium was prepared with an iodide dissociation method combined with Hunter's sodium reduction process.

In the early 1930s, a magnesium vacuum reduction process was developed for reduction of titanium tetrachloride to metal. Based on this process, the U.S. Bureau of Mines (BOM) initiated a program in 1940 to develop commercial production. Some years later, the BOM publicized its work on titanium and made samples available to the industrial community. By 1948, the BOM produced batch sizes of 104 kg. In the same year, E. I. du Pont de Nemours & Co., Inc., announced commercial availability of titanium, and the modern titanium metals industry began.<sup>1</sup>

By the mid-1950s, this new metals industry had become well established, with six producers, two other companies with tentative production plans, and more than 25 institutions engaged in research projects. Titanium, termed the wonder metal, was billed as the successor to aluminum and stainless steels. When, in the 1950s, the DOD (titanium's most staunch supporter) shifted emphasis from aircraft to missiles, the demand for titanium sharply declined. Only two of the original titanium metal plants are still in use, the Titanium Metals Corporation of America's (TMCA) plant in Henderson,

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Nevada, and National Distillers & Chemical Corporation's two-stage sodium reduction plant built in the late 1950s at Ashtabula, Ohio, which now houses the sponge production facility for RMI Corporation (formerly Reactor Metals, Inc.).

Overoptimism followed by disappointment has characterized the titanium-metals industry. In the late 1960s, the future again appeared bright. Supersonic transports and desalination plants were intended to use large amounts of titanium. Oregon Metallurgical Corporation, a titanium melter, decided at that time to become a fully integrated producer (i.e., from raw material to mill products). However, the supersonic transports and the desalination industry did not grow as expected. Nevertheless, in the late 1970s and early 1980s, the titanium-metal demand again exceeded capacity and both the United States and Japan expanded capacities. This growth was stimulated by greater acceptance of titanium in the chemical-process industry, power-industry requirements for seawater cooling, and commercial and military aircraft demands. However, with the economic recession of 1981–1983, the demand dropped well below capacity and the industry was again faced with hard times.

## 6.2 ALLOYS

Titanium alloy systems have been studied extensively. A single company evaluated over 3000 compositions in 8 years. Alloy development has been aimed at elevated-temperature aerospace applications, strength for structural applications, and aqueous corrosion resistance. The principal effort has been in aerospace applications to replace nickel- and cobalt-base alloys in the 500–900°C ranges. To date, titanium alloys have replaced steel in the 200–500°C range. The useful strength and corrosion-resistance temperature limit is ~550°C.

The addition of alloying elements alters the  $\alpha$ - $\beta$  transformation temperature. Elements that raise the transformation temperature are called  $\alpha$  stabilizers; elements that depress the transformation temperature are called  $\beta$  stabilizers; the latter are divided into  $\beta$ -isomorphous and  $\beta$ -eutectoid types. The  $\beta$ -isomorphous elements have limited  $\alpha$  solubility, and increasing additions of these elements progressively depresses the transformation temperature. The  $\beta$ -eutectoid elements have restricted beta solubility and form intermetallic compounds by eutectoid decomposition of the  $\beta$  phase. The binary phase diagram illustrating these three types of alloy systems is shown in Fig. 6.1

The important  $\alpha$ -stabilizing alloying elements include aluminum, tin, zirconium, and the interstitial alloying elements (i.e., elements that do not occupy lattice positions) oxygen, nitrogen, and carbon. Small quantities of interstitial alloying elements, generally considered to be impurities, have a very great effect on strength and ultimately embrittle the titanium at room temperature.<sup>3</sup> The effects of oxygen, nitrogen and carbon on the ultimate tensile properties and elongation are shown in Table 6.1. These elements are always present and are difficult to control. Nitrogen has the greatest effect, and commercial alloys specify its limit to be less than 0.05 wt %. It may also be present as nitride (TiN) inclusions, which are detrimental to critical aerospace structural applications. Oxygen additions increase strength and serve to identify several commercial grades. This strengthening effect diminishes at elevated temperatures and under creep conditions at room temperature. For cryogenic service, low oxygen content is specified (<1300 ppm) because high concentrations of interstitial impurities increase sensitivity to cracking, cold brittleness, and fracture temperatures. Alloys with low interstitial

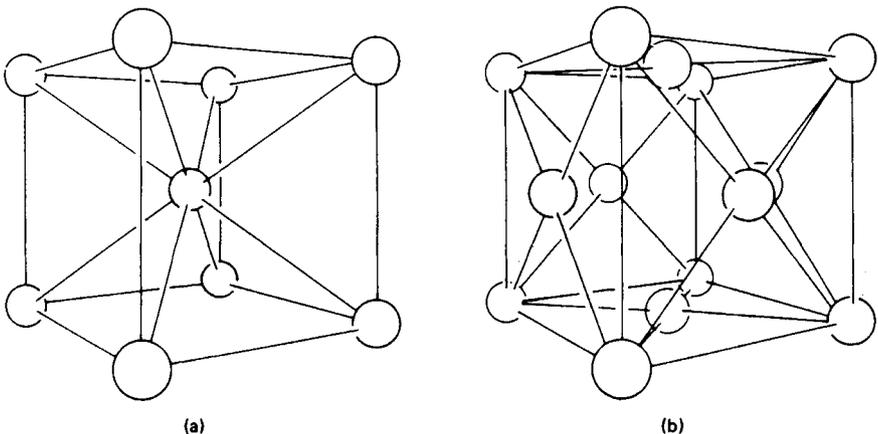


Fig. 6.1 The effect of alloying elements on the phase diagram of titanium: (a)  $\alpha$ -stabilized system, (b)  $\beta$ -isomorphous system, and (c)  $\beta$ -eutectoid system.<sup>2</sup>

**Table 6.1 Effects of O, N, and C on the Ultimate Tensile Strength<sup>2,3</sup>**

Concentration of Impurity, wt%	Oxygen <sup>b,c</sup>		Nitrogen <sup>b,c</sup>		Carbon <sup>b,c</sup>	
	UT MPa <sup>d</sup>	Elong., %	UT MPa <sup>d</sup>	Elong., %	UT MPa <sup>d</sup>	Elong., %
0.025	330	37	380	35	310	40
0.05	365	35	460	28	330	39
0.1	440	30	550	20	370	36
0.15	490	27	630	15	415	32
0.2	545	25	700	13	450	26
0.3	640	23	embrittles		500	21
0.5	790	18			520	18
0.7	930	8			525	17

<sup>a</sup> Tests were conducted using titanium produced by the iodide process.

<sup>b</sup> UT = ultimate tensile stress.

<sup>c</sup> Elongation on 2.54 cm.

<sup>d</sup> To convert MPa to psi, multiply by 145.

content are identified as ELI (extra-low interstitials) after the alloy name. 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.<sup>4</sup>

The most important alloying element is aluminum, an  $\alpha$  stabilizer. It is not expensive, and its atomic weight is less than that of titanium; hence, aluminum additions lower the density. The mechanical strength of titanium can be increased considerably by aluminum additions. Even though the solubility range of aluminum extends to 27 wt %, above 7.5 wt % the alloy becomes too difficult to fabricate and embrittles. The embrittlement is caused by a coherently ordered phase based on Ti<sub>3</sub>Al. Other  $\alpha$ -stabilizing elements also cause phase ordering. An empirical relationship below which ordering does not occur is<sup>5</sup>

$$\text{wt \% Al} + \frac{\text{wt \% Sn}}{3} + \frac{\text{wt \% Zr}}{6} + 10 \times \text{wt \% O} \leq 9$$

The important  $\beta$ -stabilizing alloying elements are the bcc elements vanadium, molybdenum, tantalum, and niobium of the  $\beta$ -isomorphous type and manganese, iron, chromium, cobalt, nickel, copper, and silicon of the  $\beta$ -eutectoid type. The  $\beta$ -eutectoid elements arranged in order of increasing tendency to form compounds are shown in Table 6.2. The elements copper, silicon, nickel, and cobalt are termed active eutectoid forms because of a rapid decomposition of  $\beta$  to  $\alpha$  and a compound. The other elements in Table 6.2 are sluggish in their eutectoid reactions.

Alloys of the  $\beta$  type respond to heat treatment, are characterized by higher density than pure titanium, and are easily fabricated. The purpose of  $\beta$  alloying is to form an all- $\beta$ -phase alloy with commercially useful qualities, form alloys with duplex  $\alpha$  and  $\beta$  structure to enhance heat-treatment

**Table 6.2  $\beta$ -Eutectoid Elements in Order of Increasing Tendency to Form Compounds<sup>2,6</sup>**

Element	Eutectoid Composition, wt %	Eutectoid Temperature, °C	Composition for $\beta$ 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	

response (i.e., changing the  $\alpha$  and  $\beta$  volume ratio), or use  $\beta$ -eutectoid elements for intermetallic hardening. The most important commercial  $\beta$ -alloying element is vanadium.

### 6.2.1 Aerospace Alloys

The alloys of titanium for aerospace use can be divided into three categories: an all- $\alpha$  structure, a mixed  $\alpha$ - $\beta$  structure, and an all- $\beta$  structure. The  $\alpha$ - $\beta$  structure alloys are further divided into near- $\alpha$  alloys (<2%  $\beta$  stabilizers). Most of the approximately 100 commercially available alloys (approximately 30 in the United States, 40 in the USSR, and 10 in Europe and Japan) are of the  $\alpha$ - $\beta$  structure type.<sup>7</sup> Some of these, produced in the United States, are given in Table 6.3 along with some wrought properties.<sup>8-10</sup> The most important commercial alloy is Ti-6 Al-4 V, an  $\alpha$ - $\beta$  alloy with a good combination of strength and ductility. It can be age-hardened and has moderate ductility, and an excellent record of successful applications. It is mostly used for compressor blades and disks in aircraft gas-turbine engines, and also in lower-temperature engine applications such as rotating disks and fans. It is also used for rocket-motor cases, structural forgings, steam-turbine blades, and cryogenic parts for which ELI grades are usually specified.

Other commercially important  $\alpha$ - $\beta$  alloys are Ti-3 Al-2.5 V, Ti-6 Al-6 V-2 Sn, and Ti-10 V-2 Fe-3 Al (see Table 6.3). As a group, these alloys have good strength, moderate ductility, and can be age-hardened.<sup>10,11</sup> Weldability becomes more difficult with increasing  $\beta$  constituents, and fabrication of strip, foil, sheet, and tubing may be difficult. Temperature tolerances are lower than those of the  $\alpha$  or near- $\alpha$  alloys. The alloy Ti-3 Al-2.5 V (called one-half Ti-6 Al-4 V) is easier to fabricate than Ti-6 Al-4 V and is used primarily as seamless aircraft-hydraulic tubing. The alloy Ti-6 Al-6 V-2 Sn is used for some aircraft forgings because it has a higher strength than Ti-6 Al-4 V. The alloy Ti-10 V-2 Fe-3 Al is easier to forge at lower temperatures than Ti-6 Al-4 V because it contains more  $\beta$ -alloying constituents and has good fracture toughness. This alloy can be hardened to high strengths [1.24-1.38 GPa or (1.8-2)  $\times 10^5$  psi] and is expected to be used as forgings for airframe structures to replace steel below temperatures of 300°C<sup>12</sup>,

**Table 6.3 Properties, Specifications and Applications of Wrought Titanium Alloys<sup>2,9,10</sup>**

Nominal Composition, wt %	CAS Registry No.	ASTM B-265	CLTE <sup>a</sup> , $\mu\text{m}/(\text{m} \cdot \text{K})$		Average Physical Properties				
			21-100°C	21-538°C	Modulus of Elasticity <sup>b</sup> , GPa <sup>c</sup>	Modulus of Rigidity <sup>b</sup> , GPa <sup>c</sup>	Poisson's <sup>b</sup> Ratio	Density, g/cm <sup>3</sup>	Condition
commercially pure									
99.5 Ti		grade 1	8.7	9.8	102	39	0.34	4.5	annealed
99.2 Ti		grade 2	8.7	9.8	102	39	0.34	4.5	annealed
99.1 Ti		grade 3	8.7	9.8	103	39	0.34	4.5	annealed
99.0 Ti		grade 4	8.7	9.8	104	39	0.34	4.5	annealed
99.2 Ti <sup>s</sup>		grade 7	8.7	9.8	102	39	0.34	4.5	annealed
98.9 Ti <sup>b</sup>								4.5	annealed
Ti-5 Al-2.5 Sn <sup>i</sup>	[11109-19-6]	grade 6	9.4	9.6	110			4.5	annealed
Ti-8 Al-1 Mo, 1 V <sup>i</sup>	[39303-55-4]		8.5	10.1	124	47	0.32	4.4	duplex annealed
Ti-6 Al-2 Sn, 4 Zr-2 Mo <sup>i</sup>	[11109-15-2]		7.8	8.1	114			4.5	annealed
Ti-3 Al-2.5 V <sup>i</sup>	[11109-23-2]		9.6	9.9	107			4.5	annealed
Ti-6 Al-4 V <sup>i</sup>	[12743-70-3]	grade 5	8.7	9.6	114	42	0.342	4.4	annealed
Ti-6 Al-6 V, 2 Sn <sup>i</sup>	[12606-77-8]		9.0	9.6	110			4.5	annealed
Ti-10 V-2 Fe, 3 Al <sup>i</sup>	[51809-47-3]				112			4.6	solution and age

<sup>a</sup> CLTE = coefficient of linear thermal expansion.

<sup>b</sup> Room temperature.

<sup>c</sup> To convert GPa to psi, multiply by 145,000.

<sup>d</sup> To convert MPa to psi, multiply by 145.

The only  $\alpha$  alloy of commercial importance is Ti-5 Al-2.5 Sn. It is weldable, has good elevated-temperature stability, and good oxidation resistance to about 600°C. It is used for forgings and sheet-metal parts such as aircraft-engine compressor cases because of weldability.

The commercially important near- $\alpha$  alloys are Ti-8 Al-1 Mo-1 V and Ti-6 Al-2 Sn-4 Zr-2 Mo. They exhibit good creep resistance and the excellent weldability and high strength of  $\alpha$  alloys; the temperature limit is ~500°C. Alloy Ti-8 Al-1 Mo-1 V is used for compressor blades because of its high elastic modulus and creep resistance; however, it may suffer from ordering embrittlement. Alloy Ti-6 Al-2 Sn-4 Zr-2 Mo is also used for blades and disks in aircraft engines. The service temperature limit of 470 °C is ~70°C higher than that of Ti-8 Al-1 Mo-1 V.<sup>5</sup>

Commercialization of  $\beta$  alloys has not been very successful. Even though alloys with high strength [up to 1.5 GPa (217,500 psi)] were made, they suffered from intermetallic and  $\omega$ -phase embrittlement. These alloys are metallurgically unstable and have little practical use above 250°C. They are fabricable but welds are not ductile. This alloy type is used in the cold-drawn or cold-rolled condition and finds application in spring manufacture (alloy Ti-13 Al-11 Cr-3 Al).<sup>13</sup> There is one commercially available alloy of the  $\beta$ -eutectoid type (Ti-2.5 Cu) that uses a true precipitation-hardening mechanism to increase strength. The precipitate is Ti<sub>2</sub>Cu. This alloy is only slightly heat treatable; it is used in engine castings and flanges.<sup>5</sup>

### 6.2.2 Nonaerospace Alloys

The nonaerospace alloys are used primarily in industrial applications. The four grades (ASTM grade 1 through grade 4) differ primarily in oxygen and iron content (see Table 6.4). ASTM grade 1 has the highest purity and the lowest strength (strength is controlled by impurities). The two other alloys of this group are ASTM grade 7, Ti-0.2 Pd, and ASTM grade 12, Ti-0.8 Ni-0.3 Mo. The alloys in this group are distinguished by excellent weldability, formability, and corrosion resistance. The strength, however, is not maintained at elevated temperatures (see Table 6.3). The primary use of alloys in this group is in industrial-processing equipment (i.e., tanks, heat exchangers, pumps, elec-

Average Mechanical Properties

Room Temperature		Extreme Temperatures			Charpy Impact Strength, J/m <sup>e</sup>	Hardness <sup>f</sup>				
Tensile Strength, MPa <sup>d</sup>	Yield Strength, MPa <sup>d</sup>	Elongation, %	Reduction in Area, %	Test Temperature, °C			Tensile Strength, MPa <sup>d</sup>	Yield Strength, MPa <sup>d</sup>	Elongation, %	Reduction in Area, %
331	241	30	55	315	152	97	32	80		HB 120
434	346	28	50	315	193	117	35	75	43	HB 200
517	448	25	45	315	234	138	34	75	38	HB 225
662	586	20	40	315	310	172	25	70	20	HB 265
434	346	28	50	315	186	110	37	75	43	HB 200
517	448	25	42	315	324	207	32			
862	807	16	40	315	565	448	18	45	26	HRC 36
1000	952	15	28	540	621	517	25	55	33	HRC 35
979	896	15	35	540	648	490	26	60		HRC 32
690	586	20		315	483	345	25			
993	924	14	30	540	531	427	35	50	19	HRC 36
1069	1000	14	30	315	931	807	18	42	18	HRC 38
1276	1200	10	19	315	1103	979	13	42		

<sup>e</sup> To convert J/m to ft-lb/in., divide by 53.38.

<sup>f</sup> HB = Brinell, HRC = Rockwell (C-scale).

<sup>g</sup> Also contains 0.2 Pd.

<sup>h</sup> Also contains 0.8 Ni and 0.3 Mo.

<sup>i</sup> Numerical designations = wt % of element.

**Table 6.4 ASTM Requirements for Different Titanium Grades<sup>2,4</sup>**

Element	Grade 1	Grade 2	Grade 3	Grade 4	Grade 7	Grade 12
nitrogen, max	0.03	0.03	0.05	0.05	0.03	0.03
carbon, max	0.10	0.10	0.10	0.10	0.10	0.08
hydrogen, max	0.015	0.015	0.015	0.015	0.015	0.015
iron, max	0.20	0.30	0.30	0.50	0.30	0.30
oxygen, max	0.18	0.25	0.35	0.40	0.25	0.25
palladium					0.21–0.25	
molybdenum						0.2–0.4
nickel						0.6–0.9
residuals, max						
each	0.1	0.1	0.1	0.1	0.1	0.1
total	0.4	0.4	0.4	0.4	0.4	0.4
titanium	remainder	remainder	remainder	remainder	remainder	remainder

trodes, etc.), even though there is some use in airframes and aircraft engines. The ASTM grade 1 is used where higher purity is desired, for example, as weld wire for grade 2 fabrication and as sheet for explosive bonding to steel. Grade 1 is manufactured from high-purity sponge. The ASTM grade 2 is the most commonly used grade of commercially pure titanium. The chemistry for this grade is easy to meet with most sponge. The ASTM grades 3 and 4 are higher strength versions of grade 2; grades 7 and 12 have better corrosion resistance than grade 2 in reducing acids and acid chlorides. However, grade 7 is expensive and grade 12 is not readily available.

### 6.2.3 Other Alloys

Other alloying ranges include the aluminides (TiAl and Ti<sub>3</sub>Al), the superconducting alloys (Ti–Nb type), the shape-memory alloys (Ni–Ti type), and the hydrogen-storage alloys (Fe–Ti). The aluminides TiAl and Ti<sub>3</sub>Al have excellent high-temperature strengths, comparable to those of nickel- and cobalt-base alloys, with less than half the density. These alloys exhibit ultimate strengths of 1 GPa (145,000 psi), and 800 MPa (116,000 psi) yield, respectively, 4–5% elongation, and 7% reduction in area. Strengths are maintained to 800–900°C. The modulus of elasticity is high [125–165 GPa, (18–24) × 10<sup>6</sup> psi], and oxidation resistance is good.<sup>8</sup> The aluminides are intended for both static and rotating parts in the turbine section of gas-turbine aircraft engines.

Titanium alloyed with niobium exhibits superconductivity, and a lack of electrical resistance below 10K. Composition ranges from 25 to 50 wt % Ti. These alloys are  $\beta$ -phase alloys with superconducting transitional temperatures at ~10 K. Their use is of interest for power generation, propulsion devices, fusion research, and electronic devices.<sup>14</sup>

Titanium alloyed with nickel exhibits a memory effect, that is, the metal form switches from one specific shape to another in response to temperature changes. The group of Ti–Ni alloys (nitinol) was developed by the Navy in the early 1960s for F-14 fighter jets. The compositions are typically Ti with 55 wt % Ni. The transition temperature ranges from –100°C to >100°C and is controlled by additional alloying elements. These alloys are of interest for thermostats, recapture of waste heat, pipe joining, etc. The nitinols have not been extensively used because of high price and fabrication difficulties.<sup>15</sup>

Titanium alloyed with iron is a leading candidate for solid-hydrate energy-storage material for automotive fuel. The hydride FeTiH<sub>2</sub> absorbs and releases hydrogen at low temperatures. This hydride stores 0.9 kW·hr/kg. To provide the energy equivalent to a tank of gasoline would require about 800 kg FeTiH<sub>2</sub>.<sup>8</sup>

## 6.3 PHYSICAL PROPERTIES

The physical properties of titanium are given in Table 6.5. The most important physical property of titanium from a commercial viewpoint is the ratio of its strength [ultimate strength > 690 MPa (100,000 psi)] at a density of 4.507 g/cm<sup>3</sup>. Titanium alloys have a higher yield strength-to-density rating between –200 and 540°C than either aluminum alloys or steel.<sup>6,16</sup> Titanium alloys can be made with strength equivalent to high-strength steel, yet with density ~60% that of iron alloys. At ambient temperatures, titanium's strength-to-weight ratio is equal to that of magnesium, one and one-half times greater than that of aluminum, two times greater than that of stainless steel, and three times greater than that of nickel. Alloys of titanium have much higher strength-to-weight ratios than alloys

**Table 6.5 Physical Properties of Titanium<sup>2</sup>**

Property	Value
melting point, °C	1668 ± 5
boiling point, °C	3260
density, g/cm <sup>3</sup>	
α phase at 20°C	4.507
β phase at 885°C	4.35
allotropic transformation, °C	882.5
latent heat of fusion, kJ/kg <sup>a</sup>	440
latent heat of transition, kJ/kg <sup>a</sup>	91.8
latent heat of vaporization, MJ/kg <sup>a</sup>	9.83
entropy at 25°C, J/mol <sup>a</sup>	30.3
thermal expansion coefficient at 20°C per °C	8.41 × 10 <sup>-6</sup>
thermal conductivity at 25°C, W/(m·K)	21.9
emissivity	9.43
electrical resistivity at 20°C, nΩ·m	420
magnetic susceptibility, mks	180 × 10 <sup>-6</sup>
modulus of elasticity, GPa <sup>b</sup>	
tension	ca 101
compression	103
shear	44
Poisson's ratio	~0.41
lattice constants, nm	
α, 25°C	a <sub>0</sub> = 0.29503
β, 900°C	c <sub>0</sub> = 0.46531
	a <sub>0</sub> = 0.332
vapor pressure, kPa <sup>c</sup>	log P <sub>kPa</sub> = 5.7904 - 24644/T - 0.000227 T
specific heat, J/(kg·K) <sup>d</sup>	C <sub>p</sub> = 669.0 - 0.037188 T - 1.080 × 10 <sup>-6</sup> T <sup>2</sup>

<sup>a</sup> To convert J to cal, divide by 4.184.

<sup>b</sup> To convert GPa to psi, multiply by 145,000.

<sup>c</sup> To convert log P<sub>kPa</sub> to log P<sub>atm</sub>, add 2.0056 to the constant.

<sup>d</sup> T > 298 K.

of nickel, aluminum, or magnesium, and stainless steel. Because of its high melting point, titanium can be alloyed to maintain strength well above the useful limits of magnesium and aluminum alloys. This property gives titanium a unique position in applications between 150 and 550°C where the strength-to-weight ratio is the sole criterion.

Solid titanium exists in two allotropic crystalline forms. The α phase, stable below 882.5°C, is a hexagonal closed-packed structure, whereas the β phase, a bcc crystalline structure, is stable between 882.5°C and the melting point of 1668°C. The high-temperature β phase can be found at room temperature when β-stabilizing elements are present as impurities or additions (see Section 6.2). The α and β phases can be distinguished by examining an unetched polished mount with polarized light. The α is optically active and changes from light to dark as the microscope stage is rotated. The microstructure of titanium is difficult to interpret without knowledge of the alloy content, working temperature, and thermal treatment.<sup>6,17,18</sup>

The heat-transfer qualities of titanium are characterized by the coefficient of thermal conductivity. Even though this is low, heat transfer in service approaches that of admiralty brass (thermal conductivity seven times greater) because titanium's greater strength permits thinner-walled equipment, relative absence of corrosion scale, erosion-corrosion resistance permitting higher operating velocities, and inherently passive film.

## 6.4 CORROSION RESISTANCE

Titanium is immune to corrosion in all naturally occurring environments. It does not corrode in air, even if polluted or moist with ocean spray. It does not corrode in soil or even the deep salt-mine-type environments where nuclear waste might be buried. It does not corrode in any naturally occurring water and most industrial wastewater streams. For these reasons, titanium has been termed the metal for the earth, and 20–30% of consumption is used in corrosion-resistance applications.

Even though titanium is an active metal, it resists decomposition because of a tenacious protective oxide film. This film is insoluble, repairable, and nonporous in many chemical media and provides excellent corrosion resistance. However, where this oxide film is broken, the corrosion rate is very rapid. However, usually the presence of a small amount of water is sufficient to repair the damaged oxide film. In a seawater solution, this film is maintained in the passive region from  $\sim -0.2$  to 10 V versus the saturated calomel electrode.<sup>19,20</sup>

Titanium is resistant to corrosion attack in oxidizing, neutral, and inhibited reducing conditions. Examples of oxidizing environments are nitric acid, oxidizing chloride ( $\text{FeCl}_3$  and  $\text{CuCl}_2$ ) solutions, and wet chlorine gas. Neutral conditions include all neutral waters (fresh, salt, and brackish), neutral salt solutions, and natural soil environments. Examples of inhibited reducing conditions are in hydrochloric or sulfuric acids with oxidizing inhibitors and in organic acids inhibited with small amounts of water. Corrosion resistances to a variety of media are given in Table 6.6.<sup>22</sup> Titanium resistance to aqueous chloride solutions and chlorine account for most of its use in corrosion-resistant applications.

Titanium corrodes very rapidly in acid fluoride environments. The degree of attack generally increases with the acidity and the fluoride content. It is attacked in boiling HCl or  $\text{H}_2\text{SO}_4$  at acid concentrations  $>1\%$  or in  $\sim 10$  wt % acid concentration at room temperature. Titanium is also attacked by hot caustic solutions, phosphoric acid solutions (concentrations above 25 wt %), boiling  $\text{AlCl}_3$  (concentrations  $>15$  wt %), dry chlorine gas, anhydrous ammonia above  $150^\circ\text{C}$ , and dry hydrogen–dihydrogen sulfide above  $150^\circ\text{C}$ .

Titanium is susceptible to pitting and crevice corrosion in aqueous chloride environments. The area of susceptibility is shown in Fig 6.2 as a function of temperature and sodium chloride content.<sup>22</sup> The susceptibility also depends on pH. The susceptibility temperature increases parabolically from  $65^\circ\text{C}$  as pH is increased from zero. With ASTM grades 7 or 12, crevice-corrosion attack is not observed above pH 2 until  $\sim 270^\circ\text{C}$ . Noble alloying elements shift the equilibrium potential into the passive region where a protective film is formed and maintained.

Titanium does not stress crack in environments that cause stress cracking of other metal alloys (i.e., boiling 42%  $\text{MgCl}_2$ , NaOH, sulfides, etc.). Some of the alloys are susceptible to hot-salt stress cracking; however, this is a laboratory observation and has not been confirmed in service. Titanium stress cracks in methanol containing acid chlorides or sulfates, red fuming nitric acid, nitrogen tetroxide, and trichloroethylene.

Titanium is susceptible to failure by hydrogen embrittlement. Hydrogen attack initiates at sites of surface iron contamination or when titanium is galvanically coupled with iron.<sup>23</sup> In hydrogen-containing environments, titanium absorbs hydrogen above  $80^\circ\text{C}$  or in areas of high stress. If the surface oxide is removed by vacuum annealing or abrasion, pure dry hydrogen reacts at lower temperatures. Small amounts of oxygen or water vapor repair the oxide film and prevent this occurrence. Molybdenum-containing alloys are less susceptible to hydrogen attack. Titanium resists this oxidation in air up to  $650^\circ\text{C}$ . Noticeable scale forms and embrittlement occurs at higher temperatures. Surface contaminants accelerate oxidation. In the presence of oxygen, the metal does not react significantly with nitrogen. Spontaneous ignition occurs in gas mixtures containing more than 40% oxygen under impact loading or abrasion. Ignition also occurs in dry halogen gases.

Titanium resists erosion–corrosion by fast-moving sand-laden water. In a high-velocity sand-laden seawater test (8.2 m/sec) for a 60-day period, titanium performed more than 100 times better than 18 Cr–8 Ni stainless steel, Monel, or 70 Cu–30 Ni. Resistance to cavitation (i.e., corrosion on surfaces exposed to high-velocity liquids) is better than by most other structural metals.<sup>21,22</sup>

In galvanic coupling, titanium is usually the cathode metal and, consequently, is not attacked. The galvanic potential in flowing seawater in relation to other metals is shown in Table 6.7.<sup>21</sup> Since titanium is the cathode metal, hydrogen attack may be of concern, as it occurs with titanium coupled to iron.

## 6.5 FABRICATION

Titanium can be fabricated similarly to nickel-base alloys and stainless steels. However, the characteristics of titanium have to be taken into account. Compared to these materials, titanium has:

1. Lower modulus of elasticity.
2. Lower ductility.
3. Higher melting point.
4. Lower thermal conductivity.
5. Smaller strain-hardening coefficient, thereby, lower uniform elongation.
6. Greater tendency to cold weld, thereby, greater tendency to gall or seize.
7. Greater tendency to be contaminated by oxygen, nitrogen, hydrogen, and carbon.

### 6.5.1 Boiler Code

The allowable stress values as determined by the Boiler and Pressure Vessel Committee of the American Society of Mechanical Engineers are listed in Tables 6.8 and 6.9 for various titanium grades and product forms.

**Table 6.6 Corrosion Data for ASTM Grade 2 Titanium<sup>2,16,21</sup>**

Media	Conc, wt %	Temperature, °C	Corrosion Rate, mm/yr
acetaldehyde	100	149	0.0
acetic acid	5–99.7	124	0.0
adipic acid	67	232	0.0
aluminum chloride, aerated	10	100	0.002
	10	150	0.03
	20	149	16
	25	20	0.001
	25	100	6.6
	40	121	109
ammonia + 28% urea + 20.5% H <sub>2</sub> O + 19% CO <sub>2</sub> + 0.3% inerts + air	32.2	182	0.08
ammonia carbamate	50	100	0.0
ammonium perchlorate aerated	20	88	0.0
aniline hydrochloride	20	100	0.0
aqua regia	3:1	RT	0.0
	3:1	79	0.9
barium chloride, aerated	5–20	100	<0.003
bromine–water solution		RT	0.0
calcium chloride		RT	0.0
	5	100	0.005
	10	100	0.007
	20	100	0.02
	55	104	0.0005
	60	149	<0.003
	62	154	0.05–0.4
	73	177	2.1
calcium hypochlorite	6	100	0.001
chlorine gas, wet	>0.7 H <sub>2</sub> O	RT	0.0
	>0.5 H <sub>2</sub> O	200	0.0
chlorine gas, dry	<0.5 H <sub>2</sub> O	RT	may react
chlorine dioxide in steam	5	99	0.0
chloroacetic acid	100	189	<0.1
chromic acid	50	24	0.01
citric acid	25	100	0.0009
copper sulfate + 2% H <sub>2</sub> SO <sub>4</sub>	saturated	RT	0.02
cupric chloride, aerated	1–20	100	<0.01
cyclohexane (plus traces of formic acid)		150	0.003
ethylene dichloride	100	boiling	0.005–0.1
ferric chloride	10–30	100	<0.1
formic acid, nonaerated	10	100	2.4
hydrochloric acid, aerated	5	35	0.04
	20	35	4.4
HCl, chlorine saturated	5	190	<0.03
HCl + 10% HNO <sub>3</sub>	5	38	0.0
HCl + 1% CrO <sub>3</sub>	5	93	0.03
hydrofluoric acid	1–48	RT	rapid
hydrogen peroxide	3	RT	<0.1
hydrogen sulfide, steam and 0.077% mercaptans	7.65	93–110	0.0
hypochlorous acid + Cl <sub>2</sub> O and Cl <sub>2</sub>	17	38	0.00003

Table 6.6 (Continued)

Media	Conc, wt %	Temperature, °C	Corrosion Rate, mm/yr
lactic acid	10	boiling	<0.1
manganous chloride, aerated	5-20	100	0.0
magnesium chloride	5-40	boiling	0.0
mercuric chloride, aerated	1	100	0.0003
	5	100	0.01
	10	100	0.001
	55	102	0.0
mercury	100	RT	0.0
nickel chloride, aerated	5-20	100	0.0004
nitric acid	17	boiling	0.08-0.1
	70	boiling	0.05-0.9
nitric acid, red fuming	<about 2% H <sub>2</sub> O	RT	ignition sensitive
	>about 2% H <sub>2</sub> O	RT	nonignition sensitive
oxalic acid	1	37	0.3
oxygen, pure			ignition sensitive
phenol	saturated	21	0.1
phosphoric acid	10-30	RT	0.02-0.05
	10	boiling	10
potassium chloride	saturated	60	<0.0002
potassium dichromate			0.0
potassium hydroxide	50	27	0.01
	50	boiling	2.7
seawater, ten year test			0.0
sodium chlorate	saturated	boiling	0.0
sodium chloride	saturated	boiling	0.0
sodium chloride, titanium in contact with Teflon	23	boiling	crevice attack
sodium dichromate	saturated	RT	0.0
sodium hypochlorite + 12-15% sodium chloride + 1% sodium hydroxide + 1-2% sodium carbonate	1.5-4	66-93	0.03
stannic chloride	5	100	0.003
	24	boiling	0.04
sulfuric acid	1	boiling	2.5
sulfuric acid + 0.25% CuSO <sub>4</sub>	5	93	0.0
terephthalic acid	77	218	0.0
urea-ammonia reaction mass		elevated temperature and pressure	no attack
zinc chloride	20	104	0.0
	50	150	0.0
	75	200	0.5
	80	200	203

### 6.5.2 Drawing

Commercially pure titanium can be cold drawn by tools required for austenitic stainless steels. Alpha-beta alloys, such as Ti-6 Al-4 V, are difficult to draw at room temperature. The following considerations should be given to drawing of titanium:

1. Slow drawing speeds are recommended.

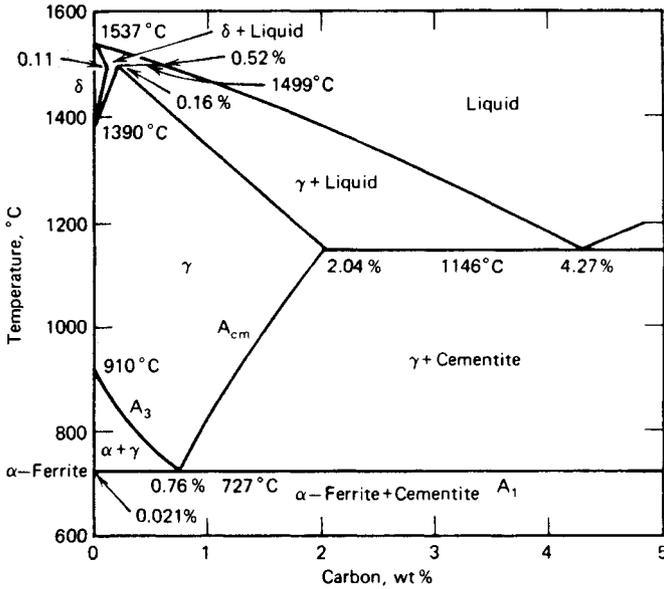


Fig. 6.2 Corrosion characteristics of titanium in aqueous NaCl solution.<sup>23</sup>

Table 6.7 Galvanic Series in Flowing Seawater 4 m/sec at 24°C<sup>2,23</sup>

Metal	Potential, V <sup>a</sup>
T304 stainless steel, passive	0.08
Monel alloy	0.08
Hastelloy alloy C	0.08
unalloyed titanium	0.10
silver	0.13
T410 stainless steel, passive	0.15
nickel	0.20
T430 stainless steel, passive	0.22
70-30 copper-nickel	0.25
90-10 copper-nickel	0.28
admiralty brass	0.29
G bronze	0.31
aluminum brass	0.32
copper	0.36
naval brass	0.40
T410 stainless steel, active	0.52
T304 stainless steel, active	0.53
T430 stainless steel, active	0.57
carbon steel	0.61
cast iron	0.61
aluminum	0.79
zinc	1.03

<sup>a</sup> Steady-state potential, negative to saturated calomel half-cell.

**Table 6.8 Maximum Allowable Stress Values in Tension for Titanium and Its Alloys<sup>24</sup>**

Form and Specification Number	Grade	Condition	Maximum Allowable Stress (ksi) for Metal Temperature (°F) Not Exceeding										
			100	150	200	250	300	350	400	450	500	550	600
Sheet, strip, plate, SB-265	1		8.8	8.1	7.3	6.5	5.8	5.2	4.8	4.5	4.1	3.6	3.1
	2	Annealed	12.5	12.0	10.9	9.9	9.0	8.4	7.7	7.2	6.6	6.2	5.7
	3	Annealed	16.3	15.6	14.3	13.0	11.7	10.4	9.3	8.3	7.5	6.7	6.0
	7		12.5	12.0	10.9	9.9	9.0	8.4	7.7	7.2	6.6	6.2	5.7
Bar, billet, SB-348	12		17.5	17.5	16.4	15.2	14.2	13.3	12.5	11.9	11.4	11.1	10.8
Pipe, SB-337	1	Seamless annealed	8.8	8.1	7.3	6.5	5.8	5.2	4.8	4.5	4.1	3.6	3.1
	2	Seamless annealed	12.5	12.0	10.9	9.9	9.0	8.4	7.7	7.2	6.6	6.2	5.7
Tubing, SB-338	3	Seamless annealed	16.3	15.6	14.3	13.0	11.7	10.4	9.3	8.3	7.5	6.7	6.0
	7	Seamless annealed	12.5	12.0	10.9	9.9	9.0	8.4	7.7	7.2	6.6	6.2	5.7
	12		17.5	17.5	16.4	15.2	14.2	13.3	12.5	11.9	11.4	11.1	10.8
Pipe, SB-337	1	Weld, annealed <sup>a</sup>	7.5	6.9	6.2	5.5	4.9	4.4	4.1	3.8	3.5	3.1	2.6
	2	Weld, annealed <sup>a</sup>	10.6	10.2	9.3	8.4	7.7	7.1	6.5	6.1	5.6	5.3	4.8
Tubing, SB-338	3	Weld, annealed <sup>a</sup>	13.9	13.3	12.2	11.1	10.0	8.8	7.9	7.1	6.4	5.7	5.1
	7	Weld, annealed <sup>a</sup>	10.6	10.2	9.3	8.4	7.7	7.1	6.5	6.1	5.6	5.3	4.8
	12		14.9	14.9	13.9	12.9	12.1	11.3	10.6	10.1	9.7	9.4	9.2
Forgings, SB-381	1		Same as Grade 1 of sheet, strip, and plate										
	F2	Annealed	Same as Grade 2 of sheet, strip and plate										
	F3	Annealed	Same as Grade 3 of sheet, strip, and plate										
	F7		Same as Grade 7 of sheet, strip and plate										
	F12		Same as Grade 12 of sheet, strip, and plate										

<sup>a</sup> 85% joint efficiency has been used in determining the allowable stress values for welded pipe and tube. Filler metal shall not be used in the manufacture of welded tubing or pipe.

**Table 6.9 Design Stress Intensity Values in Tension for Titanium and Its Alloys<sup>25</sup>**

Form and Specification Number	Grade	Condition	Design Stress Intensity (ksi) for Metal Temperature (°F) Not Exceeding										
			100	150	200	250	300	350	400	450	500	550	600
Sheet, strip, plate, SB-265	1	Annealed	11.7	10.8	9.7	8.6	7.7	6.9	6.4	6.0	5.3	4.7	4.2
	2	Annealed	16.7	16.7	16.7	13.7	12.3	10.9	9.8	8.8	8.0	7.5	7.3
	3	Annealed	21.7	20.8	19.0	17.3	15.6	13.9	12.3	11.1	9.9	8.9	8.0
	7	Annealed	16.7	16.7	16.7	13.7	12.3	10.9	9.8	8.8	8.0	7.5	7.3
Bar, billet, SB-348													
Pipe, SB-337	1	Seamless annealed	11.7	10.8	9.7	8.6	7.7	6.9	6.4	6.0	5.3	4.7	4.2
	2	Seamless annealed	16.7	16.7	16.7	13.7	12.3	10.9	9.8	8.8	8.0	7.5	7.3
Tubing, SB-338	3	Seamless annealed	21.7	20.8	19.0	17.3	15.6	13.9	12.3	11.1	9.9	8.9	8.0
	7	Seamless annealed	16.7	16.7	16.7	13.7	12.3	10.9	9.8	8.8	8.0	7.5	7.3
	1	Weld, annealed <sup>a</sup>	9.9	9.2	8.3	7.3	6.5	5.9	5.4	5.1	4.5	4.0	3.6
	2	Weld, annealed <sup>a</sup>	14.2	14.2	14.2	11.6	10.5	9.3	8.3	7.5	6.8	7.4	6.2
	3	Weld, annealed <sup>a</sup>	18.4	17.7	16.2	14.7	13.3	11.8	10.5	9.4	8.4	7.6	6.8
Forgings, SB-381	7	Weld, annealed <sup>a</sup>	14.2	14.2	14.2	11.6	10.5	9.3	8.3	7.5	6.8	6.4	6.2
	F1	Annealed	11.7	10.8	9.7	8.6	7.7	6.9	6.4	6.0	5.3	4.7	4.2
	F2	Annealed	16.7	16.7	16.7	13.7	12.3	10.9	9.8	8.8	8.0	7.5	7.3
	F3	Annealed	21.7	20.8	19.0	17.3	15.6	13.9	12.9	11.1	9.9	8.9	8.0
	F7	Annealed	16.7	16.7	16.7	13.7	12.3	10.9	9.8	8.8	8.0	7.5	7.3

<sup>a</sup> A quality factor of 0.85 has been applied in arriving at the design intensity values for this material. Filler metal shall not be used in the manufacture of welded tubing or pipe.

2. Blanks should be profiled and cleaned.
3. Cleanliness should be maintained on the dies and blanks.
4. Room-temperature deformations should be held to 8% maximum on a single draw before annealing.
5. Proper lubrication, preferably using dry-film types with antigalling constituents, should be applied to blanks.
6. The large amount of springback should be considered.

Hot drawing of titanium is capable of resulting in deeper draws, lower loads, and less distortion. The recommended drawing temperature ranges are 200–300°C for commercially pure titanium and 500–650°C for titanium alloys, such as Ti–6 Al–4 V.

### 6.5.3 Bending

Titanium can be bent with press brake equipment used for cold-forming stainless steels. The minimum bend radii for bending various titanium alloys through an angle of 105° are given in Table 6.10. More severe bends can be accomplished at 200°C or higher temperatures depending on the alloy and the bend required. The amount of springback decreases with increasing temperature. For bending operations above 550°C, a descaling operation may be necessary to remove the surface oxide layer.

Titanium tubes (<25 mm outside diameter) can be bent at a radius equal to two to three times the outside diameter of the tube. For tubes with an outside diameter larger than 25 mm, larger bend radii are recommended for room-temperature bending. Tighter bends can be obtained by heating the tube above 200°C. Owing to the low modulus, titanium has a tendency to buckle under compressive stress. Therefore, it is recommended that both the inside and outside surfaces of the bend be subjected to tension to avoid buckling.

### 6.5.4 Cutting and Grinding

Titanium can be sheared, flame cut, saw cut, and abrasive cut. Sheared edges should be examined for cracks for plates over 9.5 mm thick. Flame-cut edges are recommended with oxygen and carbon. It is recommended that at least 1.6 mm below the surface (measured from the lowest point of the cut roughness) be removed by grinding or machining. Thick plates may require removal of additional thickness. Generous amounts of coolant should be used in saw cutting and abrasive cutting to keep the workpiece cool and to minimize sparking. Water or water-soluble oil is recommended.

Abrasive grinding can be used on titanium, but care should be taken to avoid excessive heat buildup and contamination. The temperature of the grinding sparks is very high and precautionary measures should be taken accordingly.

### 6.5.5 Welding

Commercially pure titanium and most titanium alloys can be readily welded using the gas metal-arc (GMA) or gas tungsten-arc (GTA) welding process. Owing to titanium's highly reactive nature, the welding processes involving a noninert gas or a flux, such as, oxyacetylene-shielded metal arc, flux-cored arc, and submerged arc welding, are not suitable. For the same reason, welding titanium requires a clear environment and good inert-gas shielding in either GMA or GTA welding.

**Table 6.10 Minimum Bend Radius for Annealed Titanium Sheet (ASTM B-265)**

Grade	Minimum Bend Radius <sup>a</sup>	
	Under 1.8 mm Thick	1.8–4.75 mm Thick
1	1.5 $t$	2.0 $t$
2	2.0 $t$	2.5 $t$
3	2.0 $t$	2.5 $t$
4	2.5 $t$	3.0 $t$
5	4.5 $t$	5.0 $t$
6	4.0 $t$	4.5 $t$
7	2.0 $t$	2.5 $t$
10	3.0 $t$	3.0 $t$
11	1.5 $t$	2.0 $t$
12	2.0 $t$	2.5 $t$

<sup>a</sup> In multiples of sheet thickness,  $t$ , for room-temperature bending through and angle of 105°.

Common joint designs can be used for welding titanium as long as the design allows proper inert-gas shielding. The joint surfaces must be clean and free of grease, oil, moisture, visible oxides, and other contaminants. The oxides can be removed by grinding, brushing with a stainless-steel wire brush, or pickling in a room-temperature solution containing 30% nitric acid and 3% hydrofluoric acid, by weight.

A primary shield is needed for the molten weld puddle and a trailing secondary shield for the solidified weld deposit and the heat-affected zone. In addition, a backup shield is also needed for the backside of the weld and the heat-affected zone. Argon is generally preferred to helium for primary shielding because of better arc stability. Argon-helium mixtures can be used in some conditions where high voltage and deep penetration are desired. Either argon or helium can be used in the secondary and backup shielding.

The mechanical properties of the welds depend on the alloying elements. The welds generally have higher strength but less ductility than the parent metals as shown in Table 6.11.

Other than the GTA and GMA welding processes, titanium can also be welded by electron beam, resistance, plasma arc, and friction welding. In general, titanium cannot be welded with a dissimilar metal owing to the fact that it forms brittle intermetallic compounds with most other metals. Mechanical joining is recommended when joining titanium with a dissimilar metal.

## 6.6 SPECIFICATIONS, STANDARDS, AND QUALITY CONTROL

The alloys of titanium have compositional specifications tabulated by ASTM. The ASTM specification number is given in Table 6.3 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. Each aircraft company has its own set of alloy specifications.

The alloy name in the United States usually includes a company name or trademark in conjunction with the composition for alloyed titanium or the strength (ultimate tensile strength for TMCA and yield strength for other U.S. producers) for unalloyed titanium. The common alloys and company designations are shown in Table 6.12.

**Table 6.11 Comparison in Tensile Properties Between Weld and Parent Metal of Titanium Alloys<sup>26</sup>**

Alloy	Condition	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)
Grade 1	Parent metal	215	315	50.4
	Single-bead metal	255	345	37.5
	Multiple-bead weld	270	365	37.7
Grade 2	Parent metal	325	460	26.2
	Single-bead weld	380	505	18.3
	Multiple-bead weld	385	510	13.3
Grade 3	Parent metal	395	545	25.9
	Single-bead weld	475	605	15.5
	Multiple-bead weld	480	615	14.7
Grade 4	Parent metal	530	660	22.3
	Single-bead weld	580	695	16.4
	Multiple-bead weld	585	710	16.0
Grade 5	Parent metal	945	1000	11.0
	Single-bead weld	920	1060	3.5
	Multiple-bead weld	945	1090	3.2
Grade 6	Parent metal	805	850	15.7
	Single-bead weld	770	920	9.8
	Multiple-bead weld	820	935	7.5
Grade 9	Parent metal	670	705	15.2
	Single-bead weld	600	705	12.7
	Multiple-bead weld	625	745	11.2
Ti-8 Al-1 Mo-1 V	Parent metal	1020	1060	15.0
	Single-bead weld	930	1085	5.5
	Multiple-bead weld	960	1115	3.2
Ti-6 Al-6 V-2 Sn	Parent metal	1005	1060	9.8
	Single-bead weld	1255	1295	0.3
	Multiple-bead weld	—	1280	0.1

**Table 6.12 Company Names of Common Titanium Alloys<sup>2,7,9</sup>**

Alloys	ASTM	Cabot	IMI <sup>a</sup>	RMI	Timet	USSR
99.5 Ti	grade 2	CABOT Ti 40	IMI-125	RMI 40	Ti-50 A	VT1-0
99.2 Ti	grade 3	CABOT Ti 55	IMI-130	RMI 55	Ti-65 A	VT1
99.0 Ti	grade 4	CABOT Ti 70	IMI-155	RMI 70	Ti-75 A	VT1-1
Ti-5 Al-2.5 Sn	grade 6		IMI-315	RMI 5 Al-2.5 Sn	Ti-5 Al-2.5 Sn	VT5-1
Ti-6 Al-4 V	grade 5	CABOT Ti-6 Al-4 V	IMI-317	RMI 6 Al-4V	Ti-6 Al-4 V	VT6

<sup>a</sup> IMI = IMI Limited, Witton, Birmingham, UK.

Since titanium alloys are used in a variety of applications, several different material and quality standards are specified. Among them are ASTM, ASME, ASM, 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. For more stringent applications, yttrium may also be specified. In addition, control of the thermomechanical processing and subsequent heat treatment is vital to obtaining desired properties. For extremely critical applications, such as rotating parts in aircraft gas turbines, raw materials, melting parameters, chemistry, thermomechanical processing, heat treatment, test, and finishing operations must be carefully and closely controlled at each step to ensure that required characteristics are present in the products supplied.

### 6.7 HEALTH AND SAFETY FACTORS

Titanium and its corrosion products are nontoxic. A safety problem does exist with titanium grindings, turnings, and some corrosion products which are pyrophoric. 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 and, if a fire occurs, it must be extinguished with a class D extinguisher (for use against metal fires). The larger the surface area, the more pyrophoric the titanium fines. When titanium equipment is being worked on, all flammable products and corrosive products must be removed, and the area must be well ventilated. A pyrophoric corrosion product has been observed in environments or dry  $\text{Cl}_2$  gas and in dry red fuming nitric acids.

### 6.8 USES

Titanium is primarily used in the form of high-purity titanium oxide. Although the principal application of high-purity (pigment-grade)  $\text{TiO}_2$  is in paint pigments, other important uses are in plastics (for color in floor-covering products and to help protect plastic products and foodstuffs contained in plastic bags from ultraviolet radiation deterioration), in paper (as a filler and whitener), and in rubber. Future application areas include  $\text{TiO}_2$  single-crystal electrodes for water decomposition for the production of hydrogen fuel, flue-gas denitrification catalysts, and high-purity  $\text{TiO}_2$  to make barium titanate thermistors.

Titanium metal was first established as a material for aerospace, "metal-for-air" applications. In the late 1970s, it was developed as "metal-for-sea" uses. The metal-for-air and metal-for-sea designations characterize Japanese market development goals. In terms of volume, the U.S. titanium industry is still in the metal-for-air development stage; the statements about metal-for-earth and -sea reflect an optimistic outlook.

In the United States, the high strength-to-weight ratio of titanium accounts for approximately 70% of its uses. Before 1970, the high strength-to-weight ratio was the basis of over 90% of applications, such as engines, where the advantage of light weight is translated to higher flying, faster planes. Aerospace applications have shaped and controlled the titanium-metal industry.

The use of titanium in aircraft is divided about equally between engines and airframes. For engine components, titanium is limited because of temperature constraints at the compressor area where it is used as blades, casings, and disks. In the frame, it is used in bulkheads, firewall, flap tracks, landing-gear parts, wiring pivot structures, fasteners, rotor hubs, and hot-area skins. In the F-15, titanium accounts for about 32% of the structural weight. Design changes and weight savings owing to the use of titanium in Pratt and Whitney's JT3D engine, employed to power Boeing 707 and Douglas DC 8 aircraft, resulted in 42% more takeoff thrust, 13% lower specific fuel consumption, and 18% less weight than the prior JT3C engine.<sup>3</sup>

The other outstanding property of titanium metal is its corrosion resistance, although its use in corrosion-resistance applications in 1980 in the United States was a mere 5000 tons or ~0.001% of the metal used in corrosion-resistance markets. The largest application was heat-exchanger pipes and tubing (~800  $\mu\text{m}$  or 22 gauge welded) for the power industry, and marine and desalination applications, where titanium provides protection against corrosion by seawater, brackish water, and other estuary waters containing high concentrations of chlorides and industrial wastes.

Titanium metal is especially utilized in environments of wet chlorine gas and bleaching solutions, that is, in the chlor-alkali industry and the pulp and paper industries. Here, titanium is used as anodes for chlorine production, chlorine-caustic scrubbers, pulp washers, and  $\text{Cl}_2$ ,  $\text{ClO}_2$ , and  $\text{HClO}_4$  storage and piping equipment.

In the chemical industry, titanium is used in heat-exchanger tubing for salt production, in the production of ethylene glycol, ethylene oxide, propylene oxide, and terephthalic acid, and in industrial wastewater treatment. Titanium is used in environments of aqueous chloride salts ( $\text{ZnCl}_2$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , etc.), chlorine gas, chlorinated hydrocarbons, and nitric acid.

In metal recovery, titanium is used for ore-leaching solutions and as racks for metal plating. The leaching solutions contain  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  with enough ferric or cupric ions to inhibit the corrosion of titanium. In metal-plating applications, titanium is cathodically protected against  $\text{H}_2\text{SO}_4$  and chrome-plating solution corrosion. An important factor in using titanium for metal-plating applications is that the minute amount of dissolved titanium ions does not plate out as an impurity in the coatings.

In oil and gas refinery applications, titanium is used as protection in environments of H<sub>2</sub>S, SO<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub>, caustic solutions, steam and cooling water. It is used in heat-exchanger condensers for the fractional condensation of crude hydrocarbons, NH<sub>3</sub>, propane, and desulfurization products using seawater or brackish water for cooling.

Other application areas include nuclear-waste storage canisters, pacemaker castings, implantations, geothermal equipment, automotive connection rods, and ordnance.

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