We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



186,000

200M



Our authors are among the

TOP 1%





WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



Chapter

Modern Production Methods for Titanium Alloys: A Review

Hamweendo Agripa and Ionel Botef

Abstract

Titanium alloys are advanced structural materials for numerous key engineering applications in medicine (implants), aerospace, marine structures, and many other areas. The novel aspects of application potential for titanium alloys are as a result of their unique properties such as high corrosion resistance, high specific strength, low elastic modulus, high elasticity, and high hardness. This chapter examines the modern methods for production of titanium alloys. The goal of this chapter is to show the process engineers the current methods for production of titanium alloys necessary for modern applications. The chapter also presents the future methods of production for titanium and titanium alloys to meet the future demands of titanium and titanium alloys' products.

Keywords: titanium, titanium alloys, production methods

1. Introduction

Titanium (Ti) is a lustrous metal with a silver color. This metal exists in two different physical crystalline state called body centered cubic (bcc) and hexagonal closed packing (hcp), shown in **Figure 1 (a)** and **(b)**, respectively. Titanium has five natural isotopes, and these are 46Ti, 47Ti, 48Ti, 49Ti, 50Ti. The 48Ti is the most abundant (73.8%).



Figure 1. *Crystalline state of titanium: (a) bcc, and (b) hcp* [8].

Titanium has high strength of 430 MPa and low density of 4.5 g/cm³, compared to iron with strength of 200 MPa and density of 7.9 g/cm³. Accordingly, titanium has the highest strength-to-density ratio than all other metals. However, titanium is quite ductile especially in an oxygen-free environment. In addition, titanium has relatively high melting point (more than 1650°C or 3000°F), and is paramagnetic with fairly low electrical and thermal conductivity. Further, titanium has very low bio-toxicity and is therefore bio-compatible. Furthermore, titanium readily reacts with oxygen at 1200°C (2190°F) in air, and at 610°C (1130°F) in pure oxygen, forming titanium dioxide. At ambient temperature, titanium slowly reacts with water and air to form a passive oxide coating that protects the bulk metal from further oxidation, hence, it has excellent resistance to corrosion and attack by dilute sulfuric and hydrochloric acids, chloride solutions, and most organic acids. However, titanium reacts with pure nitrogen gas at 800°C (1470°F) to form titanium nitride [1, 2].

Some of the major areas where titanium is used include the aerospace industry, orthopedics, dental implants, medical equipment, power generation, nuclear waste storage, automotive components, and food and pharmaceutical manufacturing.

Titanium is the ninth-most abundant element in Earth's crust (0.63% by mass) and the seventh-most abundant metal. The fact that titanium has most useful properties makes it be preferred material of future engineering application. Moreover, the application of titanium can be extended when alloyed with other elements as described below.

2. Titanium alloys

An alloy is a substance composed of two or more elements (metals or nonmetals) that are intimately mixed by fusion or electro-deposition. On this basis, titanium alloys are made by adding elements such as aluminum, vanadium, molybdenum, niobium, zirconium and many others to produce alloys such as Ti-6Al-4V and Ti-24Nb-4Zr-8Sn and several others [2]. These alloys have exceptional properties as illustrated below. Depending on their influence on the heat treating temperature and the alloying elements, the alloys of titanium can be classified into the following three types:

2.1 Type 1: the alpha (α) alloys

These alloys contain a large amount of α -stabilizing alloying elements such as aluminum, oxygen, nitrogen or carbon. Aluminum is widely used as the alpha stabilizer for most commercial titanium alloys because it is capable strengthening the alloy at ambient and elevated temperatures up to about 550°C. This capability coupled with its low density makes aluminum to have additional advantage over other alloying elements such as copper and molybdenum. However, the amount of aluminum that can be added is limited because of the formation of a brittle titanium-aluminum compound when 8% or more by weight aluminum is added. Occasionally, oxygen is added to pure titanium to produce a range of grades having increasing strength as the oxygen level is raised. The limitation of the α alloys of titanium is non-heat treatable but these are generally very weldable. In addition, these alloys have low to medium strength, good notch toughness, reasonably good ductility and have excellent properties at cryogenic temperatures. These alloys can be strengthened further by the addition of tin or zirconium. These metals have appreciable solubility in both alpha and beta phases and as their addition does not markedly influence the transformation temperature they are normally classified as neutral additions. Just like aluminum, the benefit of hardening at ambient

temperature is retained even at elevated temperatures when tin and zirconium are used as alloying elements.

2.2 Type 2: alpha-beta (α - β) titanium alloys

These alloys contain 4–6% of β -phase stabilizer elements such as molybdenum, vanadium, tungsten, tantalum, and silicon. The amount of these elements increases the amount of β -phase is the metal matrix. Consequently, these alloys are heat treatable, and are significantly strengthened by precipitation hardening. Solution treatment of these alloys causes increase of β -phase content mechanical strength while ductility decreases. The most popular example of the α - β titanium alloy is the Ti-6Al-4V with 6 and 4% by weight aluminum and vanadium, respectively. This alloy of titanium is about half of all titanium alloys produced. In these alloys, the aluminum is added as α -phase stabilizer and hardener due to its solution strengthening effect. The vanadium stabilizes the ductile β -phase, providing hot workability of the alloy.

2.2.1 Properties of α - β titanium alloys

The α - β titanium alloys have high tensile strength, high fatigue strength, high corrosion resistance, good hot formability and high creep resistance [3].

2.2.2 Novel application of α - β titanium alloys

Therefore, these alloys are used for manufacturing steam turbine blades, gas and chemical pumps, airframes and jet engine parts, pressure vessels, blades and discs of aircraft turbines, aircraft hydraulic tubing, rocket motor cases, cryogenic parts, and marine components [4].

2.3 Type 3: beta (β) titanium alloys

These alloys exhibit the body centered cubic crystalline form shown in **Figure 1 (a)**. The β stabilizing elements used in these alloy are one or more of the following: molybdenum, vanadium, niobium, tantalum, zirconium, manganese, iron, chromium, cobalt, nickel, and copper. Besides strengthening the beta phase, these β stabilizers lower the resistance to deformation which tends to improve alloy fabricability during both hot and cold working operations. In addition, this β stabilizer to titanium compositions also confers a heat treatment capability which permits significant strengthening during the heat treatment process [4].

2.3.1 Properties of beta (β) titanium alloys

As a result, the β titanium alloys have large strength to modulus of elasticity ratios that is almost twice those of 18–8 austenitic stainless steel. In addition, these β titanium alloys contain completely biocompatible elements that impart exceptional biochemical properties such as superior properties such as exceptionally high strength-to-weight ratio, low elastic modulus, super-elasticity low elastic modulus, larger elastic deflections, and low toxicity [1, 3].

2.3.2 Novel application of beta (β) titanium alloys

The above properties make them to be bio-compatible and are excellent prospective materials for manufacturing of bio-implants. Therefore, nowadays these alloys are

largely utilized in the orthodontic field since the 1980s, replacing the stainless steel for certain uses, as stainless steel had dominated orthodontics since the 1960s [2].

2.4 Summary

Because of alloying the titanium achieve improved properties that make it to be preferred material of choice for application in aerospace, medical, marine and instrumentation. The extent of improvement to the properties of titanium alloys and ultimately the choice of area of application is influenced by the methods of production and processing as discussed in the subsequent sections.

3. Production of titanium

The base metal required for production of titanium alloys is pure titanium. Pure titanium is produced using several methods including the Kroll process. This process produces the majority of titanium primary metals used globally by industry today. In this process, the titanium is extracted from its ore rutile—TiO₂ or titanium concentrates. These materials are put in a fluidized-bed reactor along with chlorine gas and carbon and heated to 900°C and the subsequent chemical reaction results in the creation of impure titanium tetrachloride (TiCl₄) and carbon monoxide. The resultant titanium tetrachloride is fed into vertical distillation tanks where it is heated to remove the impurities by separation using processes such as fractional distillation and precipitation. These processes remove metal chlorides including those of iron, silicon, zirconium, vanadium and magnesium. Thereafter, the purified liquid titanium tetrachloride is transferred to a reactor vessel in which magnesium is added and the container is heated to slightly above 1000°C. At this stage, the argon is pumped into the container to remove the air and prevent the contamination of the titanium with oxygen or nitrogen. During this process, the magnesium reacts with the chlorine to produce liquid magnesium chloride thereby leaving the pure titanium solid. This process is schematically presented in **Figure 2**.





Kroll process for production of titanium: (a) chlorination, (b) fractional distillation [5].

The resultant titanium solid is removed from the reactor by boring and then treated with water and hydrochloric acid to remove excess magnesium and magnesium chloride leaving porous titanium sponge, which is jackhammered, crushed, and pressed, followed by melting in a vacuum electric arc furnace using expendable carbon electrode. The melted ingot is allowed to solidify in a vacuum atmosphere. This solid is often remelted to remove inclusions and to homogenize its constituents. These melting steps add to the cost of producing titanium, and this cost is usually about six times that of stainless steel. Usually the titanium solid undergo further treatment to produce titanium powder required in alloying process. The basic methods used to produce titanium powder are summarized below.

3.1 Armstrong process

The first method is called the Armstrong process, shown in **Figure 3**, in which the powder is made as the product of extractive processes that produce primary metal powder. This process is capable of producing commercially pure titanium (Ti) powder by the reduction of titanium tetrachloride (TiCl₄) and other metal halides using sodium (Na). This process produces powder particles with a unique properties and low bulk density. To improve powder properties such as the particle size distribution and the tap density, additional post processing activities such as dry and wet ball milling are applied. The narrowed particle size distributions are necessary for typical powder metallurgical processes. In addition, the resultant powder's morphology produced by the Armstrong process provide for excellent compressibility and compaction properties that result in dense compacts with increased green strength than those produced by the irregular powder. For this reason, the powders can even be consolidated by traditional powder metallurgy techniques such as uniaxial compaction and cold isostatic pressing. **Figure 4** illustration the scanning electron microscope images of the titanium powders of the



Figure 3. *Illustration of the Armstrong process* [5].

Titanium Alloys - Novel Aspects of Their Manufacturing and Processing



Figure 4. SEM micrographs of CP-Ti produced by Armstrong process [5].



Armstrong process. As seen in the figure, the powder has an irregular morphology made of granular agglomerates of smaller particles.

3.2 The hydride-dehydride process

The hydride-dehydride (HDH) process, illustrated in **Figure 5**, is used to produce titanium powder using titanium sponge, titanium, mill products, or titanium scrap as the raw material. The hydrogenation process is achieved using a batch furnace that is usually operated in vacuum and/or hydrogen atmospheric conditions. The conditions necessary for hydrogenation of titanium are pressure of one atmospheric and temperatures of utmost 800°C. This process results in forming of titanium hydride and alloy hydrides that are usually brittle in nature. These metal



Figure 6. SEM micrographs of CP-Ti produced by HDH [5].

hydrides are milled and screened to produce fine powders. The powder is resized using a variety of powder-crushing and milling techniques may be used including: a jaw crusher, ball milling, or jet milling. After the titanium hydride powders are crushed and classified, they are placed back in the batch furnace to dehydrogenate and remove the interstitial hydrogen under vacuum or argon atmosphere and produce metal powder. These powders are irregular and angular in morphology and can also be magnetically screened and acid washed to remove any ferromagnetic contamination. Finer particle sizes can be obtained, but rarely used because oxygen content increases rapidly when the powder is finer than -325 mesh. Powder finer than -325 mesh also possess more safety challenges [5]. The powder can be passivated upon completion of both the hydrogenating and dehydrogenating cycles to minimize exothermic heat generated when exposed to air.

The hydride-dehydride process is relatively inexpensive because the hydrogenation and dehydrogenation processes contribute small amount of cost to that of input material. The additional benefit of this process is the fact that the purity of the powder can be very high, as long as the raw material's impurities are reduced. The oxygen content of final powder has a strong dependence on the input material, the handling processes and the specific surface area of the powder. Therefore, the main disadvantages of hydride-dehydride powder include: the powder morphology is irregular, and the process is not suitable for making virgin alloyed powders or modification of alloy compositions if the raw material is from scrap alloys (**Figure 6**) [5].

4. Conventional methods of production for titanium alloys

4.1 Powder metallurgy

Conventional sintering, shown in **Figure 7**, is one of the widely applied powder metallurgy (PM) based method for manufacturing titanium alloys. In this method, the feedstock titanium powder is mixed thoroughly with alloying elements mentioned in Section 2 using a suitable powder blender, followed by compaction of the mixture under high pressure, and finally sintered. The sintering operation is carried out at high temperature and pressure treatment process that causes the powder



particles to bond to each other with minor change to the particle shape, which also allows porosity formation in the product when the temperature is well regulated. This method can produce high performance and low cost titanium alloy parts. The titanium alloy parts produced by powder metallurgy have several advantages such as comparable mechanical properties, near-net-shape, low cost, full dense material, minimal inner defect, nearly homogenous microstructure, good particle-to-particle bonding, and low internal stress compared with those titanium parts produced by other conventional processes [7].

4.2 Self-propagating high temperature synthesis

Self-propagating high temperature synthesis (SHS), shown in **Figure 8**, is another PM based process used to produce titanium alloys. The steps in this process include: mixing of reagents, cold compaction, and finally ignition to initiate a spontaneous self-sustaining exothermic reaction to create the titanium alloy [7].

Although the above PM processes are mature technologies for fabrication of bone implants they have difficulties of fabricating porous coatings on surfaces that are delicate or with complex geometries. In addition, these processes tend to produce brittle products because of cracks and oxides formed inside the materials. Further, the high costs and poor workability associated with these PM processes restrict their application in commercial production of bone implants. Consequently, new methods, based on additive manufacturing principles were developed [7].



Figure 8. SHS process [7].

5. Advanced methods for production of titanium alloys

The definitions of advanced methods of production is the use of technological method to improve the quality of the products and/or processes, with the relevant technology being described as "advanced," "innovative," or "cutting edge." These technologies evolved from conventional processes some of which have been developed to achieve various components of titanium base alloys and aluminides. Atomisation processes are among the most widely used cutting edge methods for production of titanium alloys [5].

5.1 Atomisation

Atomisation processes are used to make alloyed titanium powders. In these processes, the feedstock material is generally titanium, and the alloy powders produced are further processed typically to manufacture components using processes such as hot isostatic pressing (hip). As mentioned previously, it is generally believed that alloyed powders are not suitable for cold compaction using conventional uniaxial die pressing methods. Moreover, the inherent strength of the alloyed powders is too high, making it difficult to deform the particles in order to achieve desired green density. The atomisation processes produce relatively spherically shaped titanium alloy powders that are most suitable for additive manufacturing using techniques such as selective laser melting or electron beam melting. These spherical powders are also required for manufacturing titanium components using metal injection molding techniques. Typically, additive manufacturing and metal injection molding processes require particle sizes of powders to be in the range of 100 µm to ensure good flowability of the powder during operations. However, the challenge of the atomisation processes usually is that powders produced tend to have a wide particle size distribution, from a few to hundreds of micrometers. Examples of atomisation processes are gas atomisation and plasma atomisation processes described below [5].

5.1.1 Gas atomisation process

In the gas atomisation process, shown in **Figure 9**, the metal is usually melted using gas and the molten metal is atomised using an inert gas jets. The resultant fine metal droplets are then cooled down during their fall in the atomisation tower. The metal powders obtained by gas-atomization offer a perfectly spherical shape



Figure 9. Schematic diagrams of gas atomisation process [5].

Titanium Alloys - Novel Aspects of Their Manufacturing and Processing



Figure 10. Schematic diagrams of plasma atomisation process [5].

combined with a high cleanliness level. However, even though gas atomisation is, generally, a mature technology, its application need to be widened after addressing a few issues worth noting such as considerable interactions between droplets while they cool during flight in the cooling chamber, causing the formation of satellite particles. Also, due to the erosion of atomising nozzle by the liquid metal, the possibility for contamination by ceramic particles is high. Usually, there may also be argon gas entrapment in the powder that creates unwanted voids [5].

5.1.2 Plasma atomisation process

Plasma atomisation, shown in **Figure 10**, uses a titanium wire alloy as the feed material which is a significant cost contributing factor. The titanium alloy wire, fed via a spool, is melted in a plasma torch, and a high velocity plasma flow breaks up the liquid into droplets which cool rapidly, with a typical cooling rate in the range of $100-1000^{\circ}$ C/s. Plasma atomisation produces powders with particle sizes ranging from 25 to 250 µm. In general, the yield of particles under 45 µm using the plasma wire atomisation technique is significantly higher than that of conventional gas atomisation processes [5].

6. Future methods for production of titanium alloys

The future methods for production of titanium alloys depend on the demand of these products and to what extend nature will be able to provide them. The demand for titanium alloys shall also influence the number and type of technological breakthroughs, the extent of automation, robotics' application, the number of discoveries for new titanium alloys, their methods of manufacturing, and new areas of application. Automation is an important aspect of the industry's future and already a large percentage of the manufacturing processes are fully automated. In addition, automation enables a high level of accuracy and productivity beyond human ability—even in hazardous environments. And while automation eliminates some of the most

tedious manufacturing jobs, it is also creating new jobs for a re-trained workforce. The new generation of robotics is not only much easier to program, but also easier to use due to extra capabilities such as voice and image recognition during operations, they are capable of doing precisely what you ask them to do. The discovery of new titanium alloys, or innovative uses of existing ones, is essential for making progress in many of the technological challenges we face. This discovery can result in new synthesis methods of new alloy compounds and design of super alloys, theoretical modeling and even the computational prediction of titanium alloys. This discovery requires that new methods of manufacturing are developed. In light of this, "additive manufacturing" is being developed and this is viewed as a groundbreaking development in manufacturing advancement that offers manufacturers powerful solutions for making any number of products cost-effectively and with little waste. Examples of additive manufacturing technologies are cold spray, 3-D printing, electron beam melting, and selective laser melting. To fabricate alloy surfaces using these technologies, alloying elements are mixed thoroughly in the feedstock powder and the fabrication processes proceed as described in the following paragraphs [7, 8].

6.1 Cold spray

Cold spray (CS) process, schematically shown in Figures 11 and 12 can deposit metals or metal alloys or composite powders on a metallic or dielectric substrate using a high velocity (300-1200 m/s) jet of small $(5-50 \mu \text{m})$ particles injected in a stream of preheated and compressed gas passing through a specially designed nozzle. The main components of a generic CS system include the source of compressed gas, gas heater, powder feeder, spray nozzle assembly, and sensors for gas pressure and temperature. The source of compressed gas acquires the gas from an external reservoir, compresses it to desired pressure and delivers it into the gas heater. Then, the gas heater preheats the compressed gas in order to increase its enthalpy energy. The preheated gas is delivered into the spray nozzle assembly whose convergent/divergent geometry not only converts the enthalpy energy of the gas into kinetic energy but also mixes the metal powders with the gas proportionately. The powder feeder meters and injects the powder in the spray nozzle assembly. The sensors for the gas pressure and temperature are responsible for regulating the preset pressure and temperature of the gas stream. The powder injection point in the spray nozzle assembly, the gas pressure, and gas temperature distinguish the low pressure-CS system (LP-CS) from the high pressure CS (HP-CS). In the LP-CS



Figure 11. Low pressure CS process configuration [8].



Figure 12. High pressure CS process configuration [8].

Parameters	HP-CS	LP-CS
Working gas	nitrogen, air, helium	nitrogen, air, helium
Gas pressure, Mpa	0.5 - 5.0	0.5 - 1.7
Gas temperature, °C	20 - 1000	20 - 600
Gas flow rate, m^3/h	2 - 200	15 - 78
Maximum gas match no.	1 - 3	1 - 3
Powder flow rate, g/s	0.1 - 2.0	0.1 - 1.0
Particle size, μm	5 - 100	5 - 50

Table 1.

Operation parameters for CS systems [8].

system, the feedstock powder is injected in the downstream side of the convergent section of the nozzle assembly, while in the HP-CS system; the powder is injected in the upstream side of the convergent/diverging section of the nozzle assembly as illustrated in **Figures 11** and **12**. Several other parameters which contribute towards the distinguishing of the CS systems are summarized in **Table 1** [8].

6.23-D printing

3-D printing is an additive manufacturing method that applies the principle of adding material to create structures using computer aided design (CAD), part modeling, and layer-by-layer deposition of feedstock material. This cutting-edge technology is also called stereolithography, and is illustrated in **Figure 13** [8].

In this technology, the pattern is transferred from a digital 3D model, stored in the CAD file, to the object using a laser beam scanned through a reactive liquid polymer which hardened to create a thin layer of the solid. In this manner, the structure is fabricated on the desired surface. This method was proved in the laboratory setup is still being integrated in commercial set-up because 3-D printing is the most widely recognized version of additive manufacturing. For this reason, the inventors and engineers for this process have for years used machines costing anywhere from a few thousand dollars to hundreds of thousands for rapid prototyping of new products. It can be noted that all of the additive-manufacturing processes follow



Figure 14. *Electron beam melting method* [1].





this same basic layer-by-layer deposition principle but with slightly different ways such as using powdered or liquid polymers, metals, metal-alloys or other materials to produce a desired product [8].

6.3 Electron beam melting

Electron beam melting (EBM), shown in **Figure 14**, is one of the additive manufacturing processes which fabricated titanium coatings by melting and deposition of metal powders, layer-by-layer, using a magnetically directed electron beam. Though this method was proved to be successful, it has high set-up costs due to the requirement of high vacuum atmosphere [7].

6.4 Selective laser melting

Selective laser melting (SLM), shown in **Figure 15** is the second additive manufacturing method for titanium alloy coatings which completely melt the powder using a high-power laser beam. Similarly, this method is costly because it requires advanced high rate cooling systems. Moreover, the fluctuations of temperatures during processing negatively affect the quality of the products [1].

7. Conclusion

This chapter described the titanium as a metal that exists naturally with two crystalline forms. The chapter highlighted the properties of titanium metal that influence its application. The fact that titanium has advantageously unique properties that can be improved by alloying with other elements makes it to be preferred engineering material for future application in such areas as biomedical implants, aerospace, marine structures, and many others. The chapter discussed the traditional, current and future methods necessary to produce structures using titanium and titanium alloys. Further, the chapter suggested "additive manufacturing methods" as advanced methods for future manufacturing because they offer powerful solutions for making any type and number of products cost-effectively and with little waste. The examples of these methods are cold spray, 3-D printing, electron beam melting, and selective laser melting. Finally, the various processes used during fabrication of alloys using these methods were also presented.

Author details

Hamweendo Agripa and Ionel Botef*

1 Evelyn Hone College, Lusaka, Zambia

2 School of Mechanical Industrial and Aeronautical Engineering, University of the Witwatersrand, Johannesburg, South Africa

*Address all correspondence to: ionel.botef@wits.ac.za

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

[1] Sidambe AT. Biocompatibility of advanced manufactured titanium implants a review. Materials. 2014;7(12):8168-8188

[2] Yang R, Hao Y, Li S. Development and application of low-modulus biomedical titanium alloy Ti2448. Biomedical Engineering Trends. 2011;**10**:225-247

[3] Elahinia MH, Hashemi M, Tabesh M, Bhaduri SB. Manufacturing and processing of NiTi implants: A review. Progress in Materials Science. 2012;**57**:911-946

[4] Kopeliovich D. Titanium Alpha-Beta Alloys; 2018

[5] Fang ZZ, Paramore JD, Sun P, Chandran KSR, Zhang Y, Xia Y, et al. Powder metallurgy of titanium—Past, present, and future. International Materials Reviews. ISSN: 0950-6608 (Print) 1743-2804 (Online). Available from: http://www.tandfonline.com/loi/ yimr20

[6] Ovchinnikov A, Smolyak Y, Dzhugan A, Yunusov E, Ianko T, Panov S. Technology of New Generation Titanium Alloys Powder for Additive Technology; 2018. pp. 101-107

[7] Hamweendo A, Malama T, Botef I. Titanium-nickel alloys for bone tissue engineering application via cold spray. In: International Conference on Competitive Manufacturing COMA16. Vol. 2016. Stellenbosch, South Africa. pp. 273-279

[8] Hamweendo A. Fabrication of porous structures using cold gas dynamic spray technology [thesis]. Johannesburg, South Africa: University of the Witwatersrand; 2017. pp. 1-198

15