Management Systems
in
Production Engineering

2013, No 4 (12), pp 15-19

VERSATILE APPLICATIONS OF TITANIUM INCLUDING THE MEDICAL ASPECTS

Marta MIERZWA
Silesian University in Katowice

Abstract:
This article provides a review of the titanium as a material with a wide range of applications. There will be presented both lit. analysis as well as some results of my own research. In the publication will be discussed the relevant properties of titanium and expensive process for its preparation.

Key words: *titanium, titanium alloys and compounds, applications of titanium, biomaterials*

INTRODUCTION

Titanium (Ti – titanium) is the twenty-second chemical element lying in the periodic table between scandium and vanadium. Titanium is the transitory metal, and its oxides show ampholytic proprieties. Titanium atomic mass equals 47.867u, and density 4507 kg/m^3. Characteristic temperatures – melting and boiling – they carry out suitably: 1668°C and 3287°C. All parameters given relate to normal conditions (pressure 1013.25 hPa) [1].

Titanium is light and it has high mechanical resistance and resistance to corrosion. It can be added to the iron, aluminum, vanadium, molybdenum and other alloys. Titanium alloys are used in air industry (jet-propelled engines), military, automotive, medical (artificial limb dentists, orthopaedic clamps), metallurgical processes. This chemical element was discovered by William Gregor in 1791, and the name coming from the name of god from Greek mythology gave Martin Heinrich Klaproth. He affirmed that rutile contained new chemical element and decided to name it titanium.

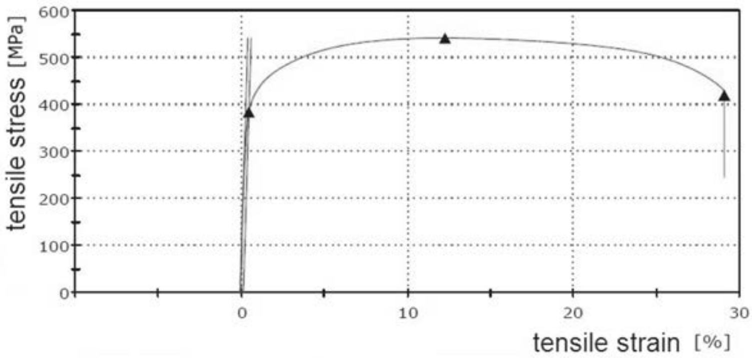
Titanium occurs in the earthly shell in quantities about 0.61%, and its mineral forms are widespread in the Earth. Its common compound – the titanium dioxide – is used in production of white pigments, e.g. the titanic whiteness which is the only pigment of titanium dioxide produced in Poland and is useful for producing: paper, food, artificial materials, cosmetics, ,porcelain, paints, enamels and as the stabiliser of the color of glazes. Another compound including the titanium is titanium tetrachloride used to smoke curtains and as the catalyst. There are two allotropic varieties of titanium, which will be discussed later in this article. Physicochemical properties of titanium are similar to zirconium.

Over the years, people attempted to obtain pure titanium, however, failed to do so by the usual methods of heating in the presence of carbon monoxide, because they arose titanium carbide instead of the expected reduction of the metal oxide. In 1910, Matthew A. Hunter reached clean (99.9%) titanium metal by heating $TiCl_4$ with sodium in a steel bomb at 700-800°C. But it was William Justin Kroll who developed as a cost-effective method for the preparation of titanium metal by reducing titanium tetrachloride with magnesium. This technology was named after his last name – Kroll process. Despite research on cheaper and more efficient process for obtaining titanium, Kroll process is still used for commercial extract the metal.

Titanium of very high purity managed to get by a team of Anton Eduard van Arkel and Jan Hendrik de Boer in the iodide already in 1925. Titanium is refined in a vacuum in a closed reactor. Iodine vapor react with titanium and form a technical titanium tetrachloride, which further decomposes into a resistively heated tungsten thin wire, and thickens it during the process.

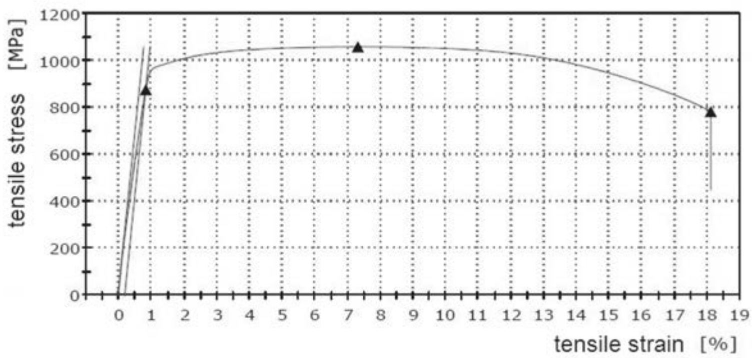
In the 50's and 60's last century, the Soviet Union pioneered the use of titanium for military purposes (such as submarines). Meanwhile, titanium has been widely used in military aircraft, particularly high performance jets engine. In the United States Department of Defense realized the great importance of titanium and began stocking the metal throughout the Cold War.

The most important information on the titanium was presented above, so we can move on to more detailed analysis presented in the next section. The next point will describe the properties of titanium divided into physical and chemical. Then will be a brief mention about the occurrence and preparation of titanium, and the last two points will be dedicated to the typical applications of titanium.



	Rm [MPa]	Strain [%]	R0,2 [MPa]
1	541,0	12,2	384,1

Fig. 1 Tensile curve for pure titanium of Class II (Grade 2)



	Rm [MPa]	Strain [%]	R0,2 [MPa]
1	1 056,8	7,3	875,2

Fig. 2 Tensile curve for titanium alloy Ti-6Al-7NB

PROPERTIES

Physical Properties

Titanium is a metallic element which is known for its high mechanical strength compared to the low weight. It is lightweight (density 4507 kg/m³), and at high purity are ductile (especially in a reducing atmosphere). Characterized by a high melting point: 1668°C. It is shiny, has a white metallic color. Commercial purity titanium 99.2% has a tensile strength of 434 MPa, as it is similar to metal alloys, but which is lighter than about 45%, while it is 60% heavier than aluminum. Tensile strength decreases when heated above the temperature of 430°C. Titanium has a high hardness (but not equal to some hardened steels), there are also difficulties in the treatment.

Metal comes in two allotropic forms α and β: α-Ti form - is stable to a temperature of 882°C, crystallizes in a hexagonal A3, Ti-β – stable than the melting point of 882°C to 1668°C and crystallizes in the regular system of spatially centered A2. The second variant has better flow properties and, therefore is suitable for mechanical processing.

As shown in these graphs (Fig. 1, 2), in the case of an alloy (due to alloying elements) mechanical resistance increases nearly doubled.

Chemical Properties

The most common chemical property of titanium is its excellent corrosion resistance, comparable to platinum. It is also resistant to the action of dilute acids such as sulfuric acid, hydrochloric acid and most of the organic acid, chlorine gas, and alkaline solutions or seawater. Pure titanium can be digested only concentrated acids. It is also one of the few elements that rapidly react with pure nitrogen. The reaction takes place above the temperature of 800°C and takes the form of titanium nitride. It is paramagnetic and has a relatively low conductivity, both electrical and thermal energy.

By the contact with oxygen, titanium is formed on the surface passivating titanium oxide layer having a thickness of approximately 2 nm. This layer also increases the resistance to corrosion.

OCCURRENCE AND RECEIVING TITANIUM

Occurence of titanium

Titanium usually occurs in ores of other elements. As far as the occurrence is concerned it is ranked as the ninth position in the world and seventh as a metal. The most common is in igneous rocks and sedimentary rocks. It is widespread and occurs mainly in the form of minerals anatase, brookite, ilmenite, perovskite, rutile, titanite, and in many iron ores. Of these minerals, only ilmenite and rutile play a very important role. Significant deposits of titanium can be found in western Australia, Canada, New Zealand, Norway and Ukraine, while large quantities of rutile are used in North America and South Africa, as illustrated in the graph above (Fig. 3). The annual production is about 90 000 tons of metal and 4.3 million tons of titanium dioxide. The total titanium resources on Earth are estimated at over 600 million tons. Titanium is also present in meteorites, his presence was noted even on the Sun.

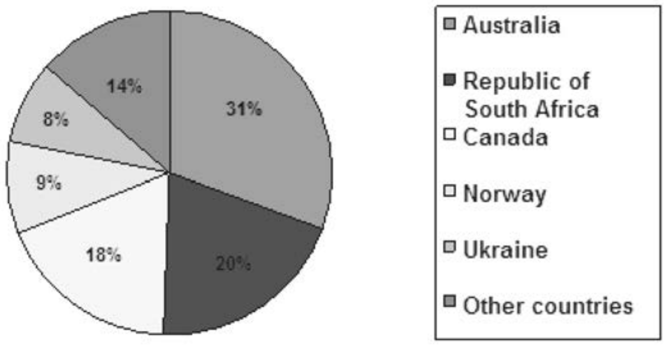


Fig. 3 Major producers of titanium in the world

Preparation of titanium

Process for the preparation of metallic titanium using the Kroll method includes five essential steps:

1) processing of titanium ore,
2) obtaining a titanium tetrachloride - $TiCl_4$,
3) reduction of $TiCl_4$ with magnesium,
4) the process of iodide, the purification of titanium,
5) melting titanium.

Titanium is reacted with oxygen at high temperatures, therefore it is not extracted by reduction of titanium dioxide. Despite the high cost, Kroll process is still used. The reactions taking place during this process:

$$2TiFeO_3 + 7Cl_2 + 6C\ (900°C) \rightarrow 2TiCl_4 + + 6CO\ 2FeCl_3$$

$$TiCl_4 + 2Mg\ (1100°C) \rightarrow 2MgCl_2 + Ti$$

A major problem is the melting process of titanium, because of its high melting point - 1668°C, and also titanium is chemically active at this temperature. Currently, melting is carried out in electric inductive, plasma and electrone furnrnaces.

COMPOUNDS AND TITANIUM ALLOYS – EXAMPLES OF NON-MEDICAL APPLICATIONS

Titanium dioxide (TiO_2 is in powder form) is the most common compound of titanium, which has a very wide range of possible applications. One of them is the steel industry – production of electrodes and alloys. Quite important role is played by the titanium dioxide in paint industry because it gives an intense white color, and for papermaking industry – high quality white paper. It is used as a pigment in paints (resistant to low temperatures and humid and salty environment), paper, and even toothpaste. Its non-toxicity allows it to be used in the production of glass fibers, and even in the food industry (E171 dye). It can be added to the cement, and well suited to the air-purifying filter or UV protection. In nature, titanium dioxide is present in the form of minerals include anatase, brookite and rutile. These minerals are soft, but durable. Rutile has a thermal stability, high refractive index, high hardness and Young's modulus [2].

Titanium dioxide is widely used – use of optical and protective – because of their high transparency, mechanical stability and chemical stability in aqueous solutions [2].

Titanium nitride (TiN) is used for coating cutting molding, slip tools. Even a small TiN layer with a thickness of 0.5 microns contributes to increased surface hardness up to 2400 HV and time-covered gear extended several times. TiN coatings can also be plasma sprayed on the working parts of turbine blades and engines.

Titanium tetrachloride ($TiCl_4$) is a colorless liquid, used for the production of titanium dioxide or titanium in the Kroll process.

Titanium carbide (TiC) was applied to the tool industry, aerospace and nuclear energy, as well as diamond-carbide composites for the cutting blade.

Barium titanate ($BaTiO_3$) is used in ultrasonic devices, microphones and devices to ignite the gas in a microwave oven.

Strontium titanate ($SrTiO_3$) is used in the manufacture of glass with a high refractive index - the lenses, prisms and jewelry.

Sodium titanate (Na_2TiO_3) is a component to cover the welding rods.

Maraging steel (MS) containing 20-25% Ni with additions 1.3-1.6% Ti, 0.15-0.30% Al, 0.3-0.5% Nb.

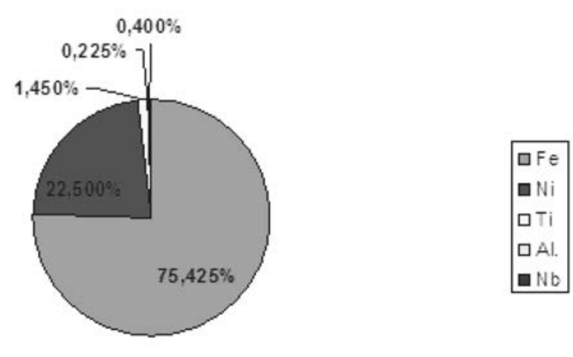


Fig. 4 Average percentage composition of maraging steel sample

Titanium in the alloy such as maraging steel is a component of strengthening (Fig. 4). These steels are used in the construction of spaceships in aviation – landing gear, fighter aircraft design, in the armaments industry (gun barrels and firearms).

Titanium and its alloys are ideal for the production of sports equipment, as they give the opportunity to achieve high strength with the minimum weight of the product, such as: equipment for mountaineering, bicycle frames, tennis rackets, skis, golf clubs and hockey, and even fishing equipment.

Titanium was also brought to jewelry – for wedding rings, earrings, bracelets and watches that do not cause allergic reactions and do not damage under the influence of the water environment.

Titanium alloy of aluminum and vanadium (Ti-6Al-4V), and alloys with other additives are found in engines and covering of aircraft (Table 1), such as engine Concorde.

Table 1
The titanium content in the sample types of aircraft

Type of aircraft	Titanium kontent in tons
Boeing 777	58
Boeing 747	43
Boeing 737	18
Airbus A340	24
Airbus A330	17
Airbus A320	12
Airbus A380	77
Ił-86	20

THE USE OF TITANIUM IN MEDICINE

A large subgroup of biomaterials are metallic biomaterials, which include: 316L steel, Co-Cr-Mo alloy and titanium alloys [3]. The properties of the latter can be shaped by the selection and implementation of appropriate surface treatment. Titanium alloys are most commonly used to perform bolts and clamps acetabular prostheses, as they ensure lightness but also strength.

Pure titanium (commercially pure – which contains small amounts of elements such as oxygen, nitrogen, carbon, hydrogen, and depending on the degree of oxygen pure titanium is divided into four classes) can also be used in medicine, particularly for the production of porous layers applied to the prostheses' mandrels and for the manufacture of dental implants. Technical titanium is mainly used in surgical implants.

On the market there are six main forms of titanium – four classes of pure titanium and two alloys, all of which are made implants:

- Class I pure titanium (cp I)
- Class II pure titanium (cp II)
- Class III pure titanium (cp III)
- Class IV pure titanium (cp IV)
- Ti-6Al-4V,
- Ti-6Al-4V (ELI – extra low interstitial).

Titanium Class I, II and III are used rarely, mainly due to the low mechanical resistance. The most common material is a titanium alloy α + β Ti-6Al-4V with 6% of aluminum (Al) and 4% of vanadium (V), because it provides a good composition properties such as corrosion resistance, mechanical resistance and flexibility. Implants made from this alloy have better structural stability than those from pure titanium and may be exposed to higher mechanical loads. This is often used in the form ELI of the alloy that has a lower content of interstitial elements, iron, hydrogen and oxygen, and thus improved corrosion resistance, although at the expense of durability. ELI form is used for the production of strongly exposed occlusal force connection elements implants, less for the manufacture of the whole implant. ELI alloy is sometimes also called Titanium class V, which falsely suggests that we are dealing with a pure titanium rather than its alloy.

Examples of medical applications of titanium alloys:

- Dental prosthetics – due to the low thermal conductivity, high hardness, mechanical strength and durability, as well as the lack of an allergic reaction and resistance to corrosion. There is the possibility of occlusion treatment of children by properly inserts made from alloys having shape memory effect, and comprising titanium in its composition. In dentistry, titanium initially used mainly in the form of finished manufactured goods (implants). The rapid development of technology has given the opportunity to perform with it most of the building restorations, such as inlays and onlays, crowns and telescopic crowns. The use of titanium implants as the pillars of the prosthesis makes it possible to rebuild a variety of missing teeth.
- Medical – surgical instruments, wheelchairs, crutches may be made of titanium alloys.
- Treatment of fractures – which are used titanium alloys with Al, Nb and Ta, and titanium with Al and Nb (Ti-6Al-7NB) – fixing of components such as screws bone fragments.
- Joint replacement, dental implants, spine implants, "artificial discs." Spine implants are particularly important for our society, as more and more people complain about the problems associated with it, lumbar pain syndromes. There is the center of gravity of the human body and have the greatest forces on the vertebrae and intervertebral discs.

Titanium and its alloys from metallic biomaterials are the best materials for all kinds of implants, have good mechanical properties and excellent corrosion resistance and biocompatibility, and compared to austenitic steels and cobalt alloys, the Titanium alloys have the lowest density of them, and even Young's modulus, which is very important in the case of implants. Good biotolerance titanium in the environment of the living organism causing the osseointegration process, and therefore the bone tissue adhesion to the surface of titanium implant occurs.

Furthermore, titanium has a high affinity for oxygen, which contributes to the formation on the surface of the passive film of TiO_2, which also protects against corrosion. However, the implementation of any of the titanium implant involves large financial outlays, which is the result of a complex manufacturing process.

Titanium alloys which are used in bioengineering can be classified in three groups:

- α-phase alloys,
- two-phase alloys α + β,
- β-phase alloys [4].

Due to the occurance in the most popular alloy Ti-6Al-4V (used in bone surgery, its trade name is Protasul 64WF) vanadium, which can be released into the body causes disturbances in the normal functioning, they began to look for new titanium alloys deprived of vanadium, where the β phase stabilizers function elements meet acceptable by the human body even in large amounts. These include niobium, tantalum and iron. New titanium alloys have an even higher corrosion resistance, are better tolerated than vanadium alloy and, of course, have a low Young's modulus and good mechanical properties – fatigue resistance, hardness. Titanium and its alloys are among the long-term biomaterials because their residence time in the body can exceed even twenty-five.

Compared to other biomaterials, titanium alloys are characterized by:

- good resistance to crevice corrosion, stress, and overall in the chloride environment – titanium, of course, is exposed to the chemical processes, including corrosion, but less than the other metals used in medicine;
- heat resistance (up to 800°C), especially in the oxidizing environment;
- the highest biotolerance of the currently used metallic biomaterials;
- a preferred ratio of tensile strength to yield strength;
- low density;
- the lowest Young's modulus of the of metallic biomaterials;
- a high tendency to naturally self-passivate;
- paramagnetic properties;
- high fatigue strength, which is important in terms of the sustainability elements for long-term stay in the human body [5].

Currently, market trend shows that manufacturers seek to increase the capacity of pure titanium Class IV, which (after treatment) equals physical parameters of titanium alloys, while maintaining the high biocompatibility and resistance to corrosion. On the basis of tests to date in vitro and in vivo showed much greater resistance to corrosion and a thicker passivation layer (TiO_2) in the case of pure titanium as compared with titanium alloys.

Allergy to titanium is intermittent, so we can basically safely use its unique properties that make it a versatile material, highly biocompatible and offer a chance of mastering new areas of application in medicine and dentistry, if only it does not contain sensitizing other metals, which may appear in trace amounts as a result of processing.

As far as the titanium allergy, there are some problems with the recognition, because there are no titanium-oriented testing. Dermal patch test, used successfully for other allergies, is not suitable in the case of titanium and works only in about 20% of cases.

SUMMARY

Titanium is not a toxic element even in very high doses and has not had any negative impact on the human body. Every day a person eats with the food of about 0.8 mg of titanium, but most of it is absorbed by the body. However, it has a tendency to accumulate in tissues that contain silica. Plants typically contain about 1 ppm of titanium, although such horsetail and nettle may contain up to 80 ppm.

Most titanium compounds is harmless, the exceptions include those with chlorine: $TiCl_2$, $TiCl_3$ and $TiCl_4$, which have hazardous properties - titanium dichloride (a form of black crystals) can undergo spontaneously combustion and titanium tetrachloride is a volatile fuming fluid. All the titanium chlorides are corrosive.

Titanium alloys are characterized by resistance to corrosion and the ability to carry heavy loads. However, titanium is still too expensive, that it can be widely used for example in the average car for a reasonable cost.

The liquid titanium reacts with oxygen, nitrogen and hydrogen, which creates difficulties for metallurgy, but favorable physical and chemical properties gave him the use in industry, medicine, oral surgery, implantology, orthodontics and prosthodontics. With the clinically observed good biocompatibility and osseointegration, titanium and its alloys are used to manufacture various components useful in various branches of medicine. Though again the economic aspect is worth noticing, the number of implanted titanium implants both in Poland and in other countries depends on the wealth of the society. Since titanium does not belong to a group of ferromagnetic, patients with implants made from it can be safely examined tomography MRI (magnetic resonance imaging).

REFERENCES

[1] Titanium. http://www.webelements.com/.
[2] Li-Chin C., Chin-Hsiang L., Shin-hao Ya. The structure and mechanical properties of thick rutile - TiO_2 films using different coating treatments. [in:] Applied Surface Science. Elsevier, 2011.
[3] Makuch K.: Analiza zawartości tytanu w błonie śluzowej pokrywającej dwuetapowe tytanowe wszczepy śródkostne w okresie ich wgajania. Wyd. Uniwersytetu Medycznego im. Karola Marcinkowskiego w Poznaniu. Poznań 2011.
[4] Materiały biomedyczne. LABORATORIUM NAUKI O MATERIAŁACH. http://www.iim.p.lodz.pl/wyklady/nowe_2010.
[5] Świeczko-Żurek B.: Ocena struktury i własności mechanicznych oraz odporności korozyjnej tworzyw metalowych na implanty dla chirurgii kostnej. http://www.pg.gda.pl/~kkrzyszt/biomat3.pdf.

inż. Marta Mierzwa
Silesian University in Katowice
Department of The Computer Science and Theory about Materials
Bankowa 12, 40-007 Katowice, POLAND
e-mail: martuniamierzwa@gmail.com

Artykuł w polskiej wersji językowej dostępny na stronie internetowej czasopisma.

The article in Polish language version available on the website of the journal