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PROPERTIES AND APPLICATIONS OF TITANIUM ALLOYS: A BRIEF REVIEW

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Abstract. This paper presents a brief review on titanium alloys, giving especial attention to Ti-6Al-4V. The mechanical and the thermal properties were highlighted, while with regard to application the emphasis was placed to the aerospace, automotive and biomedical fields. The tensile strength of the alloys under concern varies from about 200 to 1400 MPa, but for Ti-6Al-4V the range is from about 900 to 1200 MPa. Generally, the thermal conductivity varies from about 5.5 to 25 W/mK when temperature varies from near room to 200 °C, while for Ti-6Al-4V the values are about 6.6 - 6.8 W/mK at near room temperature, and about 16.0-19.0 W/mK at 800 °C. Aerospace has been the major field of application of titanium materials, being one of the major challenges the development of new alloys with improved strength and higher service temperature. In automotive parts, such alloys are used especially for weight saving, but new alloys with higher service temperature, and new surface treatment to improve wear resistance are needed. New alloys without toxic elements and with elastic modulus similar to the bone need to be developed for biomedical applications.

1. INTRODUCTION

Though a large number of titanium alloys have been developed [1], they can be grouped into three major categories such as α-alloys, β-alloys, and $\alpha + \beta$ alloys. Their properties are dependent on microstructure which, in turn, depends on the chemical composition and thermomechanical processing.

Due to their high specific strength and exceptional corrosion resistance, titanium alloys have been widely used in engineering, namely in the aerospatiale, automotive and biomedical fields [2,3]. The alloy Ti-6Al-4V, due to its biocompatibility coupled with good combination of mechanical and corrosive properties, is the most popular titanium-based material in the manufacture of biomedical components, including dental implants, prosthetic femoral components, surgical instruments, *etc.* [4-6]. Nowadays, the industry of titanium alloys seems to be mature, but new technology and applications for these alloys continue to grow [7].

Regardless of the usefulness of titanium alloys, the number of available articles addressing the subject has been limited. The aim of this paper is to perform a review on titanium alloys. The core subjects are properties and applications, with special focus on Ti-6Al-4V. Additional descriptions on elemental titanium, alloying elements, chemical composition, and classification are also provided.

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Table 1. Selected physical properties of titanium, compared to some competitor metals.

	Ti	Al	Fe	Ni
Density [g/cm^3]	4.5	2.7	7.9	8.9
Melting point [°C]	1670	660	1538	1455
Thermal conductivity [W/mK]*	15-22	221-247	68-80	72-92
Elastic modulus [GPa]	115	72	215	200
Reactivity with oxygen	high +	high	low	low
Corrosion resistance	high +	high	low	medium
Metal price	high +	medium	low	high

2. ELEMENTAL TITANIUM AND ALLOYING ELEMENTS

2.1. Elemental titanium

Elemental or pure titanium has low thermal conductivity, relatively low density and elastic modulus, moderate strength, good corrosion-resistance in various environments and high reactivity with a variety of elements. Table 1 shows selected properties [7, 8-10] of this element compared with those of some competitor metals.

At low temperatures, pure titanium has hexagonal close packed structure (hcp), called α titanium. But at high temperatures the stable structure is body-centered cubic (bcc), which is referred to as β titanium. The atomic unit cells of the referred structure are illustrated in Fig. 1. The β-transus temperature for pure titanium is around 882±2 °C [11] and is dependent on the amount of incorporated impurities [12]. The existence of the two different crystal structures is the basis for large variety of titanium alloys properties.

2.2. Alloying elements

The alloying elements for titanium alloys are classified as neutral, α-stabilizers or β-stabilizers [8,11,12], according to their influence on stabilizing α or β phases (Table 2). This Table also evidences the position of alloying element in the lattice crystal, which may be interstitial or substitutional.

The α-stabilizers rise the β-transus temperature, while β-stabilizers lower this temperature. Neutral elements have slight influence on β-transus temperature. On the other hand, β-stabilizers are divided into β-isomorphous and β-eutectoid elements. The first promote the stability of β phase along all composition of the alloy, while the last cause eutectoid transformations of β phase, as illustrated in Fig. 2.

Aluminum is the most important α-stabilizer, while molybdenum is among the main β-stabilizers. The α-stabilizers and their relative capacity to stabilize α phase are expressed as aluminum equivalence, having the molybdenum similar meaning for β phase [13].

3. CLASSIFICATION OF TITANIUM ALLOYS

3.1. Main categories

Titanium is available as commercially pure and as alloys. These alloys are usually divided into three categories: alpha (α), alpha-beta (α+β) and beta (β). This paper provides a more detailed classification, as shown in Table 3, being the data extracted from various references [8,12,14]. This Table also

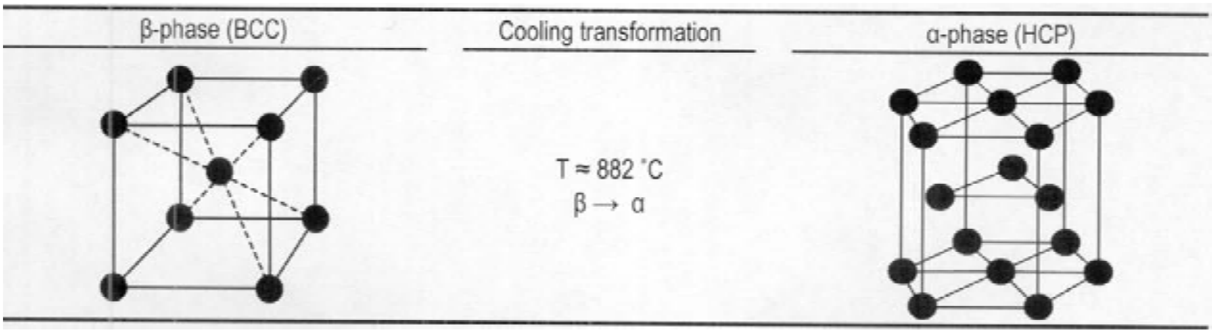


Fig. 1. Illustration of crystallographic cell and allotropic transformation of pure titanium.

Table 2. Classification of selected alloying elements used in titanium alloys.

	α-stabilizer				β-stabilizer							Neutral	
					β-eutectoid		β-isomorphous						
	Al	O	N	C	Mo	V	Fe	Cr	Mn	H	Ni	Sn	Zr
Substitutional	√				√	√						√	√
Interstitial		√	√	√			√	√	√	√	√		

Table 3. Categories of titanium materials and selected examples.

Category	Selected materials			
CP-Ti	CP-Ti (0.2Fe, 0.18O)	CP-Ti (0.3Fe, 0.25O)	CP-Ti (0.3Fe, 0.35O)	CP-Ti (0.5Fe, 0.40O)
α alloy	Ti-5Al-2.5Sn	Ti-3Al-2.5V	Ti-2Cu	Ti-0.3Mo-0.8Ni
near-α alloy	Ti-5Al-6Sn-2Zr-1Mo-0.2Si	Ti-2Al-2Sn-4Zr-2Mo	Ti-8Al-1Mo-1V	-
α+β alloy	Ti-6Al-4V	Ti-6Al-4V ELI	Ti-6Al-4V-2Sn	Ti-6Al-2Sn-4Zr-6Mo
β alloy	Ti-13V-11Cr-3Al	Ti-11.5Mo-6Zr-4.5Sn	Ti-13V-11Cr-3Al	-
near-β alloy	Ti-6Al-2Sn-4Zr-6Mo	Ti-8Mo-8V-2Fe-3Al	Ti-10V-2Fe-3Al	Ti-8Mn
Ti-Aluminides	Ti-24Al-10Nb	Ti-25Al-17Nb-1Mo	Ti-22Al-27Nb	-

presents, for each category, examples of specific materials with designation according to their chemical compositions.

3.2. Category characteristics

Commercially pure titanium (CP-Ti) contains elemental titanium plus some amount of impurities such as Nitrogen (N), Hydrogen (H), Oxygen (O), and Iron (Fe). CP-Ti materials contain essentially α -phase and are divided into numerous grades. The strength increases with increasing amount of the O and Fe elements [15].

The α-alloys are formed by single solid solution of α-phase. These alloys have good high temperature properties, but do not allow microstructural modifications by heat treatment to improve properties [12]. They are primarily used in the chemical and process engineering industry, where excellent corrosion behavior and deformability are of prime concern, while high strength-to-weight ratio only ranks second [11].

Near-α alloys contain α-phase and usually less than 10% of β-phase [16], derived from addition of small amount (1 to 2%) of β stabilizers. The β-phase improves the strength and workability of the alloys

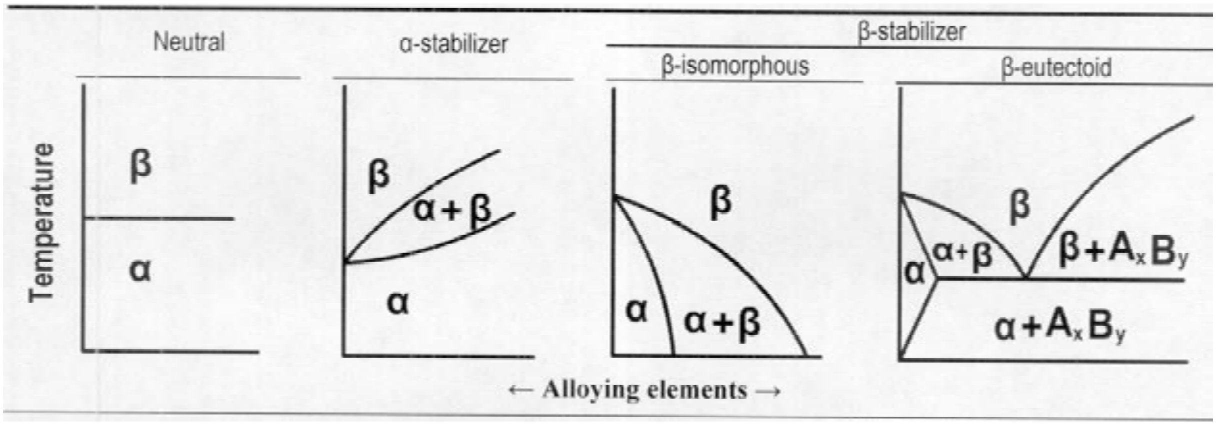


Fig. 2. Illustration of influence of alloying elements on the extent of α and β fields.

Table 4. Properties of titanium and its alloys.

Category	Chemical composition [Weight %]	Hardness [HV]	YS [MPa]	TS [MPa]	*E* [GPa]	T_β[°C]
α						
High purity Ti	99.98 Ti	100	140	235	100-145	882
CP-Ti grade 1	0.2Fe-0.18O	120	170-310	>240	-	890
CP-Ti grade 4	0.5Fe-0.40O	260	480-655	>550	100-120	950
Alloy grade 6	Ti-5Al-2.5Sn	300	827	861	109	1040
Near-α						
Ti-6-2-4-2-S	Ti-6Al-2Sn-4Zr-2Mo-0.1Si	340	990	1010	114	995
TIMETAL 1100	Ti-6Al-2.7Sn-4Zr-0.4Mo-0.4Si	-	900-950	1010-1050	112	1010
TIMTETAL 685	Ti-6Al-5Zr-0.5Mo-0.25Si	-	850-910	990-1020	120	1020
α+β						
Ti-6-4	Ti-6Al-4V	300-400	800-1100	900-1200	110-140	995
Ti-6-6-2	Ti-6Al-6V-2Sn	300-400	950-1050	1000-1100	110-117	945
Ti-6-2-4-6	Ti-6Al-2Sn-4Zr-6Mo	300-400	1000-1100	1100-1200	114	940
Ti-17	Ti-5Al-2Sn-2Zr-4Mo-4Cr	400	1050	1100-1250	112	890
Near-β						
SP 700	Ti-4.5Al-3V-2Mo-2Fe	300-500	900	960	110	900
Beta III	Ti-11.5Mo-6Zr-4.5Sn	250-450	800-1200	900-1300	83-103	760
Beta C	Ti-3Al-8V-6Cr-4Mo-4Zr	300-450	800-1200	900-1300	86-115	795
Ti-10-2-3	Ti-10V-2Fe-3Al	300-470	1000-1200	1000-1400	110	800
Ti-15-3	Ti-15V-3Cr-3Al-3Sn	300-450	800-1000	800-1100	80-100	760

T_β – Beta transus temperature; YS – Yield strength; TS – Tensile strength; *E* – Elastic modulus.

and promotes equilibrium between higher strength of α+β alloys and creep resistance of α-alloys. Today their upper operating temperature is limited to about 500 to 550 °C [11]. The most widely used commercial high temperature titanium alloys for aero-engine applications belong from this class [12].

The α+β alloys contain 4 to 16% of β-stabilizers. The most commonly used alloy included in this category is Ti-6Al-4V [12], which represents more than 50% of all titanium alloys in use today [11]. At room temperature, commercial α+β alloys typically contain 10-20% of β-phase [16].

Near-β alloys, also referred as metastable β-alloys, contain small amount of α-stabilizers and 10 to 15% of β-stabilizers [12]. According to this reference, the β-stabilizers promote the retention of β phase in metastable condition at room temperature, and these alloys can be heat-treated by ageing, leading to precipitation of a very fine α-phase dispersed in the β matrix. In addition, these alloys allow optimization for both high strength and toughness and can be hardened to strength level over 1400 MPa [11].

Titanium aluminides, referred in Table 3 as Ti-aluminides, embody a special class of alloys with exceptional set of physical and mechanical properties [17]. Based on the intermetallic compounds Ti3Al (α2) and TiAl (γ), these materials have the capacity to raise the operating temperature to about 650 °C and 800 °C, respectively. Because Ti3Al alloys have a modest longterm stability, currently the main focus of research and development on titanium aluminides is directed to TiAl-base alloys [11].

4. PROPERTIES OF TITANIUM ALLOYS

4.1. Overview

The mechanical properties of titanium alloys are influenced by individual properties of α and β phases, their arrangement and volume fraction [11]. For example, the α phase has lower density than the β phase due to the fact that the predominant element Al in a phase has lower density than the predominant

Table 5. Selected thermal properties of titanium materials.

		Temperature [°C]				
		0	200	400	600	800
Pure-Ti	*k*	22	21	21	21	-
	C	2.3-2.5	2.55-2.75	2.75-3.05	3.0-3.4	3.3-3.8
$\alpha/\alpha+\beta/\beta$	*k*	5.5-8.0	8.0-12.0	10.0-17.0	12.5-21.0	15.0-25.0
	C	2.3-2.5	2.55-2.75	2.75-3.05	3.0-3.4	3.3-3.8
Ti-6Al-4V	*k*	6.6-6.8	8.5-9.1	10.5-12.5	13.0-16.0	16.0-19.0
	C	-	-	-	-	-

k – Thermal conductivity [W/mK]; *C* – Heat capacity [MJ/m^3].

Table 6. Selected properties of Ti-6Al-4V alloy in its two main metallurgical conditions.

Material	TS [MPa]	YS [MPa]	*E* [GPa]	Hardness [HV]	*K* [W/mK]	β-Transus [°C]
Ti-6Al-4V (annealed bar)	895	825	110	340	7.3	995
Ti-6Al-4V (solution + age bar)	1035	965	-	360	7.5	995

TS – Tensile Strength; YS – Yield Strength; *E* – Elastic modulus; *C* – Thermal conductivity.

elements Mo or V in β phase. Consequently, α alloys generally have lower density than β alloys, but the values are about 4.5 g/cm^3.

Besides, the fine microstructures increase strength and ductility, retard crack nucleation and are a pre-requisite for super plastic deformation, while coarse microstructures are more resistant to creep and fatigue crack growth; equiaxed microstructures often have high ductility and fatigue strength and are ideal for super plastic deformation, whereas lamellar structures have high fracture toughness and show superior resistance to creep and fatigue crack growth; bimodal microstructures combine the advantages of lamellar and equiaxed structures, which results in a well-balanced property profiles [11]. Table 4 provides selected mechanical properties of some of the most used titanium alloys [11]. The chemical composition and β-transus temperatures are also indicated.

Table 5 provides information on the variation of thermal properties of titanium materials with temperature [18]. Increase of temperature leads to significant increase in the thermal conductivity of titanium alloys but not for pure titanium. Heat capacity of titanium alloys seems to be less influenced by change in temperature than thermal conductivity.

4.2. Properties of Ti-6Al-4V alloy

The classic Ti-6Al-4V alloy is employed generally in two metallurgical conditions: annealed and solution treated and aged [14]. Table 6 provides the magnitude of selected properties of this alloy [8, 11, 14].

Fig. 3 provides information on the Influence of temperature on properties of Ti-6Al-4V alloy [19-21]. The thermal conductivity increases to more than threefold when the temperature changes from about 10 °C to about 1200 °C (Fig. 3a), while the hardness increases rapidly as the temperature is decreased (Fig. 3b). Hong et al. [20] underlined that when temperature changes from room to liquid nitrogen temperature, tensile strength of this alloy changes from 1000 to 1700 MPa. There is an overall decrease of Young modulus with increasing temperature from above 200 °C, but this decrease is more pronounced for temperatures above 500 °C (Fig. 3c). The ultimate tensile strength (UTS) decreased from about 1000 MPa at 25 °C to about 625 MPa at 450 °C, which results in a global decrease equal to about 45% (Fig. 3d).

Other authors [22] found that the yield strength increases with increasing volume fraction of a phase while decreases with increasing thickness of a

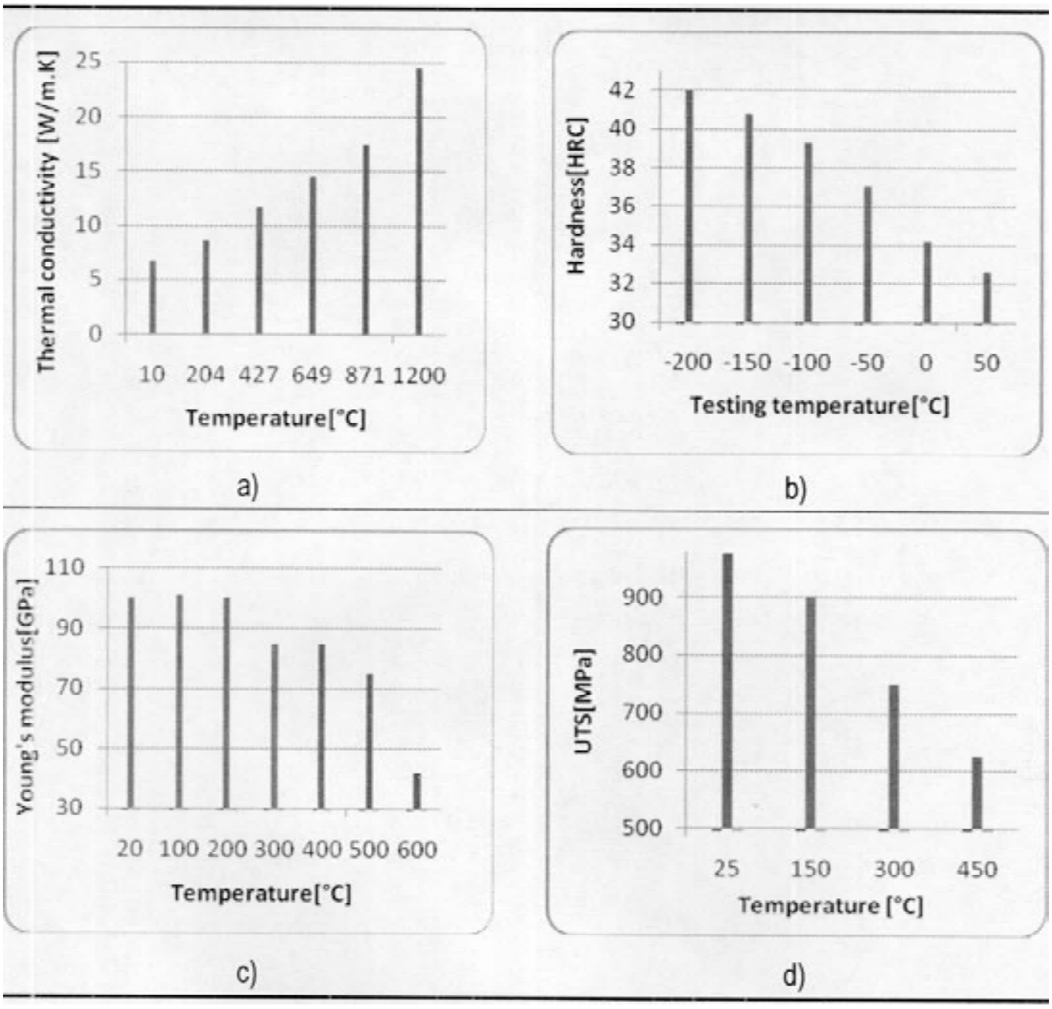


Fig. 3. Influence of temperature on selected properties of Ti-6Al-4V alloy.

phase and Feret ratio. The elongation increases with increasing volume fraction of α phase, thickness of α phase and the Feret ratio. The correlation of microstructure and mechanical properties was developed using the artificial neural network technique, being the mean absolute percentage error only 1.22%, which imply that the trained neural network is able to predict the mechanical properties of the Ti-6Al-4V alloy accurately.

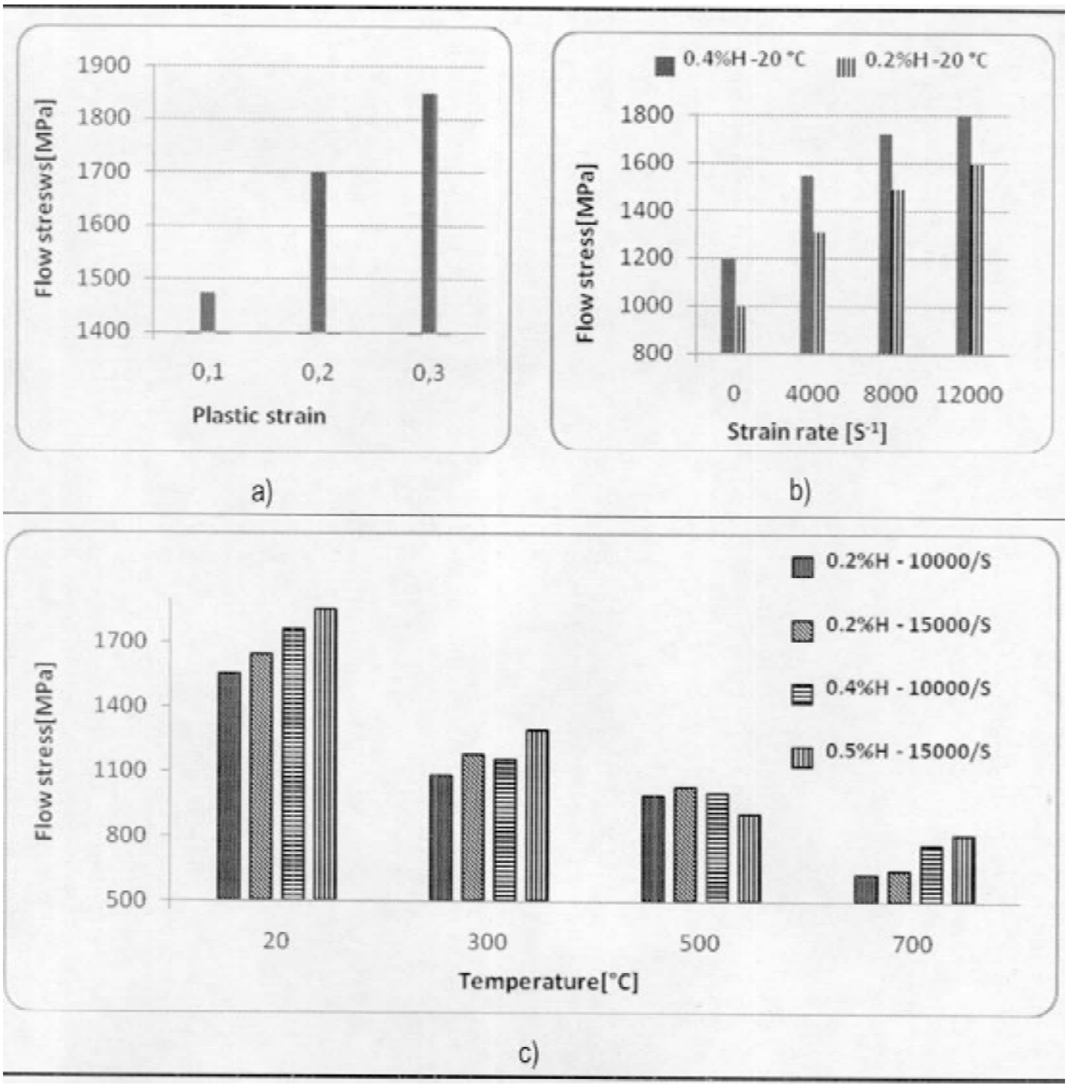
Fig. 4a provides flow stress magnitude versus strain, obtained at room temperature (300K), for strain rate equal to 1500 S^{-1} [23]. The flow stress increases with increasing strain. This behavior is usually caused by hardening phenomenon.

According to Fig. 4b, the flow stress increases with strain rate. Besides, high hydrogen content in Ti-6Al-4V alloy resulted in increase of flow stress [24].

Fig. 4c presents flow stress magnitude of Ti-6Al-4V alloy versus temperature, for different combinations of hydrogen content and strain rate. The increase of temperature leads the decrease of flow stress magnitude which, however, generally increased with increasing hydrogen content and/or strain rate, except for temperature of 500 °C [24].

Constitutive analysis of Ti–6Al–4V alloy was developed by performing hot compression tests in a wide range of temperatures (800–1050 °C) and strain rates (0.0005–1 s^{-1}) [25]. Strain showed significant influence on material constants. The developed constitutive equation can precisely predict the flow stress under most deformation conditions in α+β phase region. Almost similar prediction accuracy was also obtained in single β phase region. However, some significant deviations are observed between the experimental and the computed flow stress data for some deformation conditions in α+β phase region.

Mechanical tests performed at room temperature revealed that the hydrogen content (0.2–1.2 wt.%) has dissimilar effect on the tensile and compressive properties of Ti–6Al–4V alloy. As hydrogen content increases, the tensile properties decrease, but the compressive properties first increase and then



a) b)

c)

Fig. 4. Influence of plastic strain (a), strain rate and hydrogen content (b), temperature and hydrogen content (c) on the evolution of flow stress of Ti-6Al-4V alloy.

decrease [26]. The decrease of tensile properties with increasing hydrogen content resulted from increasing amounts of hydrides and solid solution of hydrogen at the grain and phase interfaces, which causes the decrease of the binding force at the referred interfaces. The increase of hydrogen content also causes an increase in the amount of plastic β, which result in increase of the ultimate compression strength. However, high hydrogen content in the specimen results in high amounts of hydrogen content in the form of solid solution and hydrides, which are continuously distributed along the grain boundaries and leads to the degradation of compressive properties. The optimum hydrogen content for cold forming of Ti–6Al–4V alloy for the highest ultimate compression strength was found to be in the range of 0.6–0.8 wt.% [26].

The effect of hydrogen on the cold deformation behaviors of the Ti–6Al–4V alloys (α+β type) was investigated [27]. Microstructures exhibiting large α'' martensite and metastable β phase show a better plasticity than that of the as received alloy. The deformation twins appear inside of α'' martensite in specimens containing lower than 0.45 wt.% H, which promotes the deformation. When the hydrogen concentration is further increased up to 0.9 wt.%, the metastable β phases transform to α'' martensite during the deformation, which, together with the deformation twins, increase the true strain from 30% to 60% [27].

The oxygen content also influences the mechanical properties of titanium alloys. According to Su et al. [28], deoxidation of Ti-6Al-4V alloy results in microstructure refinement and decrease of microhardness.

Fig. 5 provides nanohardness values of nitrogen ion implanted versus unimplanted Ti-6Al-4V alloy. The nanohardness values were obtained from

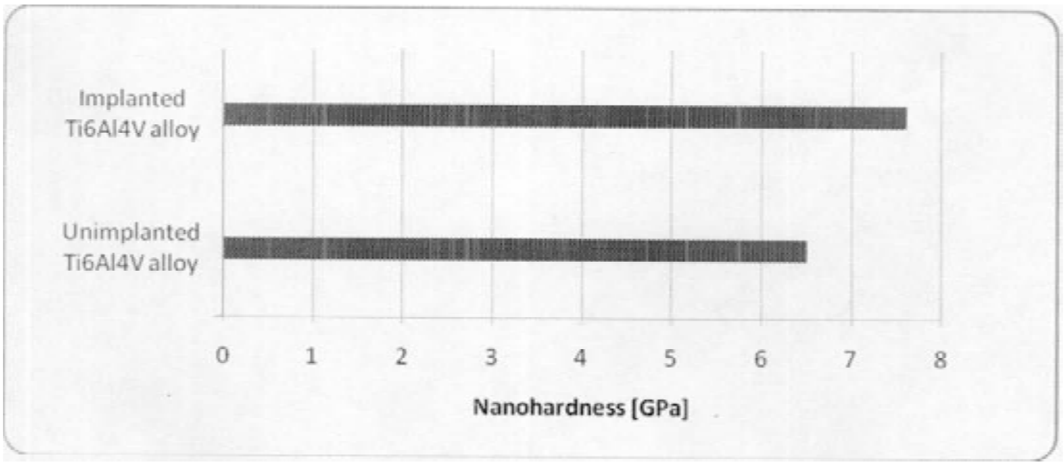


Fig. 5. Influence of nitrogen ion implantation on hardness of Ti-6Al-4V alloy.

experimental test using the applied loads of 2 mN and based on load-displacement curves according to Oliver and Pharr methods. Nitrogen ion implantation caused an increase of about 20% in nanohardness. This growth was attributed by Luo [1] to higher stiffness of hard layer of TiN formed on implanted Ti-6Al-4V substrates.

According to Adamek and Jakubowicz [29], porous materials are often used for biomedical parts and device construction. They investigated the formation of porous morphology in nanocrystalline of Ti-6Al-4V alloy. The results show that, due to the porous morphology, the nanocrystalline alloy has a nanohardness and Young modulus in the range of 993–1275 HV and 137–162 GPa, respectively.

Poondla et al. [30] measured the microhardness (Vickers scale) and macrohardness (Rockwell C scale) of commercially pure titanium (Grade 2) and Ti-6Al-4V alloy, both in the annealed condition. Marginal variation of microhardness through a cross-section of the samples was found and the authors attributed this behavior to the change in microstructure, namely the α and β phases, being the average values about 200 kg/mm^2 (1962 MPa) and 330 kg/mm^2 (3237.3 MPa), respectively for Grade 2 and Ti-6Al-4V alloy. The macrohardness across the length of machined sample gave an average value 260 kg/mm^2 (2550.6 MPa) for Grade 2 and 290 kg/mm^2 (2844.9 MPa) for Ti-6Al-4V. The microhardness values were marginally lower than the macrohardness values across the length of Grade 2 sample, but regarding the Ti-6Al-4V alloy the opposite happened. The lower value of macrohardness for Ti-6Al-4V alloy when compared to its microhardness was attributed by the authors to the physical presence of a population of processing-related artifact.

Study of Zherebtsov et al. [31] showed that the application of hydrostatic extrusion and multiaxial forging followed by cold rolling results in Ti-6Al-4V alloy with very high tensile strength of about 1500 MPa, while the multiaxial forging, and forging combined with heat treatment results in Ti-6Al-4V alloys with moderate strengths of about 1300 MPa and 1050 MPa, respectively.

Cvijovic et al. [32] studied the wear and corrosion behavior in Ringer's solution. The materials investigated were the cold-rolled Ti–13Nb–13Zr alloy with martensitic microstructure, and Ti–6Al–4V ELI alloy in martensitic and two-phase (α+β) microstructural conditions. The wear experiments were carried out at room temperature with a normal load of 40 N and sliding speeds 0.26, 0.5, and 1.0 m/s. The corrosion behavior was analyzed at 37 °C using open circuit potential-time measurements and potentiodynamic polarization. It was concluded that Ti–6Al–4V ELI alloy has a substantially higher wear resistance than Ti–13Nb–13Zr alloy in both microstructural conditions. Both alloys exhibited spontaneous passivity in Ringer's solution and the corrosion potential values are similar for all three materials. However, the corrosion resistance of Ti–13Nb–13Zr and martensitic Ti–6Al–4V ELI alloys improved comparatively to Ti–6Al–4V ELI alloy with (α+β) microstructure. The martensitic Ti–6Al–4V ELI alloy presented the best combination of both corrosion and wear resistance.

The alloy Ti–6Al–4V has the ability to substitute heavier steel in some friction and wear-critical diesel engine components like connecting rods, intake valves, movable turbocharger vanes, and pistons. This alloy also exhibits excellent corrosion resistance, good fatigue strength, and acceptable fracture toughness, but it has poor sliding characteristics. In addition, titanium alloys have a propensity to fail by galling, and often exhibit high and unstable friction coefficients. Selected surface engineering techniques were compared to determine which best enhance the tribological performance of Ti–6Al–4V alloy [33]. Candidate treatments included diffusion treatments (oxygen diffusion, nitriding, and carburizing), hard coatings (TiN and CrN), soft coating (Cu–Ni–In), titanium-matrix TiB2 in situ-formed composite and shot peening. One of the interesting conclusions is that the CrN coating had the least amount of wear [33].

Study of micromechanical behavior of Ti–6Al–4V alloy through microindentation experiments [34] revealed that the loading speed has little influence on microhardness and Young's modulus, but showed strong indentation size effects, namely an increase of indentation hardness with the decrease of indentation load or depth.

The surfaces of Ti–6Al–4V alloy component modified via CoBlast using either Al_2O_3–SiC or Al_2O_3–B_4C powder mixtures demonstrated increased hardness compared with the unmodified alloy, but wear testing performed using a pin-on-disc tribometer revealed that this treatment did not cause significant improvement in wear resistance [35].

The application of titanium alloys as implant in the bone is usually very good, but has certain restrictions because the metal ions are released from the implant and may cause local irritation of the surrounding tissues. Cell and tissue are affected not only by the chemical properties of the implant surface, but also by the implant surface topography. To overcome the problem of ion release and to improve the biological, chemical, and mechanical properties, many surface treatment techniques are used. According to Rautray et al. [36], calcium and phosphorus implantation are useful for improvement of biocompatibility of titanium. They also describe that the silver ion implantation is used for anti-bacterial applications, while nitrogen ion implantation combats wear of the titanium surface.

5. APPLICATION OF TITANIUM ALLOYS

5.1. Overview

The fascination for titanium properties started in the late 1940's and early 1950's, around the Second World War. In the USA, at TIMET (1951) and RMI (1958) for example, were developed large capacity plants for production of titanium sponge. In Europe, large scale production started in 1951 in the UK at Metals Division of Imperial Chemical Industries (later IMI and Deeside Titanium), which became the principal European titanium producer. In France, titanium sponge was produced for several years, however discontinued in 1963. In Japan, sponge production started in 1952 and two companies (Osaka Titanium and Toho Titanium) have relatively large capacity in 1954. The Soviet Union started production of titanium sponge in 1954 and considerably increased their capacity. By 1979 the Soviet Union became the World's largest titanium sponge producer [8].

The α and β categories included 26% and 4% respectively, while $\alpha+\beta$ alloy comprises 70% of all USA titanium market, being the Ti-6Al-4V alloy, which belong from the last category, covered 56% of all USA titanium market [8].

The alloy Ti-6Al-4V covers over 50% of global consumption, while the CP-titanium includes about 20 to 30% [11]. More than 100 titanium alloys are known but only about 20 to 30 of them reached commercial position, and currently there is an increasing interest in use of titanium aluminides category, more precisely the γ(TiAl)-based alloys, in the aerospace and automotive industries.

Titanium and titanium alloys are used in a wide variety of fields, systems and parts and their selection may be based on corrosion resistance or in strength features [14], with additional requirement, the biocompatibility, for biomedical implant applications [37].

Applications for corrosion resistance use normally CP-Ti (ASTM Grades 1, 2, 3, 4), which are good corrosion resistant but low strength materials. These are used in tanks, heat exchangers, reactor vessels, etc., respectively for chemical-processing, desalination and power generation plants. For some corrosion applications, ASTM Grades 7, 8, and 11 are used. In medicine field, Grade 2 is usually used in low-strength applications, whereas Grade 5 (Ti-6Al-4V) is employed usually in applications requiring higher strength [14].

Applications for high-strength performance use high-strength titanium alloys such as Ti-6Al-4V, Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-6V-2Sn, Ti-10V-2Fe-3Al, among others, but the Ti-6Al-4V alloy is unique because it merges a set of interesting properties, good workability and production experience, and high commercial availability. Therefore, this alloy was converted into the standard against which other alloys must be compared when selecting titanium alloys for specific applications [14].

Table 7. Selected aerospace system and parts versus titanium application.

Systems and parts	Materials
Airframe structures	
Hydraulic tubing	Ti-3Al-2.5V
Floors	CP-Ti
Landing gear	Ti-10V-2Fe-3Al; Ti-6-6-2
Windows frames	Ti-6Al-4V
Springs	Ti-15V-3Cr-3Sn-3Al
Gas turbine engines	
Fan discs and blades	Ti-6Al-4V; Ti-6-2-4-2S
Compressor disc	Ti-6Al-4V; Ti-6-2-4-2S
Compressor blades	Ti-6Al-4V; Ti-6-2-4-2S
Compressor stators	Ti-35V-15Cr
Nozzle assembly	TIMETAL 21S

5.2. Application of titanium in the aerospace industry

Aerospace has been the major field of application of titanium materials [38], particularly in the engine and airframe systems where it comprises 36% and 7% respectively [39]. In the USA, about 70 to 80% of all titanium requests are for aerospace and the remainder is for industrial application [7].

The primary reasons for using titanium in the aerospace industry are *decrease in weight* (primarily as a steel replacement, but also as Al replacement), *space limitation* (replace Al alloys), *operating temperature* (Al, Ni, steel alloys replacement), and *corrosion resistance* (replace Al and low alloy steels) [40]. Table 7 provides selected applications of titanium materials in the aerospace field [39, 40].

Because the strength of titanium alloys is significantly higher than Al alloys, parts made from the first alloys may have smaller transversal section, which results in weight savings. Substitution of Al alloys by Ti alloys may also be performed when operating temperatures exceed those supported by the first, which is around 130 °C for conventional aluminum alloys [40]. According to this author, this temperature condition exists for example in the nacelle and auxiliary power unit areas and wing anti-icing systems for airframe structures.

Landing gear beams on the Boeing 747 and 757 are good examples for illustrating the volume or space limitation problems and their solution by the application of titanium alloys. In fact, according to Boyer [40], the preferable alloy for this application in terms of cost is aluminum 7075, but the size required to carry the required loads is excessive and do not fit within the wing envelope. Steel could be used in expense of greater weight. So, titanium alloys should be better solution.

Titanium provides enough corrosion resistance so that the painting is not necessary, except in some cases. For example, when the titanium is in contact with aluminum or low alloy steel components paint is needed to prevent galvanic corrosion. The floor support structure under the kitchens and lavatories is submitted to a very corrosive environment which requires the use of titanium to ensure better structural durability.

Table 8 provides, by category/alloy, more details on the application of selected titanium materials in the aerospace field [40].

5.3. Application of titanium in the automotive industry

The application of titanium materials in automobile industry began with F-1 racing cars in 1980s, being the application carried out primarily in the engine

Table 8. Application of titanium alloys in the aerospace industry.

α Alloy	Application
CP-Ti	Used in the annealed conditions for floor support structure in the galley and lavatory areas, tubes or pipes in the lavatory system, clips and brackets, ducting for the anti-icing, and environmental control systems that operate at temperatures up to about 230 °C, which is too high for aluminum alloys.
Ti-3Al-2.5V	Used for high pressure hydraulic lines, replacing 21-6-9 stainless steel tubing with about a 40% weight savings. It is also used for the fabrication of honeycomb core where strength required is greater than that provided by CP-Ti.
Ti-5-2.5	Used in the annealed condition, for cryogenic applications as it retains good fracture toughness and ductility down to cryogenic temperatures, being the primary use in the hydrogen side of the high pressure fuel turbo-pump of the space shuttle.

Ti-8-1-1	Used for fan blades for military engines, as well as for tear straps on commercial airframes, usually in the duplex annealed condition.
Ti-6-2-4-2S	Used primarily in the gas turbine engine parts, including blades, discs and rotors at temperatures up to about 540 °C, and in the high pressure compressor at temperatures too high for Ti-6-4, which is above about 315 °C for structural applications. Beyond about 540 °C, the temperatures are too high for titanium, and Ni-based alloys are used.
IMI 829 (Ti-5.5A1-3.5Sn-3Zr-1Nb-0.25Mo-0.3Si)	Used at operating temperatures up to 540 °C in the β-solution treated and aged condition for some of the compressor discs, blades and spacers of the RB-211-535E4 engine, which powers the Boeing 757.
IMI 834 (Ti-5.SA1-4Sn-3.5Zr-.7Nb-0.5Mo-0.35Si-0.06C)	Used at maximum temperature of 600 °C in the RR Trent 800 for compressor discs in the last two stages of the intermediate pressure compressor, and the first four stages of the high pressure compressor.
Timetal-II00 (Ti-6Al-2.8Sr-4Zr-0.4Mo-0.4Si)	It is a modification of Ti-6-2-4-2S for use up to 600 °C, for example in Allison Gas Turbine Engines.

α+β Alloy	Application
Ti-6Al-4V	Used in the gas turbine engines for static and rotating components, including all sections of the aircraft, namely fuselage, nacelles, landing gear, wing, and empennage, and also in the floor support structure, including areas of galleys and lavatories.
Ti-6Al-2Sn-2Zr-2Mo-2Cr + Si (Ti-6-22-22)	It was developed by RMI in the early i970's as a deep hardenable alloy. It has recently been resurrected as a moderate strength-damage tolerant alloy for the Lockheed/Boeing F-22 program.
Ti-6-2-4-6	Can be used for moderate temperatures, up to about 315 °C. It is used primarily for military engines, such as the F-100 and F-119, at a yield strength level of 1035 MPa. The damage tolerance characteristics of this alloy are not as good as those of Ti-6-4 or Ti-6-2-4-2 so it is not used in commercial engines.
Ti-5Al-2Sn-2Zr-4Mo-4Cr	It is used below 400 °C for fan and compressor discs.

β Alloy	Application
Ti- 13V- 11Cr-3A1 (Ti-13-11-3)	It was used extensively on the SR-71 airplane, for wing and body skins, frames, longerons, bulkheads, ribs, rivets and essentially in the main and nose landing gears.
Ti-15-3	For springs made from flat product, such as clock-type springs, Ti-15-3 is used because strip is a standard product for this alloy. Strip is the primary product form for Ti-15-3.
Ti-10-2-3	Almost the entire main landing gear of the 777 is fabricated from Ti-10-2-3, resulting in a weight savings of about 270 kg per airplane, and elimination of the potential of stress corrosion cracking associated with the steel. Also, Bell, Westland, Sikorsky and Eurocopter are all using Ti-10-2-3 in their rotor systems.
Timetal 21S (β-21S)	The normal operating temperature is in the range of 480-565 °C. It is used on the aft cowl and plug and nozzle for all three 777 engines (P&W 4084, GE-90, and the Trent 800), all skin and stringer type structures. These applications save about 74 kilograms per airplane.
Alloy C	This alloy has the advantage of high ignition resistance, which allows it to be used in areas previously requiring nickel-based alloys, for example in the vectored exhaust structure and cast compressor components on the Fl19 engine, which powers the Lockheed/Boeing F-22.

Table 9. Selected titanium materials and its automotive application.

Systems and parts	Materials
Frame structures	
Suspension springs	Ti-6.8Mo-4.5Fe-1.5Al; Ti-6Al-4V
Armor	Ti-6Al-4V
Body	CP-Ti (Grade 4); Ti-6Al-4V
Engines	
Outlet valves	γ(TiAl); Grade 2; Ti-6Al-4V; Ti-6Al-2Sn-4Zr-2Mo-0.1Si
Intake valves	Ti-6Al-4V
Turbocharger rotors	γ(TiAl)
Connecting rods	Ti-6Al-4V
Exhaust system	Grade 2

parts [41]. However, due to high cost of titanium alloys, their applications in automobile have been restricted, except for racing and special-purpose cars, despite the strong interest shown in these materials by the industry in terms of lightweight, fuel efficiency, and performances. In recent years, however, titanium and its alloys have been actively used for a variety of automobile parts [42]. Table 9 provides an interesting selection of these applications [41-43].

According to Fujii et al. [42], a considerable amount of titanium intake valves, being the majority of them made of Ti-6Al-4V alloy, have been mounted on many cars and motorcycles. But problems were found and the major of them is the development of surface treatment in order to improve wear resistance and, therefore, overcome the well-know low wear resistance of titanium alloys. These authors also underline that the use of hard TiN coating, Mo thermal spray coating, and Cr plating have been carried out in several cases, but these surface treatments are expensive and not suitable for prolonged wear resistance. Thus, it was decided to employ oxidizing treatment based on diffusion of concentrated oxygen into titanium surface layer, which enhance hardness as a result of formation of thick hardened layer.

Regarding the exhaust valves, which are usually exposed to high temperature, the typical heat-resistant alloy Ti-6Al-2Sn-4Zr-2Mo-0.1Si (6242S) is usually used. However, in the case of mass-produced motorcycles the exigencies are more because the referred components are exposed to higher temperature for a prolonged period of time. So, the study on the application of TIMETAL@1100 (Ti-6Al-2.7Sn-4Zr-0.4Mo-0.45Si), one of the most heat resistant materials among the titanium alloys, was carried out. It was found that the service temperature of this alloy is only to the extent of 600 °C, but the heat resistance up to about 800 °C is required in the case of the exhaust valves of motorcycles.

Table 10 provides information on adoption of titanium alloys by automakers in their industries [41]. Weight reduction is the major benefit targeted when using titanium in automobile parts.

New alloys for application in automobile parts are currently under study [42]. These include Super-TIX, Super-TIX51AF (Ti-5%Al-1%Fe), Super-TIX800 (Ti-1%Fe-0.35%O-0.01%N) and TIMETAL@LCB (Ti-4.5Fe-6.8Mo-1.5Al), among others.

5.4. Application of titanium in the medical devices

Titanium alloys started gaining extensive usage in biomedical implant in the early 1970s and their forms and material specifications are described in a

Table 10. Manufacturers versus application of titanium materials in automotive parts.

Manufacturer	Application	Introduction
Mitsubishi	Ti-22V-4Al in the AMG engine retainers of the Gallant 1	1989
Honda Motors	Ti-3Al-2.5V + REM in the connecting rods of the sport cars NSX	1990
Toyota	Sintered titanium alloys Ti-6Al-4V/TiB and Ti-Al-Zr-Sn-Nb-Mo-Si/TiB in the intake and exhaust engine valves, respectively, in the Altezza	1998
Nissan Motor	Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-Si in engine inlet and exhaust valves, respectively, for the CIMA	2000
Volkswagen	Ti-4.5Fe-6.8Mo-1.5Al in suspension spring of Lupo FS	2001
Kawasaki	Titanium alloys in the muffler of the large sports-type motorcycle ZX-9	1998
General Motors	Titanium alloys in dual mufflers of the Corvette Z06	2001

Table 11. Selected titanium biomaterials and their mechanical properties.

Material	Condition	TS [MPa]	YS [MPa]	Hardness
CP-Ti Grade 1 (α)	Annealed (700 °C)	241	172	70 RB
CP-Ti Grade 2 (α)	Annealed (700 °C)	345	276	80 RB
CP-Ti Grade 3 (α)	Annealed (700 °C)	448	379	90 RB
CP-Ti Grade 4 (α)	Annealed (700 °C)	552	483	100 RB
Ti-3Al-2.5V (α+β)	Annealed (700 °C)	690	586	24 RC
Ti-6Al-4V (α+β)	Annealed (700 °C)	931	862	32 RC
Ti-6Al-4V ELI (α+β)	Annealed (940 °C)	862	793	32 RC
Ti-6Al-7Nb (α+β)	Annealed (700 °C)	862	793	32 RC
Ti-15Mo (β)	Annealed (800 °C)	793	655	24 RC
Ti-15Mo-2.8Nb-0.2Si (β)	Annealed (800 °C)	793	655	24 RC
Ti-12Mo-6Zr-2Fe (β)	Annealed (760 °C)	1000	965	33 RC
Ti-35Nb-7Zr-5Ta (β)	Annealed (700 °C)	827	793	35 RC

TS – Tensile strength; YS – Yield strength; RB – Rockwell B; RC – Rockwell C.

Table 12. Some applications of titanium and its alloys in medical parts.

Parts	Materials
Joints	
Hip and knee joints	Ti-6Al-4V
Dental	
	TiMo11Zr6Sn4; Ti-6Al-4V CP-Ti (Grades 1, 2, 3 and 4)
Heart	
Valves and connectors	CP-Ti

number of literatures, including ASTM and BS7252/ ISO 5832 standards [37]. The use of titanium alloys as biomaterials increased due to their reduced elastic modulus, superior biocompatibility, high strength to weight ratio, and enhanced corrosion resistance when compared to conventional stainless steel and Co-Cr alloys [44]. The CP-Ti and Ti-6Al-4V alloy are the most used titanium material in medicine [37] and some authors [45] consider that the CP-Ti is the best biocompatible metallic material because its surface properties result in the spontaneous build-up of a stable and inert oxide layer. Table 11 provides a set of selected titanium biomaterials and their main mechanical properties [46].

The data provided by Table 12, extracted from various sources [37,44,45,47], indicates selected parts and common titanium-based materials used as implant. Commercially pure titanium (CP-Ti) has been used for dental implant and maxillofacial applications [37]. Nowadays, the applications of Ti-6Al-4V alloy include hip and knee prostheses, trauma fixation devices (nails, plates, screws, and wires), instruments, and dental implants. The cardiac valve prostheses, pacemakers, and artificial hearts are also made from titanium alloys, according to Elias et al. [45].

Due to its relatively poor wear resistance, the Ti-6Al-4V alloy is not suitable for bearing surface applications such as hip heads and femoral knees, without a coating or surface treatment [37]. In addition, numerous recent researches showed that the elastic behavior of α+β type alloys is not totally suitable for orthopedic applications [48,49]. For example, the Ti-6Al-4V alloy has elastic modulus around 110 GPa while the elastic modulus of a cortical bone is close to 18 GPa [50]. So, the use of this alloy as implant cause inadequate load transfer from implant device to the adjacent bone, which in turn result in degradation of this later, according to the suggestion of some studies [51].

Also, it was found that the V and Al elements are toxic to the human body. Thus, β alloys free of vanadium such as Ti-6Al-7Nb and Ti-5Al-2.5Fe were developed [37]. Besides better biocompatibility, these alloys present additional advantages over Ti-6Al-4V alloy such as higher fatigue strength and lower elastic modulus [8]. In recent years, efforts have been made to develop â alloy completely free of the toxic elements Al and V. Some of these alloys are Ti-13Nb-13Zr, Ti-12Mo-6Zr-2Fe and Ti-29Nb-13Ta-4.6Zr [49].

According to some authors [51,52], the use of suitable heat treatment and addition of biocompatible alloying elements like Nb, Ta and Zr to titanium is the base for obtaining titanium alloys with appropriate mechanical properties, namely low elastic modulus, and good biocompatibility.

6. CONCLUSIONS

This paper addressed the review on titanium alloys. The main topics discussed were the properties and the applications, but additional subjects such as elemental titanium, alloying elements and titanium categories were also briefly described. The classic alloy, Ti-6Al-4V, received special attention. With regard to application, the emphasis was given to the aerospace, automotive and biomedical fields. Below are presented the main conclusions obtained.

Properties

- Tensile strength of titanium materials varies normally from about 200 MPa for pure titanium to about 1400 MPa for near-β alloys, while for Ti-6Al-4V the values vary between 900 and 1200 MPa.
- Thermal conductivity varies from about 5.5 to 25 W/mK when temperature varies from near room to 200 °C, but for Ti-6Al-4V the values are about 6.6 - 6.8 W/m.K for near room temperature and about 16.0-19.0 W/mK for 800 °C.
- Flow stress of Ti-6Al-4V increases substantially with increasing strain and with increasing strain rate, but decreases with increasing temperature.
- Titanium alloys are used in several fields, systems, and parts and their selection is based essentially on corrosion resistance and/or strength, but in the case of biomedical application, the biocompatibility is also an important requisite.

Aerospace application

- Aerospace has been the major field of application of titanium materials, particularly in the engine and airframe systems where it comprises 36% and 7% respectively.
- In parts subjected to aggressive conditions of corrosion, but not submitted to high mechanical and thermal demands, as are the cases of support structure under the kitchens and lavatories, the CP-Ti is usually used.
- In parts subjected to high mechanical and/or thermal demands, including engine components and airframe, the higher strength and heat resistant alloys are used, for example Ti-6Al-4V, Ti-6-2-4-2S, Ti- 13V- 11Cr-3Al, and IMI 834, among others.
- The major challenge has been to develop new alloys with improved strength and higher service temperature.

Automotive application

- The application of titanium materials in automobile industry began with F-1 racing cars in 1980s, being the application carried out primarily in the engine parts.
- Recently, titanium and its alloys are actively used for intake and exhaust valves, connecting rods, retainers, and others, being the weight saving the major benefits of such applications.
- The major need is the development of new alloys with higher service temperature, for example up to 800 °C for motorcycle exhaust valves application, and new surface treatment to improve wear resistance.
- New alloys for application in the automobile parts are currently under study, including Super-TIX, Super-TIX51AF, Super-TIX800, and TIMETAL@LCB, among others.

Biomedical application

- The use of titanium alloys as biomaterials has growing due to their reduced elastic modulus, good biocompatibility, excellent strength to weight ratio, and enhanced corrosion resistance when compared to conventional stainless steel and Co-Cr alloys.
- The CP-Ti and the Ti-6Al-4V are the most used titanium material in medicine, being the first considered the best biocompatible metallic material.
- Improving the biocompatibility through the elimination of potential toxic elements such as Al and V, and lowering the elastic modulus to a value similar of the bone are among the major problems on development of new titanium alloys for biomedical applications.

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