

SURFACE MODIFICATION OF Ti6Al4V TITANIUM ALLOY FOR BIOMEDICAL APPLICATIONS AND ITS EFFECT ON TRIBOLOGICAL PERFORMANCE – A REVIEW

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Abstract. Since its first introduction in the 1950s, Ti6Al4V became the most favorable titanium alloy due to its attractive mechanical and physicochemical properties and is currently extensively used e.g. in biomedical industry. However, its poor tribological properties limit its use in orthopedic applications. Hence, a variety of attempts have been made in order to improve tribological performance of titanium alloys, especially focusing on surface modification. This paper represents an overview of surface modification techniques applied on Ti6Al4V alloy during the last 15 years. The effects of oxidizing, deposition of carbon-based amorphous coatings, nitrogen-based layers and other surface modification techniques have been reviewed. According to the provided information, the durability, efficiency and reliability of popular anti-wear coatings strongly depends not only on the type of surface modification, research methods or experiment setup, but also on the experiment conditions, such as sliding velocity or applied load. Due to that, it is recommended to develop unified standards for wear tests of biomedical alloys used in orthopedic-related applications, e.g. arthroplasty.

1. INTRODUCTION

Modern engineering materials, such as metallic alloys, ceramics, composites, and plastics are often subjected to harsh working conditions during their operation, what results in wear, corrosion development and fatigue. Active work on removing or minimizing materials' failures is nowadays necessary due to existing raw materials and energy shortage. Among all engineering materials, titanium and its alloys are considered attractive materials in numerous branches of industry, due to their excellent properties such as high strength-to-weight ratio, low elastic modulus, anti-magnetic properties, high biocompatibility and acceptable corrosion resistance [1-10]. Hence, since its first introduction in the early 1950s [11,12], Ti6Al4V has become the most favorable titanium alloy. Ti6Al4V alloy covers about 50%

of total titanium world production [11] and today is extensively used in automotive, aerospace, chemical, marine and biomedical industries [5,11,12]. However, the main alloy's drawback - arising from inherent nature of Ti - poor tribological properties, such as: high and unstable coefficient of friction (COF) [4], low abrasive and adhesive wear resistance [4,13], low hardness [5,14], strong tendency to galling [15], low load-carrying capacity [7,15] significantly limit its use in wear-related engineering applications. Insufficient tribological properties are considered as key disadvantage when using Ti6Al4V also as an implant material. According to the *primum non nocere* primary ethical medical standard, patient's health and safety are a priority in the treatment process. References give examples of complications resulting from poor wear resistance of Ti6Al4V alloy, e.g. damage done to human tissues

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due to toxicity of aluminum and vanadium [1], coupling between metallic implants [3] and their aseptic loosening [6,10], inflammation of surrounding tissues [7,10], and, as a result, osteolysis [6-7,10].

However, wear of metallic implants is connected not only with patient's pain, but also with consequent loss of accuracy and implant failure [7,16]. Therefore, prosthesis failure avoidance is one of the main goals of these materials, and one of the recurrent approaches is minimizing wear on the biomaterial's surface. This necessitates enhancement of surface hardness as well as reduction of friction coefficient between contacting surfaces. Hence, a variety of attempts have been made in order to improve tribological performance of titanium alloys, especially focusing on surface modification. For this purpose, many studies have been carried out to modify the bearing surface of Ti6Al4V alloy, such as nitriding [2,9], ion implantation [2,6,9,16-17], thermal oxidation [6,9,17], laser surface treatments [2,9,17], and others.

In this paper, an attempt to systematize and summarize surface modification techniques applied on Ti6Al4V alloy during the last 15 years and their impact on its wear resistance has been made.

2. OXIDIZING

The excellent biocompatibility of titanium alloys is widely associated with the naturally formed surface oxide properties. Nonetheless, the few nanometers thick [18-19], composed mainly of TiO_2 [18] and accompanied by some Ti_2O_3 and TiO [20], spontaneously formed in ambient air oxide layer is too thin to effectively prevent the *in vivo* release [21] of cytotoxic vanadium and causing neurological disorders aluminum ions [21-24] and can be easily damaged. One of the methods to solve problems connected with abrasion wear debris coinciding with Al and V metal ions is to deposit thicker ceramic films, able to increase wear and corrosion resistance of the titanium alloy [21]. In recent years, oxidation processes have attracted many scientists' attention due to high solubility of oxygen in titanium. Nowadays, oxidation treatments are the most popular titanium alloy surface modification techniques, which allow to produce a relatively thick coating for final goods surface protection [25]. Processes such as anodic oxidation (AO), thermal oxidation (TO), plasma immersion ion implantation (PIII), plasma electrolytic oxidation (PEO) and plasma oxidation (PO) [26-27] have been used to improve tribological properties of titanium alloys.

Anodic oxidation (AO) is a traditional surface modification method, suitable for all valve-metals,

by which an oxide film grows *in-situ* on material [27,28]. In the potentiostatic method, the oxide layer is directly related to the anodizing voltage: the higher the voltage, the thicker the film [28]. Its low production cost [29] and ease of operation, as well as ability to improve wear, adhesion and corrosion [27,28], make it an advantageous method for use in mass production. The use of this surface modification technique results even in tenfold thickening of the film [30]. The oxide film is reported to act as a solid lubricant [27], but in some severe friction conditions, anodized films are unable to meet the standards desirable in friction of mechanical parts. Thin oxide films are susceptible to fracture due to scratches, fretting and loading – their biocompatibility deteriorates when the material is plastically deformed [28].

Wear behavior of anodically oxidized Ti6Al4V alloy was studied by Li et al. [27], who carried out tribological tests with a ball-on-flat contact configuration under dry conditions at a room temperature (Table 1). It was stressed that wear of TiO_2 films is of abrasive form. The authors demonstrated that when using surface modification by anodic oxidation it is reasonable to introduce nanoparticles in order to improve surface layer's hardness and resistance to wear. The authors suggested that introducing SiC nanoparticles significantly reduces ball penetration, tear and wear debris volume, which results in even 5-fold reduction of wear.

Another way to introduce oxide to Ti6Al4V alloy surface layer is to apply thermal oxidation. It is believed to be a simple and cost-effective method based on a formation of a thick and hard oxide rutile-based film on the surface [31,32]. According to Wang et al. [31] rutile ceramic coatings are characterized by higher bonding strength and relatively higher thickness than naturally formed oxide layers. Thermal oxidation temperature and time are the leading factors in the wear performance of oxidized layer [31]. However, due to high temperatures and prolonged duration of the process, debonding stratification between oxide scales and interface is observed [32-34]. Some authors also claim that TO processes are time-consuming and the thick oxygen diffusion zone obtained in the technological process is susceptible to deteriorate the mechanical properties of the substrate [35].

Several attempts to determine tribological properties of thermal oxidized titanium alloys were made by Wang et al. in their three recent works [6,31,32]. In one of the studies, the research couple was UHMWPE ball (spherical pin) and TO Ti6Al4V [31]. It occurred that even without lubrication, COF of oxidized alloy is relatively low (0.17) and highly

Table 1. Tribological properties of oxidized Ti6Al4V (COF – coefficient of friction, Y – year of publication).

Friction couple	Oxidizing method	Experimental setup	Lubrication	COF	Wear rate	Additional information	Y	Ref
Si ₃ N ₄ / TiO ₂ Ti6Al4V	AO	Ball-on-flat	-	-	2.1×10 ⁻⁵ μm ³ /Nm	Si ₃ N ₄ φ2 mm ball, 4 N load, oscillating amplitude of 6 mm, 30 min test duration	2014	[27]
Si ₃ N ₄ / TiO ₂ /SiC Ti6Al4V	AO	Ball-on-flat	-	-	0.3×10 ⁻⁵ μm ³ /Nm	Si ₃ N ₄ φ2 mm ball, 4 N load, oscillating amplitude of 6 mm, 30 min test duration	2014	[27]
UHMWPE / TiO ₂ Ti6Al4V	TO	Ball-on-disc	Distilled water	0.1	2.32×10 ⁶ μm ³	UHMWPE pin (20 mm radius, with spherical crown of 14 mm radius), 90 N load, 6 h of constant sliding, 0.05 m/s sliding speed, 8 mm stroke	2014	[32]
UHMWPE / TiO ₂ Ti6Al4V	TO	Ball-on-disc	25-wt % bovine serum	0.05	1.10×10 ⁶ μm ³	UHMWPE pin (20 mm radius, with spherical crown of 14 mm radius), 90 N load, 6 h of constant sliding, 0.05 m/s sliding speed, 8 mm stroke	2014	[32]
UHMWPE / TiO ₂ Ti6Al4V	TO	Ball-on-disc	-	0.17	2.93×10 ⁶ μm ³	UHMWPE pin (20 mm radius, with spherical crown of 14 mm radius), 90 N load, 6 h of constant sliding, 0.05 m/s sliding speed, 8 mm stroke	2014	[32]
UHMWPE / TiO ₂ Ti6Al4V	TO	Ball-on-disc	Distilled water	0.1	2.32×10 ⁶ μm ³	UHMWPE pin (20 mm radius, with spherical crown of 14 mm radius), load of 90 N, 6 h of constant sliding, 0.05 m/ s sliding speed, 8 mm stroke	2014	[6]
UHMWPE / TiO ₂ Ti6Al4V	TO	Ball-on-disc	25-wt % bovine serum	0.05	1.10×10 ⁶ μm ³	UHMWPE pin (20 mm radius, with spherical crown of 14 mm radius), load of 90 N, 6 h of constant sliding, 0.05 m/ s sliding speed, 8 mm stroke	2014	[6]
UHMWPE / TiO ₂ Ti6Al4V	TO	Ball-on-disc	-	0.17	2.93×10 ⁶ μm ³	UHMWPE pin (20 mm radius, with spherical crown of 14 mm radius), load of 90 N, 6 h of constant sliding, 0.05 m/ s sliding speed, 8 mm stroke	2014	[6]
ZrO ₂ / TiO ₂ Ti6Al4V	TO	Ball-on-disc	-	0.413	3.769×10 ⁸ μm ³	Load of 3 N, 1 h test, 0.08 m/s sliding speed, 4 mm stroke, ZrO ₂ φ6.35 mm ball	2014	[6]
ZrO ₂ / TiO ₂ Ti6Al4V	TO	Ball-on-disc	25-wt% bovine serum	0.197	7.337×10 ⁷ μm ³	Load of 3 N, 1 h test, 0.08 m/s sliding speed, 4 mm stroke, ZrO ₂ φ6.35 mm ball	2014	[6]
ASI 52100 / TiO ₂ Ti6Al4V	PEO	Ball-on-disc	-	0.65	-	AlSI 52100 φ5.5 mm ball, load of 2 N, 4 mm stroke diam- eter, 0.075 m/s sliding speed, 300 m track	2013	[25]
ASI 52100 / TiO ₂ Ti6Al4V	PEO	Ball-on-disc	-	0.8	1.7×10 ⁻⁵ μm ³ /Nm	AlSI 52100 φ3 mm ball, load of 2 N, oscillating amplitude of 5 mm for 30 min	2013	[9]

AlSi 52100 / TiO ₂ /MoS ₂ Ti6Al4V	PEO	Ball-on-disc	-	0.12	5.5 × 10 ⁻⁶ μm ³ /Nm	AISI 52100 φ3 mm ball, load of 2 N, oscillating amplitude of 5 mm for 30 min	2013 [9]
Al ₂ O ₃ -TiO ₂ (plasma sprayed) /TiO ₂ Ti6Al4V	PEO	Flat-on-cylinder	-	0.24	-	PEO Ti6Al4V stationary sliders (5×5×70 mm), 0.6 m/s sliding speed, 5000 m sliding distance, load of 35 N	2008 [38]
AlSi 52100 / TiO ₂ Ti6Al4V	PEO	Ball-on-disc	-	0.2	-	AISI 52100 φ4.75 mm ball, load of 100 N, 1000 rpm rota- tion speed, 10 min of sliding, 0.42 m/s sliding speed	2009 [41]
AlSi 52100 / TiO ₂ Ti6Al4V	PBII	Ball-on-disc	-	0.4	0.39×10 ⁻⁶ μm ³ /Nm	AISI 52100 φ6 mm ball, load of 0.784 N, 14 mm diameter of wear stroke, 0.12 m/s sliding speed, 1000 s time	2006 [46]
AlSi 52100 / TiO ₂ Ti6Al4V	PBII	Ball-on-disc	-	0.7	2.5 × 10 ⁻⁴ μm ³ /Nm	AISI 52100 φ5 mm ball, load of 0.196 N, 7 mm diameter of wear track, 73.3 m/s sliding speed, 35 min experiment	2011 [47]
Al ₂ O ₃ / TiO ₂ Ti6Al4V	PBII	Ball-on-disc	Hank's solution	0.09	2.441×10 ⁻³ μm ³ /Nm	Al ₂ O ₃ φ3 mm ball, load of 100 g, 30 000 cycles, linear speed of 0.1 m/s	2009 [42]
WC-Co / TiO ₂ Ti6Al4V	TPO	Ball-on-plate	-	0.9	9.05×10 ⁻⁶ μm ³	WC-Co φ10 mm ball, 5 Hz frequency, speed of 0.1 m/s, stroke length of 10 mm, load of 4 N, 1500 m sliding dis- tance	2011 [26]

stable. As the authors claim, the wear mechanism during dry sliding may be attributed to the mixture of mechanism of adhesion and abrasive wear. However, examples of spalling have also been provided. Compared to the untreated specimen, a significant decrease in friction and wear has been observed. The authors proposed two explanations for such behavior – first, they attributed decrease in wear to restriction of plastic and elastic deformation during friction when applying thermal oxidation. Second, they paid attention to oxygen deficiency of the rutile phase that decreases the friction by causing a low shear strength. Similar studies were made also in distilled water and bovine serum [32]. According to the authors, the best tribological performance was observed during the tests with bovine serum. Wang et al. [32] suggested that applying thermal oxidation results in increase of oxidized layers wettability, therefore enabling albumin absorption to the surface and forming the mixed or boundary lubrication film. According to Dong et al. [36] the wettability of the specimens increases with increasing ionic character of the surface. The rutile oxide formed during the TO treatment possesses much higher wettability than titanium alloys [36]. Findings by Wang et al. [32] were also confirmed in studies where ZrO_2 balls instead of UHMWPE pins were used [6].

The next worth mentioning oxidizing technique is derived from conventional anodic oxidation [37] plasma electrolytic oxidation (PEO), often also referred to as microarc oxidation (MAO). According to Ceschini et al. [38] it is “a novel surface modification technique based on the interaction between ceramic, anatase-rutile film growing on the anodic metal and spark arc microcharges initiated at the potentials exceeding the dielectric breakdown voltage of the film in almost neutral aqueous electrolyte”. Compared with the traditional anodizing, its main advantages are low process temperatures, which do not exceed 100 °C [38], ability to obtain thick oxidized films (1-100 μm) [35,38], high productivity and economic efficiency [35]. The technology has also its drawbacks, along which especially high porosity [38-40] and high friction coefficients under unlubricated conditions are mentioned [35]. Thus, numerous investigations in obtaining anti-frictional coatings on titanium alloys by plasma electrolytic oxidation have been performed.

According to Ceschini et al. [38], PEO treated Ti6Al4V displays significantly lower COF than TiAlN, TiN and superlattice CrN/NbN modified one. In this research, tribological behavior of MAO-treated material has been investigated in dry sliding conditions against ceramics during the flat-on-cylinder tests.

The authors stressed that PEO coatings have displayed superior tribological properties, even under high applied loads (35 N). The researchers claim that observed tribological behavior of MAO-modified material is related to the thickness of the layer – according to the authors, the main wear mechanism was micropolishing. Different results were obtained by Mu et al. [9] and Wang et al. [35] in the ball-on-disc dry sliding tests with AISI 52100 steel as a counter material. In contrast with findings by Ceschini et al. [38] that stated stability of COF of PEO layers under dry sliding, Mu et al. [9] and Wang et al. [35] have reported gradual increase of COFs during sliding up to 0.8. These findings were confirmed also by Chen et al. in recently developed impact-sliding tests [25]. What is more, Chen et al. [25] and Fei et al. [41] suggest pre-polishing of the substrate in order to obtain best tribological performance of the layers. According to Ceschini et al. [38], a typical value of COF for thick-coated alloys before the removal of the coating and beginning of severe wear damage varies in the range from 0.5 to 0.8. Nevertheless, Mu et al. [9] reported that the main wear mechanism of TiO_2 layer was abrasive wear, caused by detachment and brittle fracture of the TiO_2 coating. In order to improve insufficient tribological properties of oxidized layer obtained by the MAO method, the authors [9] suggested addition of solid lubricant MoS_2 particles to the structure. Introduction of TiO_2/MoS_2 composite layer resulted in one order of magnitude reduction of wear rate. Nevertheless, it ought to be stressed that addition of MoS_2 particles is not suitable for biomedical applications.

Oxidizing is currently performed also by ion implantation methods, considered as advanced treatments to improve tribological properties of materials for biomedical applications [42]. There are two most commonly used ion implantation techniques: traditional, beam-line ion implantation (BLII) and plasma based ion implantation (PBII), known also by the name of plasma immersion ion implantation (PIII) [43]. Due to the fact that ion beam systems are characterized by having a preferred direction (line-of-sight process), they constitute as perfect method to obtain surface modification in planar substrate like wafers, but are useless for treatment of three-dimensional objects because the substrate would have to be constantly moved to achieve required uniformity of the layer [43]. In plasma immersion ion implantation technique, the substrate is immersed in the plasma and by biasing it, it becomes a part of an ion source [43]. Therefore, it circumvents problems connected with line-of-sight

requirements and is applicable on large and complex-shaped components, and is considered as potentially more economical [44,45].

According to Li et al. [46] there are several reports on biocompatibility of oxygen-rich layers obtained by PIII, but there has been lack of information to study the effect of biasing the substrate on titanium alloys tribological properties. In their tribotests, they used AISI 52100 steel balls as counter-specimens. According to their findings, wear resistance of oxygen-implanted specimens increases with implanted voltage, reaching maximum at voltage of -50 kV ($0.39 \times 10^{-6} \text{ mm}^3/\text{Nm}$). Similar studies were conducted by Feng et al. [47] – the same pulse voltage, repeat frequency, implantation time and experiment setup (ball-on-disc) have been applied as in Li's experiment. In general, studies differed mainly in predefined conditions of wear studies (applied load, linear sliding speed). This resulted in significantly different outcome – in Feng's study, COF stabilized at ca. 0.7, but in Li's – varied from 0.3 to 0.4. What is more, Feng reported wear rate of $\text{O}_2\text{-PBII}$ layers of $25 \times 10^{-5} \text{ mm}^3/\text{Nm}$, but in Li's research it amounted only to $0.39 \times 10^{-6} \text{ mm}^3/\text{Nm}$. This implies that selection of test method and experiment conditions eminently determines results of frictional studies.

The last oxidizing method we would like to mention is triode plasma oxidation (TPO). This process differs from conventional plasma oxidizing methods through the use of tungsten hot filament as a third electrode. The tungsten, negatively biased electrode, mainly enhances the degree of plasma ionization through electron impact ionization effect. The increased number of oxygen ions then bombard the surface of the substrate and form a dense layer of good adhesion [26]. According to Banfield et al. [26] the TPO-obtained layers exhibit no flaking or spalling. Despite observed very high COF during the tribological tests, a small volume loss over large sliding distances was observed.

For comparison purposes, results from the wear resistance tests of oxidized Ti6Al4V alloy were presented in Table 1. As it can be seen, the authors determine wear in the means of wear volume calculated from depth and width of scars (e.g. [32]) or calculate wear coefficient, referred also to wear rate, from equation

$$W = V / PL \text{ in } \text{mm}^3/\text{Nm} \quad [46 - 47], \quad (1)$$

where V is wear volume (mm^3), P is perpendicular force (N), and L is total sliding distance (m). According to the provided results, the lowest wear rate

in the means of wear volume were obtained by Wang et al. [6,32] in studies where UHMWPE/TO Ti6Al4V tribological couple was lubricated by 25 wt.% bovine serum. Among tests conducted in ambient air, the best tribological properties by the means of calculated wear rate exhibits tribological pair consisting of AISI 52100 ball and PBII-O₂ Ti6Al4V. As one may have observed, most of the presented tribological studies are conducted in ball-on-disc configuration. Taking into account mentioned earlier problems with comparing results, it would be reasonable to perform comparative research, in which the same friction materials tribological properties, e.g. AISI 5200 steel/AO Ti6Al4V, would be tested in different experiment setups, e.g. ball-on-disc, pin-on-disc and ring-on-disc.

3. CARBON-BASED AMORPHOUS LAYERS

In modern literature, several names are attributed to describe amorphous carbon films. These include a:C (amorphous carbon), containing less than 1% hydrogen, a-C:H (amorphous hydrogenated carbon), containing up to about 50 at.% or i:C (ion bombarded carbon) [48,49]. Unlike diamond, which is a crystal with pure sp³ bonding [49], DLC films contain significant fractions of sp³ bonds, providing them attractive mechanical and physical properties [48]. The a-C films contain sp³ fractions greater than 85%, while the a-C:H layers typically contain less than 50% of sp³ bonds [48]. The amorphous hydrogenated carbon (a-C:H) films are often referred to as "DLC" in order to separate hydrogen-containing layers from the non-hydrogenated carbon (a-C), commonly called as ta-C [48].

Generally, mechanical properties of the carbon-based amorphous layers significantly differ from the ones of pure titanium or titanium alloys [50,51]. Under high loads, hard carbon-based films are unable to follow the elastic and plastic deformation of the titanium alloy substrate without fracture and delamination [4,50-52]. What is more, carbon amorphous layers typically exhibit high residual compressive stresses [51,53-58] which significantly limit their thickness, adhesion and, in the long-run, contribute to their tribological failure. Hence, some ways to improve the load-bearing of amorphous carbon layers/Ti6Al4V alloy by the means of enhancing the alloy's hardness have been proposed [50-52,55,56,60].

Numerous studies were performed to determine the tribological properties of carbon-based amorphous layers. To begin with a-C layers, an attempt

Table 2. Tribological properties of carbon-based amorphous layers (COF – coefficient of friction, Y – year of publication).

Friction couple	Sputtering method	Experiment setup	Lubrication	COF	Wear rate	Additional information	Y	Ref
Ti-6Al-4V / a-C Ti-6Al-4V	DC unbalanced magnetron sputtering	Ball-on-disc	-	0.10 $0.4 \pm 0.3 \times 10^{-6}$ $\mu\text{m}^3/\text{Nm}$	Ti6Al4V $\phi 8$ mm ball, load of 1 N, linear speed of 20 cm s^{-1} , 10 000 cycles	2013 [50]		
Ti-6Al-4V / a-C:Zr (7% Zr)	DC unbalanced magnetron sputtering	Ball-on-disc	-	0.15 $0.6 \pm 0.4 \times 10^{-6}$ $\mu\text{m}^3/\text{Nm}$	Ti6Al4V $\phi 8$ mm ball, load of 1 N, linear speed of 20 cm s^{-1} , 10 000 cycles	2013 [50]		
Ti-6Al-4V	Closed field unbalanced magnetron sputtering	Ball-on-disc	-	0.140 1.86×10^{-6} $\mu\text{m}^3/\text{Nm}$	Si_3N_4 $\phi 4$ mm ball, load of 5 N, 0.25 m/s sliding velocity, 30 000 cycles	2013 [56]		
Si_3N_4 / a-C/a-C:Ti (40 nm bilayer period) Ti6Al4V	Closed field unbalanced magnetron sputtering	Ball-on-disc	-	0.092 2.48×10^{-7} $\mu\text{m}^3/\text{Nm}$	Si_3N_4 $\phi 4$ mm ball, load of 5 N, 0.25 m/s sliding velocity, 30 000 cycles	2013 [56]		
Si_3N_4 / a-C/a-C:Ti (40 nm bilayer period) Ti6Al4V	Closed field unbalanced magnetron sputtering	Ball-on-disc	-	0.080 1.95×10^{-7} $\mu\text{m}^3/\text{Nm}$	Si_3N_4 $\phi 4$ mm ball, load of 10 N, 0.25 m/s sliding velocity, 30 000 cycles	2013 [56]		
Si_3N_4 / a-C/a-C:Ti (40 nm bilayer period) Ti6Al4V	Closed field unbalanced magnetron sputtering	Ball-on-disc	Hank's solution	0.074 4.25×10^{-8} $\mu\text{m}^3/\text{Nm}$	Si_3N_4 $\phi 4$ mm ball, load of 10 N, 0.25 m/s sliding velocity, 30 000 cycles	2013 [56]		
Si_3N_4 / a-C/a-C:Ti (12 nm bilayer period) Ti6Al4V	Closed field unbalanced magnetron sputtering	Ball-on-disc	-	0.09 8.06×10^{-8} $\mu\text{m}^3/\text{Nm}$	Si_3N_4 $\phi 4$ mm ball, load of 10 N, 0.2 m/s sliding velocity, 15 000 cycles	2014 [54]		
Si_3N_4 / a-C/a-C:Ti gradient composite Ti6Al4V	Closed field unbalanced magnetron sputtering with bias-graded voltage	Ball-on-disc	-	0.080 3×10^{-7} $\mu\text{m}^3/\text{Nm}$	Si_3N_4 $\phi 4$ mm ball, load of 10 N, 0.25 m/s sliding velocity, 30 000 cycles	2013 [55]		
Si_3N_4 / a-C/a-C:Ti gradient composite Ti6Al4V	Closed field unbalanced magnetron sputtering with bias-graded voltage	Ball-on-disc	Hank's solution	0.082 0.4×10^{-7} $\mu\text{m}^3/\text{Nm}$	Si_3N_4 $\phi 4$ mm ball, load of 10 N, 0.2 m/s sliding velocity, 30 000 cycles	2013 [55]		
SiC / DLC Ti6Al4V	Pulsed vacuum arc plasma deposition	Ball-on-disc	-	0.07 -	SiC $\phi 6$ mm ball, load of 0.98 N, 10 cm/s rotation speed, 6 mm rotation radius	2003 [61]		
UHMWPE / gradient DLC Ti6Al4V	Plasma source ion implantation-ion beam enhanced deposition	Pin-on-disc	-	0.137 0.8×10^{-6} $\mu\text{m}^3/\text{Nm}$	$\phi 10$ mm UHMWPE pin, 200 N load, 2000 m stroke	2004 [60]		
UHMWPE / gradient DLC Ti6Al4V	Plasma source ion implantation-ion beam enhanced deposition	Pin-on-disc	Bovine serum	0.128 0.6×10^{-6} $\mu\text{m}^3/\text{Nm}$	$\phi 10$ mm UHMWPE pin, 200 N load, 2000 m stroke	2004 [60]		

UHMWPE / gradient DLC Ti6Al4V	Plasma source ion implantation- ion beam enhanced deposition	Pin-on-disc	0.9-wt. % NaCl _{aq}	0.110	1.25×10^{-6} μm ³ /Nm	φ10 mm UHMWPE pin, 200 N load, 200 m stroke	2004 [60]
AlSI 52100 / DLC Ti6Al4V	Plasma assisted chemical vapor deposition	Ball-on-disc	-	0.08	2.6×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]
AlSI 52100 / DLC/TPN Ti6Al4V	Plasma assisted chemical vapor deposition-triode plasma nitriding	Ball-on-disc	-	0.06	1.4×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]
AlSI 52100 / DLC/TiN Ti6Al4V	Plasma assisted chemical vapor deposition-plasma assisted physical vapor deposition	Ball-on-disc	-	0.19	0.67×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]
AlSI 52100 / DLC/TiN/ TPN Ti6Al4V	Plasma assisted chemical vapor deposition-plasma assisted physical vapor deposition-triode plasma nitriding	Ball-on-disc	-	0.15	0.65×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]
AlSI 52100 / DLC/CrN Ti6Al4V	Plasma assisted chemical vapor deposition-plasma assisted physical vapor deposition	Ball-on-disc	-	0.21	1.2×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]
AlSI 52100 / DLC/CrAIN/ TPN Ti6Al4V	Plasma assisted chemical vapor deposition-plasma assisted physical vapor deposition-triode plasma nitriding	Ball-on-disc	-	0.16	1.1×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]
AlSI 52100 / DLC/CrAlN Ti6Al4V	Plasma assisted chemical vapor deposition-plasma assisted physical vapor deposition	Ball-on-disc	-	0.21	1.1×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]
AlSI 52100 / DLC/CrAlN/ TPN Ti6Al4V	Plasma assisted chemical vapor deposition- triode plasma nitriding	Ball-on-disc	-	0.12	1.0×10^{-7} μm ³ /Nm	100Cr6 φ10 mm steel ball, load of 5 N, 10 cm/s linear speed, 1256 m sliding distance (50 000 cycles)	2006 [51]

WC-Co / Ti-DLC Ti6Al4V	Closed field unbalanced magnetron sputtering	Ball-on-disc -	0.20	1.3×10^{-6} $\mu\text{m}^3/\text{Nm}$	WC-Co $\phi 5$ mm ball, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2010 [4]
WC-Co / Ti-DLC/PN Ti6Al4V	Closed field unbalanced magnetron sputtering-plasma nitriding	Ball-on-disc -	0.25	5×10^{-7} $\mu\text{m}^3/\text{Nm}$	WC-Co $\phi 5$ mm ball, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2010 [4]
Al_2O_3 / DMF (dimethylformamide) DLC Ti6Al4V	Electrochemical deposition	Ball-on-plate -	0.8	-	Al_2O_3 $\phi 7.75$ mm ball, load of 2 N, 1 Hz frequency, 1.5 mm track length, 1800 cycles	2012 [62]
Al_2O_3 / ACN (acetonitrile) DLC Ti6Al4V	Electrochemical deposition	Ball-on-plate -	0.75	-	Al_2O_3 $\phi 7.75$ mm ball, load of 2 N, 1 Hz frequency, 1.5 mm track length, 1800 cycles	2012 [62]
Al_2O_3 / DLC Ti6Al4V	Radio frequency plasma assisted physical vapor deposition	Ball-on-plate -	0.38	1.8×10^{-7} $\mu\text{m}^3/\text{Nm}$	Al_2O_3 $\phi 5$ mm ball, load of 16 N, sliding velocity of 32 mm/s, 8 mm track length, test performed for 2 h or until coating failure	2013 [52]
Al_2O_3 / DLC/nitrided Ti6Al4V	Radio frequency plasma assisted physical vapor deposition	Ball-on-plate -	0.43	1.76×10^{-7} $\mu\text{m}^3/\text{Nm}$	Al_2O_3 $\phi 5$ mm ball, load of 16 N, sliding velocity of 32 mm/s, 8 mm track length, test performed for 2 h or until coating failure	2013 [52]
Ti-6Al-4V / DLC Ti-6Al-4V sputtering	DC unbalanced magnetron	Ball-on-disc -	0.14	not measurable	Ti6Al4V $\phi 8$ mm ball, load of 1 N, linear speed of 20 cm s^{-1} , 10 000 cycles	2013 [50]
Ti-6Al-4V / DLC:Zr (7% Zr) Ti-6Al-4V ZrO ₂ / DLC Ti6Al4V ELI	DC unbalanced magnetron sputtering	Ball-on-disc -	0.15	$0.16 \pm 0.02 \times 10^{-6}$ $\mu\text{m}^3/\text{Nm}$	Ti6Al4V $\phi 8$ mm ball, load of 1 N, linear speed of 20 cm s^{-1} , 10 000 cycles	2013 [50]
ZrO ₂ / DLC Ti6Al4V ELI	Physical vapor deposition	Ball-on-disc -	0.083	3.111×10^{-7} μm^3	ZrO ₂ $\phi 6.35$ mm ball, load of 3 N, 0.08 m/s sliding speed, 4 mm stroke, 1 h test	2014 [6]
ZrO ₂ / DLC Ti6Al4V ELI	Physical vapor deposition	Ball-on-disc 25 - wt. % bovine serum	0.108	1.541×10^{-7} μm^3	ZrO ₂ $\phi 6.35$ mm ball, load of 3 N, 0.08 m/s sliding speed, 4 mm stroke, 1 h test	2014 [6]

to define their wear resistance was made by Escudero et al. [50]. In order to improve mechanical properties of obtained layer, before depositing carbon two transition layers – pure Ti and TiN/TiNC were sputtered. What is more, some of the a-C layers were co-sputtered with Zr. According to the results, pure a-C films presented higher elasticity than a-C:Zr films. As can be seen in Table 2, this translated to greater wear resistance of a-C layers. In order to overcome problems connected with delamination of a-C layers, Cai et al. [56] and Bai et al. [54] deposited a-C/a-C:Ti nanomultilayers. In the ball-on-disc studies performed by Cai et al. [56] the superlattice, Ti-containing amorphous film of 40 nm bilayer period was characterized by better wear resistance and lower COF than pure a-C layer (Table 2). What is more, application of Hank's solution as lubricant resulted in further improvement of tribological properties of the superlattice layer. Similar studies were performed by Bai et al. [54]. According to Table 2, a-C/a-C:Ti films with bilayer periods of 12 nm are characterized by the lowest wear rate during dry sliding among a-C/a-C:Ti films. Cai et al. [55] have also made an attempt to determine tribological properties of Ti-contained a-C gradient composite films. Provided results (Table 2) show that a-C:Ti composite is characterized by low COF and low wear rate. According to the authors [55] low friction coefficients of a-C films are related to the sp^3 to graphite-characteristic sp^2 phase transformation, possibly induced by stresses produced by the friction contacts.

DLC layers, due to their high inertness and excellent mechanical properties [52,60,61] are considered as attractive modern biomedical materials. Leng et al. [61] reported that when fabricating diamond-like-carbon by pulsed vacuum arc plasma deposition their performance highly depends on argon flow – the more argon, the lower the wear resistance. Samples prepared with the highest argon amount were characterized by immediate failure due to spalling. In the research made by Jiang et al. [60] the pin-on-disc setup was chosen for wear resistance analyses. Similarly to the research performed by Wang et al. [32] on thermal oxidized Ti6Al4V, the use of bovine serum reduces wear rate and friction coefficient of DLC layers. The same relationship between use of bovine serum as lubricant and reduction of friction coefficient and wear was observed by Wang et al. [6]. What is important, Jiang et al. [60] proved that not every lubricant fulfills its anti-frictional role (Table 2). The authors claim that under dry condition, debris was liable to be absorbed by UHMWPE pins and because of that,

the release of wear products was prevented. Avelar-Batista et al. [51] made an attempt to improve the load support of DLC coatings on Ti6Al4V substrates by using intermediate layers between the DLC top coat and metallic substrate. According to the results presented in Table 2, the best wear resistance was obtained by combining triode plasma nitriding (TPN) with DLC film. The validity of sputtering intermediate layers was also investigated by Yetim et al. [4]. In their research, a diffusion nitrides layer of 100 μm beneath the compound of Ti-DLC/PN (plasma nitrided) film improved the load-bearing capacities of the alloy and resulted in reduction of its wear in one order of magnitude (Table 2). On the contrary, Manhabosco et al. [52] reported failure of DLC/nitrided layer after first 16 minutes of the frictional test, which corresponded to a 0.02-0.03 km lifetime in the ball-on-plate study. Another way to improve tribological properties of DLC films is to introduce metallic elements. In the study by Escudero et al. [50] Zr-doping of hydrogenated a-C film resulted in increase of the layer hardness and reduction of friction coefficient and wear (Table 2).

In order to obtain a-C:H films not only physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods are used, but also electrodeposition techniques [62], although layers obtained by this process are not characterized by excellent frictional properties (Table 2).

As seen in Table 2, the best anti-wear properties among all amorphous carbon layers under both the dry and the lubricated conditions exhibit a-C/a-C:Ti superlattice layers. Compared with oxidized layers, COFs of amorphous carbon layers are similar, but wear rate significantly decreases. What is important, in every research where the amorphous carbon layers and untreated substrate were compared, carbon films deposition resulted in significant decrease in wear.

4. NITROGEN-BASED LAYERS

Tribological properties of Ti-based components are often commercially improved by the means of introduction of nitrogen to their surface [63]. In the case of the Ti6Al4V alloy, the nitrogen-based layers are formed by plasma nitriding (PN) [2,3,5,64,65], PVD [63], PIII [45,47,66,67], and BLII [42] methods.

Plasma nitriding is a diffusional process, in which a continuous hardness profile is obtained [3,68]. After the nitriding treatment of titanium alloys, the hard, consisting of TiN and Ti_2N layer forms on the material surface [3,5]. The layer does not only significantly improve the corrosion and wear resistance

Table 3. Tribological properties of nitrogen-based layers (COF – coefficient of friction, Y – year of publication).

Friction couple	Nitriding method	Experiment setup	Lubrication	COF	Wear rate	Additional information	Y	Ref
WC-Co / PN (650 °C, 1 h) Ti6Al4V	PN	Pin-on-disc	-	0.42-0.46	3.34×10^{-6} $\mu\text{m}^3/\text{Nm}$	5 mm diameter WC-Co pin, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2008	[3]
WC-Co / PN (650 °C, 4 h) Ti6Al4V	PN	Pin-on-disc	-	0.48-0.52	1.82×10^{-6} $\mu\text{m}^3/\text{Nm}$	5 mm diameter WC-Co pin, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2008	[3]
WC-Co / PN (700 °C, 1 h) Ti6Al4V	PN	Pin-on-disc	-	0.44-0.47	2.13×10^{-6} $\mu\text{m}^3/\text{Nm}$	5 mm diameter WC-Co pin, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2008	[3]
WC-Co / PN (700 °C, 4 h) Ti6Al4V	PN	Pin-on-disc	-	0.46-0.50	0.67×10^{-6} $\mu\text{m}^3/\text{Nm}$	5 mm diameter WC-Co pin, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2008	[3]
WC-Co / PN (750 °C, 1 h) Ti6Al4V	PN	Pin-on-disc	-	0.50-0.55	0.14×10^{-6} $\mu\text{m}^3/\text{Nm}$	5 mm diameter WC-Co pin, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2008	[3]
WC-Co / PN (750 °C, 4 h) Ti6Al4V	PN	Pin-on-disc	-	0.49-0.55	0.62×10^{-6} $\mu\text{m}^3/\text{Nm}$	5 mm diameter WC-Co pin, load of 10 N, 141 m sliding distance, 0.078 m/s sliding speed, 10 mm wear track diameter	2008	[3]
Al ₂ O ₃ / PN (750 °C, 1 h) Ti6Al4V	PN	Ball-on-disc	Ringer's solution	0.7	4.5×10^{-9} $\mu\text{m}^3/\text{Nm}$	Al ₂ O ₃ φ6 mm ball, load of 2 N, sliding velocity of 5 cm/s, sliding distance of 142 m	2009	[2]
Al ₂ O ₃ / PN (800 °C, 10 h) Ti6Al4V	PN	Ball-on-plate	-	0.41	2.4×10^{-6} μm^3	Al ₂ O ₃ φ5 mm ball, load of 4 N, sliding velocity of 8 mm/s, 8 mm sliding distance, 2 h test	2011	[65]
Si ₃ N ₄ / PN (cathode assisting discharge)	PN	Ball-on-disc	-	1.0	8.9×10^{-6} μm	Si ₃ N ₄ φ5 mm ball, load of 10 N, 141 m total sliding distance, 0.1 m/s sliding speed, 4 mm wear track diameter	2013	[64]
Ti6Al4V	PN	Ball-on-disc	-	0.45	8.9×10^{-8} μm	Si ₃ N ₄ φ5 mm ball, load of 10 N, 141 m total sliding distance, 0.1 m/s sliding speed, 4 mm wear track diameter	2013	[64]

Al_2O_3 / Ti/TiN Ti6Al4V	Cathodic Arc Evaporation (CAE) PVD	Ball-on-disc	-	4.60×10^{-5} $\mu\text{m}^3/\text{Nm}$	$\text{Al}_2\text{O}_3 \phi 4$ mm ball, load of 10 N, sliding speed of 0.05 m/s, 200 m total sliding distance, 4 mm radius of the track	2008 [63]
Al_2O_3 / Ti/TiN +WC-Co Ti6Al4V	CAE PVD (TiN)+HVOF (WC-Co)	Ball-on-disc	-	3.86×10^{-6} $\mu\text{m}^3/\text{Nm}$	$\text{Al}_2\text{O}_3 \phi 4$ mm ball, load of 10 N, sliding speed of 0.05 m/s, 200 m total sliding distance, 4 mm radius of the track	2008 [63]
AlSi 52100 / oxynitrided Ti6Al4V	PII	Ball-on-disc	0.65	8.5×10^{-5} $\mu\text{m}^3/\text{Nm}$	AlSi 52100 $\phi 5$ mm ball, load of 0.196 N, 7 mm diameter of wear circle, 73.3 m/s sliding speed, 35 min experiment	2011 [47]
Al_2O_3 / N_2 -implanted Ti6Al4V	BLII	Ball-on-disc	Hank's solution	2.441×10^{-4} $\mu\text{m}^3/\text{Nm}$	$\text{Al}_2\text{O}_3 \phi 3$ mm ball, load of 0.98 N, linear speed of 0.1 m/s, 30 000 cycles	2009 [42]

of the Ti6Al4V alloy [3], but also helps to reduce the amount of Al and V concentrations on the implant surface near zero [69]. Yildiz et al. [3] conducted the study in which wear properties of plasma nitrided in different conditions Ti6Al4V alloy were determined. According to the authors, the friction coefficient did not show an important change after nitriding, but the wear resistance of the alloy increased with the presence of TiN in the compound layer. What is more, the wear rate decreased with increase of the process temperature (Table 3). Compared to the bare alloy, the wear resistance of nitrided samples improved. In the next study by Yildiz et al. [2] the frictional properties of the nitrided layer were compared with TiAlN and Al_2O_3 sputtered films. According to the authors, the highest COF, higher even of that of bare material, was obtained for nitrided sample. It was also noted that all surface treatments improved the wear resistance of Ti6Al4V alloy, but the lowest wear rate was achieved for alumina coating. Yetim et al. [5] confirmed the anti-wear properties of plasma nitrided Ti6Al4V, but the best frictional properties were exhibited by oxynitrided samples, obtained in a combination of plasma nitriding and oxidizing. The greatest diffusion zone depth of oxynitrided samples and formation of both oxides and nitrides improved load-bearing capacity of the alloy and reduced the risk of adhesion between the pin and the substrate [5]. Moreover, in the ball-on-plate wear tests performed by Manhabosco et al. [65] it was stressed that, compared to the bare material, plasma nitriding reduced wear volume of the substrate approximately 900 times. The wear tracks of nitride samples showed a narrow, smooth and shallow wear track with an expressive reduction of wear debris. No adhesive wear mechanism was observed. Tang et al. [64] investigated the effect of plasma nitriding by the cathode assisting discharge nitriding (CAN) and conventional DC plasma nitriding (CPN) methods. The results indicated that the CAN layers are characterized by greater wear resistance than the CPN film at high loads (Table 3). The wear resistance measured in volume loss of the CAN diffusion layers was about 2 orders of magnitude increased due to their high load-bearing ability, higher TiN phase rate, greater surface microhardness and nitrogen ion flux in the depth of the substrate.

An attempt to obtain duplex coating Ti/TiN+WC-Co by the means of PVD and high velocity oxygen fuel (HVOF) was made by Bemporad et al. [63] (Table 2). The authors pointed out that after wear tests complete delamination of Ti/TiN layer was

observed, while no delamination occurred after introduction of WC-Co interlayer. Compared with the uncoated alloy, after introducing WC-Co to the substrate its wear rate decreased two orders. However, according to the recent studies, cobalt toxicity has been reported in patients who became recipients of cobalt-containing hip prostheses [70,71]. What is more, according to Witten et al. [72] chronic exposure to tungsten may result in severe health problems.

Nitriding is performed also by ion implantation techniques [42,66,67]. Since its first introduction in the 1980s [67], PIII has evolved to a mature surface modification method that contributed to significant achievements in the field of biomedical applications [73,74]. Currently it is a popular method for obtaining oxynitrided and duplex Ti-O/Ti-N coatings. In the research by Feng et al. [47] oxynitriding by PIII technique resulted in 5-fold reduction of wear rate compared with untreated substrate. Comparing the wear track of the implanted sample and the untreated one, after oxynitriding the main wear mechanism changes from adhesive to ploughing.

The traditional beam-line ion implantation (BLII) technique was used by Díaz et al. [42] to introduce nitrogen to the surface of the Ti6Al4V alloy (Table 2). It was mentioned that nitrogen-implanted substrate decreased in hardness compared with the reference one. What is more, no significant decrease in wear rate was observed.

According to Table 3, the lowest COF value was obtained in wear test where lubricated by Hank's solution BLII N₂-implanted Ti6Al4V coupled with Al_2O_3 balls. At the same time, the wear rate calculated from Eq. (1) was the greatest in this study. The lowest wear rate under dry conditions amongst all nitrogen-based layers was observed by Yildiz et al. [3] for plasma nitrided specimens.

Considering nitrogen-based coatings, we would also like to mention the problem that was shown in recent research by Saravanan et al. [75] on the effect of wear parameters and their effects on TiN coated surface sliding against Ti6Al4V alloy. It has been observed that the minimal wear mass loss is identified at 2 N load and 0.75 m/s sliding velocity. However, the minimum coefficient of friction was registered with the maximum applied load and higher sliding distance. This implies that not only mechanical properties of the substrate and the coating or the experiment setup affect wear resistance of surface modified alloys, but also working conditions, such as sliding velocity, determine performance of coated metallic alloys.

5. OTHER MODIFICATION TECHNIQUES

As mentioned in the Introduction, titanium and its alloys are characterized by poor friction and wear properties, such as high friction coefficient, severe adhesive wear and low abrasion resistance in harsh or *in vivo* conditions [76]. In order to improve their insufficient tribological properties, many more than only oxidizing, amorphous carbon-based or nitrogen-based layers modification techniques are used. In this chapter the less-popular or, to the authors' best knowledge, not proven to be biocompatible, but promising for application in the mechanical industry surface modification techniques will be presented.

Over the past few years, boriding, a diffusion-based thermochemical treatment has been increasingly used to improve the performance of biomedical ferrous and non-ferrous alloys [77,78]. Boriding titanium alloys may be beneficial for biomedical applications due to the high hardness and excellent wear of titanium borides [79], but according to Campos-Silva et al. [78] literature lacks information about the biocompatibility of these films.

In the research by Lee et al. [79] it was pointed out that wear rate of titanium balls coated with a dual layer boride ($TiB_2 + TiB$) mated against alumina was 40 times less than that of alumina balls mated against alumina. The borided material wore by an abrasive process, resulting in a relatively smooth wear surface. However, the research was conducted in the light mineral oil, which is not suitable for use in biomedical applications. Excellent anti-wear properties of borided films were also proven by Atar et al. [11] and Qin et al. [15]. According to Atar et al. [11] the wear mode of borided titanium alloy changes from ploughing to polishing. The authors stressed that borided Ti6Al4V exhibit superior tribological performance in both dry and lubricated conditions (Table 4). Moreover, Qin et al. [15] stated that boriding of Ti6Al4V alloy results in significant improvement of its tribological properties, resulting in about 35 times greater wear resistance compared to the uncoated alloy coupled with corundum ball.

The other group of popular anti-wear coatings are Cr-based thin layers, which are already in use for machining tools [80], mainly of Cu-, Al-, and Ti-based alloys [81]. According to the literature, the most popular ones, CrN coatings, are characterized by good thermal stability, sufficient corrosion resistance and high toughness [82]. However, its usage in wide variety of biomedical applications is

limited due to its relatively low hardness [81] and concerns regarding toxicity of chromium [83]. To improve wear performance of CrN coatings on Ti6Al4V alloy, multilayers are often formed [82,84]. In the research by Chang et al. [82], it was stated that the CrN/Cr transitional coatings are characterized by good anti-abrasive properties and high micro-hardness. However, in their study wear tests lasted for 5 minutes, what corresponds to total sliding distance of 4.8 m. Nie et al. [84] deposited rutile on the surface of Ti6Al4V alloy in order to act as load-bearing interphase in CrN/TiO₂ composite coatings. It was stressed that relatively hard CrN coatings need an intermediate support layer on soft substrates (e.g. Ti alloys) for wear-related applications. According to the authors, the duplex process of reactive unbalanced magnetron sputtering of CrN and micro-arc oxidation results in significant decrease in wear Ti6Al4V alloy. However, a relatively high wear rate ($5.69 \times 10^{-4} \text{ mm}^3/\text{Nm}$) of CrN-coated reference specimens was observed after 500 m of sliding distance. On the contrary, superior anti-wear properties of CrN coatings were presented in the research by Yang et al. [81]. After 2000 m of total sliding distance, CrN layer deposited on Ti6Al4V alloy exhibited higher dry sliding wear resistance even than TiN coatings. Nevertheless, the authors stated that the best anti-wear properties were obtained for CrTiAlN nanolayered coating (Table 4).

6. CONCLUSIONS

In this paper, an attempt to systematize and summarize surface modification techniques applied on Ti6Al4V alloy during the last 15 years and their impact on its wear resistance has been made. Amongst all the results discussed in this study, the lowest wear rates in tribological tests are observed for amorphous carbon layers. Although it is described in the literature, that DLC and ta-C coatings are unable to follow plastic deformation of titanium alloys under high loads, after deposition on Ti6Al4V alloy they exhibit superb anti-wear performance even without application of transition layers or introducing selected atomic elements. In comparison with other surface modification methods suitable for biomedical products, carbon-based amorphous layers provide reduction of wear rate over of few orders of magnitude. Nevertheless, it ought be stressed that DLC layers deposited electrochemically are not suitable for orthopedic applications due to very high COFs when mated against alumina.

On the other hand, far worse anti-wear performance is exhibited by the nitrided titanium alloy or

Table 4. Tribological properties of other selected layers (COF – coefficient of friction, Y – year of publication).

Friction couple	Modification technique	Experiment setup	Lubrication	COF	Wear rate	Additional information	Y	Ref
Borided Ti6Al4V / Al ₂ O ₃	Solid-state diffusion	Ball-on-disc	Light mineral oil	0.1095	6.08 × 10 ⁻⁸ μm ³ /Nm	Ti6Al4V φ6.35 mm borided ball, Al ₂ O ₃ disc, load of 49 N, velocity of 0.12 m/s, 1000 m sliding distance, room temperature	2008	[79]
Sapphire (Al ₂ O ₃) / Borided Ti6Al4V	Pack boriding	Ball-on-flat	-	0.4	-	Al ₂ O ₃ φ10 mm ball, Ti6Al4V 10×10×10 mm cubic borided samples, load of 12 N, 8 mm stroke, 0.02 m/s sliding speed, testing time of 150 min	2008	[11]
Sapphire (Al ₂ O ₃) / Borided Ti6Al4V	Pack boriding	Ball-on-flat	Boundary lubrication with synthetic oil	0.1	-	Al ₂ O ₃ φ10 mm ball, Ti6Al4V 10×10×10 mm cubic borided samples, load of 20 N, 8 mm stroke, 0.02 m/s sliding speed, testing time of 150 min	2008	[11]
Al ₂ O ₃ / Borided Ti6Al4V	Double glow plasma boriding	Ball-on-disc	-	5.41 × 10 ⁻⁶ μm ³ /Nm	Al ₂ O ₃ φ5 mm ball, borided Ti6Al4V discs, load of 5 N, 11 mm wear track radius, 138 mm/s sliding speed of the ball, 100 m total sliding length	2013	[15]	
Si ₃ N ₄ / CrN/Cr Ti6Al4V	Arc ion plating	Ball-on-disc	-	0.4	-	Si ₃ N ₄ φ4 mm ball, CrN/Cr Ti6Al4V discs, load of 3 N, sliding displacement amplitude of 4 mm, sliding frequency of 4 Hz, test duration of 5 min	2011	[82]
WC-Co / CrN Ti6Al4V	Reactive magnetron sputtering	Ball-on-disc	-	0.70	3.6 × 10 ⁻⁷ μm ³ /Nm	WC-6%Co ball, CrN Ti6Al4V substrates, load of 10 N, sliding speed of 20 cm/s, total sliding distance of 2 000 m	2008	[81]
WC-Co / CrTiAlN Ti6Al4V	Reactive magnetron sputtering	Ball-on-disc	-	0.86	2.6 × 10 ⁻⁸ μm ³ /Nm	WC-6%Co ball, CrN Ti6Al4V substrates, load of 10 N, sliding speed of 20 cm/s, total sliding distance of 2 000 m	2008	[81]
AlSi 52100 / CrN Ti6Al4V	Micro-arc oxidation + unbalanced magnetron sputtering	Ball-on-disc	-	0.61	5.69 × 10 ⁻⁴ μm ³ /Nm	AlSi 52100 φ10 mm ball, CrN Ti6Al4V substrates, load of 10 N, sliding speed of 0.1 m/s, sliding distance of 500 m	2000	[84]
AlSi 52100 / CrN/TiO ₂ Ti6Al4V	Micro-arc oxidation + unbalanced magnetron sputtering	Ball-on-disc	-	0.57	-	AlSi 52100 φ10 mm ball, CrN/TiO ₂ Ti6Al4V substrates, load of 10 N, sliding speed of 0.1 m/s, sliding distance of 500 m	2000	[84]

by the extremely popular in orthopedic applications coatings formed during oxidizing processes. However, their anti-wear properties are strongly dependent on surface modification process parameters. For example, coefficient of friction of oxide coatings formed in plasma electrolytic oxidation (PEO) process mated against AISI 52100 steel can vary from 0.2 to 0.8. On the other hand, plasma nitrided Ti6Al4V is characterized by relatively high (>0.4), but stable COFs. Nonetheless, wear of nitrided surfaces is two orders of magnitude lower than that of lubricated N₂-implanted surfaced, despite of their four times higher COFs and work in dry conditions.

Moreover, our study showed that high variety in experiment conditions can be observed. Experiments are carried out in setups such as ball-on-disc, ball-on-flat, flat-on-cylinder, ball-on-plate, pin-on-disc, amongst which the most common one (ca. 90% of all research) is ball-on-disc. Nevertheless, it is virtually impossible to compare volumetric wear or wear rate of tribological systems when conditions of the experiments vary dramatically. Even if the same friction couple, e.g. AISI 52100 vs. PO Ti6Al4V, is analyzed in two separate studies, the counter specimens can be of different diameters, specific loads are applied, sliding speeds or number of cycles differ significantly.

In view of provided information, the described durability, efficiency and reliability of anti-wear coatings strongly depend on the research methods and experiment conditions. Taking into account safety of the patients, it is recommended to develop unified and as close as possible to the actual operating conditions standards for wear tests of surface modified biomedical alloys, especially the ones used in orthopedic applications.

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REFERENCES

- [1] X. Zeng, T. Yamaguchi and K. Nishio // *Surf Coat Tech* **262** (2015) 1.
- [2] F. Yildiz, A.F. Yetim, A. Alsaran and I. Efeoglu // *Wear* **267** (2009) 695.
- [3] F. Yildiz, A.F. Yetim, A. Alsaran and A. Çelik // *Surf Coat Tech* **202** (2008) 2471.
- [4] A.F. Yetim, A. Çelik and A. Alsaran // *Surf Coat Tech* **205** (2010) 320.
- [5] A.F. Yetim, F. Yildiz, Y. Vangolu, A. Alsaran and A. Celik // *Wear* **267** (2009) 2179.
- [6] S. Wang, Z. Liao, Y. Liu and W. Liu // *Surf Coat Tech* **252** (2014) 64.
- [7] V. Sáenz de Viteri, M.G. Barandika, U. Ruiz de Gopegui, R. Bayón, C. Zubizarreta, X. Fernández, A. Igartua and F. Agullo-Rueda // *J Inorg Biochem* **117** (2012) 359.
- [8] G. Perumal, M. Geetha, R. Asokamani and N. Alagumurthi // *Wear* **311** (2014) 101.
- [9] M. Mu, J. Liang, X. Zhou and Q. Xiao // *Surf Coat Tech* **214** (2013) 124.
- [10] A. Fan, Y. Ma, R. Yang, X. Zhang and B. Tang // *Surf Coat Tech* **228** (2013) S419.
- [11] E. Atar, E.S. Kayali and H. Cimenoglu // *Surf Coat Tech* **202** (2008) 4583.
- [12] A. Zhecheva, W. Sha, S. Malinov and A. Long // *Surf Coat Tech* **200** (2005) 2192.
- [13] K.G. Budinski // *Wear* **151** (1991) 203.
- [14] M. Niinomi // *Sci Technol Adv Mater* **4** (2003) 445.
- [15] L. Qin, C. Liu, K. Yang and B. Tang // *Surf Coat Tech* **225** (2013) 92.
- [16] Y. Qin, D. Xiong, J. Li and R. Tyagi // *Tribol Int* **82** (2015) 543.
- [17] D. Xiong, Y. Yang and Y. Deng // *Surf Coat Tech* **228** (2013) S442.
- [18] M. Masmoudi, M. Assoul, M. Wery, R. Abdelhedi, F. El Halouani and G. Monteil // *Appl Surf Sci* **253** (2006) 2237.
- [19] L. Mohan and C. Anandan // *Appl Surf Sci* **282** (2013) 281.
- [20] M.T. Mohammed, Z.A. Khan and A.N. Siddiquee // *Procedia Mater Sci* **6** (2014) 1610.
- [21] Y.X. Leng, J.Y. Chen, P. Yang, H. Sun and N. Huang // *Nucl Instrum Meth B* **257** (2007) 451.
- [22] H.M. Silva, S.G. Schneider and C. Moura Neto // *Mat Sci Eng C-Bio S* **24** (2004) 679.
- [23] J.C. Pessoa, S. Etcheverry and D. Gambino // *Coordin Chem Rev* **301-302** (2015) 24.
- [24] M. Belen Suárez-Fernández, A.B. Soldado, A. Sanz-Medel, J.A. Vega, A. Novelli and M.T. Fernández-Sánchez // *Brain Res* **835** (1999) 125.
- [25] Y. Chen, T. Cheng and X. Nie // *J Alloy Compd* **578** (2013) 336.
- [26] S. Banfield, J.C. Avelar-Batista Wilson, G. Cassar, A. Leyland, A. Matthews and J. Housden // *Surf Coat Tech* **206** (2011) 1955.
- [27] Song-mei Li, Xiu-mei Yu, Jian-hua Liu, Mei Yu, Liang Wu and Kang Yang // *J Cent South Univ* **21** (2014) 4415.

- [28] M. Łepicka, M. Grądzka-Dahlke and A. Sobolewski // *MP Mater Test* **57** (2015) 393.
- [29] A. Karambakhsh, A. Afshar, S. Ghahramani and P. Malekinejad // *J Mater Eng Perform* **20** (2011) 1690.
- [30] J.L. Ong, L.C. Lucas, G.N. Raikar and J.C. Gregory // *Appl Surf Sci* **72** (1993) 7.
- [31] S. Wang, Z. Liao, Y. Liu and W. Liu // *Surf Coat Tech* **240** (2014) 470.
- [32] S. Wang, Y. Liu, C. Zhang, Z. Liao and W. Liu // *Tribol Int* **79** (2014) 174.
- [33] P.A. Dearnley, K.L. Dahm and H. Çimenoglu // *Wear* **256** (2004) 469.
- [34] D.S.R. Krishna, Y.L. Brama and Y. Sun // *Tribol Int* **40** (2007) 329.
- [35] Y.M. Wang, B.L. Jiang, T.Q. Lei and L.X. Guo // *Surf Coat Tech* **201** (2006) 82.
- [36] H. Dong and T. Bell // *Wear* **238** (2000) 131.
- [37] F. Liu, J.L. Xu, D.Z. Yu, F.P. Wang and L.C. Zhao // *J Alloy Compd* **487** (2009) 391.
- [38] L. Ceschini, E. Lanzoni, C. Martini, D. Prandstraller and G. Sambogna // *Wear* **264** (2008) 86.
- [39] A.L. Yerokhin, A. Leyland and A. Matthews // *Appl Surf Sci* **200** (2002) 172.
- [40] T.H. Teh, A. Berkani, S. Mato, P. Skeldon, G.E. Thompson, H. Habazaki and K. Shimizu // *Corros Sci* **45** (2003) 2757.
- [41] C. Fei, Z. Hai, C. Chen and X. Yangjian // *Prog Org Coat* **64** (2009) 264.
- [42] C. Díaz, J. Lutz, S. Mändl, J.A. García, R. Martínez and R.J. Rodríguez // *Nucl Instrum Meth B* **267** (2009) 1630.
- [43] J. Pelletier and A. Anders // *IEEE Transactions on Plasma Science* **33** (2005) 1.
- [44] Y.X. Leng, J.Y. Chen, Z.M. Zeng, X.B. Tian, P. Yang, N. Huang, Z.R. Zhou and P.K. Chu // *Thin Solid Films* **377** (2000) 573.
- [45] Y.X. Leng, P. Yang, J.Y. Chen, H. Sun, J. Wang, G.J. Wang, N. Huang, X.B. Tian and P.K. Chu // *Surf Coat Tech* **138** (2001) 296.
- [46] J. Li, M. Sun, X. Ma and G. Tang // *Wear* **261** (2006) 1247.
- [47] X. Feng, M. Sun, X. Ma and G. Tang // *Appl Surf Sci* **257** (2011) 9904.
- [48] A. Grill // *Diam Relat Mater* **8** (1999) 428.
- [49] A. Gangopadhyay // *Tribol Lett* **5** (1998) 25.
- [50] A. Escudeiro, T. Polcar and A. Cavaleiro // *Thin Solid Films* **538** (2013) 89.
- [51] J.C. Avelar-Batista, E. Spain, G.G. Fuentes, A. Sola, R. Rodriguez and J. Housden // *Surf Coat Tech* **201** (2006) 4335.
- [52] T.M. Manhabosco, A.P.M. Barboza, R.J.C. Batista and B.R.A. Neves, I.L. Müller // *Diam Relat Mater* **31** (2013) 58.
- [53] S.J. Cho, J.W. Chung and K.R. Lee // *Diam Relat Mater* **14** (2005) 1270.
- [54] W.Q. Bai, J.B. Cai, X.L. Wang, D.H. Wang, C.D. Gu and J.P. Tu // *Thin Solid Films* **558** (2014) 176.
- [55] J.B. Cai, X.L. Wang, W.Q. Bai, X.Y. Zhao, T.Q. Wang and J.P. Tu // *Appl Surf Sci* **279** (2013) 450.
- [56] J.B. Cai, X.L. Wang, W.Q. Bai, D.H. Wang, C.D. Gu and J.P. Tu // *Surf Coat Tech* **232** (2013) 403.
- [57] G. Dearnaley and J.H. Arps // *Surf Coat Tech* **200** (2005) 2518.
- [58] M.G. Kovaleva, A.Y. Kolpakov, A.I. Poplavskii, I.Y. Goncharov, M.S. Prozorova, M.Y. Arseenko and M.Y. Smolyakova // *J Frict Wear* **33** (2012) 260.
- [59] V.N. Inkin, G.G. Kirpilenko, A.A. Dementjev and K.I. Maslakov // *Diam Relat Mater* **9** (2000) 715.
- [60] Shu-wen Jiang, Bin Jiang, Yan Li, Yan-rong Li, Guang-fu Yin and Chang-qiong Zheng // *Appl Surf Sci* **236** (2004) 285.
- [61] Y.X. Leng, J.Y. Chen, P. Yang, H. Sun, G.J. Wan and N. Huang // *Surf Sci* **531** (2003) 177.
- [62] T. Falcade, T.E. Shmitzhaus, O.G. dos Reis, A.L.M. Vargas, R. Hübler, I.L. Müller and C. de Fraga Malfatti // *Appl Surf Sci* **263** (2012) 18.
- [63] E. Bemporad, M. Sebastiani, M.H. Staia and E. Puchi Cabrera // *Surf Coat Tech* **203** (2008) 566.
- [64] J.G. Tang, D.X. Liu, C.B. Tang and X.H. Zhang // *Sci China Technol Sc* **56** (2013) 1858.
- [65] T.M. Manhabosco, S.M. Tamborim, C.B. dos Santos and I.L. Müller // *Corros Sci* **53** (2011) 1786.
- [66] M.M. Silva, M. Ueda, L. Pichon, H. Reuther and C.M. Lepienski // *Nucl Instrum Meth B* **257** (2007) 722.
- [67] M. Ueda, R.M. Oliveira, J.O. Rossi, C.B. Mello, Rita C.C. Rangel and M.S. Vieira // *Surf Coat Tech* **229** (2013) 97.
- [68] M. Łepicka and M. Grądzka-Dahlke // *Acta Mechanica et Automatica* **8** (2014) 156.

- [69] F. Galliano, E. Galvanetto, S. Mischler and D. Landolt // *Surf Coat Tech* **145** (2001) 121.
- [70] A. Harris, J. Johnson, P.K. Mansuripur and R. Limbird // *Arthroplasty Today* **1** (2015) 89.
- [71] S.M. Bradberry // *Medicine* **44** (2016) 182.
- [72] M.L. Witten, P.R. Sheppard and B.L. Witten // *Chem-Biol Interact* **196** (2012) 87.
- [73] P.K. Chu // *Surf Coat Tech* **203** (2009) 2793.
- [74] P.K. Chu // *Surf Coat Tech* **204** (2010) 2853.
- [75] I. Saravanan, A.E. Perumal, R.F. Issac, S.C. Vettivel and A. Devaraju // *Mater Design* **92** (2016) 23.
- [76] W. Wang, M. Wang, Z. Jie, F. Sun and D. Huang // *Opt Laser Eng* **46** (2008) 810.
- [77] B. Sivakumar, R. Singh and L.C. Pathak // *Mater Sci Eng C Mater Biol Appl* **48** (2015) 243.
- [78] I. Campos-Silva, D. Bravo-Bárcenas, A. Meneses-Amador, M. Ortiz-Dominguez, H. Cimenoglu, U. Figueroa-López and J. Andraca-Adame // *Surf Coat Tech* **237** (2013) 402.
- [79] C. Lee, A. Sanders, N. Tikekar and K.S. Ravi Chandran // *Wear* **265** (2008) 375.
- [80] B. Podgornik, M. Sedlaček and D. Mandrino // *Tribol Int* **96** (2016) 247.
- [81] Q. Yang, L.R. Zhao, F. Cai, S. Yang and D.G. Teer // *Surf Coat Tech* **202** (2008) 3886.
- [82] Z.K. Chang, X.S. Wan, Z.L. Pei, J. Gong and C. Sun // *Surf Coat Tech* **205** (2011) 4690.
- [83] Q. Wang, F. Zhou, C. Wang, M.F. Yuen, M. Wang, T. Qian, M. Matsumoto and J. Yan // *Mater Chem Phys* **158** (2015) 74.
- [84] X. Nie, A. Leyland and A. Matthews // *Surf Coat Tech* **133-134** (2000) 331.