Tribology International 130 (2019) 359–365

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Tribological and corrosive investigations of perfluoro and alkylphosphonic self-assembled monolayers on Ti incorporated carbon coatings

M. Cichomski[a,*], B. Burnat[b], M. Prowizor[a], A. Jedrzejczak[c], D. Batory[d], I. Piwoński[a], W. Kozłowski[e], W. Szymanski[c], M. Dudek[c]

[a] University of Lodz, Faculty of Chemistry, Department of Materials Technology and Chemistry, Pomorska 163, 90-236, Lodz, Poland
[b] University of Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Tamka 12, 91-403, Lodz, Poland
[c] Lodz University of Technology, Institute of Materials Science and Engineering, Stefanowskiego 1/15, 90-924, Lodz, Poland
[d] Lodz University of Technology, Department of Vehicles and Fundamentals of Machine Design, Stefanowskiego 1/15, 90-924, Lodz, Poland
[e] University of Lodz, Faculty of Physics and Applied Informatics, Department of Solid State Physics, Pomorska 149/153, 90-236, Lodz, Poland

A R T I C L E I N F O

Keywords:
Titanium incorporated carbon coatings
Self-assembled monolayers
Corrosion
Tribology

A B S T R A C T

This paper presents tribological and corrosion properties of perfluoro and alkylphosphonic self-assembled monolayers formed on Ti incorporated carbon coatings. The Ti-DLC incorporated coatings were deposited on Ti6Al4V substrates by Radio Frequency Plasma Enhanced Chemical Vapour Deposition (RF PECVD) method using combination of methane (CH_4) and titanium (IV) isopropoxide (Ti [$OCH(CH_3)_2]_4$) atmospheres. The obtained coatings were subsequently modified by perfluoro and alkylphosphonic self-assembled layers having hydrocarbon or perfluorocarbon chains (DP and PFDP). Presented results show that application of these compounds on the top of Ti-DLC coatings significantly improves their tribological properties. After 1000 m of ball-on-disc test the DP- and PFDP- modified coatings presented low coefficient of friction, showing particularly more stable and lower value in case of PFDP while the unmodified coating was worn out already after 160 m of the test under the same conditions. The corrosion tests show varied results for both modifiers. In the case of PFDP an increased reactivity of the coating is observed, whereas for DP the results prove the anti-corrosive effect of this self-assembled layer.

1. Introduction

The development of new production technologies requires new functional materials possessing good mechanical, tribological and anti-corrosion parameters. One of the ways leading to improve these parameters of engineering materials is the modification of their surface with adequate single, multilayer and nanocomposite coatings using chemical or physical vapour deposition techniques. Here, the low friction and high wear resistant materials are particularly interesting, as every improvement of these properties ensures beneficial effect in widely understood, long-term perspective of durability. Diamond like carbon coatings (DLC), due to their excellent mechanical, chemical and tribological properties [1–8], play an important role in the contemporary technique. Moreover, further their modifications based on the incorporation of different elements into their amorphous structure noticeably improve their properties [9–12]. Here, special attention deserve silicon and titanium incorporated carbon coatings, presenting a remarkably low coefficient of friction and decreased level of residual stress [9–11]. Titanium incorporated carbon coatings are characterized by chemical inertness which is extremely important and desirable in biomedical and biological applications. These coating are good candidate to improve surface characteristic of Ti6Al4V alloy which despite commonly used in biomedical application, show problems in direct contact with blood (for instance, thrombogenesis and protein adsorption) [13–16]. Moreover, apart from physicochemical and biological properties, friction coefficient and wear resistance are another critical parameters that have to be considered while dealing with medical implants, especially the load bearing ones.

An interesting way of further improvement of the functional parameters of the coatings is modification of their surface by organic thin layers, exhibiting good antifriction and anticorrosion properties. Good candidates for this purpose are technologically attractive perfluoro and alkylphosphonic acids due to their lubricating properties, thermal stability, possibility of controlling their ordering and interactions at the molecular level, and finally simplicity of deposition methods [17–19]. Alkylphosphonic acids ($RPO(OH)_2$) as self-assembled monolayers

* Corresponding author.
E-mail address: mcichom@uni.lodz.pl (M. Cichomski).

https://doi.org/10.1016/j.triboint.2018.10.010
Received 25 July 2018; Received in revised form 23 September 2018; Accepted 8 October 2018
Available online 09 October 2018

(SAMs) are built of three groups: a head group that reacts with a substrate, a backbone molecular chain group and a terminal group, that interacts with the outer surface of the film [20,21]. Such structure allows to use them as thin layers deposited on various substrates. The stability of alkylphosphonic acids on the native oxide surfaces of different metal substrates such as magnesium, aluminum, copper nickel, titanium and their alloys is determined by covalent bonds between molecules and the surface as well as interactions between the neighboring molecules consisting of three or two reactive atoms in the head group [22,23]. The optimal choice of each group will provide the monolayer exhibiting the best performance, namely low adhesion, friction and wear [24,25]. The interactions between the backbone chain groups of different molecules, such as van der Waals forces or hydrogen bonding, contribute to the formation and stability of the deposited layers with hydrophilic or hydrophobic character. Thin layers of perfluoro and alkylphosphonic acids deposited on the surface can act as nanometer-scale lubricants decreasing friction and protecting the substrate against wear. Furthermore, an ultrathin organic layer appears to be appropriate to control the interface regions between the surface and environment. This, in turn, makes SAMs an effective method of improving the corrosion resistance [26].

In this work titanium-incorporated diamond like carbon coatings (Ti-DLC) were deposited on Ti6Al4V substrates by RF PECVD method using different combinations of methane (CH_4) and titanium (IV) isopropoxide (Ti $[OCH(CH_3)_2]_4$) atmosphere. The obtained coatings were subsequently modified by self-assembled monolayers of phosphonic acids. Here, the titanium atoms incorporated in DLC were supposed to play the role of adhesion promoting centers between the amorphous carbon matrix and self-assembled monolayers of phosphonic acids. Two types of compounds with different functional groups: *n*-decylphosphonic acid (DP) and 1H, 1H, 2H, 2H-perfluorodecylphosphonic acid (PFDP) were used in the investigation. The obtained DP and PFDP modified Ti-DLC coatings were investigated in terms of corrosion and tribological properties.

2. Materials and methods

2.1. Ti-DLC coating deposition process

Titanium incorporated DLC coatings were deposited on Ti6Al4V substrates (6 mm thick and one inch in diameter discs) by RF PECVD (RF, 13.56 MHz) method. Prior to the deposition process the samples surfaces were grinded on sandpapers with a gradation between 80 and 2000 and polished with colloidal silica suspension using an automatic polishing machine – surface roughness (R_a) measured by Hommel Tester T1000 profilometer was equal to 0.021 ± 0.001 µm. The samples were then ultrasonically cleaned in acetone bath and placed on the water cooled RF electrode. The vacuum chamber was pumped to a base pressure of 2 Pa. Before the deposition process samples were cleaned and activated by Ar ions of the high intensity RF plasma discharge for 10 min at the negative self-bias of 1100 V and 4 Pa of the residual pressure. The deposition of Ti-DLC coatings was performed under 400 V of the negative self-bias potential and pressure of 20 Pa from a mixture of CH_4 and Ti $[OCH(CH_3)_2]_4$. The chemical composition of the coatings was controlled by changing the methane and titanium (IV) isopropoxide (TIP) flow ratio in the working gas atmosphere (see Table 1). The flow rate of methane was controlled by a mass flowmeter, whereas TIP flow was controlled by a needle valve – after establishing a flow of methane, vapours of TIP were introduced to the deposition chamber to obtain the operating pressure of 20 Pa (see Table 1). The temperature of bubbler with TIP was PLC controlled and kept at the level of 85 °C, whereas the rest of the gas supplying system connecting the bubbler with the deposition chamber was heated up to 100 °C. The thickness of the coatings was optimized for further investigations by choosing an appropriate duration of the deposition time. For the purpose of tribological investigations the thickness of coatings was set to 1000 nm, whereas for the corrosion measurements to 100 nm. In order to improve the adhesion of the coatings to the substrate, prior to deposition of Ti-DLC coatings for the tribological investigations, Ti interface layer having the thickness of 100 nm was deposited by a magnetron sputtering technique.

Table 1
Combinations of methane and TIP atmospheres used for the deposition of titanium incorporated carbon coatings.

Coating	CH_4 flow (sccm)	Ratio of TIP pressure to total pressure, p_{TIP}/p_{total}	Total pressure (Pa)
DLC	20	0	20
Ti-DLC1	18	0.05	20
Ti-DLC2	15	0.17	20
Ti-DLC3	14	0.21	20

2.2. Ti-DLC modification process

Two types of self-assembled monolayers were formed on the surface of Ti-DLC coatings. These chemicals were chosen to compare the effect of terminal group structure on the tribological and corrosion performance. The modifiers were purchased from ABCR, GmbH & Co. KG, Karlsruhe. In the first preparation step, the surface of Ti-DLC coating was activated by an air plasma, resulting in creation of hydroxyl and Ti–O groups playing the role of anchoring centers for modifying compounds, necessary for the creation of stable covalent bonds between the modifier molecules and the coating surface [27,28]. The plasma process was performed with the use of Diener Electronic Plasma-Surface-Technology, Zepto, 40 Hz, 100 W. Phosphonic acid layers were produced on the surface of Ti-DLC coatings by the liquid phase deposition (LPD) method. DP and PFDP solutions having the concentration from 0.05% (wt.%) and 0.5% (wt.%) were prepared by dissolving the solid phosphonic acid in ethanol at room temperature under ambient conditions for 60 minutes. After immersion of Ti-DLC coatings in DP and PFDP solution the samples were removed and rinsed several times in fresh ethanol to remove physisorbed molecules from the surface. Finally, the modified Ti-DLC coatings were blown with dry argon and annealed at 60 °C for 24 h. Details concerning the optimization of these layers deposition procedure, including such parameters as time and base solutions and concentration were reported in our previous publication [29].

2.3. Characterisation methods

The thickness of Ti-DLC coatings was determined by X-ray reflectivity (XRR) method. The XRR tests were performed with use of the Empyrean X-ray diffractometer (PANalytical) working with Cu Kα radiation (λ = 0.15418 nm). The data processing was done using X'Pert Reflectivity software. The hardness and Young's modulus of the coatings were determined by nanoindentation method exploiting the continuous stiffness measurement (CSM) technique. The tests were performed with the use of the Nano Indenter G200 (MTS Systems Corp.) equipped in the Berkovich pyramid. The data were analyzed using the Oliver and Pharr approach [30]. The tests were performed at room temperature and about 40% of humidity.

The chemical structure of titanium incorporated carbon coatings was investigated with the use of Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR). The tests were performed by the Renishaw in Via Raman Microscope equipped with 532 nm laser arranged in a backscattering geometry. The investigated wavenumber ranged from 750 to 2100 cm^{-1}. All measurements were carried out in air at room temperature. FT-IR measurements were performed with the use of Nicolet iS50 FTIR spectrophotometer with ultra-high sensitive, low noise, linearized mercury-cadmium-telluride (MCT) detector. The VariGATR™ grazing angle ATR accessory equipped in reflectance Ge