Surface & Coatings Technology 460 (2023) 129409

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Effect of a DLC film on the sliding-wear behaviour of Ti6Al4V: Implications for dental implants

Fernando Rodríguez-Rojas [a], Miroslavna Kovylina [b], Elena Pinilla-Cienfuegos [b,**], Óscar Borrero-López [a,*], Avi Bendavid [c], Philip J. Martin [c], Mark Hoffman [d]

[a] Departamento de Ingeniería Mecánica, Energética y de los Materiales, Universidad de Extremadura, 06006 Badajoz, Spain
[b] Nanophotonics Technology Center, Universitat Politècnica de València, Valencia E46022, Spain
[c] CSIRO Manufacturing, Lindfield, NSW 2070, Australia
[d] School of Engineering, University of Newcastle, Newcastle 2308, Australia

ARTICLE INFO

Keywords:
Dental implants
Ti6Al4V
Diamond-like carbon (DLC)
Wear
Durability

ABSTRACT

Titanium alloys are widely used in parts of dental implants, such as screws and abutments. In practice, unwanted relative sliding between contacting implant parts can cause excessive wear, which may lead to early failure. The effect of a submicron diamond-like carbon (DLC) coating on the friction and wear of Ti6Al4V alloys under sliding contact in artificial saliva was investigated. Critically, the DLC film suppressed adhesion between contacting surfaces, significantly lowered the coefficient of friction and contact stress, and ultimately the wear rate, relative to uncoated Ti6Al4V, while maintaining good film-substrate bonding and undergoing a limited extent of fracture. Results are explained within the framework of contact mechanics. Implications for the development of durable dental implants are discussed.

1. Introduction

Owing to their biocompatibility and osseointegration capacity, high corrosion resistance, strength, and machinability, titanium alloys (especially Ti6Al4V) are widely used in the more internal parts of dental implants, namely the screw and the abutment [1]. The connection between screw and abutment is intended to be fixed and motionless, *i.e.*, experiencing static friction only. However, unwanted relative rotation in practice can result in sliding contact. Even if such contact is of small amplitude, the dynamic friction associated with sliding inevitably causes wear. If excessive, this wear may loosen the connection between screw and abutment and contribute to early failure [2–7].

Titanium alloys typically show strong adhesion in sliding contacts against metals, resulting in high friction and severe wear (galling) [8,9]. Secondary abrasion can also take place, typically controlled by plastic deformation, but also assisted by fracture when brittle tribolayers form [10]. Moreover, under certain conditions—including conditions which may occur in the human oral environment [11,12]—titanium can also be subject to corrosion, harmful for human health. Accordingly, ceramic coatings and films (with primarily ionic-covalent atomic bonding) have been considered in order to decrease friction and wear and to impart chemical protection for Ti-based implant parts [12,13]. Among these, diamond-like carbon (DLC) presents a unique combination of mechanical and tribological properties and, being biocompatible and bioinert, has demonstrated potential for use in both orthopaedics and dental implants [2,4,14–18]. However, some studies have indicated that DLC bonds relatively poorly to Ti-based substrates, which can limit the durability of the coating [17,19–22]. Moreover, DLC films can be significantly harder and stiffer than Ti-alloys. Property mismatch thus results in relatively large stresses at the film/substrate interface upon cyclic loading, which limits their use to relatively low loads [23].

Previous work [8] investigated the sliding-wear of DLC/Ti6Al4V *vs* Ti6Al4V cylinders by means of galling tests, using high loads (up to 200 N), without external lubrication. The DLC films effectively prevented adhesion at low and intermediate loads, thereby reducing friction and resulting in significantly greater galling loads compared with uncoated contacts. Galling was related to film delamination at high contact pressures. These films provided increased protection relative to other surface treatments such as thermal oxidation and TiN films. In this tribosystem wear rates are dependent on load/contact pressure and sliding

* Corresponding author number 1.
** Corresponding author number 2.
E-mail addresses: epinilla@ntc.upv.es (E. Pinilla-Cienfuegos), oborlop@unex.es (Ó. Borrero-López).

https://doi.org/10.1016/j.surfcoat.2023.129409
Received 26 January 2023; Received in revised form 2 March 2023; Accepted 4 March 2023
Available online 11 March 2023

speed, with wear transitions related to tribochemical reactions [24].

In the field of biomedical engineering, much of the research on the tribological aspects of DLC-coated titanium has focused on orthopaedic implants, typically employing a counter-body other than titanium, such as ceramic (*e.g.*, [25–28]) or polymer (*e.g.*, [29–31]), and lubrication by some form of simulated body fluid. In general, the application of a DLC coating to orthopaedic Ti-based implant parts under sliding was found to protect against the severe adhesion and oxidation occurring in uncoated systems, and to result mostly in moderate abrasion [10,26,27,29]. As a result, DLC films generally decreased friction and wear compared to uncoated tribopairs by up to various orders of magnitude (*e.g.*, by factors of ~10 [10,32], $\sim 10^2$ [25,26], and $\sim 10^3$ [27]), with specific wear rates dependent on the particular contact and environmental conditions employed.

Work in the dental field has focused on actual screw-abutment contacts involving DLC films (*e.g.*, [2,4,33,34]). One of the issues with such studies is that the contact configuration is complex and there are competing failure modes, *e.g.* plastic yield, fatigue, fracture, wear, and corrosion. This hinders comparison, and can lead to contradictory results, with some studies concluding that DLC coatings significantly improve the resistance to screw loosening [2,33] while others find no difference between coated and uncoated groups [4,34]. Moreover, studies in dentistry generally provide limited information on wear mechanisms. Investigations using model systems under simplified contact conditions (*e.g.*, pin-on-disk) have the advantage of allowing specific effects of friction and wear to be assessed independently [35,36]. Employing such systems, it was reported that, also under artificial saliva lubrication, a DLC coating suppressed oxidation and adhesion and minimized abrasion of Ti6Al7Nb alloys against Si_3N_4 antagonists, leading to reductions by factors of up to 5 in the coefficient of friction (CoF) and 15 in the wear rate compared with uncoated systems [37]. When tested against ZrO_2 antagonists, relatively thick (in excess of 1 μm) polycrystalline diamond coatings resulted in reductions by up to a factor of 3 in the CoF of Ti6Al4V alloys [6].

Given the above, the present study was aimed at contributing fresh experimental friction and wear results in the Ti6Al4V *vs* DLC/Ti6Al4V tribopair under artificial saliva lubrication by means of pin-on-disk engineering tests, as a simple model of dental implant against abutment sliding contacts. Effects of a thin (less than 1 μm thickness) DLC film are investigated with a view to providing guidelines for the development of durable dental implants. Wear tests are supplemented with microscopy observations of both the surface and the cross-section for detailed analysis of the damage modes and mechanisms. Results are explained within the framework of contact mechanics.

2. Materials and methods

Ti6Al4V alloy substrates were employed (Shaanxi CXMET Technology Co. Ltd., China). The chemical composition of the substrates was Al: 6.0 wt%, V: 4.0 wt%, Fe: 0.05 wt%, C: 0.01 wt%; N: 0.009 wt%; H: 0.001 wt%; O: 0.06 wt%, Ti: balance. Substrates were ground and initially polished using 15 μm diamond suspension and then finely-polished using an oxide suspension consisting of 2.0 ml ammonia and 1.0 ml hydrogen peroxide. Polished substrates were subsequently washed with isopropanol and nitrogen dried.

DLC films were deposited onto TiAl4V substrates using a custom-made radio-frequency plasma enhanced chemical vapour deposition (RF-PECVD) system [38], equipped with a turbo pump. The vacuum achieved in the chamber was 1×10^{-3} Pa. Acetylene (C_2H_2), argon (Ar), and tetramethylsilane (TMS) were employed as process gases. Mass flow controllers were employed to control the individual gas flow into the chamber. The deposition pressure was controlled by adjusting a throttle valve. All specimens were sputter cleaned *in-situ* prior to the deposition of a hydrogenated amorphous silicon carbide (a-SiC:H) bonding layer, obtained from a TMS precursor, at a pressure of 3.3 Pa, with the TMS flow rate set to 80 standard cubic centimetres per minute (sccm) at 200 W for 3 min (~75 nm thickness). For the DLC films, deposition conditions were: pressure of 6.6 Pa, C_2H_2 flow rate of 100 sccm, RF power of 200 W, and deposition duration 10 mins. The self-bias voltages during the deposition of a-SiC:H and DLC were 650 V and 450 V, respectively.

The thickness of the deposited DLC films was measured from Focused-Ion Beam, FIB (AURIGA Compact, ZEISS, Germany), micrographs to be 800 nm. DLC films' elastic modulus and hardness are ≈106 GPa, and ≈12.8 GPa, respectively, and contain an equibiaxial, compressive, residual stress of ≈1 GPa [39]. The elastic modulus and hardness of Ti6Al4V are 110 GPa, and 3.4 GPa, respectively [40].

The surface of the materials prior to tribological testing was inspected by Atomic-Force Microscopy, AFM (Bruker Multimode 8), operated in PeakForce Tapping mode, and optical profilometry (Profilm, Filmetrics, San Diego, CA). Average roughness (R_a) values of 0.031 ± 0.003 μm and 0.039 ± 0.009 μm were measured on uncoated Ti6Al4V substrates, and DLC/Ti6Al4V systems, respectively.

Sliding-wear experiments were conducted using a pin-on-disk test equipment (THT, Anton Paar, Graz, Austria) [41]. Precision Ti6Al4V spheres (grade 200) of radius $R = 3$ mm (Goodfellow Cambridge Ltd., UK) were used as pin, and plane-parallel DLC-coated and uncoated Ti6Al4V specimens as disk. The normal load selected was $F = 20$ N, within the 5 N–100 N interval typically used in *in-vitro* wear testing of dental systems [42]. The load employed in this study lies within the lower range of that interval as being assumed to be representative of the load transferred to an individual implant upon chewing. The radius of wear scar and sliding speed were 3 mm and 10 mm·s^{-1}, respectively. The sliding distance was $L = 150$ m. A commercial artificial saliva solution (Lacer S.A., Spain), with a viscosity of 3.22 mm^2·s^{-1} at 20 °C, was employed as lubricant. For each tribosystem, tests were performed three times. The wear volume (V) of the disks was calculated from direct measurements on the scars using the profilometer, as indicated in greater detail elsewhere [43]. The wear volume of the pins was estimated from the diameter of the wear scar, d, measured by optical microscopy (Epiphot 300, Nikon, Tokyo, Japan), in accordance to $V = \frac{\pi d^4}{64R}$ [41]. Specific wear rates (SWR) were calculated as $SWR = \frac{V\ (mm^3)}{F(N) \bullet L(m)}$.

The surface and cross-section of the specimens after testing were inspected by High Resolution Field Emission Scanning Electron microscopy (HRFESEM, Quanta 3D FEG, FEI, The Netherlands, and GeminiSEM 500, Zeiss, Germany) and FIB microscopy, respectively. The SEM observations were made using secondary electrons at accelerating voltages up to 15 kV. The FIB cross-section milling was done using intensities of 10 nA; with the milled cross-sections subsequently being polished using intensities of 100 pA, and finally imaged with secondary electrons. Specimens were not metal-coated prior to microscopy.

Relevant contact stresses were simulated using the commercial software package FilmDoctor® (SIO®, Saxonian Institute of Surface Mechanics, Ruegen, Germany). The software calculates stress fields in substrate-film(s) systems, from the contact conditions and the materials' elastic property values, using the extended Hertzian model for layered materials [44].

3. Results

Fig. 1 shows representative AFM micrographs of the surface of uncoated (Fig. 1(A)) and DLC-coated (Fig. 1(B)) Ti6Al4V substrates used as disk specimens in the pin-on-disk tests. Both surfaces are very smooth, showing asperities of heights less than 9 nm, with slightly greater mean and dispersion in the coated specimen. These values are consistent with the low R_a values measured by profilometry (0.031 ± 0.003 μm and 0.039 ± 0.009 μm, in the uncoated Ti6Al4V substrates and the DLC films, respectively).

Fig. 2 shows the coefficient of friction (CoF) data measured from the pin-on-disk tests for the tribosystems Ti6Al4V (pin) *vs* Ti6Al4V (disk), hereafter 'Uncoated', and Ti6Al4V (pin) *vs* DLC/Ti6Al4V (disk), hereafter 'Coated'. Compared with the 'Coated' system, the friction curve for

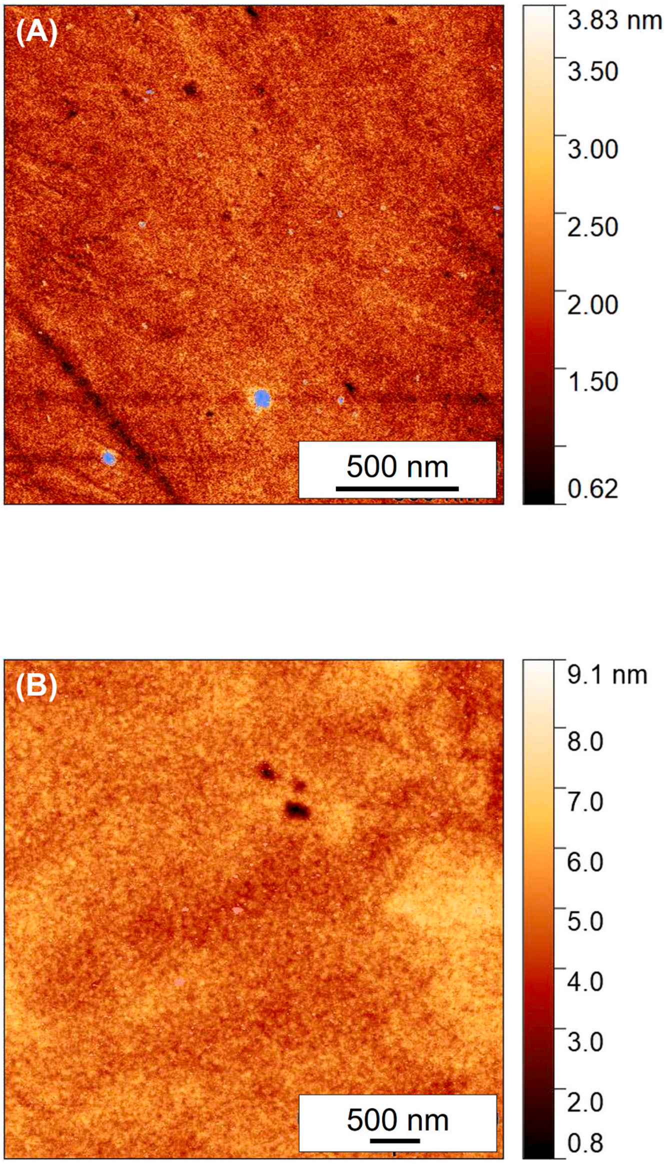

Fig. 1. AFM topography micrographs of the surface of (A) uncoated Ti6Al4V substrate; and (B) DLC-coated Ti6Al4V. Shading indicates height contours.

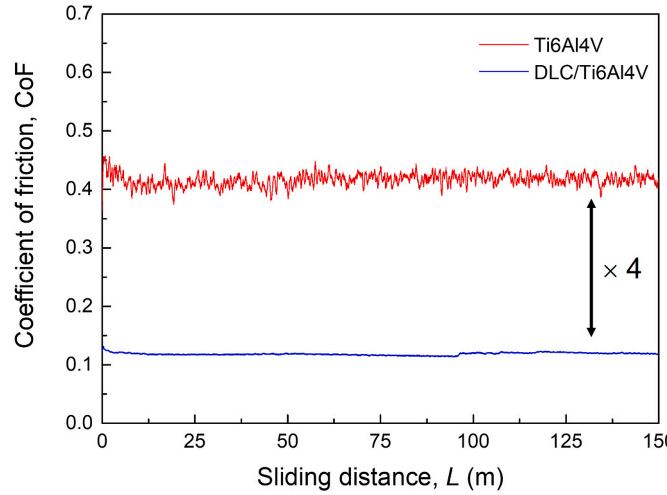

Fig. 2. Representative curves of coefficient of friction *vs* sliding distance obtained from pin-on-disk tests in the Ti6Al4V *vs* Ti6Al4V ('Uncoated', red line) and Ti6Al4V *vs* DLC/Ti6Al4V ('Coated', blue line) tribosystems. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

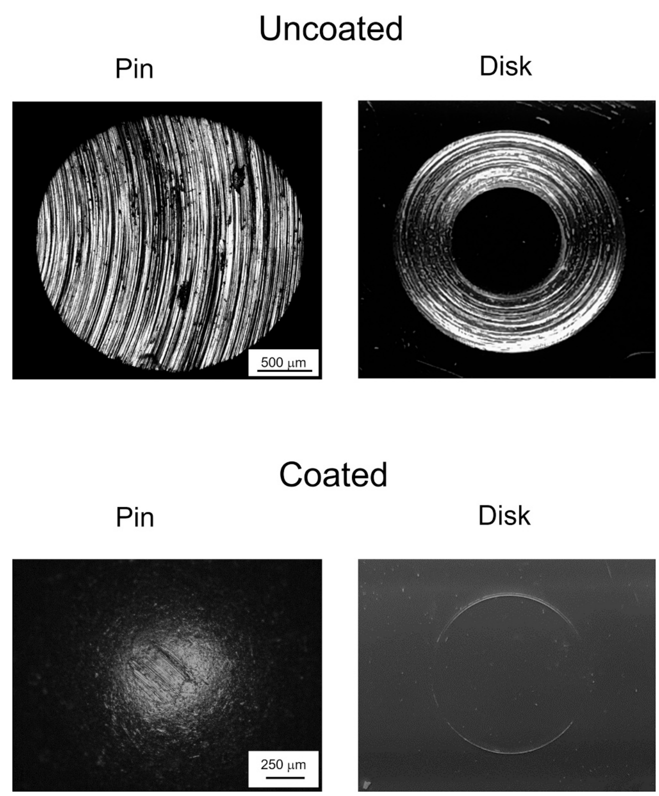

Fig. 3. Low-magnification optical microscopy images, obtained at the end of the wear tests, representative of the wear damage on the contact surface of both pin and disk in the Ti6Al4V *vs* Ti6Al4V ('Uncoated') and Ti6Al4V *vs* DLC/Ti6Al4V ('Coated') tribosystems. The disk specimens (right) have a width of 2 cm.

the 'Uncoated' system is somewhat more irregular, showing small amplitude peaks and valleys which suggest the occurrence of stick-slip processes and abrasion by relatively hard (oxide) debris. The average values of CoF are 0.42 ± 0.02 ('Uncoated'), and 0.11 ± 0.06 ('Coated'). The introduction of a DLC film in the tribosystem thus results in a 4-fold reduction in the CoF.

Fig. 3 shows representative low-magnification optical microscopy images of the wear damage at the conclusion of the sliding tests on the surface of both pin and disk. They illustrate the protective effect of the DLC film. While the wear track on the Ti6Al4V disks in the 'Uncoated' system is very wide, the disks in the 'Coated' systems merely show a slight, barely visible, scratch on the surface. The DLC film appears to remain well adhered to the substrate by the end of the wear tests, after 150 m of continuous sliding contact. Similarly, the wear scar observed on the contact surface of the Ti6Al4V pins in 'Coated' systems is dramatically reduced compared with 'Uncoated' systems. Abrasive marks on the worn surface of all the uncoated Ti6Al4V specimens are observed in both systems.

Fig. 4 shows profilometry images typical of the wear scars obtained on disks. The 3-D images reveal that, in addition to being of greater width, the wear scar observed on the Ti6Al4V disks in the 'Uncoated' system (Fig. 4(A)) is significantly deeper than that observed on the 'Coated' disks (Fig. 4(B)). For direct comparison of the differences in scar size, the 2-D profiles are shown in Fig. 4(C). The profilometry images confirm the presence of abrasive scratches on the wear surface of the specimens, which are of comparatively greater depth in the

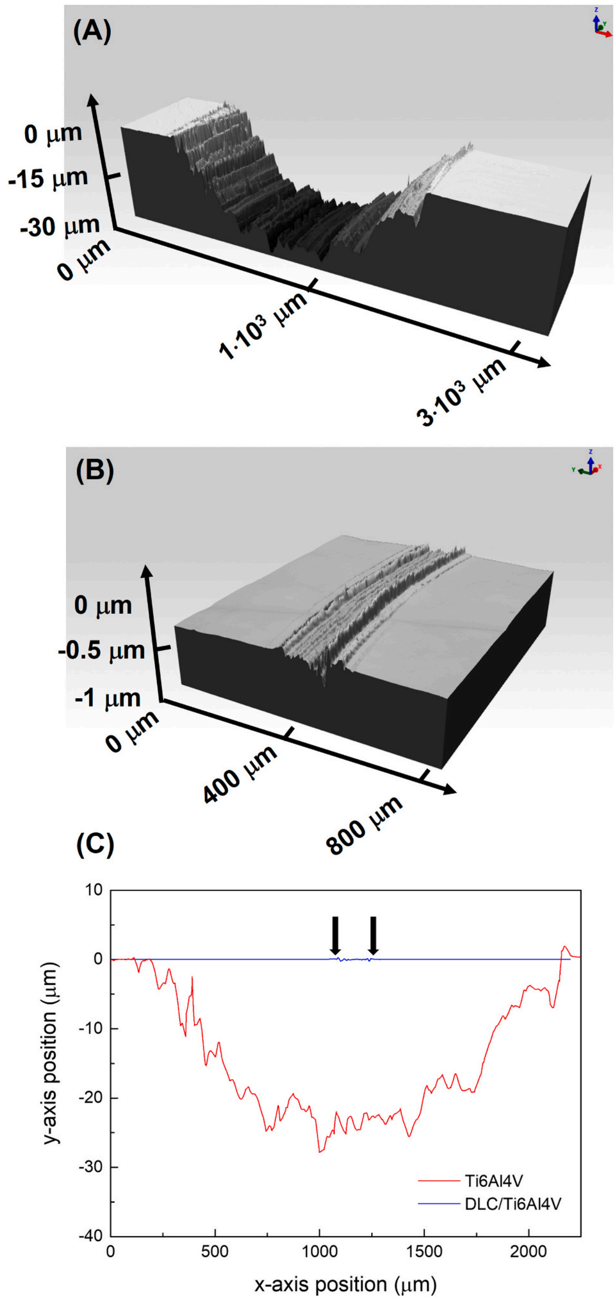

Fig. 4. Typical profilometry images of the wear scar on a (A) Ti6Al4V disk specimen from a Ti6Al4V *vs* Ti6Al4V ('Uncoated') tribosystem, and a (B) DLC/Ti6Al4V disk specimen from a Ti6Al4V *vs* DLC/Ti6Al4V ('Coated') tribosystem, obtained at the end of the sliding-wear experiments. Shading represents height contours. (C) Two-dimensional (*xy*, Cartesian, with *y* being the normal loading direction) profiles of the cross-section of the above wear scars. The black arrows mark the width of the wear scar in the 'Coated' disk specimen.

'Uncoated' system.

Fig. 5 shows the wear volume in both 'Uncoated' and 'Coated' tribosystems at the end of the pin-on-disk tests. It can be seen that the presence of a DLC film has a dramatic effect on the wear of TiAl64V parts under sliding contact in saliva. In particular, in the 'Coated' system, the DLC/Ti6Al4V disks experienced a reduction of 99.97 % in wear volume compared to Ti6Al4V disks in the 'Uncoated' system. Moreover, the Ti6Al4V counter spheres in the 'Coated' system show a reduction of 99.99 % in wear volume compared to the Ti6Al4V counter spheres in the 'Uncoated' system. In the 'Uncoated' system, the experimental wear volumes result in SWR values of $2.0 \cdot 10^{-4}$ mm^3/N·m (Ti6Al4V disks)

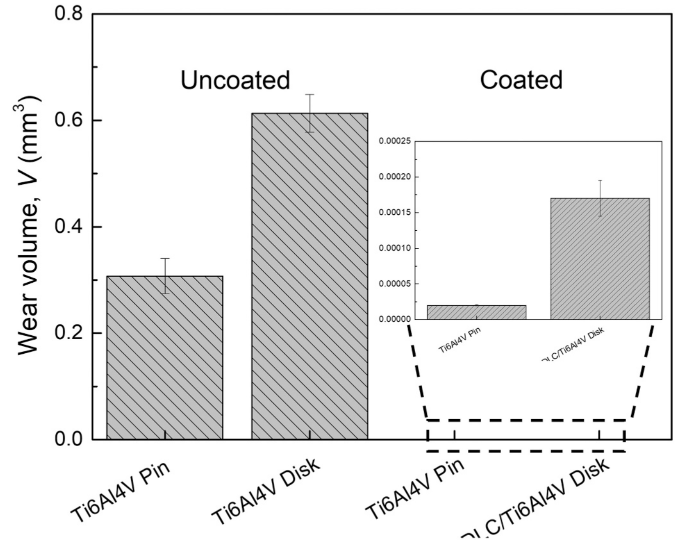

Fig. 5. Wear volume bar chart, computed from microscopy and profilometry images, of the pin and disk materials in the Ti6Al4V *vs* Ti6Al4V ('Uncoated') and Ti6Al4V *vs* DLC/Ti6Al4V ('Coated') tribosystems investigated in this study, at the conclusion of the sliding-wear tests. The values plotted are the mean and standard deviation of the wear volumes for the four categories of material (3 samples in every category).

and $1.0 \cdot 10^{-4}$ mm^3/N·m (Ti6Al4V pins), which indicate severe wear [45]. By contrast, in the 'Coated' system, the experimental wear volumes result in over 4 orders of magnitude lower SWR values, of $5.7 \cdot 10^{-8}$ mm^3/N·m (DLC/Ti6Al4V disks) and $6.7 \cdot 10^{-9}$ mm^3/N·m (Ti6Al4V pins), which pertain to mild wear.

Fig. 6 shows high magnification details of the wear damage on the surface of Ti6Al4V pins in 'Uncoated' systems, obtained by HRFESEM. There are three main types of damage modes at the microscopic scale: (i) scratches of micrometric width, extending parallel to the sliding direction; and relatively large (diameter over ~10 μm) scattered (ii) pits and (iii) material pile-ups (higher magnification detail in Fig. 6(B)). The extent of the damage on the surface of Ti6Al4V pins is significantly decreased in 'Coated' systems, with scratches of smaller width and frequency than in 'Uncoated' systems, and with pits and pile-ups essentially suppressed.

Fig. 7 shows representative HRFESEM images of the wear damage in the Ti6Al4V disks in 'Uncoated' systems, on both the surface and the cross-section (milled and polished by FIB). As anticipated from Fig. 6, it can be observed that the wear surface is relatively rough, with noticeable 'macro' steps (boxed area) indicating substantial plastic deformation, in addition to the micro scratches parallel to the sliding direction. Material pile-ups on the surface can also be observed. The cross-sections appear to be free of cracks and damage other than plastic deformation.

In contrast, the amount of plastic deformation, in both the DLC film and the Ti6Al4V substrate of 'Coated' systems, is greatly reduced, as seen in Fig. 8. Low magnification HRFESEM images show that the wear surfaces in 'Coated' systems are significantly smoother than those in 'Uncoated' systems. Microscratches parallel to the sliding surface can also be observed, although to a much lesser extent. A few scattered debris particles of submicron size, adhered to the wear surface of DLC-coated disks, are visible in Fig. 8(B).

Higher magnification details (Fig. 9) confirm that the surfaces of both the DLC film and the Ti6Al4V substrate remain smooth by the end of the wear tests. Moreover, as anticipated from the optical images, the FIB cross-sectional observations reveal that the DLC films remain very well attached to the substrates after 150 m of sliding contact, with smooth and seemingly pristine film-substrate interfaces. No damage other than mild deformation is observed in the coated TiAl64V substrates (Fig. 9(A)). On the other hand, the DLC films show two types of

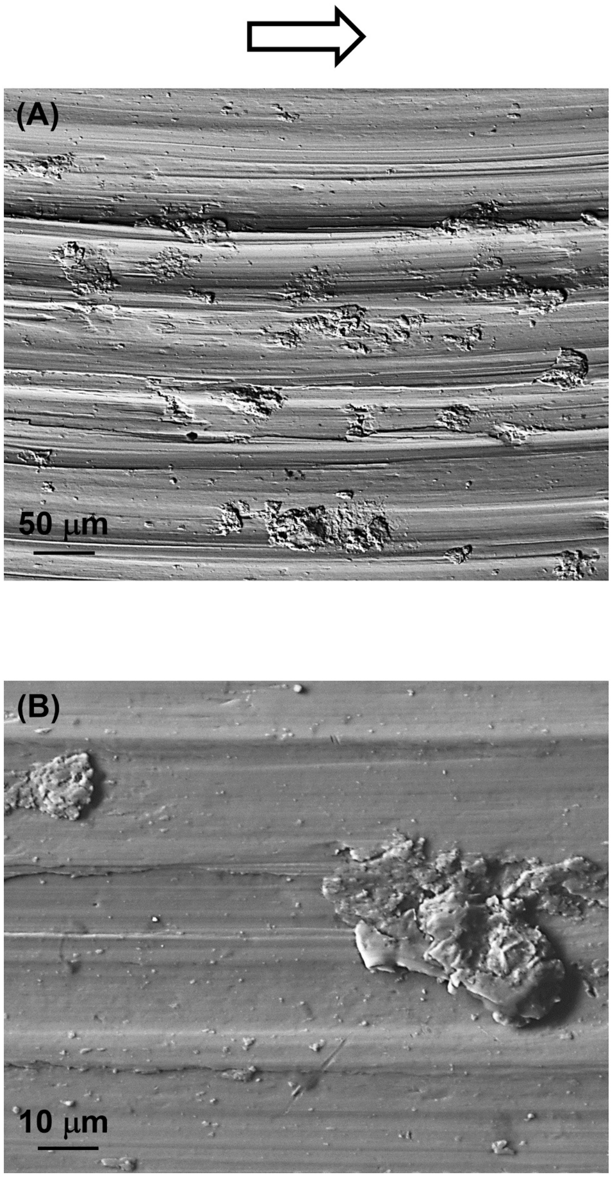

Fig. 6. HRFESEM images at (A) intermediate-high and (B) high magnifications representative of the wear damage on the surface of a Ti6Al4V pin from a Ti6Al4V *vs* Ti6Al4V ('Uncoated') tribosystem, at the end of a pin-on-disk test. The arrow indicates the sliding direction.

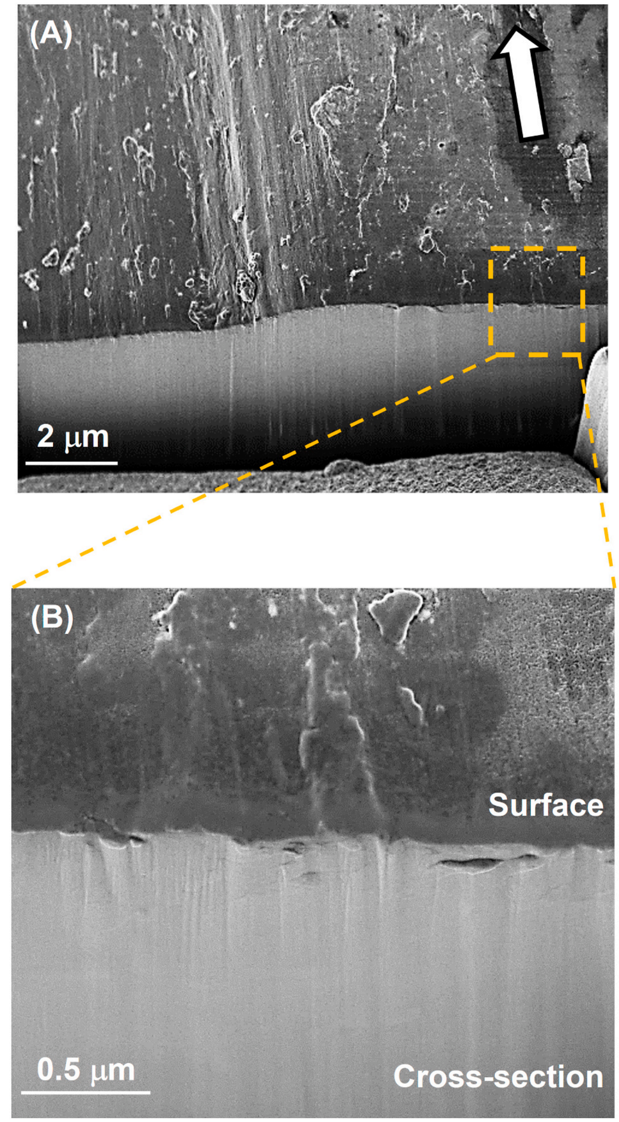

Fig. 7. HRFESEM images at (A) intermediate-high and (B) high magnifications representative of the wear damage at the cross-section (milled by FIB) of a Ti6Al4V disk from a Ti6Al4V *vs* Ti6Al4V ('Uncoated') tribosystem, at the end of a pin-on-disk test. The arrow indicates the sliding direction. The specimen is tilted 52° with respect to the observation axis.

brittle damage modes, as observed at the cross-section. First, some of the microscratches observed on the surface appear to be crack-like and propagate into the film cross-section, forming an angle with respect to the axial loading axis (*e.g.*, '1' in Fig. 9(A)). Such cracks are not catastrophic. In most instances, they arrest before reaching the film-substrate interface (Fig. 9(B)). When cracks do reach the interface, they do not propagate into the substrate, but rather deflect at the interface. Importantly, crack deflection at the interface only results in very localized detachment which does not compromise the adhesion of the DLC film, as observed in Fig. 9(E). In addition to cracks generated on the surface, radial cracks generated at the film-substrate interface are also observed (*e.g.*, '2' in Fig. 9(A) and (C)). Again, such cracks are relatively stable and not catastrophic, and arrest before they can reach the film surface and form significant wear particles. The submicron wear particles observed on the surface (Fig. 8(B)) largely correspond to DLC debris from relatively wider scratches (*e.g.*, '3' in Fig. 9(A) and (D)).

4. Discussion

The experimental results unambiguously show the beneficial effect of a DLC film to impart protection from excessive wear to Ti6Al4V parts under sliding contact, such as those in dental implants. In particular, in our experiments the application of a DLC film to a Ti6Al4V *vs* Ti6Al4V tribosystem under lubrication with artificial saliva reduced the SWR by over 4 orders of magnitude in both the pin and the disk. This can be attributed to three causes. First, the presence of the DLC film physically separates the contacting titanium surfaces, thus changing the wear mode from mixed abrasion and adhesion (in 'Uncoated') to abrasion only (in 'Coated'). The latter is evidenced by the microscopic markings observed on the wear surfaces (Figs. 6–8): microscratches caused by the asperities of the counter sphere and hard oxide debris, and adhesive deposits (*i.e.*, material transfer) in 'Uncoated' systems *vs* microscratches only (of smaller size and lesser frequency) in 'Coated' systems. Adhesion between uncoated titanium contacts is well known and leads to severe wear [8,46]. Second, the suppression of adhesion by the DLC film lowers the coefficient of friction [46] by a factor 4, from an average value of

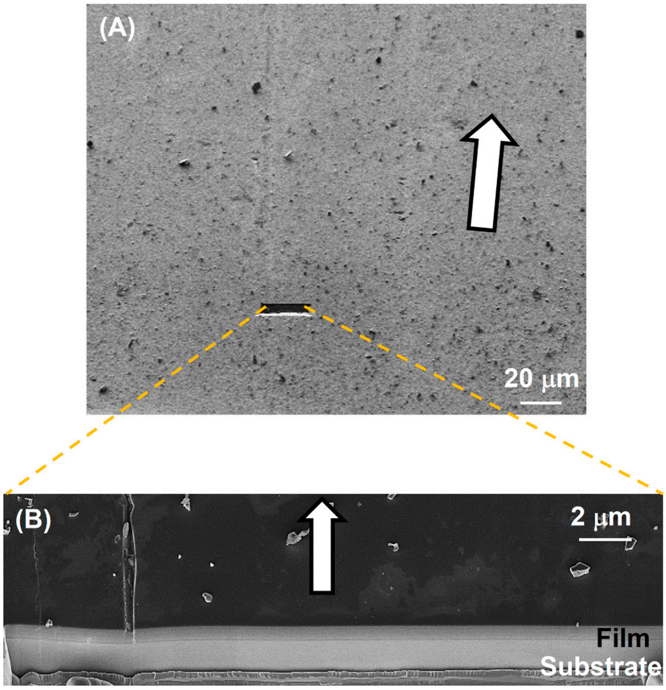

Fig. 8. (A) Low magnification SEM image of the wear track on the surface of a DLC/Ti6Al4V disk specimen from a Ti6Al4V *vs* DLC/Ti6Al4V ('Coated') tribosystem. (B) Low magnification HRSEM image of the damage at the cross-section milled by FIB. The images were obtained at the end of a pin-on-disk test. The arrows indicate the sliding direction.

≈0.4 ('Uncoated') to ≈0.1 ('Coated'). In turn, decreasing the coefficient of friction results in lower values of the critical macro-contact stresses [47]: both the surface tensile stress at the rear edge of the contact and the sub-surface shear stress ahead of the contact are relatively lower in the 'Coated' than in the 'Uncoated' system. And third, the low surface roughness (*e.g.*, Fig. 9(A)) and intrinsic high hardness and resistance to wear of DLC[1] [14] contribute to the limited extent of abrasion of both Ti6Al4V counter sphere and film in the 'Coated' system (Fig. 3). The combination of suppressed adhesion, decreased friction and macro-contact stress, and reduced abrasion associated with the presence of the DLC film effectively shift the wear regime of Ti6Al4V sliding contacts, from severe in the 'Uncoated' system to mild in the 'Coated' system.

The application of a DLC film to Ti6Al4V sliding contacts could also have some potential downsides. Among them are poor bonding between film and substrate, and increased susceptibility to fracture in the relatively brittle film. The former is typically a result of large compressive residual stresses in the film and/or the presence of impurities at the interface which may be introduced during deposition [21]. In contrast, the RF-PECVD DLC films employed in this work showed excellent bonding to the Ti6Al4V substrate, as seen in the cross-sectional FIB images taken at the conclusion of the wear tests after 150 m of sliding contact (Fig. 8(B)). Underlying the stability of our DLC films is the preferential formation of Si—C bonds on the interlayer, which enhances the chemical affinity of a-SiC:H with the DLC film, and reduces the elastic modulus mismatch with the substrate [26,49,50]. Note that good film bonding was achieved here even on highly polished substrates (*i.e.*, without mechanical interlocking).

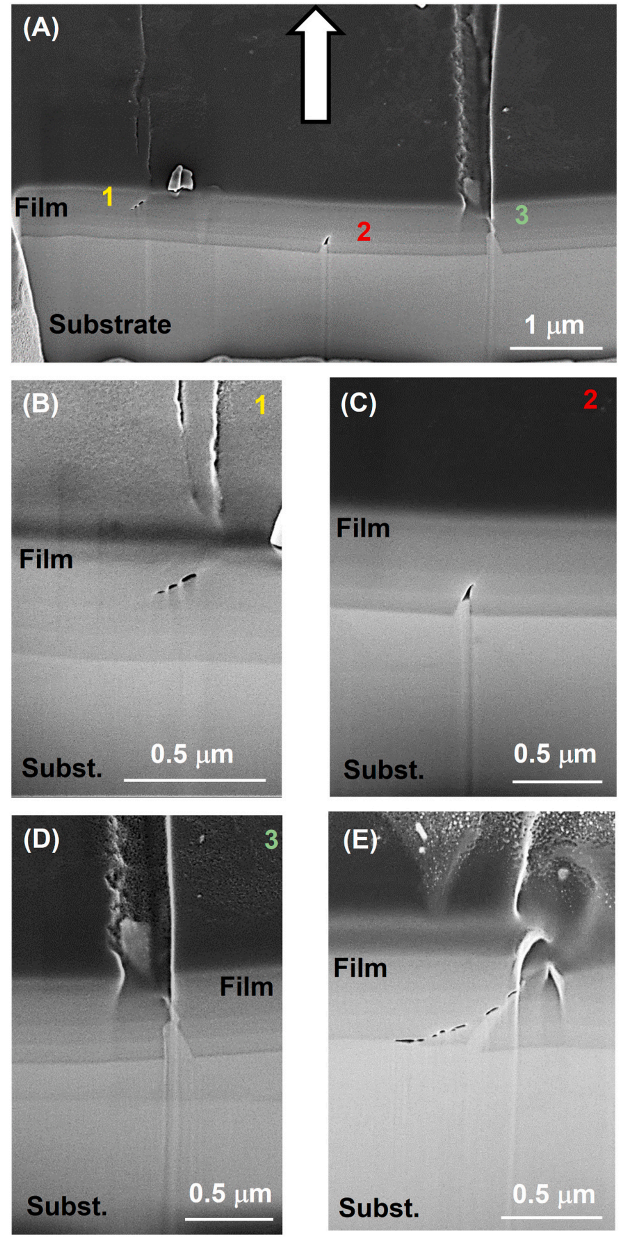

Fig. 9. (A) Intermediate-high magnification HRFESEM image showing representative damage modes at the cross-section of a DLC/Ti6Al4V disk specimen from a Ti6Al4V *vs* DLC/Ti6Al4V ('Coated') tribosystem. (B), (C), and (D) are high magnification details of sites labelled '1', '2', and '3', respectively, in (A). (E) High magnification detail of a crack reaching the DLC-Ti6Al4V interface. All images were obtained at the conclusion of a pin-on-disk test. The arrow indicates the sliding direction. The specimen is tilted 52° with respect to the observation axis.

With regards to fracture, a ceramic DLC film is comparatively harder and more brittle [14] than the Ti6Al4V substrate, and thus more prone to the initiation of cracks. The cross-sectional FIB examinations revealed two basic fracture modes: (i) cracks generated at the contact surface, which subsequently propagate 'downwards' at an angle through the film thickness; and (ii) cracks generated at the film-substrate interface, which subsequently propagate 'upwards' perpendicular to the surface (*i.e.*, radial cracks [51]). To ascertain the origin of such cracks, numerical simulations were made of the stress field upon sliding. Because surfaces are not ideally flat, the contact between a Ti6Al4V sphere and a DLC/Ti6Al4V disk is actually effected at the asperity level [48,52–54], *i.e.*, micro-contacts between the asperities of the sphere and the coated disk.

[1] According to Archard's law, the resistance to abrasive wear is inversely proportional to the materials' hardness [48]. Thus, DLC shows increased resistance to abrasion compared with uncoated Ti6Al4V mostly as a result of its greater hardness.

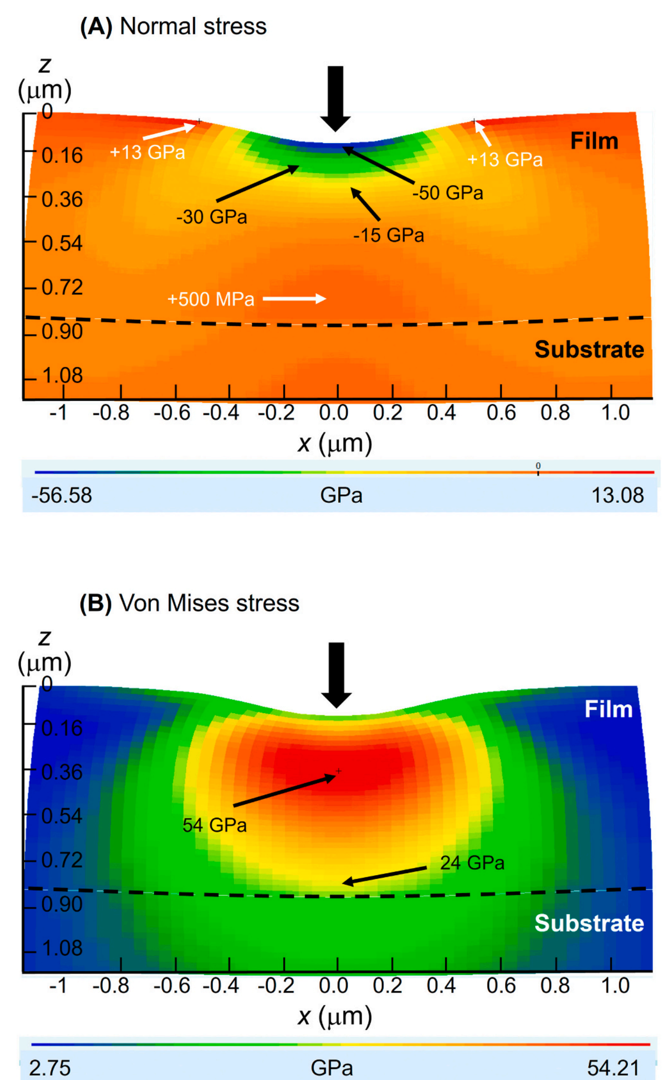

Fig. 10. FilmDoctor® simulations (contour plots) of relevant components of the stress field induced on a DLC/Ti6Al4V system by a relatively sharp indenter/particle (marked by the vertical black arrow) of radius 0.5 μm applying a normal load of 50 mN. Cross-sectional view *xz* (Cartesian), with *z* being the loading direction. The dashed line marks the film-substrate interface. Stress units are GPa, with positive values indicating tensile stress and negative values compressive stress. (A) Normal stress in *x*-direction, with white arrows pointing at regions under tensile stress; and (B) Von Mises stress.

Fig. 10 shows a simulation of the relevant components of the stress field caused in the DLC/Ti6Al4V system investigated in this work by a sub-micrometric asperity or micro-contact, modelled as a conical (angle 45°) indenter with a tip of radius 0.5 μm (*i.e.* relatively sharp), applying a reference normal load of 50 mN[2] [55]. The normal stress at the cross-section (Fig. 10(A)) shows relatively high positive values (*i.e.*, tensile) on the film surface, outside the contact circle, as well as near the film/substrate interface due to film bending. The former open tensile cracks at the surface, such as ‘1’ in Fig. 9(A) and (B), which propagate through the film cross-section at an angle of ~45° with respect to the normal axis [56]. The latter open radial cracks at the film-substrate interface, such as ‘2’ in Fig. 9(A) and (C), which propagate normal to the interface [51]. The dominance of contact over bending and the magnitude of the tensile stresses depend on film thickness and the film-substrate property mismatch: thicker films favour contact-induced surface cracks over bending-induced radial cracks, and tensile stresses increase with increasing film stiffness [51,57]. With regards to the shear stress, Fig. 10 (B) shows that the Von Mises stress is greatest just below the contact surface, along the normal loading axis. High shear stresses induce plastic deformation at the asperity level and are thus responsible for the abrasive microscratches in the film (such as ‘3’ in Fig. 9(A) and (D)) [48].

In addition to their relatively low resistance to crack initiation, their amorphous structure and reduced dimension (thickness) mean that, in principle, DLC films lack the extrinsic mechanisms which are present in some engineering ceramics and natural hard tissues to resist crack propagation [58,59]. However, none of the fracture modes observed in the DLC/Ti6Al4V system appear to be catastrophic. Cracks generated on the contact surface typically arrest before reaching the film-substrate interface (Fig. 9(B)). When they do reach the interface, they deflect (without compromising bonding at a macroscopic scale) and do not propagate through the substrate (Fig. 9(E)). Similarly, radial cracks generated at the film-substrate interface are effectively arrested before reaching the contact surface. The observed resistance of the DLC film to the propagation of radial cracks is attributable to the through-thickness, equibiaxial (in-plane), compressive residual stress, as well as to the compressive component of the micro-contact stress field under the contact and in the mid cross-section of the film (Fig. 10(A)). Fatigue effects could take place in cyclic, sliding contacts of greater duration.

The results of this work have important implications for the development of durable, Ti-based dental implant parts. Indeed, as mentioned above, adhesion-induced severe wear (galling) between contacting titanium screw and abutment parts can result in early failure. The deposition of a thin DLC film is effective at physically separating metallic surfaces and suppressing adhesion, and significantly reduces friction, macro-contact stresses and ultimately wear. To ensure the stability of the system, good bonding between the film and the substrate must be achieved. In dental tribosystems, this is hindered by the low surface roughness of precision implant parts, but this problem can be overcome by employing an effective interlayer during RF-PECVD deposition, such as a-SiC:H, as is it was demonstrated in this work, or by doping DLC with such elements as fluorine [38].

The main issue associated with the introduction of a ceramic film such as DLC which could affect the long-term performance of the system is property mismatch with the substrate. This results in increased susceptibility to fracture in the relatively brittle film, especially at the contact surface and interface. Because such fracture is largely due to tensile stresses introduced at the micro-contact or asperity level, it follows that contact surfaces should be polished as smoothly as possible in order to minimize the extent of fracture in the film, while maintaining good bonding between film and substrate. Moreover, in coated systems, cyclic stresses during mastication can result in cumulative strain of the film-substrate interface which could lead to delamination. This issue is minimized in the present DLC/TTi6Al4V systems, since the DLC films deposited by RF-PECVD have elastic moduli that are similar to those of Ti6Al4V. Alternatively, gradient film structures could be attempted [50], with relatively high modulus and hardness values at the contact surface for greater load-bearing capacity and abrasion resistance, progressively decreasing through the film thickness for toughening, and equating the substrate modulus at the interface for improved adhesion, thus emulating the highly durable and damage -resistant structure of human enamel (*i.e.*, bio-mimetic design) [60,61].

5. Conclusions

The effect of a DLC thin film on the wear behaviour of Ti6Al4V disks in contact with sliding Ti6Al4V spheres under artificial saliva lubrication was investigated. The main conclusions are:

[2] For simplicity, the relatively low frictional force was excluded from the simulation, as it only adds a small shift of the maxima of the stress field components [47], and thus does not affect the damage modes significantly.

1. A submicron DLC film effectively separates Ti6Al4V surfaces under sliding contact, thus changing the wear mode from mixed abrasion and adhesion (uncoated system) to abrasion only (coated system).
2. The suppression of adhesion by the DLC film lowers the coefficient of friction by a factor of 4, and in turn reduces the contact stress.
3. The DLC film improves the abrasion resistance of Ti6Al4V due to its greater hardness.
4. Under the conditions simulated in this study, suppressed adhesion, lower friction and contact stress, and reduced abrasion by the DLC film decrease the specific wear rate of uncoated Ti6Al4V by over 4 orders of magnitude.
5. Potential downsides associated with the incorporation of a DLC film to dental tribosystems are poorer film-substrate bonding, and increased susceptibility to fracture in the relatively brittle film. The former can be improved by suitable interlayers or dopants, and the latter by engineering the film's properties to minimize the micro-contact stress.

CRediT authorship contribution statement

Fernando Rodríguez-Rojas: Investigation, Visualization, Writing – review & editing. **Miroslavna Kovylina:** Investigation, Visualization, Writing – review & editing. **Elena Pinillia-Cienfuegos:** Conceptualization, Methodology, Formal analysis, Writing – review & editing. **Óscar Borrero-López:** Investigation, Visualization, Conceptualization, Methodology, Formal analysis, Writing – original draft, Supervision, Writing – review & editing. **Avi Bendavid:** Investigation, Visualization, Conceptualization, Methodology, Formal analysis, Writing – review & editing. **Philip J. Martin:** Conceptualization, Methodology, Formal analysis, Writing – review & editing. **Mark Hoffman:** Conceptualization, Methodology, Formal analysis, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This study was supported by the Ministry of Science and Innovation, Spain (Grant No. PID2019-105377RB-I00). E.P.-C. gratefully acknowledges funding from the Generalitat Valenciana (Grant No. SEJIGENT/2021/039).

References

[1] G. Chahine, M. Koike, T. Okabe, P. Smith, R. Kovacevic, The design and production of Ti-6Al-4V ELI customized dental implants, JOM 60 (11) (2008) 50–55.
[2] S.K. Kim, J.B. Lee, J.Y. Koak, S.J. Heo, K.R. Lee, L.R. Cho, S.S. Lee, An abutment screw loosening study of a diamond like carbon-coated CP titanium implant, J. Oral Rehabil. 32 (5) (2005) 346–350.
[3] Y.S. Al Jabbari, R.A. Fournelle, S. Zinelis, A.M. Iacopino, Biotribological behavior of two retrieved implant abutment screws after long-term use in vivo, Int. J. Oral Maxillofac. Implants 27 (6) (2012) 1474–1480.
[4] D. Bordin, P.G. Coelho, E.T.P. Bergamo, E.A. Bonfante, L. Witek, A.A.D. Cury, The effect of DLC-coating deposition method on the reliability and mechanical properties of abutment's screws, Dent. Mater. 34 (6) (2018) E128–E137.
[5] A.M. Prado, J. Pereira, F.S. Silva, B. Henriques, R.M. Nascimento, C.A.M. Benfatti, J. Lopez-Lopez, J.C.M. Souza, Wear of Morse taper and external hexagon implant joints after abutment removal, J.Mater.Sci.Mater.Med. 28 (5) (2017).
[6] Y.N. Xie, J. Zhou, Q.P. Wei, Z.M. Yu, H. Luo, B. Zhou, Z.G. Tang, Improving the long-term stability of Ti6Al4V abutment screw by coating micro/nano-crystalline diamond films, J. Mech. Behav. Biomed. Mater. 63 (2016) 174–182.
[7] P. Corne, P. De March, F. Cleymand, J. Geringer, Fretting-corrosion behavior on dental implant connection in human saliva, J. Mech. Behav. Biomed. Mater. 94 (2019) 86–92.
[8] U. Wiklund, I.M. Hutchings, Investigation of surface treatments for galling protection of titanium alloys, Wear 251 (2001) 1034–1041.
[9] D.G. Bansal, M. Kirkham, P.J. Blau, Effects of combined diffusion treatments and cold working on the sliding friction and wear behavior of Ti-6Al-4V, Wear 302 (1–2) (2013) 837–844.
[10] W.H. Kao, Y.L. Su, J.H. Horng, C.Y. Chang, Tribological, electrochemical and biocompatibility properties of Ti6Al4V alloy produced by selective laser melting method and then processed using gas nitriding, CN or Ti-C:H coating treatments, Surf.Coat.Technol. 350 (2018) 172–187.
[11] J.C.M. Souza, S.L. Barbosa, E. Ariza, J.P. Celis, L.A. Rocha, Simultaneous degradation by corrosion and wear of titanium in artificial saliva containing fluorides, Wear 292 (2012) 82–88.
[12] C. Fares, S.M. Hsu, M.H. Xian, X.Y. Xia, F. Ren, J.J. Mecholsky, L. Gonzaga, J. Esquivel-Upshaw, Demonstration of a SiC protective coating for titanium implants, Materials 13 (15) (2020).
[13] M. Montazerian, F. Hosseinzadeh, C. Migneco, F. Baino, M.V.L. Fook, Bioceramic coatings on metallic implants: an overview, Ceram. Int. 48 (7) (2022) 8987–9005.
[14] A. Erdemir, C. Donnet, Tribology of diamond-like carbon films: recent progress and future prospects, J. Phys. D. Appl. Phys. 39 (18) (2006) R311–R327.
[15] G. Dearnaley, J.H. Arps, Biomedical applications of diamond-like carbon (DLC) coatings: a review, Surf.Coat.Technol. 200 (7) (2005) 2518–2524.
[16] R. Hauert, A review of modified DLC coatings for biological applications, Diam. Relat. Mater. 12 (3–7) (2003) 583–589.
[17] O.V. Penkov, V.E. Pukha, S.L. Starikova, M. Khadem, V.V. Starikov, M.V. Maleev, D.E. Kim, Highly wear-resistant and biocompatible carbon nanocomposite coatings for dental implants, Biomaterials 102 (2016) 130–136.
[18] G. Kamath, Increase dental implant longevity with bio-functional TiN and DLC coatings, in: Medical Design Briefs, SAE Media Group (SMG), New York, NY, 2008.
[19] S. Nissen, J. Heeg, M. Warkentin, D. Behrend, M. Wienecke, The effect of deposition parameters on structure, mechanical and adhesion properties of a-C:H on Ti6Al4V with gradient Ti-a-C:H:Ti interlayer, Surf.Coat.Technol. 316 (2017) 180–189.
[20] C.C. Chou, Y.Y. Wu, J.W. Lee, J.C. Huang, C.H. Yeh, Mechanical properties of fluorinated DLC and Si interlayer on a Ti biomedical alloy, Thin Solid Films 528 (2013) 136–142.
[21] J.A. Santiago, I. Fernandez-Martinez, A. Wennberg, J.M. Molina-Aldareguia, M. Castillo-Rodriguez, T.C. Rojas, J.C. Sanchez-Lopez, M.U. Gonzalez, J.M. Garcia-Martin, H. Li, V. Bellido-Gonzalez, M.A. Monclus, R. Gonzalez-Arrabal, Adhesion enhancement of DLC hard coatings by HiPIMS metal ion etching pretreatment, Surf.Coat.Technol. 349 (2018) 787–796.
[22] E. Lukina, M. Kollerov, J. Meswania, P. Panin, A. Khon, G. Blunn, The influence of TiN and DLC deposition on the wear resistance of nitinol-Ti6Al4V combination for the medical application, Mater.TodayProc. 4 (3) (2017) 4675–4679.
[23] J.C. Avelar-Batista, E. Spain, G.G. Fuentes, A. Sola, R. Rodriguez, J. Housden, Triode plasma nitriding and PVD coating: a successful pre-treatment combination to improve the wear resistance of DLC coatings on Ti6Al4V alloy, Surf.Coat. Technol. 201 (7) (2006) 4335–4340.
[24] P.A. Radi, L.V. Santos, L.F. Bonetti, G.C. Rodrigues, V.J. Trava-Airoldi, Friction and wear maps of titanium alloy against a-C:H20% (DLC) film, Surf.Coat.Technol. 203 (5–7) (2008) 741–744.
[25] M. Kheradmandfard, O.V. Penkov, S.F. Kashani-Bozorg, J.S. Lee, C.L. Kim, M. Khadem, S.W. Cho, A.Z. Hanzaki, D.E. Kim, Exceptional improvement in the wear resistance of biomedical ?-type titanium alloy with the use of a biocompatible multilayer Si/DLC nanocomposite coating, Ceram. Int. 48 (12) (2022) 17376–17384.
[26] A. Hatem, J.L. Lin, R. Wei, R.D. Torres, C. Laurindo, P. Soares, Tribocorrosion behavior of DLC-coated Ti-6Al-4V alloy deposited by PIID and PEMS plus PIID techniques for biomedical applications, Surf.Coat.Technol. 332 (2017) 223–232.
[27] R. Bayon, A. Igartua, J.J. Gonzalez, U.R. de Gopegui, Influence of the carbon content on the corrosion and tribocorrosion performance of Ti-DLC coatings for biomedical alloys, Tribol. Int. 88 (2015) 115–125.
[28] V. Kashyap, P. Ramkumar, DLC coating over pre-oxidized and textured Ti6Al4V for superior adhesion and tribo-performance of hip implant, Surf.Coat.Technol. 440 (2022).
[29] T. Xu, L. Pruitt, Diamond-like carbon coatings for orthopaedic applications: an evaluation of tribological performance, J.Mater.Sci.Mater.Med. 10 (2) (1999) 83–90.
[30] S. Affatato, M. Frigo, A. Toni, An in vitro investigation of diamond-like carbon as a femoral head coating, J. Biomed. Mater. Res. 53 (3) (2000) 221–226.
[31] L. Franta, J. Fojt, L. Joska, J. Kronek, L. Cvrcek, J. Vyskocil, Z. Cejka, Hinge-type knee prosthesis wear tests with a mechanical load and corrosion properties monitoring, Tribol. Int. 63 (2013) 61–65.
[32] J. Wu, L. Chen, X.B. Wei, C.M. Ning, G.Z. Wu, Z.G. Wu, Z.B. Lu, G.A. Zhang, Simultaneously improved bio-tribological and biological corrosion properties of taC film coated on Ti6Al4V by sealing with ALD, Diam. Relat. Mater. 120 (2021).
[33] P.H. Corazza, A.D. Silva, J.R.C. Queiroz, S.M.S. Marocho, M.A. Bottino, M. Massi, R. Souza, Carbon film coating of abutment surfaces: effect on the abutment screw removal torque, Implant. Dent. 23 (4) (2014) 434–438.
[34] J.S.V. Diez, V.C. Brigagao, L.G. Cunha, A.C.C. Neves, L.R. da Silva-Concilio, Influence of diamondlike carbon-coated screws on the implant-abutment interface, Int. J. Oral Maxillofac. Implants 27 (5) (2012) 1055–1060.

[35] F. Rodriguez-Rojas, O. Borrero-Lopez, E. Sanchez-Gonzalez, F. Guiberteau, Effects of the test method on wear measurements in dental enamel/ceramic tribosystems, Ceram. Int. 48 (2) (2022) 2744–2754.
[36] Y. Zheng, K. Bashandeh, A. Shakil, S. Jha, A.A. Polycarpou, Review of dental tribology: current status and challenges, Tribol. Int. 166 (2022).
[37] X.Y. Zheng, Y.R. Zhang, B.R. Zhang, Effect of N-ion implantation and diamond-like carbon coating on fretting wear behaviors of Ti6Al7Nb in artificial saliva, Trans. Nonferrous Metals Soc. China 27 (5) (2017) 1071–1080.
[38] A. Bendavid, P.J. Martin, L. Randeniya, M.S. Amin, The properties of fluorine containing diamond-like carbon films prepared by plasma-enhanced chemical vapour deposition, Diam. Relat. Mater. 18 (1) (2009) 66–71.
[39] O. Borrero-Lopez, M. Hoffman, A. Bendavid, P.J. Martin, Substrate effects on the mechanical properties and contact damage of diamond-like carbon thin films, Diam. Relat. Mater. 19 (10) (2010) 1273–1280.
[40] Titanium Alloys - Ti6Al4V Grade 5. https://www.azom.com/properties.aspx?ArticleID=1547.
[41] ASTM G99-05, Standard Test Method for Wear Testing With a Pin-on-Disk Apparatus, ASTM International, West Conshohocken, PA, 2005.
[42] J.A. Arsecularatne, M. Hoffman, On the wear mechanism of human dental enamel, J. Mech. Behav. Biomed. Mater. 3 (4) (2010) 347–356.
[43] F. Rodríguez-Rojas, O. Borrero-López, E. Sánchez-González, M. Hoffman, F. Guiberteau, On the durability of zirconia-reinforced lithium silicate and lithium disilicate dental ceramics under severe contact, Wear 508–509 (2022), 204460.
[44] N. Schwarzer, The extended Hertzian theory and its uses in analyzing indentation experiments, Philos. Mag. 86 (33–35) (2006) 5179–5197.
[45] G.W. Stachowiak, A.W. Batchelor, in: Engineering Tribology, 3rd Edition, Engineering Tribology, 3rd Edition, 2005, pp. 1–801.
[46] J. Heinrichs, M. Olsson, I.Z. Jenei, S. Jacobson, Transfer of titanium in sliding contacts-new discoveries and insights revealed by in situ studies in the SEM, Wear 315 (1–2) (2014) 87–94.
[47] G.M. Hamilton, L.E. Goodman, Stress field created by a circular sliding contact, J. Appl. Mech. 33 (2) (1966) 371.
[48] O. Borrero-Lopez, A. Pajares, P.J. Constantino, B.R. Lawn, A model for predicting wear rates in tooth enamel, J. Mech. Behav. Biomed. Mater. 37 (2014) 226–234.
[49] V.J. Trava-Airoldi, L.F. Bonetti, G. Capote, L.V. Santos, E.J. Corat, A comparison of DLC film properties obtained by r.f. PACVD, IBAD, and enhanced pulsed-DC PACVD, Surf. Coat. Technol. 202 (3) (2007) 549–554.
[50] R.K. Singh, Z.F. Zhou, L.K.Y. Li, P. Munroe, M. Hoffman, Z.H. Xie, Design of functionally graded carbon coatings against contact damage, Thin Solid Films 518 (20) (2010) 5769–5776.
[51] H. Chai, B.R. Lawn, Fracture mode transitions in brittle coatings on compliant substrates as a function of thickness, J. Mater. Res. 19 (6) (2004) 1752–1761.
[52] I. Hutchings, P. Shipway, in: Tribology: Friction and Wear of Engineering Materials, 2nd Edition, Tribology: Friction and Wear of Engineering Materials, 2nd Edition, 2017, pp. 1–388.
[53] O. Ben-David, S.M. Rubinstein, J. Fineberg, Slip-stick and the evolution of frictional strength, Nature 463 (7277) (2010) 76–79.
[54] K. Holmberg, A. Matthews, H. Ronkainen, Coatings tribology - contact mechanisms and surface design, Tribol. Int. 31 (1–3) (1998) 107–120.
[55] O. Borrero-Lopez, F. Guiberteau, Y. Zhang, B.R. Lawn, Wear of ceramic-based dental materials, J. Mech. Behav. Biomed. Mater. 92 (2019) 144–151.
[56] B.R. Lawn, Indentation of ceramics with spheres: a century after Hertz, J. Am. Ceram. Soc. 81 (8) (1998) 1977–1994.
[57] B.R. Lawn, Fracture and deformation in brittle solids: a perspective on the issue of scale, J. Mater. Res. 19 (1) (2004) 22–29.
[58] B.R. Lawn, Fracture of Brittle Solids, Cambridge University Press, Cambridge, UK, 1993.
[59] R.O. Ritchie, Toughening materials: enhancing resistance to fracture, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 379 (2203) (2021).
[60] O. Borrero-Lopez, P.J. Constantino, M.B. Bush, B.R. Lawn, On the vital role of enamel prism interfaces and graded properties in human tooth survival, Biol. Lett. 16 (8) (2020).
[61] V.P. Thompson, The tooth: an analogue for biomimetic materials design and processing, Dent. Mater. 36 (1) (2020) 25–42.