Contents lists available at ScienceDirect





Surface & Coatings Technology

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

Tribological, anti-corrosive properties and biocompatibility of the micro- and nano-crystalline diamond coated Ti6Al4V



Jingqing Wang ^a, J. Zhou ^{b,c}, H.Y. Long ^a, Y.N. Xie ^a, X.W. Zhang ^a, H. Luo ^a, Z.J. Deng ^a, Qiuping Wei ^{a,d,*}, Z.M. Yu ^{a,d,*}, J. Zhang ^{b,c}, Z.G. Tang ^{b,1}

^a School of Materials Science and Engineering, Central South University, Changsha 410083, PR China

^b Xiangya Stomatological Hospital, Central South University, Changsha 410078, PR China

^c Xiangya Stomatological Hospital, Changsha 410008, PR China

^d State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China

ARTICLE INFO

Article history: Received 17 April 2014 Accepted in revised form 9 July 2014 Available online 15 July 2014

Keywords: Diamond film Titanium alloy Tribological behavior Corrosion resistance Cytotoxicity

1. Introduction

Since osseointegration theory was put forward by Branemark half a century ago, implanting denture has evolved into the currently most effective way to defeat dentition repair [1]. However, lots of clinical complications and accidents come easily because of superstructure complex and multi-component [2,3]. The most frequent complication is component loosening, especially the screws, with reported incidence ranging from 2% to 45% [4,5]. Without timely treatments, generation, transmission, and abnormal distribution of stress will lead to break the screws, implants and even osseointegration, namely implantation failure. Therefore, to strengthen the stability of the abutment screw becomes a key to improve the chance of success.

Currently screws are made of titanium alloy materials, Ti6Al4V (TC4). As known, titanium alloys are often chosen for biomedical materials, because of their unusually high corrosion resistance, high mechanical strength, good biocompatibility and low density. However, the fatigue embrittlement under loading and poor friction and wear behavior are detrimental for a long-life using especially as threads. Under cyclic forces of repeated chewing, abrasion of components will occur as a result of small displacement among the implant, abutment screw and denture,

tangzhangui@aliyun.com (Z.G. Tang). ¹ Tel.: + 86 731 8830335; fax: + 86 731 8876692.

ABSTRACT

Diamond coatings may provide a way to strengthen the stability of the titanium abutment screw in dentistry for improving its lifespan. Microcrystalline diamond (MCD) and nanocrystalline diamond (NCD) films were deposited on Ti6Al4V (TC4) by hot-filament-assisted chemical vapor deposition (HFCVD). The morphology and quality of the diamond films were evaluated by SEM, AFM and Raman spectroscopy, respectively. Friction and corrosion experiments of MCD, NCD coated and uncoated TC4 samples were conducted in artificial saliva. The results indicate that diamond coating lowers the friction coefficient from 0.28 on TC4 to 0.2 on MCD and 0.1 on NCD. They also promote the corrosion resistance, in which NCD films present more efficient improvements. Cell proliferation (mitochondrial function, CCK-8 assay), the pattern of cell growth and cell apoptosis with L929 fibroblast cell culture systems proved that both MCD and NCD films provide suitable and cytotoxicity-free surfaces. © 2014 Elsevier B.V. All rights reserved.

and repeated tightening and slacking. In addition, microbial corrosion and electrochemical corrosion will generate by the penetration of saliva, substances in food, decomposition and fermentation from food debris, bacteria, gingival crevicular fluid, etc. [6]. This long-term joint effect of wear and corrosion, will affect the suitability of the interface among the implant, abutment screw and denture, lost the pre-load [7], and eventually lead to screw loosening or breakage. Hence, improving the surface performances of titanium alloys is of great clinical significance. According to the above, to avoid abutment screw loosening, the ideal surface of thread should meet the following requirements: lower friction coefficient, greater wear resistance, stronger corrosion resistance and excellent biocompatibility.

To date, lots of studies revealed that diamond, more specifically the chemical vapor deposition (CVD) diamond, is as biocompatible as titanium and stainless steel, which has great biocompatibility and is frequently used in implantable devices [8–12]. On clinical applications of dentistry, researches have been published about micro-crystalline diamond (MCD) coated dental burrs [13], CVD micro/nanocrystalline diamond (MCD/NCD) bilayer for dental tools [14] and so on. As so far reported, diamond-coated titanium parts can overcome drawbacks of titanium alloys due to the extreme hardness, strength, corrosion resistance and low friction coefficient nature of diamond in ambient air [15], which completely satisfies the requirement of screw's surface. However, conventionally CVD grown MCD films exhibit a rough surface morphology, therefore show poor friction coefficients, which are especially unfavorable for wear resistant coatings. This problem has been

^{*} Corresponding authors. Tel.: +86 731 8830335; fax: +86 731 8876692. E-mail addresses: qiupwei@csu.edu.cn (Q. Wei), zhiming@csu.edu.cn (Z.M. Yu),

addressed by NCD film with no sharp crystal facets, but high hardness and polycrystalline morphology, which enable the material to minimize crystallographic cleavage in applications [16]. To improve the performance and lifespan of screws, the set of properties envisage a higher potential of NCD films for biotribological purposes compared with MCD films. Much attention has been paid to NCD films in previous studies, particularly on implants for dentistry [17–22].

To the best of our knowledge, most of researches focused on only biological, mechanical or corrosive aspects of the coating. There are few literatures for comparative study of MCD and NCD films on improving titanium abutment screws. In this work, for better component fit, extremely thin MCD and NCD films were deposited on TC4 substrates by HFCVD. Scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy were employed to evaluate morphology and quality of diamond films. In order to provide a comprehensive performance evaluation of MCD and NCD coated titanium alloy compared with the uncoated ones, the tribological and corrosion resistance tests were conducted in a simulated oral environment, instead of in ambient air which were mostly done by many researchers, and the biocompatibility has been assessed by cytotoxicity assessment and flow cytometry assessment. MCD and NCD films with superior performance are found and would provide more possible clinical applications.

2. Experimental procedures

Ti6Al4V wafers with a diameter of 9 mm and thickness of 1 mm were mechanically mirror polished. The substrates were corroded in an aqueous solution of 2% HF + 2% HNO₃ for 15 s then ultrasoniccleaned in deionized water for 10 min. After that, the etched substrates were treated by ultrasonication in acetone with nano-diamond powder for 30 min and cleaned in ethanol consecutively. All the above procedures were to improve the nucleation as well as the adhesion between the diamond films and the titanium alloy substrates. The pretreatments were done before drying and surface roughness of 28 nm was obtained.

Diamond films were grown by using a hot-filament-assisted chemical vapor deposition (HFCVD) reactor system designed and manufactured by the Department of Physics at the Royal Institute of Technology, Stockholm (Sweden). The detailed deposition parameters are listed in Table 1.

Diamond films were characterized by Raman spectroscopy (LabRAM ARAMIS), Solver P47 AFM and FEI Sirion200 field emission scanning electron microscopy (FE-SEM). Micro-Raman spectrometer probes with argon excitation of 532 nm laser, power of 21 mW and a spot size of 1 μ m. The surface morphology was investigated by SEM and AFM. The surface roughness was evaluated from the analyses of 2 \times 2 μ m² AFM images obtained in tapping mode.

The friction and wear tests were carried out by a ball-on-disk tribometer with a chrome steel ball in artificial saliva environment. The ball was 9.5 mm in diameter. The sliding velocity was 180 r \cdot min⁻¹ and the normal applied load, L, was 5 N. Diamond coated and uncoated Ti6Al4V samples were used as disks. Friction was monitored with the aid of a load cell and was recorded on chart paper in a computer throughout the tests.

Anodic polarization curve measurements were performed using a CHI660E Apotentiostat (CH Instruments, Austin, TX) to measure the

Table 1

Deposition conditions for diamond films on Ti6Al4V substrates.

Deposition parameters	MCD	NCD
Gas composition (sccm)		
CH ₄	2	4
H ₂	98	36
Ar	N/A	60
Gas pressure (kPa)	3	2
Deposition temperature (°C)	650	600-620
Deposition time (h)	1.5	2

corrosion resistance of as-deposited diamond films and uncoated Ti6Al4V. Double distilled ultrapure water (>18 M Ω at 25 °C) was used for cleaning the surface and electrodes. Prior to the measure, the samples were immersed in artificial saliva for 24 h for surface stability. Then the anodic polarization curve measurements were made in a single-compartment glass beater with a titanium sheet counter electrode and a saturated Ag/AgCl reference electrode. Artificial saliva was used as the electrolytic solution. The glass cell was placed in a constant temperature water bath and kept at 37 °C. The scan rate was 1 mV \cdot s⁻¹ range in 2 V.

The cell line L929, constituted by a highly proliferative population allowing rapid screening assays, was chosen to evaluate the biocompatibility of MCD and NCD coated and bare Ti6Al4V alloys. The fibroblast cell line L929 was cultured in α -minimal essential medium (α -MEM) containing 10% fetal bovine serum (FBS) 50 µg/ml ascorbic acid, 50 µg/ml gentamicin and 2.5 µg/ml fungizone, at 37 °C, in a humid atmosphere of 5% CO₂ in air. For subculture, the cell monolayer was washed twice with phosphate-buffered saline (PBS) and incubated with trypsin-EDTA solution (0.05% trypsin, 0.5% EDTA), resuspended in culture medium and cultured (10⁴ cells/cm²) for 8 days in standard plastic culture plates and on the surface of the samples of groups. The medium was changed every 2–3 days.

The proliferation behavior was measured by a cell counting kit-8 (CCK-8). Five groups were introduced to this experiment. Group A: blank control group (standard tissue culture plates), Group B: Ti6Al4V alloy, Group C: MCD-TC4 (Ti6Al4V alloy coated with MCD film), Group D: NCD-TC4 (Ti6Al4V alloy coated with NCD film), and Group E: Cu (fine copper). All the samples were fabricated to disk-shape (diameter = 9 mm, thickness = 1 mm) and cleaned with dehydrated alcohol and subsequently Ultra Violet (UV) sterilized for 1 h to ensure the absence of any contamination. The cell proliferation behavior was measured by CCK-8 after the cells were cultured on samples for 24 h, 48 h and 72 h. The optical density (OD) was then measured at 450 nm in an Enzyme-linked Immunosorbent Assay (ELISA) reader. The results were normalized in terms of macroscopic area and expressed as A \cdot cm⁻².

The apoptosis of the cells was measured by Flow Cytometry (FCM) with Annexin V-FIFC/PI double fluorescence staining. The cell was cultured as described above. After the 5 groups of cells were inoculated on the samples as described above for 72 h, they were collected and washed twice with PBS and were then centrifugated. The cells were resuspended in a binding buffer: 5 μ L of Annexin V and 5 μ L of PI, and incubated at room temperature for 10 min in the dark. The samples were monitored by FCM and analyzed with CellQuest software.

3. Results and discussion

3.1. Characterization of diamond films

Fig. 1 shows typical top-view electron microscopy images of the asgrown diamond films coated TC4. It can be obtained that both MCD and NCD films are compact, continuous, crack free and able to act as protective coatings. But their difference is clear to identify. Fig. 1(a) shows the well faceted crystallites of MCD film. The dominant morphological characteristic of NCD shown in Fig. 1(b) is the formation of agglomerates of a cauliflower-like structure. These agglomerates are composed of nanometer crystallites with a fine texture, or denoted as secondary nucleation processes [23]. It is obvious that the grain size declines from micrometer scale (200 nm $-1 \mu m$ in Fig. 1(a)) to nanometer scale (<100 nm in Fig. 1(b)). Fig. 2 shows the AFM images of these two samples. Surface root-mean-square (r.m.s) roughness of MCD film in Fig. 2(a) is about 50 nm and that of NCD film in Fig. 2(b) is approximately 34 nm. The NCD film is smoother than MCD film. This decrease in roughness can be directly related to the grain size decrease. Generally, the thicker the film is, the larger the grain size is and the rougher the surface of the diamond films in MCD is. M. Wiora etc. [16] reported



Fig. 1. FE-SEM images of a) MCD and b) NCD films deposited on Ti6Al4V substrates.

that the NCD films, unlike MCD films, did not increase the grain size or roughness when increasing its thickness from 1 μ m to 17 μ m. In this paper, the thickness of MCD film is about 1.5 μ m and of NCD film is about 0.5 μ m. The roughness of pretreated TC4 substrate is 28 nm that indicated NCD films inherit the substrate surface morphology and would not affect the surface roughness of thread.

Fig. 3 shows the Raman spectra of MCD and NCD films. MCD spectrum shows an intense peak at 1348 cm⁻¹. Compared with typical diamond peak at 1332 cm⁻¹, the peak of MCD has a shift and partial splitting due to the compressive stress which is calculated to be approximately -7.84 GPa [24] and mainly ascribed to a difference in the thermal expansion coefficients between a diamond film and TC4 substrate. Correspondingly, the NCD spectra have a less intense and broadening diamond peak at 1338 cm^{-1} . The lower shift means decreased residual stresses of calculated value of -2.94 GPa, which is beneficial for adhesion between the NCD film and substrate. This broadening was attributed to the decrease of the grain size [25]. Spectra show other broad peaks around 1140 cm^{-1} , 1350 cm^{-1} , 1480 cm^{-1} and 1550 cm^{-1} as well. The 1140 cm⁻¹ and 1480 cm⁻¹ shoulders are always associated with transpolyacetylene, a polymeric compound formed at the grain boundaries. which is a reliable indirect evidence of NCD exist [26]. The 1350 cm^{-1} and $1550 \,\mathrm{cm}^{-1}$ are D peak and G peak of disordered carbon [23] coming from sp² bonded carbon residing at grain boundaries and their sequence changing, respectively. The diamond grain size and Raman spectra characteristics largely depend on the CH₄/H₂ ratio [27]. With the increase of CH₄/H₂ ratio, the crystal size decreases, the grain boundaries increase and result in the rise of amorphous carbon $(sp^2 C)$ fraction. Therefore, the intensity of the diamond peak becomes weak, D peak becomes strong and overlaps with the diamond peak. That means the amount of non-diamond carbon is greater in NCD than that in MCD. Taking the resonance Raman Effect into account, the Raman sensitivity for sp² phase is approximately 50 times higher than sp³ phase [28]. Although abundant sp² carbon has been identified, the high intensity of diamond peak in Raman spectra indicates that as-deposited films are mainly diamond.

3.2. Tribological properties

To simulate oral cavity conditions, the friction tests were conducted in an artificial saliva environment. The variation of the friction coefficients (COF) of each specimen with the time are shown in Fig. 4. As shown, a graph of SUB is steady since the beginning of the test due to the polish process, while stabilized linearity of MCD and NCD comes after a period of fluctuation. A run-in period is required for as-deposited films to reach a low steady-state value, attributed to the surface roughness and the average grain size, generating the abrasive cutting and ploughing effects to the sharp surface asperities. After a run-in distance, the first flattened friction coefficients of MCD and NCD decrease to a range of 0.20-0.25. After 940 s, NCD keeps reducing to 0.10-0.15. The final persistent values of the steady friction coefficients are shown: SUB is found to be 0.28 while it reduces to 0.2 in MCD and 0.1 in NCD. On the other hand, wear rate is another important performance indicator in the friction test. But wear of the tested diamond films was too low to be measured. Due to plugging, micro abrasion is possible; when the film has higher hardness and elastic modulus compared with the ball, the wear loss from the ball surface may be higher than diamond film surface [29]. In consequence, specimens coated with diamond film apparently present superior tribological properties than uncoated TC4

Comparing MCD with NCD film, surface roughness and microstructure of the films have a significant effect on the friction and wear of diamond films [30]. Firstly, the difference of the friction coefficient in films is dependent on their initial roughness. In general, the higher the



Fig. 2. AFM images of the different diamond films deposited on Ti6Al4V substrates: a) MCD; and b) NCD.



Fig. 3. Raman spectra of the deposited MCD and NCD films (spectra have been normalized with respect to diamond peak intensity).

surface roughness is, the greater the friction and wear losses are [31]. Secondly, after running in, the NCD surface is almost atomically smooth $(Ra \approx 6 \text{ Å})$, and the friction coefficient represents the pure adhesive friction component. An explanation for the low adhesive component is that the so-called dangling carbon bonds at the surface are terminated by hydrogen [32]. If the hydrogen atoms are detached from the surface, the friction of self-mated diamond increases. Conventional CVD diamond like MCD contains small amounts of hydrogen (0.5%), compared to the present NCDs, which contain about 5 at.%. This could be caused by self-supply of hydrogen to the surface and thereby improved tribological properties [33]. Furthermore, low friction is directly related to the amorphization/graphitization of diamond near the sliding contact point [34,35]. It is observed that it undergoes the transition from sp³ to sp² resulting in an amorphous adlayer that depends on surface orientation and sliding direction, when diamond is polished. The structural phase transformation and amorphization influence the friction and wear performances. Enhanced amorphization/graphitization of carbon reduces the shear resistance and hence lowers the friction coefficient. Thus the low friction coefficient in the final stabilized liner can be attributed to the formation of a continuous lubricating amorphous carbonaceous layer. The large amount of grain boundaries, sp² polyaromatic and amorphous carbon due to the re-nucleation in NCD film lead to a much more obvious reaction and change. On the other hand, the lowfriction character of diamond is largely attributed to the highly passive nature of its sliding surface [31]. The test was done in artificial saliva. Active gaseous species such as water vapor can be adsorbed and passivate the dangling surface bonds of most carbon materials, which prohibit the formation of bond between specimens and counterparts.

With the increase of load, the friction coefficient would decrease according to Kumar N. et al. [36]. As diamond undergoes plasticity induced amorphization/graphitization, the extent of phase transformation is expected to increase with the increase of applied load. More asperities would appear at high normal load, resulting in intimate contact between specimens and counterparts. As a consequence, the thickness of the transfer layer will increase and the COF will decrease.

As mentioned in Section 3.1, with film thickness increasing, both grain size and roughness of NCD films stay constant while those of MCD would increase simultaneously [16]. As a result, the tribological property of NCD films with various thickness remains unchanged, indicating higher stability than MCD films.

Comprehensively, all these characteristics of diamond films are beneficial to biological applications and also meet the requirements for the ideal surface of screws. For reducing friction, diamond coated TC4 is better than TC4 itself. And NCD film is testified to be more advantageous than MCD film since it gains a longer working life.

3.3. Electrochemistry

Fig. 5 shows the corrosion resistance measured by the anodic polarization curve.

First of all, self-corrosion potential, a stable potential measured in corrosion system without the applied voltage, was set as an initial potential. Secondly, anodic polarization curve based on kinetic corrosion, features reflects characteristics of passivation and pitting tendency. From Fig. 5, no activation area is found in the three measured polarization curves, indicating that the surfaces of three kinds of materials have been passivated by 24 h immersion pretreatment in artificial saliva, which proves to good corrosion resistance. During the scanning process, the current increases with the increase of potential. When it rises to the initial steady state potential (E_p) , the current reaches a passivation state. According to the theory of electrochemistry, reduction of the initial steady state potential and passive current density, as well as broadening the range of passive potential correspond to improving the corrosion resistant. In Fig. 5, the initial steady state potential from negative to positive is in order of NCD, MCD and SUB. NCD shows minimum initial steady state potential and maximum passive potential range, while SUB presents maximum initial steady state potential and minimum passive potential range. It is also noted that the range of passive potential of coated samples, especially NCD, is wider than that of the uncoated. Therefore, NCD owns the best corrosion resistance



Fig. 4. Variations of friction coefficients of chrome steel balls during sliding against MCD film, NCD film and uncoated Ti6Al4V substrate (3 Hz frequency, 5 N normal load, and in artificial saliva for 30 min).



Fig. 5. Anodic polarization curve of different diamond films and uncoated substrate in artificial saliva at 37 °C, the scan rate was $1 \text{ mV} \cdot \text{s}^{-1}$.

under this condition. In clinical application, potential in oral environment generally does not exceed 600 mV [37]. Correspondently, current density of NCD under 600 mV in this test is nearly 0 μ A \cdot cm⁻², and that of MCD and SUB are also under 5 μ A \cdot cm⁻².

It is known that titanium possesses excellent corrosion resistance due to the generation of a TiO₂ passivation film on the surface, which is stable and compact, with a high oxidation potential and healing to mechanical damage [38]. However, corrosion resistance of metal surfaces is directly affected by the surface state. The surface passivation film is prone to break as a consequence of textured surface presented by processing, probably resulting in the metal ion release and harm to the normal metabolism [39]. After deposition of the compact and stable diamond films, the surface steady state is greatly improved and the precipitation of metallic elements is effectively prevented. Besides, NCD film exhibits superior performance over MCD film.

3.4. Biocompatibility

3.4.1. Cytotoxicity assessment

In this study, the mouse fibroblast cell line (L929 cells) were used to assess the cytotoxicity profile of MCD films (Group C) and NCD films (Group D) deposited on Ti6Al4V, compared with titanium alloy (Group B) as a negative control material and fine copper (Group E) as a positive control material. Group A was the blank control group used as another negative control group. Results regarding cell proliferation (CCK-8 assay) are represented in Figs. 6 and 7. The absorbance is proportional to the number of viable cells with the doping of the



Fig. 6. Cell viability/proliferation of L929 fibroblast cells cultured on the MCD film, NCD film, uncoated Ti6Al4V substrate and fine copper substrate surface for 72 h. Open bars, control. From left to right, in proper order was Group A (blank control), Group B (TC4), Group C (MCD film), Group D (NCD film), Group E (fine copper) (*: statistically different from the control).



Fig. 7. Viabilities of L929 fibroblast cells cultured on surface of Group B (TC4), Group C (MCD film), Group D (NCD film) and Group E (fine copper) for 72 h.

electronic coupling reagent. Proliferation quantity and rate of the cell line are the main factors that influence the results of the tests. The cell line exhibits deeper color when more and faster cell proliferation is generated, which is also an indication of less cytotoxicity.

From Fig. 6, L929 cells in Group B presented a great deal of proliferation almost comparable to that of the blank control group A. On the contrary, Group E as the positive control group shows the lowest proliferation. The values of Groups C and D are in the range but much closer to Groups A and B which well proved their low cytotoxicity. Moreover, it can be observed that the amount of cells on MCD is a little more than that on NCD. This phenomenon should be explained by the difference in surface energy and grain boundaries of MCD and NCD. For both films, cultures reached confluence and soon after formed a dense cell layer that was easily lost during a routine medium change [40]. NCD film has a relatively larger surface area creating more surface energy, which leads to more adsorption on the substances then more lost. The calculated viabilities of Groups B. C and D are all over 70% of blank group A shown in Fig. 7. Group E as positive control is reduced to <70%, meaning that it has a cytotoxic potential. The present work addressing the biological profile of diamond coatings regarding the response of cell line L929 is in agreement with the standard ISO guidelines for in vitro cytotoxicity evaluation of medical devices [41,42].

After comprehensive analysis of Figs. 6 and 7, L929 cells presented a profile of cell viability/proliferation representative of the cell populations: a permanent cell line with high growth rate from the beginning of the incubation. In addition, the unique surface properties of nanomaterial, namely a larger specific surface area, more surface defects (such as edge/corner sites and particle boundaries) and higher proportions of surface electron delocalization will enhance initial protein interactions that control cell adhesion [43,44], which is a determinant factor for the subsequent cell proliferation and function so that NCD film can support wider applications in biomedicine.

3.4.2. Flow cytometry assessment

Apoptosis occurs at the same time on cell's culture, as another evaluation indicator for materials' biocompatibility. Experimental groups are the same as the cytotoxicity assessment, blank control group (A), titanium alloy (B), MCD (C), NCD (D) and fine copper (E). Results are shown in Fig. 8. Total rate of apoptosis consisted of two parts, upperright portion shows mid-late apoptosis rate, and the lower-right portion is on behalf of early apoptosis rate. As shown, Group B, a negative control, has the lowest apoptosis which is close to Group A. Groups C and D are in the next approximate row position without sensible difference. Group E as a positive control induces the highest apoptosis, much higher than other groups. According to Fig. 8, though Groups C and D have higher apoptosis rate than Groups A and B, they still have very low apoptosis rate, which demonstrates that MCD and NCD exhibit a low apoptosis.



Fig. 8. Flow cytometer for apoptosis of L929 fibroblast cells cultured on a) blank control, b) TC4. c) MCD film, d) NCD film, and e) fine copper for 72 h.

In the evaluation of biocompatibility, cell apoptosis has a relevant effect with materials nature and constitution [45]. Apoptosis analysis helps to understand interactions between tissues and implants, as well as evaluate the biological performance of materials. It has been noted that cell apoptosis are mainly caused by the metal ions, accompanied by a concentration-dependence and time-dependence. As mentioned before, friction wear and corrosion will easily occur at thread surface, resulting in the metal ion release. With a diamond film coat, preferably an NCD film, which shows a similar apoptosis resistance but more compact, stable, better friction and corrosion resistance, this issue can be prevented. Meyer et al. [46] proposed that increasing the corrosion resistance of the alloy is also an effective way to improve the biocompatibility.

4. Conclusion

In the present study, both MCD and NCD films show compact, continuous surface and low surface roughness. Their surface roughness and microstructure then play a major role in improving the TC4 tribological behavior. The final steady friction coefficients reduce from 0.28 of TC4 to 0.2 of MCD, 0.1 of NCD. Electrochemical experiments demonstrate that surfaces coated with diamond films can effectively promote the corrosion resistance. The advanced corrosion resistance and compact, stable surface will further improve the biocompatibility of diamond films. Meanwhile, in these evaluations, NCD films all display a better performance than MCD films. Cytotoxicity assessment shows that diamond films provide a suitable surface for cell attachment, spreading and proliferation. Their low apoptosis further supports cytotoxicity-free and well biocompatibility. In conclusion, the cellular biocompatibility of diamond films, allied with the excellent physicochemical performance, anticipates a wide range of applications in the dental biomedical field. NCD films present a more superior combined property than MCD films to extend the life of metal specimen for dental restorations in clinical significance. By the way, there are some other important criteria that the coatings must meet to be useful as dental implants such as fracture strength of the coatings and their modulus mismatch with the titanium alloys, which will be the factors we study in the future.

Conflict of interest

There is no conflict of interest.

Acknowledgment

The authors are grateful to the Nature Science Foundation of China (no. 21271188 & no. 51301211), the China Postdoctoral Science Foundation (no. 2012M521541), and the State Key Laboratory of Powder Metallurgy (no. 20110933K) for their financial support. We acknowledge School of Stomatology, Central South University for the corporation on biomedicine and technical support.

References

- S.-H. Choi, Y.-C. Jeon, H.-S. Hwang, C.-M. Jeong, J. Korean Res. Soc. Dent. Mater. 27 [1] (2000) 117-127.
- [2] R.E. Jung, A. Zembic, B. Pjetursson, M. Zwahlen, D.S. Thoma, Clin. Oral Implants Res. 23 (Suppl. 6) (2012) 2-21.
- A. Singer, V. Serfaty, Int. J. Oral Maxillofac. Implants 11 (1996).
- T. Jemt, P. Pettersson, Am. J. Dent. 21 (1993) 203-208. [4]
- H.J. Kim, H.C. Choe, C.H. Chung, J. Korean Acad. Prosthodont. 45 (2007) 329-338. [6]
- Ş. Canay, M. Öktemer, Quintessence Int. 23 (1992).
- T. Guda, T.A. Ross, L.A. Lang, H.R. Millwater, J. Prosthet. Dent. 100 (2008) 183-193. L. Tang, C. Tsai, W.W. Gerberich, L. Kruckeberg, D.R. Kania, Biomaterials 16 (1995) [8] 483-488
- [9] P. Ariano, P. Baldelli, E. Carbone, A. Gilardino, A. Lo Giudice, D. Lovisolo, C. Manfredotti, M. Novara, H. Sternschulte, E. Vittone, Diam. Relat. Mater. 14 (2005) 669-674
- [10] G. Heinrich, T. Grögler, S. Rosiwal, R. Singer, Surf. Coat. Technol. 94 (1997) 514–520. R. Müller, M. Adamschik, D. Steidl, E. Kohn, S. Thamasett, S. Stiller, H. Hanke, V.
- Hombach, Diam. Relat. Mater. 13 (2004) 1080-1083. [12]
- C.G. Specht, O.A. Williams, R.B. Jackman, R. Schoepfer, Biomaterials 25 (2004) 4073-4078
- [13] C.A.R. Carvalho, T.C. Fagundes, V.J. Trava-airoldi, M.F.L. Navarro, J. Esthet. Restor. Dent. 19 (2007) 19-29.
- [14] E. Salgueiredo, F. Almeida, M. Amaral, A. Fernandes, F. Costa, R. Silva, F. Oliveira, Diam. Relat. Mater. 18 (2009) 264-270.
- [15] J. Wilks, E. Wilks, Properties and applications of diamond, Butterwood-Heinemann, Oxford, 1991
- [16] M. Wiora, K. Brühne, A. Flöter, P. Gluche, T. Willey, S. Kucheyev, A. Van Buuren, A. Hamza, J. Biener, H.-J. Fecht, Diam. Relat. Mater. 18 (2009) 927-930.
- X. Xiao, J. Wang, C. Liu, J.A. Carlisle, B. Mech, R. Greenberg, D. Guven, R. Freda, M.S. Humayun, J. Weiland, J. Biomed. Mater. Res. B 77 (2006) 273-281.
- [18] D. Steinmüller-Nethl, F.R. Kloss, M. Najam-Ul-Haq, M. Rainer, K. Larsson, C. Linsmeier, G. Köhler, C. Fehrer, G. Lepperdinger, X. Liu, Biomaterials 27 (2006) 4547-4556
- [19] S. Wenmackers, P. Christiaens, M. Daenen, K. Haenen, M. Nesládek, M. van deVen, V. Vermeeren, L. Michiels, M. Ameloot, P. Wagner, Phys. Status Solidi A-Appl. Mat. 202 (2005) 2212-2216.
- [20] P.S. Siew, K.P. Loh, W.C. Poh, H. Zhang, Diam. Relat. Mater. 14 (2005) 426-431.
- S. Mitura, K. Mitura, P. Niedzielski, P. Louda, V. Danilenko, J. Achiev. Mater. Manuf. [21] Eng. 16 (2006) 9-16.
- [22] W. Okrój, M. Kamińska, L. Klimek, W. Szymański, B. Walkowiak, Diam. Relat. Mater. 15 (2006) 1535-1539
- [23] N. Braga, C. Cairo, N. Ferreira, M. Baldan, V. Trava-Airoldi, Diam. Relat. Mater. 19 (2010) 764 - 767
- [24] F. Ahmed, K. Bayerlein, S. Rosiwal, M. Göken, K. Durst, Acta Mater. 59 (2011) 5422-5433
- [25] R. Dumpala, M. Chandran, N. Kumar, S. Dash, B. Ramamoorthy, M. Rao, Int. J. Refract. Met. Hard Mater. 37 (2013) 127-133
- M. Amaral, A. Fernandes, M. Vila, F. Oliveira, R. Silva, Diam. Relat. Mater. 15 (2006) [26] 1822-1827
- [27] Z. Sun, J. Shi, B. Tay, S. Lau, Diam. Relat. Mater. 9 (2000) 1979-1983.
- [28] P. Bou, L. Vandenbulcke, J. Dismukes, Proc. Electrochem, Soc. 89 (1989) 610.
- K. Panda, N. Kumar, B. Panigrahi, S. Polaki, B. Sundaravel, S. Dash, A. Tyagi, I.-N. Lin, [29] Tribol. Int. 57 (2013) 124-136.
- [30] S. Kulesza, J. Patyk, F. Rozpłoch, Chem. Phys. Lett. 391 (2004) 56-59.

- [31] A. Erdemir, C. Bindal, G. Fenske, C. Zuiker, A. Krauss, D. Gruen, Diam. Relat. Mater. 5 (1996) 923–931.
- [32] S.V. Pepper, J. Vac. Sci. Technol. 20 (1982) 643-646.
- [33] P. Hollman, O. Wänstrand, S. Hogmark, Diam. Relat. Mater. 7 (1998) 1471–1477.
 [34] L. Pastewka, S. Moser, P. Gumbsch, M. Moseler, Nat. Mater. 10 (2011) 34–38.
- [35] D.S. Grierson, R.W. Carpick, Nano Today 2 (2007) 12–21.
- [36] N. Kumar, K. Panda, S. Dash, C. Popov, J. Reithmaier, B. Panigrahi, A. Tyagi, B. Raj, AIP Adv. 2 (2012) 032164.
- [37] P. Corso, R. German, H. Simmons, J. Dent. Res. 64 (1985) 854–859.
 [38] L. Reclaru, J.-M. Meyer, Am. J. Dent. 22 (1994) 159–168.

- [40] A. Learsen, M. Stoltenberg, G. Danscher, Histochem. Cell Biol. 128 (2007) 1–6.
 [40] M. Amaral, A. Dias, P. Gomes, M. Lopes, R. Silva, J. Santos, M. Fernandes, J. Biomed. Mater. Res. A 87 (2008) 91–99.
- [41] International Organization for Standardization, ISO 7405: dentistry-preclinical evaluation of biocompatibility of medical devices used in dentistry-test methods for dental materials, 2008. (Geneva).
- [42] International Organization for Standardization, ISO 10993-5: biological evaluation of medical devices. Part 5. Tests for cytotoxicity: in vitro methods, 2009. (Geneva).
- [43] T.J. Webster, C. Ergun, R.H. Doremus, R.W. Siegel, R. Bizios, Biomaterials 21 (2000) 1803-1810.
- [44] T.J. Webster, C. Ergun, R.H. Doremus, R.W. Siegel, R. Bizios, J. Biomed. Mater. Res. A [45] J.E. Gough, C.A. Scotchford, S. Downes, J. Biomed. Mater. Res. A 61 (2002) 121–130.
- [46] R.D. Meyer, J. Meyer, LJ. Taloumis, J. Prosthet. Dent. 69 (1993) 141-143.