

Tribology in Industry

Effect of CVD-Diamond on the Tribological and Mechanical Performance of Titanium Alloy (Ti6Al4V)

S.H. Din^a, M.A. Shah^b, N.A. Sheikh^a

^aDepartment of Mechanical Engineering, National Institute of Technology Srinagar 190006, India,

^bDepartment of Physics, National Institute of Technology Srinagar 190006, India.

Keywords:

Hot filament CVD
Nanocrystalline
Microcrystalline
Coefficient of friction
Wear track
Tribo-layer

A B S T R A C T

Nano-crystalline diamond and microcrystalline diamond films have been separately deposited on chemically treated titanium alloy (Ti6Al4V) substrates from methane/hydrogen (CH₄/H₂) gas mixture, using hot filament chemical vapor deposition technique. The coatings have architecture of Ti6Al4V/NCD and Ti6Al4V/MCD. The as grown nanocrystalline diamond and microcrystalline diamond films were characterized using high resolution scanning electron microscope and Raman's spectroscopy. The residual stresses along the surface of nanocrystalline diamond coatings and micro-crystalline diamond coatings are compressive in nature as shown by the Raman spectroscopy. Nanoindentation tests were also conducted using Berkovich nanoindenter for the purpose of measurement of hardness and elastic modulus values. The indentation depth for microcrystalline diamond coating was 65 nm, whereas for nanocrystalline diamond coating, it was 72 nm. Microcrystalline diamond and nanocrystalline diamond coatings have yielded the super-hardness of ~55 G Pa and ~38 G Pa respectively. The average coefficient of friction of microcrystalline diamond and nanocrystalline diamond coatings decrease from 0.305-0.27 to 0.068-0.053, respectively, when the load is increased from 1 N to 10 N. However, for conventional Ti6Al4V substrate the average coefficient of friction changes from 0.625 to 0.38 under the same input conditions.

Corresponding author:

Sajad Hussain Din
Department of Mechanical
Engineering, National Institute of
Technology Srinagar 190006, India.
E-mail: sajad_08phd12@nitsri.net

© 2016 Published by Faculty of Engineering

1. INTRODUCTION

Many researchers are working on the deposition of diamond coatings on metallic substrates because of their applications in medical field [1-5]. Among these metals titanium and its alloys are best suited for joint implants. The materials

used in joint implants need to have a good biocompatibility, good fixation, chemical inertness and load transfer capacity. Titanium and its alloys have exceptional properties such as: good specific strength, creep resistance, corrosion resistance and biological inertness. Due to these properties titanium and titanium

alloys are widely used in medicine, aeronautics, astronautics, chemical industry, power industry and food industry [6-10]. Titanium and its alloys are preferred for implants and surgical devices because of its biocompatibility, resistance and tolerance to body fluids. The mechanical and tribological properties of titanium alloys combine to provide implants that are extremely damage-tolerant. The durability and service performance of titanium by chemical vapor deposition can markedly be enhanced [11-14]. By altering the microstructures of the substrate materials the gas reactants severely deteriorate the mechanical properties [15-19]. Hydrogen is crucial to synthesize quality diamond as it preferentially etches non diamond carbon species. But hydrogen also readily dissolves into titanium and induces phase transformation and increase brittleness. [20-25]. A new hetero-interface is introduced which complicates the adhesion failure models of diamond coatings. Thus preventing the formation of an intermediate titanium carbide layer at the early stage of CVD processing [26,27]. For smoothing the surface of diamond films, various methods have been developed. Various effective tools to improve the tribological behavior of the diamond film and lower the surface roughness are nanocrystalline diamond (NCD) film, substrate pretreatment, activated hydrogen etching on surface, diamond polishing, growth parameters control, addition of interlayers, solid lubrication composite coating on diamond films and alternate deposition of poly/nanocrystalline diamond multilayer [28-35]. With the development of the technique of CVD diamond films, synthesis of nanocrystalline diamond (NCD) and microcrystalline diamond (MCD) films have gained wide spread research interest [36,37]. NCD films possess fine diamond crystals with small grain sizes ranging few nanometers [38,39]. Compared with microcrystalline diamond (MCD) films, NCD films have lower hardness than MCD films due to the presence of graphitic carbon in the films. Moreover, due to high grain boundary density the NCD coatings show surface hardness reduction [40-46]. Further, NCD films have smoother surface and lower friction coefficient, which makes them ideal coatings for tribological applications. K. D. Bouzakis et al. studied the application of inclined impact test for evaluating the temperature dependent fatigue strength of NCD coatings' interface [47]. Moreover, it clarified the

influence of the NCD film's adhesion on wear of NCD-coated tools in milling aluminum alloy AA 7075 T6, which is a characteristic material for aerospace applications. The NCD coating-substrate interface fatigue strength is a key aspect for measuring the coated tool life in milling. The NCD coating-interface fatigue was probed using inclined impact tests at ambient and elevated temperatures. The investigations of milling AA 7075 T6 showed that the NCD film-substrate interface strength at elevated temperatures is a key factor for explaining the wear behaviour. An insufficient adhesion leads rapidly to a delamination of the NCD-coating and to a substrate revelation. The inclined impact test is an efficient test method facilitating the assessment of the NCD film substrate interface at ambient and elevated temperatures [48-51]. Z. Doni et al. studied the evolution of the functional integrity state in a comparative way for two contact pairs (Ti_6Al_4V/Al_2O_3 and $Ti_6Al_4V/steel$ ball) in dry and corrosive environment [52]. The investigation showed the behavior of Ti_6Al_4V alloy under reciprocating wear sliding conditions in a comparative way for two different counter materials, bearing steel and ceramic balls (Al_2O_3 - 99.6 %) in dry and corrosive environment (an aqueous solution of 3.5 % NaCl). It aimed to highlight the tribological characteristics that showed invariability during the test and provided a high level of functional integrity of the surface. The conclusions drawn from this work were as follows; (a) in dry condition the Ti_6Al_4V/Al_2O_3 contact pair showed a high functional integrity degree of the surfaces in terms of surface quality, characterized by roughness parameters S_a , S_q and S_y , while for the $Ti_6Al_4V/steel$ ball based on the roughness parameter S_v ; (b) in the case of $Ti_6Al_4V/steel$ ball contact pair a better functional integrity (evaluated based on the weight loss) occurred for higher applied loads than in the case of lower loads; (c) from the point of view of the electrochemical behavior a higher functional integrity occurred in the case of Ti_6Al_4V/Al_2O_3 contact pair at lower applied loads (assessed through parameters E_{corr} and I_{corr}); (d) the electrochemical parameters for Ti_6Al_4V/Al_2O_3 contact pair are at a lower level than those of the $Ti_6Al_4V/steel$ ball contact pair; (e) the evolution of the roughness parameters and the structural affinity between Ti_6Al_4V alloy and the bearing ball conduced to a higher functional integrity level from the point of view

of the evolution of COF by comparison to Ti6Al4V/Al₂O₃ contact pair [53-56].

A comparison has been documented between nanocrystalline diamond (NCD) and microcrystalline diamond (MCD) coatings on titanium alloy (Ti6Al4V) substrates with architectures of Ti6Al4V/NCD and Ti6Al4V/MCD, using hot filament chemical vapor deposition (HFCVD) technique. A detailed analysis of friction and wear behavior in ambient air for the two separate coatings has been studied. Their tribological behavior is studied as a function of the diamond coatings characteristics. The effect of diamond quality on the tribological behavior of the two types of coatings has been investigated. The friction characteristics of the diamond coated Ti6Al4V substrates has been compared with uncoated one, using ball on disc type linear reciprocating micro-tribometer, sliding against smooth alumina (Al₂O₃) ceramic ball under dry sliding conditions. Al₂O₃ is a promising ceramic material used at high temperature because of its excellent chemical stability, good mechanical and electrical properties, and wear and corrosion resistance.

2. EXPERIMENTAL DETAILS

Titanium alloy (Ti6Al4V) samples of 25 mm X 25 mm in dimensions were polished using silicon carbide (SiC) and cleaned with deionized water. The samples were etched in the solution of HF: H₂O₂: DI water. The samples were rinsed in deionized water three times for three minutes each. The samples were removed and blown dry with air gun. The mirror finish was obtained by polishing the samples by diamond paste (1μm). An ultrasonicator was used to clean the samples with acetone for 30 minutes and then dried thoroughly by a hot drier. Dimethyl sulphoxide (DMSO) solution containing diamond seedings of size 4 μm were used. Before deposition of nano-diamond films, the titanium alloy samples were dispersed in it. This is done by using a low power ultrasonicator for 15 minutes. The samples were again cleaned with ethanol in an ultra-sonicator for 1 minute and placed inside the cold walled aluminum chamber of hot filament chemical vapor deposition (HFCVD) system (sp₃ Diamond Technologies Inc. USA). An array of 31 parallel wires of (0.12 mm) diameter filaments, with 12 mm wire to wire spacing and standoff distance of

17 mm, was placed above the samples. A rotary pump was used to continuously pump the hot filament chemical vapor deposition (HFCVD) chamber, while methane (45 sccm) diluted in excess of hydrogen (2250 sccm), were quantified in at carefully controlled rates. The assembly of gas distribution allowed the control of the gas flow patterns in and around both the filament assembly and the sample to ensure uniformness in the coatings. A two color pyrometer monitored the temperature of tungsten filament. It was found to be 2200 °C. A k-type thermocouple was used to measure the temperature of titanium alloy samples. The thermocouple was located beneath the titanium alloy samples. It was found to be 800 °C. The whole growth process was performed for 3 hours and the thickness of the film was estimated to be 3 μm. The detailed growth parameters for depositing MCD and NCD films are listed in Table 1.

Table 1. Growth parameters for the deposition of MCD and NCD coatings.

Coating type	Substrate Pressure (Torr)	Substrate Temp. (°C)	Filament Temp. (°C)	Methane Conc. (CH ₄ /H ₂) %	Duration (hrs)
MCD	36	800-850	2200	2	3
NCD	12	800-850	2200	4	3

Raman spectra of the deposited films were recorded using a confocal microscope (Alpha 300, Witec) with an excitation radiation of 532 nm of a Nd:YAG laser operated at less than 20 mW. The surface roughness and microstructure were observed using a field emission SEM (Quanta 3D, FEI). The detailed experimental conditions are given in Table 2.

Table 2. Experimental conditions.

S. No.	Parameters	Operating Conditions
1	Normal Load	1, 5, 10 N
2	Sliding Velocity	8 cm/s
3	Relative Humidity	70 (± 5)%
4	Duration of Rubbing	15 minutes
5	Surface Condition	Dry
6	Materials Tested	Ti6Al4V, MCD and NCD
7	Ball Material	Alumina (Al ₂ O ₃)
8	Diameter of ball	6 mm
9	Stroke length	5 mm
10	Frequency	2 Hz
11	Temperature	30±1 °C
12	Roughness Factor (R_a) Ti6Al4V NCD MCD	0.38 μm 0.18 μm 0.26 μm

2.1 Method of deposition

Hot filament chemical vapor deposition system (HFCVD, Model 650 series, sp₃, Diamond Technologies) with excellent process control unit system was used for the deposition of diamond films, using the growth rate of 1 μm/hr. Deposition parameters such as chamber pressure and methane concentration were controlled easily during the experiment by using throttle valve and mass flow controllers respectively. Hydrogen (H₂) and methane (CH₄) were used as the precursor gases and their flow rates were completely controlled using mass flow controllers. An arrangement of tungsten wires (diameter 0.12 mm) in systematic order were used as hot filaments for the activation of these precursor gases and the distance between filament and substrate was kept 17 mm. The grain size of the diamond films were automatically controlled by maintaining both methane concentration and chamber pressure. The toxic by product gases or exhaust gases produced after the deposition process from the HFCVD chamber were diluted using nitrogen (N₂) gas. However, N₂ gases were used before and after the diamond growth process of flush the chamber. CVD chamber was made of aluminum with cooling channels and the temperature of the chamber was maintained at ~55 °C using a circulating water chiller.

3. RESULTS AND DISCUSSIONS

The friction measurement was carried out for the total sliding time of 20 minutes using ball on disc type linear reciprocating micro-tribometer, sliding against smooth alumina (Al₂O₃) ceramic ball, under the application of increased normal load. After friction measurement the wear tracks formed on the surfaces of NCD, MCD and Ti6Al4V were characterized using Raman Spectroscopy and scanning electron microscopy (SEM) techniques. However, the compositional analysis for the formation of tribo-layer observed on the wear tracks of NCD and MCD coatings were confirmed using energy dispersive spectroscopy (EDS) technique after friction measurement. Also nanoindentation tests were carried out using Berkovich nanoindentation data. In this research, it is aimed to find the variations in frictional characteristics with the duration of rubbing

when sliding against smooth Al₂O₃ ceramic ball, under the application of 1-10 N loads.

3.1 Scanning Electron Microscopy

The scanning electron microscopy was used to study the morphology and grain size of diamond films. With the increase in methane concentration, secondary nucleation takes place which changes the nature of existing grains from microcrystalline to nanocrystalline. Therefore, a cauliflower type of morphology is generally shown by the top-layer (NCD) of multilayer CVD diamond coatings [57]. The MCD coating exhibits clear multi-facet diamond crystals. Fig. 1 (a) shows the general surface morphology of the NCD coating, whereas Fig. 1 (b) shows the surface morphology of the MCD coating.

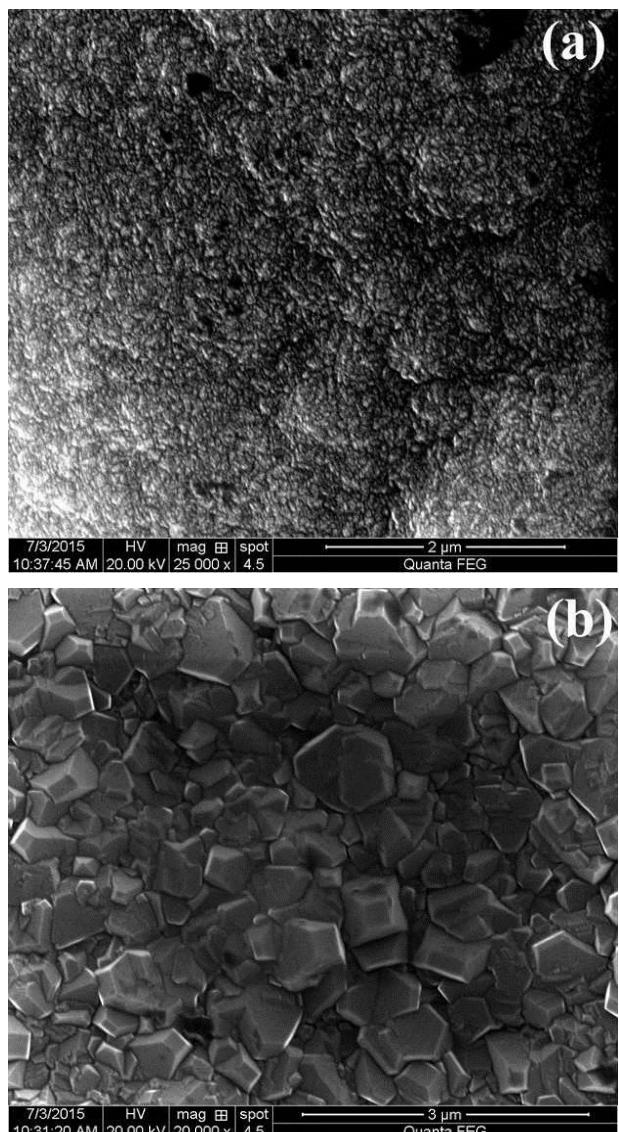


Fig. 1. CVD-diamond coatings, (a) Surface morphology of NCD coatings, (b) Surface morphology of MCD coatings.

3.2 Raman Spectroscopy

Raman spectroscopy was used to identify the chemical structure and crystalline quality of the diamond coatings. In this respect, stress free crystalline diamond coating exhibits Raman peak at 1332 cm^{-1} corresponding to the first-order phonon mode of T2g symmetry [42]. Raman spectrum of MCD coating confirms the microcrystallinity. First order Raman peak shift towards higher side centered at 1333 cm^{-1} is indicative of the presence of residual compressive stress in both the coatings (Fig. 2). Mainly, this compressive residual stress is due to the difference in thermal expansion coefficients of the substrate and coating [30-31].

Residual stresses can be calculated from $\sigma = -0.348(v_m - v_0)\text{ GPa}$ for fundamental Raman peak at v_m , where $v_0 = 1332\text{ cm}^{-1}$ and $v_m = 1333\text{ cm}^{-1}$. Thus both MCD and NCD diamond coatings contain a compressive stress of -0.348 GPa , where negative sign indicates compressive stress. MCD exhibits columnar structure of grains and faceted form of surface morphology. In case of NCD coatings, two other peaks v_1 and v_3 are characteristics of in-plane (C-H) and

stretching (C-C) vibrational modes, respectively. The presence of these modes was ascribed to the formation of transpolyacetylene (TPA) chain in the grain boundaries which is a well-known characteristic of NCD coatings. A cauliflower type of growth is generally seen with the NCD coatings [36-46].

3.3 Mechanical and Tribological Properties

Figures 3 (a) and (b) show the load-displacement curves for the polished NCD and MCD coatings. Indentation tests were performed on each coating using nanoindentation technique. It was evident from the load-displacement curves that the NCD coating was less resistant to deformation in comparison to the MCD coating. The indentation depth for MCD coating was 65 nm, whereas for NCD coating, it was 72 nm. The hardness of NCD and MCD coatings were found to be $\sim 38\text{ GPa}$ and $\sim 55\text{ GPa}$, respectively and these values are in agreement with the earlier reports on diamond films [58-60]. Hardness of NCD coatings was found to be inferior to that of MCD coatings because of the presence of non-diamond phases at the grain boundaries.

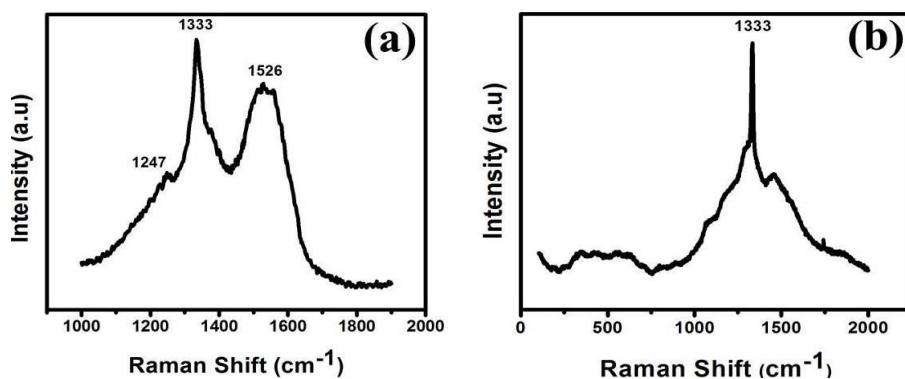


Fig. 2. Raman spectra of CVD-diamond coatings, (a) NCD and (b) MCD.

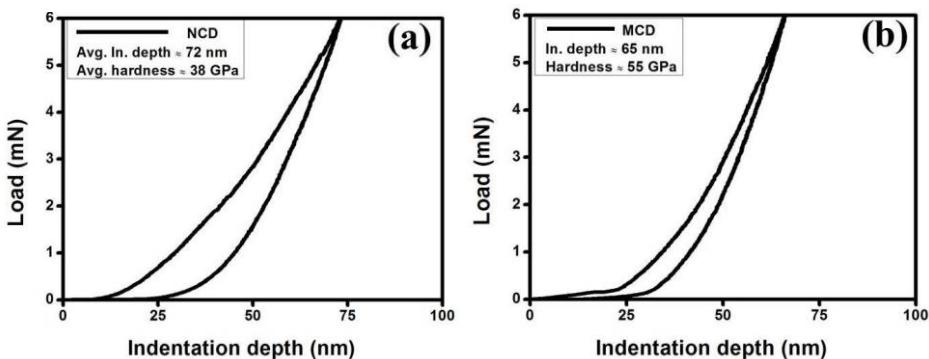


Fig. 3. (a) Load-displacement curve for NCD coating, (b) Load-displacement curve for MCD coating.

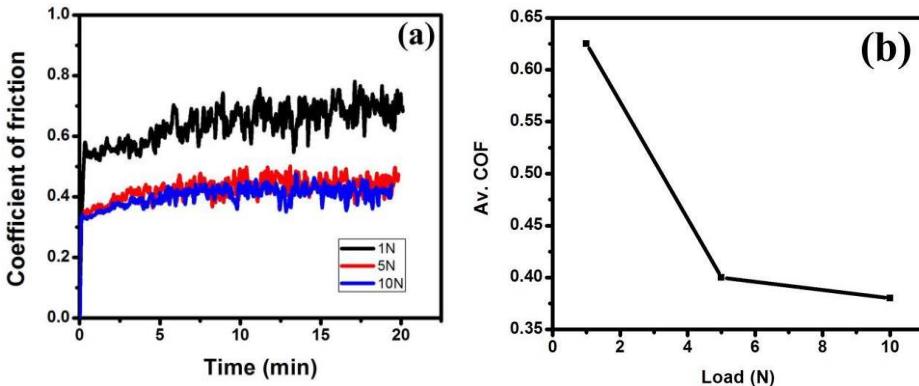


Fig. 4. Tribological characteristics of Ti6Al4V substrates sliding against alumina ball. (a) Coefficient of friction vs duration of rubbing at 1 N, 5 N and 10 N, (b) Average coefficient of friction vs. normal load.

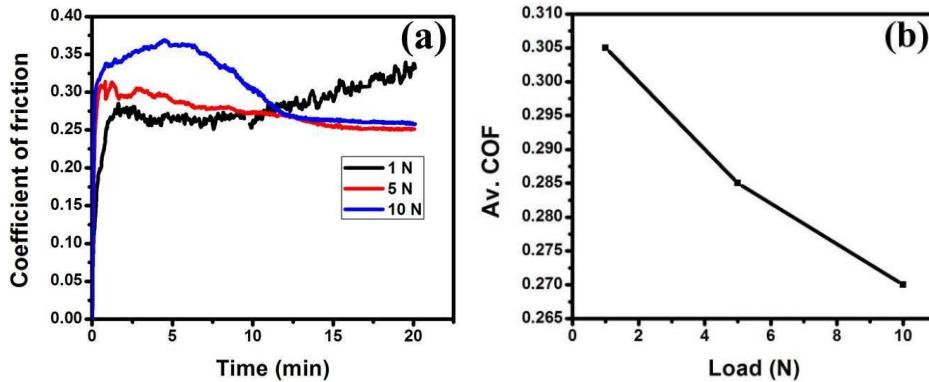


Fig. 5. Tribological characteristics of MCD coatings sliding against alumina ball. (a) Coefficient of friction vs duration of rubbing at 1 N, 5 N and 10 N, (b) Average coefficient of friction vs. normal load.

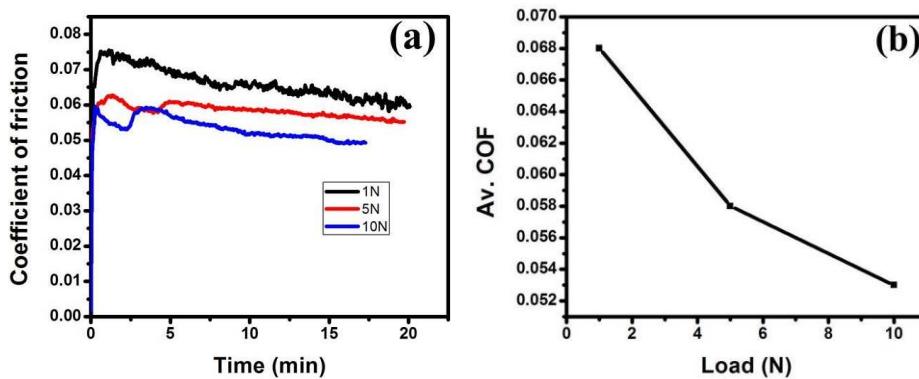


Fig. 6. Tribological characteristics of NCD coatings sliding against alumina ball, (a) Coefficient of friction vs duration of rubbing at 1 N, 5 N and 10 N, (b) Average coefficient of friction vs. normal load.

3.4 Friction Characteristics of the NCD and MCD Coatings against Alumina Balls

Frictional characteristics of uncoated Ti6Al4V, MCD and NCD were studied, sliding against smooth Al_2O_3 ceramic ball using ball on disc type linear reciprocating micro-tribometer, for a sliding speed of 8 m/s and a load of 1 N, 5 N and 10 N. The average values of coefficient of friction corresponding to virgin substrate, MCD and NCD coatings were calculated as $\sim 0.625-0.38$,

$\sim 0.305-0.27$ and $0.068-0.053$, respectively by increasing the normal load from 1-10 N, for the total duration of 20 minutes. Tribological characteristics of Ti6Al4V substrate sliding against alumina ball is shown in figure 4. The coefficient of friction decreases with increase in load, shown in Fig. 4 (a) and the average coefficient of friction, shown in Fig. 4 (b) decreases from 0.625 to 0.38. Similarly, the values of coefficient of friction corresponding to MCD coating decrease under the same input

operating conditions, as shown in Fig. 5 (a). The average coefficient of friction in MCD coatings decrease from 0.305 to 0.27, as shown in Fig. 5 (b). Tribological characteristics of NCD coatings against alumina ball are shown in Fig. 6. The NCD coatings show least coefficient of friction among all the tested materials. The values of coefficient of friction corresponding to NCD coatings decrease under the same conditions. As the load increases the coefficient of friction decreases. The average coefficient of friction decreases from 0.068 to 0.053. This observed low friction coefficient of NCD coating in comparison to that of MCD coating was observed due to the presence of graphitic carbon phases at the grain boundaries and also due to small grain size. However, in case of MCD coating, the observed initial higher value of friction coefficient is mainly due to high surface roughness which becomes smoother with sliding time.

The noisy fluctuations of the friction coefficient have been observed at 1 N. These fluctuations are due to surface roughness. At the beginning of the applied load we can observe a peak which corresponds to the adaptation of the contact of both counter-faces. After the tests carried out in these conditions, the diamond coating on the disc is found to be intact as shown by the optical microscope in Fig. 7 and indicated by the surface roughness values which remain constant. Figure 7 (a), (b) and (c) show the surface morphology of the wear tracks corresponding to virgin Ti6Al4V substrate, MCD and NCD coatings at 10 N load, respectively. It has been clearly observed from all the wear tracks that with the increase in load the track width increases, and therefore corresponding coefficient of friction decreases for both the types of coatings. At the end of the test carried out at 10 N, a wear track of 966 μm , 673 μm and 426 μm in width was formed on the Ti6Al4V substrate, MCD and NCD diamond coated discs, respectively. The detailed mechanical and tribological experimental results are listed in Table 3.

Table 3. Mechanical and tribological results.

Material	Hardness (H)	Elastic Modulus	Variation in Coefficient of Friction
Ti6Al4V	~10 GPa	~510	~0.625-0.38
MCD	~55 G Pa	~1150	~0.305-0.27
NCD	~ 38 G Pa	~1050	~0.068-0.053

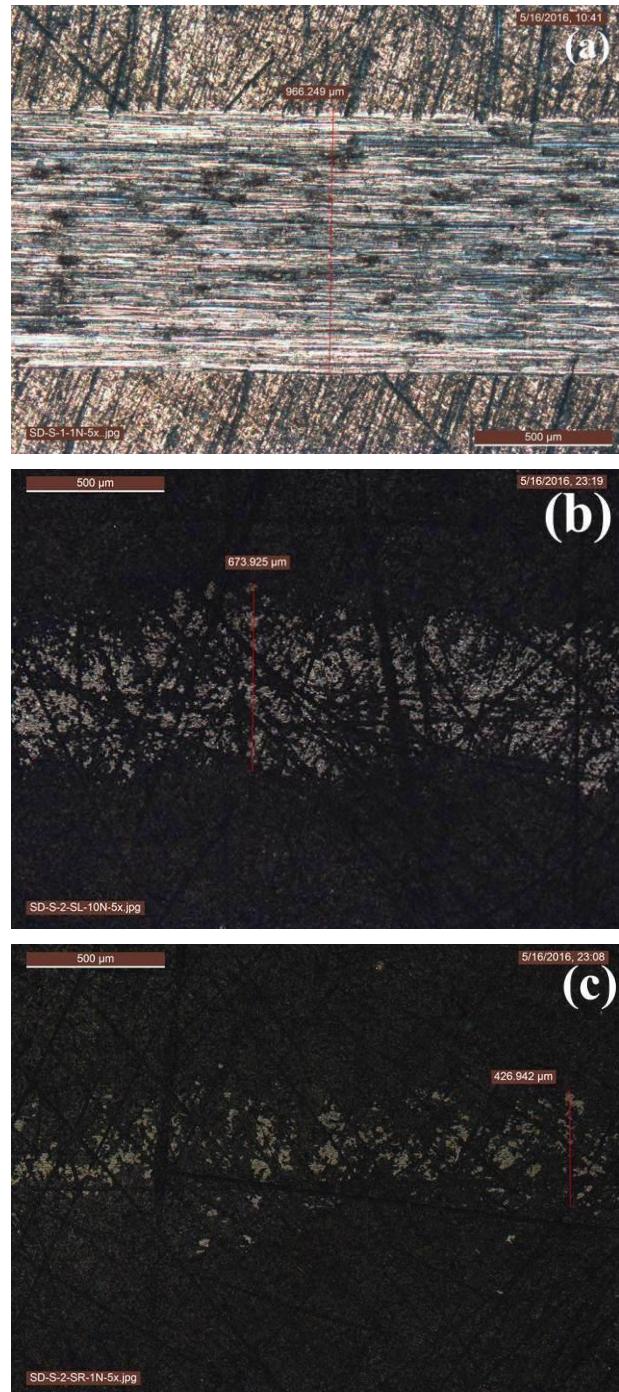


Fig. 7. Images of wear track of CVD-diamond coatings, (a) surface morphology of virgin substrate, (b) Surface morphology of NCD coatings, (c) Surface morphology of MCD coatings.

No variation of the total volume wear rate as a function of sliding distance was evidenced during the test because the vertical displacement was weak, a few micrometers at the end of the test. At this point, the final wear rate of the ball is indeed about $3 \times 10^{-17} \text{ m}^3 / (\text{N} \cdot \text{m})$. The wear of the diamond coated disc is too low to be measured and the wear track is just

polished, as observed by SEM. This lack of coating wear of the disc results from the short test duration due to the ball wearing more quickly. Alumina is a chemically inert ceramic compound and sliding interaction of diamond coatings against alumina material is purely mechanical. The stable and low friction coefficient of the NCD coating was attributed to the chemical inertness of the mating materials and also due to the continuous availability of the lubricious non-diamond graphitic phases at the grain boundaries of NCD coating. On the other hand, slightly high and unstable friction behavior was observed during the sliding of MCD coating against alumina ball. The high run-in friction behavior of the MCD coating was attributed to its sharp and rough surface asperities.

The tribological characteristics of CVD diamond coatings depend on their grain size, grain boundary strength and the presence of non-diamond phases [61]. Also, the wear and friction behavior of the tribo-contact pairs during dry sliding depends on the extrinsic conditions such as normal load, sliding velocity and mainly on the type of interaction, whether mechanical or chemical [62]. The contact between two sliding surfaces occurs at asperities and these asperities act as stress concentrators. CVD diamond coatings are highly wear resistant and chemically inert while sliding against most of the ceramics and undergo only mechanical wear by means of asperity fracture and abrasive damage [63]. Grooves may form on the wear surfaces in sliding contact due to the abrasive micro-wear mechanisms [64]. Purely mechanical wear produces rough contact surfaces and generally shows stable friction behavior. Whereas, the tribo-chemical interactions or tribo-oxidation of the mating parts produces tribo-debris or tribo-layer at the contact interface and modify the contact stresses [65]. These tribolayers of the reaction products are generally softer than the substrate and affect the wear and friction properties, especially under un-lubricated conditions [66]. The friction characteristics of diamond coating mainly depend on the counter face material. In the case of non-diamond sliders, the friction is influenced by the formation of a transfer layer during run-in period. Bull *et al.* found that the initial friction between CVD diamond coating and sapphire was ~ 0.2 , but raised rapidly to ~ 0.6 , which was attributed to

the formation of thick transfer layer [67]. Diamond is considered as self-lubricating material and the low friction coefficient values attained by many researchers is mainly due to its extreme chemical inertness (no chemical interaction/bonding) and sliding induced graphitization or re-hybridization of carbon. The chemistry of the sliding environment such as relative humidity and use of vacuum, inert gases or any other gases may affect the friction and wear characteristics of the diamond films [68-69]. The wear and friction of diamond coatings are found to be normally low only in air and relatively dry inert gas environment, whereas, in vacuum and at high temperatures, the friction and wear are much higher [70-71]. Gaseous adsorbates such as hydrogen or oxygen can effectively passivate the free σ -bonds on the surface of diamond. When these σ -bonds become highly passive, then the adhesion component of the friction significantly reduces and such diamond surface exhibits low friction coefficient [72]. Roy *et al.* investigated the friction response of the H-terminated and O-terminated NCD films and found that the H-terminated diamond films show low friction coefficient in comparison to that of O-terminated NCD films, which was attributed to the hydrophobic nature of the former one [73].

High surface roughness of the faceted MCD coatings has a detrimental effect on the friction and wears characteristics [74]. However, these coatings hardly show any wear but severely abrade counter face materials due to the hard and sharp asperities [75]. Generally MCD coatings exhibit high run-in friction behavior and stabilize to the lower value after a long sliding distance. In the case of NCD coatings, the friction coefficient falls to a much lower steady state value soon after a short run-in period. The low friction coefficient of the NCD coating is due to the presence of non-diamond carbon phases that are present at the grain boundaries. The roughness of the NCD coatings will have less detrimental effect on friction and wear characteristics in comparison to MCD coatings [76].

3.5 Wear track Analysis by Raman Spectroscopy and EDS

Figures 8(a) and 8(b) show the Raman spectra of wear tracks corresponding to NCD and MCD

coatings at 10 N loads. The presence of residual stresses in NCD and MCD wear tracks are calculated from $\sigma = -0.348 (v_m - v_0)$ GPa for the fundamental Raman peak at $V_m = 1334 \text{ cm}^{-1}$ [77]. Hence, wear track of both diamond coatings contain residual compressive stresses of -0.348 GPa, under the application of normal load.

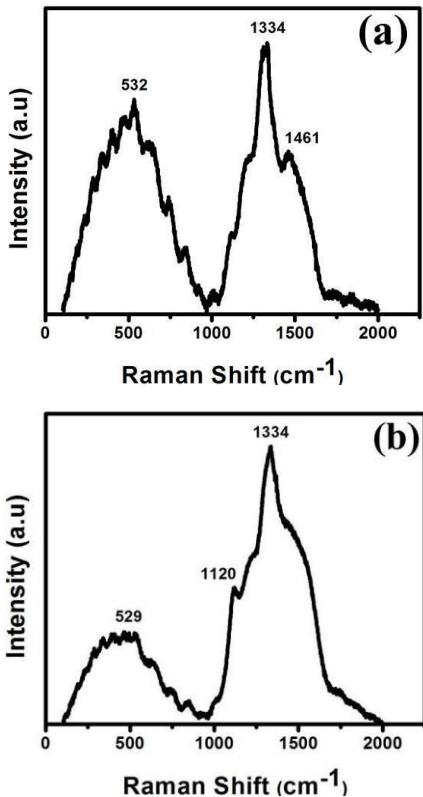


Fig. 8. Raman spectra of wear track of CVD-diamond coatings, (a) NCD and (b) MCD.

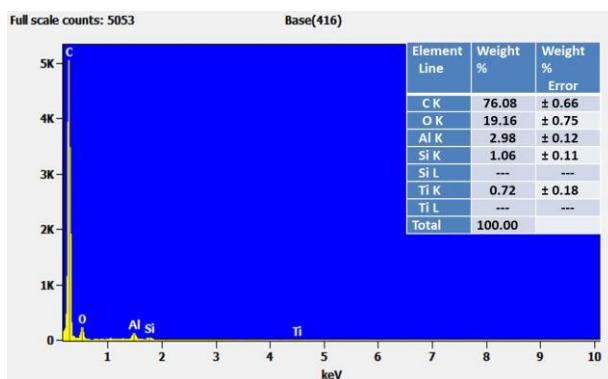


Fig. 9. Energy dispersive X-ray analysis (EDXA) of MCD Coatings.

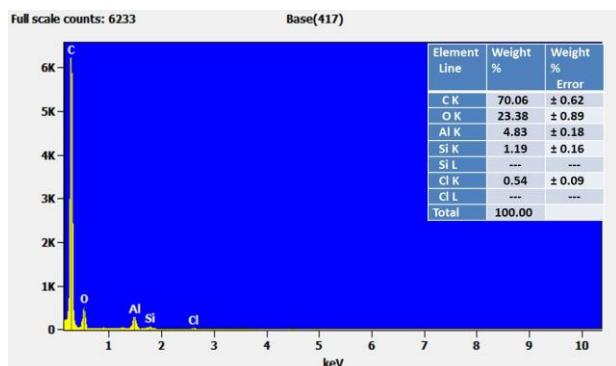


Fig. 10. Energy dispersive X-ray analysis (EDXA) of NCD Coatings.

Figures 9 and 10 show the compositional analysis of the tribo-layer formed on the MCD and NCD coatings, respectively. Tribo-chemical wear and tribo-oxidation of Al_2O_3 under unlubricated conditions is a well-known phenomenon and formation of tribo-debris or tribo-layer is anticipated. Tribo-layer formation was obvious from images of the wear tracks. Tribo-layer formation was not continuous and it was localized according to the contact asperities and observed as smooth and shiny flakes [78]. No tribo-layer formation was observed on the Al_2O_3 ball and the wear was mainly due to the mechanical fragmentation and tribo-oxidation. These small fragments and the tribo-products of the Al_2O_3 ball are transferred to the wear track on the NCD and MCD coatings [79]. Further, the small fragments are mechanically smeared and thermally treated during multi-cycle sliding process to form glassy amorphous tribo-layer [80]. Wear of the NCD and MCD coatings was negligible during the sliding test, except the blunting/crushing of sharp asperities/peaks of the NCD and MCD coatings during the run-in time. Further, the surface of the NCD and MCD coatings was completely protected by the tribo-layer formed with the aid of oxide tribo-products from the Al_2O_3 ball. The wear of the Al_2O_3 ball was mainly tribo-oxidation wear and the possible mechanical (abrasive) wear only during run-in time due to the interaction with the sharp asperities of the NCD and MCD coatings.

4. CONCLUSION

MCD and NCD coatings have yielded the super-hardness of ~55 GPa and ~38 GPa, respectively. The observed low hardness of the NCD coating in comparison to that of MCD coating was attributed to the presence of non-diamond

graphitic phases at the grain boundaries. NCD coatings show low average friction coefficient of ~0.068-0.053 at different loads, when sliding against Al₂O₃ ball, whereas MCD show average friction coefficient of ~0.305-0.27, when sliding against Al₂O₃ ball. The present analysis reveals that the coefficient of friction of CVD-diamond coatings decreases with the increase of load, and becomes steady after certain duration of sliding. The observed low coefficient of friction of NCD coating is due to the presence of graphitic carbon phases at the grain boundaries, and also because of its small grain size. However, MCD coating has shown the higher value of coefficient of friction but higher hardness. It can be concluded that NCD coatings increase the tribological properties while as the MCD coatings enhance the mechanical properties. Therefore, maintaining an appropriate level of normal load and using appropriate type of diamond coating, friction may be kept to some lower value to improve mechanical processes. These coatings are of great interest for further analysis because of their combination of hardness, low friction coefficient and elastic modulus.

Acknowledgment

The Authors would like to thank Prof. M. S. Ramachandra Rao, R. K. Dumpala, MSRC lab, IIT Madras, for the deposition of coatings and Dr. C. Anandan (Surface Engineering Division, NAL, Bangalore, India) for carrying out tribological tests, Prof. Kamal K. Kar, IIT Kanpur and G. N. Lolpuri, A. H. Sofi, NIT Srinagar.

REFERENCES

- [1] D. Rats, L. Vandenbulcke, R. Herbin, R. Benoit, R. Erre, V. Serin and J. Sevely, 'Characterization of diamond films deposited on titanium and its alloys', *Thin Solid Films*, vol. 270, pp. 177-183, 1995.
- [2] M.I. De Barros, L. Vandenbulcke and J.J. Bléche, 'Influence of diamond characteristics on the tribological behaviour of metals against diamond-coated Ti-6Al-4V alloy', *Wear*, vol. 249 no. 1-2, pp. 67-77, 2001.
- [3] M. Geetha, A.K. Singh, R. Asokamani and A.K. Gogia, 'Ti based biomaterials, the ultimate choice for orthopaedic implants - a review', *Progress in Materials Science*, vol. 54, pp. 397-425, 2009
- [4] C.B. Collins, F. Davanloo, T.J. Lee, D.R. Jander, J.H. You, H. Park and J.C. Pivin, 'The bonding of protective films of amorphic diamond to titanium', *Journal of Applied Physics*, vol. 71, pp. 3260, 1992.
- [5] T.P. Ong and R.P. Chang, 'Properties of diamond composite films grown on iron surfaces', *Applied Physics Letters*, vol. 58, pp. 358, 1991.
- [6] P.S. Weiser, S. Prawer and A. Hoffman, 'Carbon diffusion in uncoated and titanium nitride coated iron substrates during microwave plasma assisted chemical vapor deposition of diamond', *Journal of Applied Physics*, vol. 72, pp. 4643, 1992.
- [7] J. Spinnewyn, M. Nesladek and C. Asinari, 'Diamond nucleation on steel substrates', *Diamond and Related Materials*, vol. 2, no. 2-4, pp. 361-364, 1993.
- [8] X. Lei, B. Shen, S. Chen, L. Wang and F. Sun, 'Tribological behavior between micro-and nanocrystalline diamond films under dry sliding and water lubrication', *Tribology International*, vol. 69, pp. 118-127, 2014.
- [9] F. Zivic, M. Babic, S. Mitrovic and P. Todorovic, 'Interpretation of the Friction Coefficient During Reciprocating Sliding of Ti6Al4V Alloy Against Al₂O₃', *Tribology in Industry*, vol. 33, no. 1, pp. 36-42, 2011.
- [10] J. Chrąpionski and W. Szkliniarz, 'Quantitative metallography of two-phase titanium alloys', *Materials characterization*, vol. 46, pp. 149- 154, 2001.
- [11] Y.S. Li, C.Z. Zhang, H.T. Ma, L.Z. Yang, L.L. Zhang, Y. Tang, X.J. Li, L.L. He, R. Feng, Q. Yang and A. Hirose, 'CVD nanocrystalline diamond coatings on Ti alloy: A synchrotron-assisted interfacial investigation', *Materials Chemistry and Physics*, vol. 134, no. 1, pp. 145- 152, 2012.
- [12] M.I. De Barros, L. Vandenbulcke, J. Fontaine, G. Farges, M. Vayer and R. Erre, 'Tribological performance of diamond coated Ti-6Al-4V alloy with respect to diamond characteristics', *Surface Coating Technology*, vol. 127, no. 2-3, pp. 193- 202, 2000.
- [13] S.J. Askari, 'Tribological characteristics of nanocrystalline diamond films grown on titanium', *Surface Engineering*, vol. 25, pp. 482- 486, 2009.
- [14] L. Chandra, M. Chhowalla, G.A.J. Amaratunga and T.W. Clyne, 'Residual stresses and debonding of diamond films on titanium alloy substrates', *Diamond and Related Materials*, vol. 5, no. 6-8, pp. 674-681, 1996.

- [15] T. Grogler, E. Zeiler, M. Dannenfeldt and S.M. Rosiwal, R.F. Singer, 'Growth stages of chemical vapor deposited diamond on titanium alloy Ti6Al4V', *Diamond and Related Materials*, vol. 6, no. 11, pp. 1658-1667, 1997.
- [16] X.L. Peng and T.W. Clyne, 'Formation and adhesion of hot filament CVD diamond films on titanium substrates', *Thin Solid Films* vol. 293, no. 1-2, pp. 261-269, 1997.
- [17] S.S. Perry, J.W. Ager II., G.A. Somorjai, R.J. McClell, M.D. Drory, 'Interface characterization of chemically vapor deposited diamond on titanium and Ti-6Al-4V', *Journal of Applied Physics*, vol. 74, no. 12, pp. 7542-7550, 1993.
- [18] S.J. Askari, F. Akhtar, G.C. Chen, Q. He, F.Y. Wang, X.M. Meng and F.X. Lu, 'Synthesis and characterization of nano-crystalline CVD diamond film on pure titanium using Ar/CH₄/H₂ gas mixture', *Materials Letters*, vol. 61, no. 11-12, pp. 2139-2142, 2007.
- [19] M.A. Lowe, A.E. Fischer and G.M. Swain 'Formation of a crack-free and debonding-resistant boron-doped diamond thin film on titanium using a dual-coating strategy', *Jounal of Electrochemical Society*, vol. 153, no. 11, pp. 506-511, 2006.
- [20] E. Tal-Gutelmacher and D. Eliezer, 'Hydrogen cracking in titanium-based alloys', *Journal of Alloys and Compounds*, vol. 404-406, pp. 621-625, 2005.
- [21] D.S. Shin, I.M. Robertson and H.K. Birnbaum, 'Hydrogen embrittlement of α titanium: in situ TEM studies', *Acta Metallurgica*, vol. 36, pp. 111-124, 1988.
- [22] E. Buccioni, E. Braca, J.M. Kenny and M.L. Terranova, 'Processing-structure-adhesion relationship in CVD diamond films on titanium substrates', *Diamond and Related Materials*, vol. 8, no. 1, pp. 17-24, 1999.
- [23] Y.S. Li, Y. Tang, Q. Yang, C. Xiao and A. Hirose, 'Growth and adhesion failure of diamond thin films deposited on stainless steel with ultra-thin dual metal interlayers', *Applied Surface Science*, vol. 256, no. 24, pp. 7653-7657, 2010.
- [24] A.C. Ferrari and J. Robertson, 'Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond', *Philos. Trans. Royal Society of London A*, vol. 362, pp. 2477-2512, 2004.
- [25] W. Kulisch, C. Popov, S. Boycheva, L. Buforn, G. Favaro and N. Conte, 'Mechanical properties of nanocrystalline diamond/amorphous carbon composite films prepared by microwave plasma chemical vapor deposition', *Diamond and Related Materials*, vol. 13, no. 11-12, pp. 1997-2002, 2004.
- [26] S.J. Askari, G.C. Chen, F. Akhtar and F.X. Lu, 'Adherent and low friction nano-crystalline diamond film grown on titanium using microwave CVD plasma', *Diamond and Related Materials*, vol. 17, no. 3, pp. 294-299, 2008.
- [27] Q.P. Wei, Z.M. Yu, L. Ma, D.F. Yin and J. Ye, 'The effects of temperature on nanocrystalline diamond films deposited on WC-13wt.% Co substrate with W-C gradient layer', *Applied Surface Science*, vol. 256, no. 5, pp. 1322-1328, 2009.
- [28] C. Y. Wang, F.L. Zhang, T. C. Kuang and C. L. Chen, 'Chemical/mechanical polishing of diamond films assisted by molten mixture of LiNO₃ and KNO₃', *Thin Solid Films*, vol. 496, no. 2, pp. 698-702, 2006.
- [29] Q.F. Su, J.M. Liu, L.J. Wang, W.M. Shi and Y.B. Xia, 'Effects of activated hydrogen etching on surface roughness and optical properties of diamond films', *Scripta Materialia*, vol. 54, no. 11, pp. 1871, 2006.
- [30] S.K. Sarangi, A. Chattopadhyay and A.K. Chattopadhyay, 'Effect of pretreatment methods and chamber pressure on morphology, quality and adhesion of HFCVD diamond coating on cemented carbide inserts', *Applied Surface Science*, vol. 254, no. 13, pp. 3721-3733, 2008.
- [31] F.J.G. Silva, A.J.S. Fernandes, F.M. Costa, A.P.M. Baptista and E. Pereira, 'A new interlayer approach for CVD diamond coating of steel substrates', *Diamond and Related Material*, vol. 13, no. 4-8, pp. 828-833, 2004.
- [32] S.H. Seo, T.H. Lee and J.S. Park, 'Roughness control of polycrystalline diamond films grown by bias-enhanced microwave plasma-assisted CVD', *Diamond and Related Materials*, vol. 12, no. 10-11, pp. 1670-1674, 2003.
- [33] S.A. Catledge, P. Baker, J.T. Tarvin and Y.K. Vohra, 'Multilayer nanocrystalline/microcrystalline diamond films studied by laser reflectance interferometry', *Diamond and Related Materials*, vol. 9, no. 8, pp. 1512-1517, 2000.
- [34] M. Vojs, M. Vesely, R. Redhammer, J. Janik, M. Kadlec'íkova, T. Danis, M. Marton, M. Michalka and P. Sutta, 'Double bias HF CVD multilayer diamond films on WC-Co cutting tools', *Diamond and Related Materials*, vol. 14, no. 3-7, pp. 613-616, 2005.
- [35] S. Takeuchi, S. Oda and M. Murakawa, 'Synthesis of multilayer diamond film and evaluation of its mechanical properties', *Thin Solid Films*, vol. 398-399, pp. 238-243, 2001.

- [36] Y.Q. Hou, D.M. Zhuang, G. Zhang, M.S. Wu and J.J. Liu, 'Tribological performances of diamond film and graphite/diamond composite film', *Wear*, vol. 253, no. 7-8, pp. 711-719, 2002.
- [37] K. Uppireddi, B.R. Weiner and G. Morell, 'Synthesis of nanocrystalline diamond films by DC plasma-assisted argon-rich hot filament chemical vapor deposition', *Diamond and Related Materials*, vol. 17, no. 1, pp. 55-59, 2008.
- [38] P. Bruno, F. Benedic, A. Tallaire, F. Silva, F.J. Oliveira, M. Amaral, A.S. Fernandes, G. Cicala and R.F. Silva, 'Deposition of nanocrystalline diamond films on silicon nitride ceramic substrates using pulsed microwave discharges in Ar/H₂/CH₄ gas mixture', *Diamond and Related Materials*, vol. 14, no. 3-7, pp. 432-436, 2005.
- [39] P.W. May, J.A. Smith and Y.A. Mankelevich, 'Deposition of NCD films using hot filament CVD and Ar/CH₄/H₂ gas mixtures', *Diamond and Related Materials*, vol. 15, no. 2-3, pp. 345-352, 2006.
- [40] Y.P. Ma, F.H. Sun, H.G. Xue, Z.M. Zhang and M. Chen, 'Deposition and characterization of nanocrystalline diamond films on Co-cemented tungsten carbide inserts', *Diamond and Related Materials*, vol. 16, no. 3, pp. 481-485, 2007.
- [41] T. Sharda, T. Soga, T. Jimbo and M. Umeno, 'Growth of nanocrystalline diamond films by biased enhanced microwave plasma chemical vapor deposition', *Diamond and Related Materials*, vol. 10, no. 9-10, pp. 1592-1596, 2001.
- [42] F. Sun, Y. Ma, B. Shen, Z. Zhang and M. Chen, 'Fabrication and application of nano-microcrystalline composite diamond films on the interior hole surfaces of Co cemented tungsten carbide substrates', *Diamond and Related Materials*, vol. 18, no. 2-3, pp. 276-282, 2009.
- [43] S. Prawer and R.J. Nemanich, 'Raman spectroscopy of diamond and doped diamond', *Philos Trans R Soc Lond A*, vol. 362, pp. 2537-2565, 2004.
- [44] J. Gunnars and A. Alahelisten, 'Thermal stresses in diamond coatings and their influence on coating wear and failure', *Surf Coat Technol*, vol. 80, pp. 303-312, 1996.
- [45] R. Polini, E. Traversa, A. Marucci, G. Mattei and G. Marcheselli, 'A Raman Study of Diamond Film Growth on Co-Cemented Tungsten Carbide', *J Electrochem Soc*, vol. 144, no. 4, pp. 1371-1375, 1997.
- [46] H. Kuzmany, R. Pfeiffer, N. Salk and B. Günther, 'The mystery of the 1140 cm⁻¹ Raman line in nanocrystalline diamond films', *Carbon*, vol. 42, no. 5-6, pp. 911-917, 2004.
- [47] K.D. Bouzakis, G. Skordaris, E. Bouzakis, D. Tasoulas, P. Charalampous, T. Kotsanis, S. Kombogiannis and O. Lemmer, 'Explanation of the Wear Behaviour of NCD Coated Carbide Tools Facilitated by Appropriate Methods for Assessing the Coating Adhesion Deterioration at Elevated Temperatures', *Tribology in Industry*, vol. 37, no. 3, pp. 309-319, 2015.
- [48] M.A. Chowdhury, D.M. Nuruzzaman, A.H. Mia and M.L. Rahaman, 'Friction Coefficient of Different Material Pairs Under Different Normal Loads and Sliding Velocities', *Tribology in Industry*, vol. 34, no. 1, pp. 18-23, 2012.
- [49] V. Bria, D. Dima, G. Andrei, I.G. Birsan and A. Circiumaru, 'Tribological and Wear Properties of Multi-Layered Materials', *Tribology in Industry*, vol. 33, no. 3, pp. 104-109, 2011.
- [50] S. Mitrović, M. Babic, D. Adamović, F. Zivic, D. Dzunic and M. Pantic, 'Wear Behaviour of Hard Cr Coatings for Cold Forming Tools Under Dry Sliding Conditions', *Tribology in Industry*, vol. 34, no. 1, pp. 44-48, 2012.
- [51] M. Merklein, T. Schrader and U. Engel, 'Wear Behavior of PVD-Coatings', *Tribology in Industry*, vol. 34, no. 2, pp. 51-56, 2012.
- [52] Z. Doni, M. Buciumeanu and L. Palaghian, 'Topographic and Electrochemical Ti6Al4V Alloy Surface Characterization in Dry and Wet Reciprocating Sliding', *Tribology in Industry*, vol. 35, no. 3, pp. 217-224, 2013.
- [53] K. Bobzin, N. Bagcivan, M. Ewering and R.H. Brugnara, 'Vanadium Alloyed PVD CrAlN Coatings for Friction Reduction in Metal Forming Applications', *Tribology in Industry*, vol. 34, no. 2, pp. 101-107, 2012.
- [54] A. Sagalovych, V. Sagalovych, A. Kononyhin, V. Popov, A. Lubchenko and A. Olejnik, 'The Tribological Investigations of Multicomponent Multilayered Ion-Plasma Coatings Avinit', *Tribology in Industry*, vol. 33, no. 2, pp. 79-86, 2011.
- [55] A.A. Minewitsch, 'Some Developments in Tribooanalysis of Coated Machine Components', *Tribology in Industry*, vol. 33, no. 4, pp. 153-158, 2011.
- [56] F. Živić, N. Grujović, S. Mitrović, D. Adamović, V. Petrović, A. Radovanović, S. Đurić and N. Palić, 'Friction and Adhesion in Porous Biomaterial Structure', *Tribology in Industry*, vol. 38, no. 3, pp. 61-67, 2016.
- [57] W. Kulisch and C. Popov, 'On the growth mechanisms of nanocrystalline diamond films', *Phys Status Solidi A*, vol. 203, no. 2, pp. 203-219, 2006.

- [58] R. Dumpala, N. Kumar, C.R. Kumaran, S. Dash, B. Ramamoorthy and M.S. Ramachandra Rao, 'Adhesion characteristics of nano-and micro-crystalline diamond coatings: Raman stress mapping of the scratch tracks', *Diamond and Related Materials*, vol. 44, pp. 71-77, 2014.
- [59] R. Ramesham, T. Roppel and R.W. Johnson, 'Characterization of polycrystalline diamond thin films grown on various substrates', *Thin Solid Films*, vol. 212, no. 1-2, pp. 96-103, 1992.
- [60] W.C. Oliver, G.M. Pharr, 'An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments', *Journal of Materials Research*, vol. 7, pp. 1564-1583, 1992.
- [61] S.J. Bull and A. Matthews, 'Diamond for wear and corrosion applications', *Diamond and Related Materials*, vol. 1, no. 10-11, pp. 1049-1064, 1992.
- [62] V.A. Muratov, T. Luangvaranunt and T.E. Fischer, 'The tribochemistry of silicon nitride: effects of friction, temperature and sliding velocity', *Tribology International*, vol. 31, no. 10, pp. 601-611, 1998.
- [63] S.J. Bull, 'Tribology of carbon coatings: DLC, diamond and beyond', *Diamond and Related Materials*, vol. 4, no. 5-6, pp. 827-836, 1995.
- [64] K. Kato, 'Micro-mechanisms of wear — wear modes', *Wear*, vol. 153, no. 1, pp. 277-295, 1992.
- [65] A.S. Blomberg, S. Hogmark and J. Lu, 'An electron microscopy study of worn ceramic surfaces', *Tribology International*, vol. 26, pp. 369-381, 1993.
- [66] T.E. Fischer and H. Tomizawa, 'Interaction of tribochemistry and microfracture in the friction and wear of silicon nitride', *Wear*, 105, 29-45, 1985.
- [67] S.J. Bull, P.R. Chalker, C. Johnston and V. Moore, 'The effect of roughness on the friction and wear of diamond thin films', *Surface and Coatings Technology*, vol. 68-69, pp. 603-610, 1994.
- [68] A. Erdemir, M. Halter, G.R. Fenske, C. Zuiker, R. Csencsits, A.R. Krauss and D.M. Gruen, 'Friction and Wear Mechanisms of Smooth Diamond Films During Sliding in Air and Dry Nitrogen', *Tribology Transactions*, vol. 40, pp. 667-675, 1997.
- [69] N. Kumar, R. Radhika, A.T. Kozakov, K.J. Sankaran, S. Dash, A.K. Tyagi, N.H. Tai and I.N. Lin, 'Humidity-dependent friction mechanism in an ultrananocrystalline diamond film', *Journal of Physics D: Applied Physics*, vol. 46, no. 27, pp. 275501, 2013.
- [70] S. Chandrasekar and B. Bhushan, 'The role of environment in the friction of diamond for magnetic recording head applications', *Wear*, vol. 153, pp. 79-89, 1992.
- [71] K. Miyoshi, R.L.C. Wu, A. Garscadden, P.N. Barnes and H.E. Jackson, 'Friction and wear of plasma-deposited diamond films', *Journal of Applied Physics*, vol. 74, pp. 4446-4454, 1993.
- [72] A. Erdemir, 'Friction and wear of diamond and diamond-like carbon films', *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, vol. 216, pp. 387-400, 2002.
- [73] M. Roy, S. Ghodbane, T. Koch, A. Pauschitz, D. Steinmüller-Nethl, A. Tomala, C. Tomastik and F. Franek, 'Tribological investigation of nanocrystalline diamond films at low load under different tribosystems', *Diamond and Related Materials*, vol. 20, pp. 573-583, 2011.
- [74] H. Miki, A. Tsutsui, T. Takeno and T. Takagi 'Friction properties of partially polished CVD diamond films at different sliding speeds', *Diamond and Related Materials*, vol. 24, pp. 167-170, 2012.
- [75] I.P. Hayward, I.L. Singer and L.E. Seitzman, 'Effect of roughness on the friction of diamond on cvd diamond coatings', *Wear*, vol. 157, pp. 215-227, 1992.
- [76] I.S. Forbes and J.I.B. Wilson, 'Diamond and hard carbon films for microelectromechanical systems (MEMS)—a nanotribological study', *Thin Solid Films*, vol. 420-421, pp. 508-514, 2002.
- [77] R. Polini, E. Traversa, A. Marucci, G. Mattei and G. Marcheselli, 'A Raman Study of Diamond Film Growth on Co-Cemented Tungsten Carbide', *Journal of the Electrochemical Society*, vol. 144, pp. 1371-1375, 1997.
- [78] K. Holmberg, A. Matthews and H. Ronkainen, 'Coatings tribology—contact mechanisms and surface design', *Tribology International*, vol. 31, pp. 107-120, 1998.
- [79] M. Godet, 'The third-body approach: A mechanical view of wear', *Wear*, vol. 100, pp. 437-452, 1984.
- [80] A. Blomberg, S. Hogmark and J. Lu, 'An electron microscopy study of worn ceramic surfaces', *Tribology International*, vol. 26, pp. 369-381, 1993.