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Effect of relative humidity and temperature on the tribology of multilayer micro/nanocrystalline CVD diamond coatings

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ABSTRACT

The tribological behavior of tenfold micro/nanocrystalline CVD diamond multilayers is here investigated in self–mated configuration using ball-on-plate reciprocating wear testing. The effects of relative humidity (RH) and temperature (T) on friction and wear coefficients are assessed. The strongest effect of humidity was found on the value of the critical load (no delamination) that triples from 40 N at 10%RH to 120 N at 90%RH. Evaluation of the wear coefficients of the plates was only possible with the use of 3D optical profilometry. A valley-shaped evolution is observed for the wear coefficient of the plates, within the 10% to 90% RH range, with a minimum of about $1.7x10^{-7}$ $mm^3N^{-1}.m^{-1}$, indicative of a mild wear regime, whereas the balls have lower values in the very mild wear regime of $k \sim 10^{-8}$ $mm^3N^{-1}.m^{-1}$. The clearest difference between the RH and temperature experiments is observed for the critical loads, limited to the range 40-55 N at 50-100°C, while at room temperature a value of 120 N was reached. However, the critical loads at high temperature are similar to those attained under dry conditions (≤25% RH) highlighting the absence of water as the load bearing medium.

1. Introduction

Diamond, particularly due to some superior properties such as extreme hardness, highest bulk modulus, highest thermal conductivity, superior wear resistance, low coefficient of friction and chemical inertness is a preferred candidate for tribological applications in the form of diamond coatings [1–3]. Although the adhesion of microcrystalline diamond is usually high and acceptable for most applications, the major problem is that it produces rough surfaces on the workpiece materials. Moreover, although microcrystalline diamond (MCD) obtained by CVD processes has excellent wear resistance, its fracture toughness is not so high since it grows into a columnar shape and during mechanical or tribological applications, the cracks can easily propagate in the growth direction [4]. The coarse crystals and thus rough surface, may easily lead to a high friction coefficient during sliding [5–7], which increases the probability of coating failure. However, microcrystalline diamond can be used as the adhesion (first) layer to the substrate surface [1] in multilayered coatings. For tribological applications such as cutting tools, mechanical seal rings, or even in optics and microelectronics, it is very important to grow diamond film layers with a smooth surface [3]. Important characteristics of nanocrystalline diamond (NCD) films include the surface smoothness of a thin continuous film without voids or non-uniformities [8]. The multilayer coating design can avoid the columnar structure of MCD and therefore smoothen the surface [9]. In addition, these may have high adhesion strength coupled with low internal stress and improved fracture toughness [10,11].

Several investigations on multilayered diamond coating on WC-Co substrates consisting of alternating layers of micro and nanocrystalline diamond coatings are reported with low surface roughness, good adhesion and low friction coefficient [12–18]. The results of Dumpala and coworkers [18] indicated that a nano– and microcrystalline dual layer composite diamond coatings has low and stable friction coefficient of ~ 0.06 against a silicon nitride ceramic after a sliding distance of 100 m in comparison with microcrystalline diamond (MCD) coatings showed friction coefficient more than 0.1.

Salgueiredo et al. [19] carried out diamond self–mated tribological tests with a reciprocating sliding configuration without lubrication at room temperature and ambient humidity. Bi– and fourfold layer of micro and nanocrystalline diamond films were deposited onto the silicon nitride substrates. Fourfold composite coatings exhibited a superior critical load before delamination (130–200 N), when compared to the mono (60–100 N) and bilayer coatings (110 N). Their findings showed that for the multilayer composite coating, the top nanocrystalline diamond layer wears out progressively performing a sacrificial role, while

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the underneath harder microcrystalline diamond layer keeps the residual stresses at low levels. Other authors compared the tribological behaviour of silicon nitride substrates coated with monolayer micrometric, monolayer submicrometric and multilayer microcrystalline HFCVD diamond coatings [20]. The reduction of friction coefficient for the multilayer micrometric coated Si_3N_4 substrates was related to the high purity diamond crystals. In addition, differences of the friction coefficient between multilayer micrometric and monolayer submicrometric coated Si_3N_4 substrates were very small, although multilayer micrometric diamond coatings demonstrate higher wear resistance than the monolayer submicrometric diamond coatings, which results from the decrease in the hardness of the monolayer submicrometric diamond coatings.

Diamond is suited for harsh applications with poor lubrication, particularly for low humidity conditions (5% RH) where very low friction coefficients of ~0.04 were reported [21]. In the present work, besides the effects of relative humidity (10-90%), the temperature (25-250°C) effects on the self-mated friction and wear coefficients of multilayered micro/nanocrystalline diamond coatings are investigated. Ten-fold MCD/NCD multilayer coatings with a total thickness of ~10 μm were developed and tested. The large number of layers prevents the excessive growth of columnar MCD crystals and increases the number of MCD/NCD interfaces. These also enhance the fracture toughness of the coating due to their crack-arresting role [2,22].

A relevant and innovative approach of the research is the use of 3D optical profilometry to measure the extremely low wear volumes of the diamond coated flat plates, thus allowing the calculation of this component's wear coefficient, a feat unreachable by conventional methods such as weighing or AFM.

2. Materials and methods

2.1. Production of diamond coated flat plates and balls

Disc–shaped (∅10 mm; 3 mm thick) flat silicon nitride ceramic plates were produced in-house by powder technology (α–$Si_3N_4/Y_2O_3/Al_2O_3$ in 89.3/7.0/3.7 % weight proportion; pressureless sintered at 1750°C/2 h/ 0.1 MPa nitrogen atmosphere). The surfaces were ground with a 46 μm diamond wheel and lapped with 15 μm diamond paste. The surface of the commercial balls (∅5 mm; KemaNord) was roughened by polishing with a 15 μm diamond suspension. The plates and the balls were plasma etched (CF_4) for 10 min using a RF generator (Emitech K1050X). The last step, diamond seeding, was done by ultrasonic agitation with nano–diamond powder suspension for 1 h in ethanol.

A large, home–made HFCVD system with 50 cm diameter made of stainless steel coupled with a 400 A DC power supply, a vacuum rotary pump and gas feed connectors, uses tungsten wires for the production of CVD diamond coatings on flat and ball Si_3N_4 ceramic specimens. In this semi-industrial apparatus the deposition area may be as large as 20x30 cm^2. Tungsten filaments 300 μm in diameter were used to make a horizontal arrangement over the Si_3N_4 ceramic substrates. The distance between each W–filament was 5 mm. The DC power supply in current control mode was used to heat them to about 2250–2300°C, as measured using a two colour pyrometer (Raytek), and the required current is typically in the range 10–11 A/filament during deposition. For the carburization of W filaments, done before the deposition, they were heated up to 2400°C in the reactor chamber under methane (CH_4) and hydrogen (H_2) gas mixture with methane to hydrogen ratio of 4 and a total flow of 1000 ml.min^{-1}. During carburization of W, the filaments are kept away from the substrate to prevent the deposition of amorphous or undesired components. After carburization of the W filaments, the reactant gases were removed from the reactor chamber, the substrates were place in position and the deposition conditions were then imposed according to the scheduled experiment. The substrate temperature was measured using a thermocouple mounted just below the substrate holder and the substrate–filament was kept at 5–7 mm.

In summary, there are many parameters such as filament ($T_{fil.}$) and substrate temperatures ($T_{sub.}$), total flow (F) of reactant gases, chamber pressure (P), and methane to hydrogen ratio, affecting the CVD process. Many experiments were performed in order to optimise the conditions of the experiment for the desired morphology of the coated diamond on substrate. The final set of parameters used in the present work are given in Table 1 to produce the alternating MCD/NCD coating with a total of ten layers. Monolayer MCD and NCD films having the same total thickness (around 10 μm) were also produced using these conditions for comparison of properties.

2.2. Characterization of diamond–coated Si_3N_4 ceramic samples

Field emission scanning electron microscopy (FE–SEM) was carried out using a Hitachi SU–70 or a Hitachi S4100 system for surface morphology characterization of top view and cross section of the diamond coated Si_3N_4 ceramic components. UV μ–Raman spectroscopy (Horiba Jobin Yvon HR 800UV), using the line 532 nm from a He–Cd permits the identification of the carbon phases i.e. diamond, DLC and graphitic phases.

In the evaluation of diamond adhesion, the method of Brale indentation was performed, with the indenter tip (diamond, cone angle of 120° and tip radius of 0.2 mm) coupled to a universal mechanical testing machine (Zwick/Roell Z020) for applying increasing force values.

2.3. Tribological testing

Self–mated wear tests were performed in a ball–on–plate adapted tribometer (Plint 67/R) using linear reciprocating sliding with constant frequency (1 Hz) and stroke length (8 mm). Normal applied loads varied in the 40–150 N range and relative humidity changed from 10–92%. The effect of temperature was studied in the 25°C-100°C range. Fig. 1 illustrates this wear test configuration, showing one plate/ball pair after a few tests having been conducted. Above 100°C and up to 250°C, circular sliding tests were conducted. Table 2 illustrates the wear test conditions regarding load (W), time (t), total sliding distance (X), relative humidity (RH), temperature (T) and linear velocity (v).

The friction force was measured by a load cell, calibrated before testing, its signal amplified and processed by a personal computer. The coefficient of friction (COF) is given by the ratio of the friction force and the normal load. The wear coefficient (k) of the ball specimens was estimated from the wear volume (V), obtained from circular wear scars of diameter (d) measured by optical microscopy micrographs and the ball radius (r), divided by the applied normal load (W) and the sliding distance (L), following Archard's equation of wear:

$$k = \frac{V}{W \times L} = \frac{\pi \times d^4}{64 \times r \times W \times L}$$

In the case of the plates, a 3D optical profilometer (Sensofar S-neox) was used to acquire topographic images of the entire tracks with

Table 1
HFCVD conditions for multilayer diamond deposition on Si_3N_4 large disc and ball ceramic substrates (5 MCD + 5 NCD).

	MCD layers	NCD layers
$T_{fil.}$(°C)	2260	2330
$T_{sub.}$(°C)	850	750
CH_4/H_2	0.02	0.04
F (ml.min^{-1})	1800	900
P (mbar)	75	25
t (min)/layer	60	84
t (h)/total	5	7