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Full Length Article

Low friction and wear behaviour of non-hydrogenated DLC (a-C) sliding against fluorinated tetrahedral amorphous carbon (ta-C-F) at elevated temperatures

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ABSTRACT

The low coefficient of friction (COF) of sp^2 rich non-hydrogenated diamond-like carbon (a-C) coatings make them suitable for tribological applications including machining of lightweight alloy castings and for certain components in internal combustion engines. Retaining the low COF of a-C at temperatures >100 °C is however a challenge that has limited further industrial applications of these coatings. This study examines the high temperature stability of a non-hydrogenated a-C coating (H < 2 at.%) sliding against a sp^3 rich fluorinated tetrahedral amorphous carbon (ta-C-F) and tool steel counterfaces using ball-on-disk type experiments. It was shown that a-C coated balls run against ta-C-F maintained a low steady state COF that varied between 0.1 and 0.2 up to 300 °C while a-C sliding against uncoated tool steel resulted in high COF values accompanied with high wear rates of a-C coating. Transfer layers were formed on the a-C coatings' contact surfaces sliding against ta-C-F and these layers consisting of fluorine incorporating carbonaceous material remained stable up to 300 °C. The results suggested that a low COF in this tribological system can be achieved at elevated temperatures as a result of passivation of the surface carbon atoms.

1. Introduction

Non-hydrogenated diamond-like carbon (a-C) coatings have an amorphous structure with carbon atoms primarily forming sp^2 type of bonding, and contain typically less than 2 at.% H [1,2]. The a-C coatings show low coefficient of friction (COF) under the ambient [3–5], high relative humidity (RH) [4–6] atmospheres, as well as aqueous environments [7,8] when tested against counterfaces made of Al-, Mg-, Ti- alloys and steel. The a-C coatings also exhibit low COF values when tested under the boundary lubrication [9] and hydrodynamic lubrication [6]. Thus, a-C coatings have been successfully applied to surfaces operating under lubricated sliding [10] and to the tools used for machining of Al- and Mg-alloys [8,11]. By taking advantage of the low COF values and excellent adhesion mitigating properties that a-C coatings displayed under humid atmospheres, a minimum quantity lubrication (MQL) method for drilling of components made of lightweight castings has been developed [7]. The operating temperature, however, is a limiting factor for the use of a-C coatings because of the rapid deterioration of the tribological properties of these coatings at temperatures ≥100 °C [10,12]. Various manufacturing processes such as shaping, warm forming are conducted at elevated temperatures [13–15]. Also a-C coated machine tools may be susceptible to oil starvation periods during which contact temperatures increase above 100 °C [16–18]. In order to expand the working temperature range of a-C coatings it is important to understand the mechanisms responsible for the friction of a-C coatings at elevated temperatures.

It is pertinent to review the tribo-chemical mechanisms responsible for the low COF of DLC coatings. The low COF (0.10–0.15) of a-C coatings, under an ambient air (25–50% RH) atmosphere could be attributed to the passivation of surface C atoms by OH and H radicals dissociated from atmospheric moisture during sliding [19–21]. Also, during sliding carbonaceous transfer layers were often observed to form on the contact surfaces of the counterfaces. The stability of these layers and their contribution to the low friction of the tribosytem depend on the passivation state of the carbon surfaces [10,12,19] by the dissociated water molecules. As this mechanism was observed to cease at temperatures above 100 °C, the a-C coatings exhibited high values of COF ranging between 0.3 and 0.5 for temperatures up to 300 °C – above which the

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coating disintegrated [10,12]. DLC coatings can be made more stable at elevated temperatures by modifying their microstructure. For example, tetrahedral amorphous carbon, with a predominantly high sp^3 type bonding does not readily undergo a graphitization process and these coatings remain stable up to 450 °C, and exhibit low COF because of the occurrence of local sliding-induced sp^2 transformation at the contact surface [22,23]. On the other hand, 20 at.% W containing a-C showed remarkably low COF values of 0.07–0.08 against titanium alloys at temperatures ranging between 400 and 500 °C due to the formation of a WO_3 layer on the contact surface [24–26] but not at other temperatures where the surface oxidation was not prevalent.

At a temperature range between 200 and 400 °C, the COF and wear rates for sp^2 type a-C coatings could be improved by running them against a fluorinated counterface that would promote passivation of the dangling carbon atoms at the interface during sliding contact. It was shown that F (3–12 at.%) incorporating DLC sliding against steel counterfaces displayed a low COF of 0.21 [27–29] and the passivation of dangling carbon bonds by F led to the formation of fluorocarbon groups as observed by the X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) [27–29]. First principle calculations, on the other hand, revealed that two F-terminated diamond (F/F) surfaces sliding against each other would exert higher repulsive forces compared to those repulsion between C/C, H/H and C/F interfaces [30,31]. Thus, it can be expected that sliding of fluorine containing DLC coatings would generate F incorporating transfer layers and lead to F/F repulsive interactions at the interfaces resulting in low friction. A recent study [23] carried on F incorporated tetrahedral amorphous carbon (ta-C-F) coatings showed that the atomic fraction of F transferred to an Al alloy (319 Al) contact surface increased by 50% when the sliding contact temperature increased to 400 °C from 25 °C. As a result of F transfer, the running-in COF ($\mu_R = 0.38$) of ta-C-F tested at 400 °C was lower than the $\mu_R = 0.65$ of the same a-C coating without F when both coatings were tested under the same loads and speeds. It was suggested that formation of transfer layers incorporating sp^2 rich carbon bonds passivated by F atoms was responsible for the low COF of ta-C-F at elevated temperatures (200–400 °C).

Based on the above literature review, the ta-C-F system emerges as a suitable counterface for the tests that were used in this study to examine the sliding friction behaviour of a-C at elevated temperatures. Specifically, the following factors were considered for the selection of ta-C-F for this purpose; (i) high propensity of F to transfer to the carbon surface at elevated temperatures; (ii) passivating capability of F by forming C—F bonds and, (iii) inherent high temperature stability of sp^3 type coatings. Thus, an experimental program has been undertaken on the premise that a-C coatings when sliding against ta-C-F should be able to provide low COF throughout the temperature range of 25–400 °C. The COF values of this system as well as those of the a-C coatings sliding against an uncoated steel counterface were determined. Chemical and microstructural changes that occurred at the contact surfaces were observed using X-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy, cross-sectional transmission electron microscopy (TEM) and associated characterization techniques.

2. Experimental approach

The samples studied in this work, namely the a-C coatings (aka NH-DLC coatings) were deposited on AISI 52100 grade bearing steel balls of 6.00 mm diameter using an unbalanced magnetron sputtering system equipped with one chromium and two graphite targets. A 0.40 ± 0.02 μm thick Cr interlayer was deposited on the AISI 52100 steel ball to promote coating adhesion. This was followed by the deposition of 1.75 ± 0.03 μm thick a-C coating as measured from the cross-section excised by focused ion beam (FIB) as described in [23]. The average surface roughness (R_a) of the a-C coatings was 40.0 ± 2.0 nm. The hydrogen concentration of the a-C coating was <2.00 at.% according to elastic recoil detection (ERD) analysis. The hardness and the elastic modulus of the coatings were calculated from the loading–unloading curves obtained from the indentation tests that used Berkovich type nano-indenter that penetrated to a maximum depth of 200 nm below the surface. The average hardness and elastic modulus values obtained in this way were 13.00 ± 1.10 GPa and 158.55 ± 6.82 GPa.

The ta-C-F coatings were deposited on flat surfaces of 25.10 mm diameter WC-Co cylindrical coupons by a laser-induced pulsed arc deposition technique using a fluorine doped graphite cathode. The fluorine concentration of the coating determined using Rutherford backscattering spectroscopy (RBS) was 12 at.%. The thickness of the ta-C–F coating was 1.75 ± 0.13 μm and the R_a was 160.0 ± 12.0 nm. The hardness and elastic modulus of ta-C–F were determined as 6. 21 ± 2.00 GPa and 170.00 ± 20.51 GPa using the nano-indentations tests.

A high temperature pin-on-disk tribometer was used to measure the COF of a-C/ta-C-F tribosystem using a sliding speed of 0.12 m/s and a normal load of 5.00 N for 5000 revolutions. Sliding friction tests were also performed on a-C/uncoated 52100 steel system for comparison. The sliding friction tests were carried out at different constant temperatures consisting of 25 °C (54% RH), 100 °C, 200 °C, 300 °C, 400 °C and 500 °C. The average of the steady-state COF, μ_s, of each friction curve was calculated, e.g. typically after 2000 revolutions at 25 °C. The maximum value of COF attained during the initial portion of the friction curve, i.e., in the running-in stage was determined and the running-in COF was designated as μ_R. The μ_R and μ_S values reported for each tribosystem tested at each temperature (see Fig. 1) are the mean COF values obtained from three tests conducted at a constant temperature. The wear losses were calculated from the volume of the material removed from the wear tracks. The average volumetric wear loss was estimated from the area of the wear track at eight different locations along a circular sliding track of radius 1.5 mm using a white light interferometry technique [32,33].

Energy-dispersive X-ray spectroscopy (EDS) was used to determine the compositions of the tribolayers formed at the sliding interfaces. An FEI Quanta 200 FEG scanning electron microscope (SEM) equipped with an EDAX SiLi detector was used for this purpose. An EDS mapping technique was used to estimate the areal distribution of elements in the composition of material from the contact surfaces of ta-C-F that were transferred to the contact surfaces of a-C during sliding. Raman spectroscopy was also used to characterize the transfer layers using a 50 mW Nd-YAG solid state laser (532.0 nm excitation line) through the 50X objective lens of a Horiba Raman micro-spectrometer. Cross-sections of transfer layers were obtained by focused ion beam (FIB) milling (Carl Zeiss NVision 40 CrossBeam) and observed by using FEI Titan 80–300 HR-TEM operated at 300 kV. Details of this technique can be found in [23,24,34,35]. Electron Energy Loss Spectrscopy (EELS) analyses were also performed on the TEM cross-sections milled to about 25 nm. For O-K edge analyses, the TEM samples were cooled cryogenically in liquid N_2. The spectra were obtained by cumulative acquisition (10–15 spectra) with an acquisition time of up to 1 s per spectrum.

The characterization techniques used also included X-ray photoelectron spectroscopy (XPS) studies on selected samples using Kratos Axis Ultra system with an Al X-ray source (characteristic energy = 1.4867 keV) and the charge correction was carried out using a carbon reference. The survey scans of the samples were conducted using a pass energy of 160 eV over a surface were of