

Tema A2a Materiales: (Ingeniería de Superficies)

“H-DLC thin film deposited on AISI 52100 steel: tribological behaviour under dry conditions”

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RESUMEN

Las películas delgadas del tipo carbón hidrogenado quasi-diamante (H-DLC) son bastante utilizadas en elementos de máquinas donde existe contacto continuo y no se permite el uso de lubricantes líquidos. En el presente reporte se realiza un análisis cuantitativo del comportamiento tribológico bajo condiciones secas del recubrimiento depositado sobre acero AISI 52100 con el proceso de la deposición química de vapores con plasma mejorado excitado con microondas. Para el análisis se empleó la relación matemática de Clapeyron para determinar las temperaturas flash, así como la de grafitización del par H-DLC/acero. Para validar los resultados analíticos, se llevó a cabo la experimentación en relación con el comportamiento de grafitización, utilizando espectroscopía Raman y microscopía de barrido, donde se confirmó el contacto carbón-carbón debido a la formación de una tribocapa sobre las huellas ocasionadas por el desgaste tanto en el recubrimiento como en el perno de acero.

Palabras clave: Carbón hidrogenado quasi-diamante (H-DLC), tribología, acero 52100, fricción, desgaste.

ABSTRACT

Hydrogenated Diamond-Like Carbon (H-DLC) thin films are very much used due to their application in machine elements subjected to continuous contact where fluid lubricant films are not permitted. In this paper a quantitative analysis of the tribological behaviour under dry conditions of duplex layered H-DLC coating sequentially deposited by microwave excited plasma enhanced chemical vapour deposition on AISI 52100 steel was carried out. The existing Clapeyron mathematical relationship was used to determine the graphitisation temperature of the coating/steel contact as well as the flash temperature. In order to further corroborate the analytical findings, experimental observations regarding the graphitisation behaviour through Raman spectroscopy and electron microscopy were implemented from where it was confirmed the carbon-carbon contact, due to a tribolayer formation on the wear scars of the coating and pin.

Keywords: H-DLC, Tribology, AISI 52100 steel, Friction, Wear.

1. Introduction

Emission of greenhouse gases (CO₂, NO_x, CH₄, etc.) is primarily responsible for the greenhouse effect and hence global warming. Use of transportation is such a human activity which is woven into nearly every aspect of life but accounts for a massive greenhouse emission (approximately 14% of total annual emissions). Reducing greenhouse emissions from transportation presents special challenges because it requires reduction of fuel consumption which, in turn, depends on the reduction of mechanical loss (friction loss) in engines. Introducing new materials and coatings

having excellent tribological properties accompanied by optimised engine designs and/or appropriate lubrication strategies can potentially offer high fuel economy and better environment.

The use of high wear resistant and low friction materials or coatings has been identified as the most popular strategy that not only reduces dependence on the harmful components of lubricants but also provides improved durability of engine components. The thin films as the non-stoichiometric hydrogenated amorphous carbon (a-c:H) or also termed diamond-like carbon (H-DLC) has gained widespread use on the performance/life of steel components

[1, 2], in which specific properties at particular locations are needed without compromising the bulk material strengths. These coatings usually show high hardness, optical transparency, dielectric properties, high corrosion resistance, high thermal and chemical stability, low friction properties, high wear resistance and excellent running-in properties [3, 4]. The deposition of DLCs is commonly obtained by plasma decomposition of a hydrocarbon-rich atmosphere at low substrate temperatures and high deposition rates. This later is a major advantage for most of steels because the annealing temperature is not reached ($<200\text{ }^{\circ}\text{C}$) and therefore substrate hardness is not affected. From the number of techniques to deposit hard DLC films, PECVD (plasma enhanced chemical vapour deposition) process is extensively utilised due to the nature of the hydrocarbon gas used as the coatings incorporate more sp^2 and H bonds which makes the films softer than the majority of tetrahedral ta-C ones [1, 5]. It is clear that with the introduction of DLC coatings in existing engineering systems, the main objective for their effective application is to ensure a consistent performance under dry and oil-lubricated conditions. In this context, some of the important studies have been carried out with quite controversial outcomes and/or are not practical for industrial applications because the election of normal loads and sliding velocities are away from real engineering conditions [6]. Evidently, some of these discrepancies may result from different and varying DLCs under investigation. In light of the aforementioned, in this study, a hydrogenated DLC coating has been investigated for its graphitisation performance in dry sliding under different normal loads. As far as the authors know, there is no study on tribological characteristics of an H-DLC coating with the same composition of layers that resembles the H-DLC coating architecture reported in this paper. Understanding of the tribological behaviour of this particular coating with the appropriate working conditions will enable expansion in mechanical components coated with functional coatings.

2. Materials and experimental methods

An H-DLC thin film was deposited on AISI 52100 steel plates of dimensions $7 \times 7 \times 3\text{ mm}^3$ using an industrial scale Microwave excited Plasma Enhanced Chemical Vapour Deposition (MW-PECVD) Flexicoat 850 system (Hauzer Techno Coating, the Netherlands). The continuous deposition procedure includes deposition of an adherent Cr interlayer (by DC magnetron sputtering) followed by an intermediate hard tungsten carbide (WC) layer (by DC magnetron sputtering and gradual introduction of acetylene gas to chamber). This industrial scale PVD/CVD system incorporates two 1000 W microwave plasma sources (2.45 GHz). The negative bias voltage used was 420 V. The substrate was maintained at less than $200\text{ }^{\circ}\text{C}$. During deposition, control of the substrates temperature is very important for heat sensitive metallic materials such as the steel used in this study. The substrates were cleaned by Ar^+ plasma using pulsed DC bias prior to deposition of the

adhesion layer. The thickness of the coating was determined by means of the abrasion ball cratering technique utilizing a Calotester apparatus (tribotechnic, France) as can be seen in Fig. 1. The total thickness of the H-DLC layer was $2.8 \pm 0.2\text{ }\mu\text{m}$.

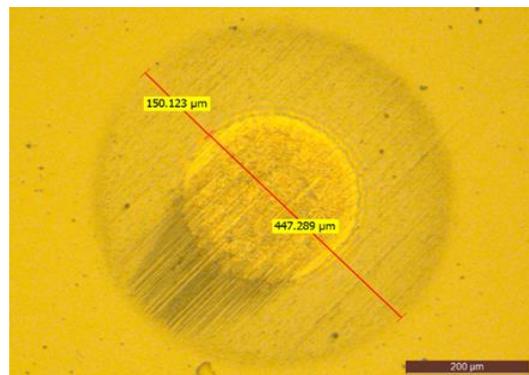


Figure 1 Produced crater on the coating from Calotest apparatus.

The hardness and elastic modules were measured by depth-sensing Nano indentation (MicroMaterials, Wrexham UK), an enclosed box platform with temperature regulated, software suite and micro capture camera. The diamond indenter was a Berkovich tip. The load was incremental with depth from 1 to 100 mN and a matrix of 50 indents was used. The Renishaw Raman spectrometer was used to characterise the bonding structure of the DLC films. The extended and static modes were used to detect chemical compound formation and the carbon peaks (disorder D and amorphous graphitic G peaks), both for the coating structure before and after wear tests. All measurements were carried out in air at room temperature ($20 \pm 2\text{ }^{\circ}\text{C}$), 35-50% RH and with a wavelength of 488 nm and 2 mW power. Assessment of the surface chemical composition and coating's cross section was carried out with the energy dispersive spectroscopy (EDS) and also with glow discharge optical emission spectroscopy (GDOES). It should be specified that the quantitative EDS and GDOES analysis had the limitation of light elements ($Z < 11$) and could not be routinely analysed. Thus, hydrogen ($Z = 1$) did not have characteristic X-rays and therefore it is not shown both in the corresponding EDX analysis and the composition profiles.

Sliding friction and wear tests of the HC-DLC under dry conditions were carried out on a pin-on-plate tribometer (Cameron Plint TE77 reciprocating friction rig) in linear/bidirectional motion. The tribological experiments were carried out using a loaded pin and reciprocated against a stationary H-DLC coated steel. Prior experimental set up all holders (both for the sample and for the pin) were sonically cleaned in acetone for 20 min. This later procedure was also utilized for the cleaning of the samples and pins. Pins were AISI 52100 steel of 20 mm in length, diameter 6 mm with one semi spherical end of 110-120 mm in radius. The stroke length was set up to 5mm. The friction force data was collected every 5 min (1000 data points) for 6 h. To

evaluate the friction, tests were repeated at least three times for each load.

The pin-on-plate configuration used was to emulate the sliding conditions of a piston ring contact of internal combustion engine [1]. Thus, the initial Hertzian contact pressure used in this study and the experimental running conditions are as follows: Normal loads of 10, 30, 40 and 50 N. In terms of Hertzian pressure would be 0.1, 0.16, 0.17 and 0.19 GPa. The frequency utilised was 10 Hz. The average velocity was 0.1 ms⁻¹. The average temperature was 20±2 °C. All tests were carried out for 6 h.

A Renishaw Raman spectrometer was used to characterise the bonding structure of the DLC films. The extended and static modes were used to detect chemical compound formation and the carbon peaks (disorder D and amorphous graphitic G peaks), both for the coating structure before and after wear tests. All measurements were carried out in air at room temperature (20 ±2 °C), 35-50% RH and with a wavelength of 488 nm and 2 mW power.

3. Results and analysis

In Fig. 2, the specific wear rates of the H-DLC coatings are depicted. Under the same sliding velocity condition (0.1 m/s), with the increase in normal load, the average specific wear rates decrease. The maximum and minimum specific wear rates are 14×10^{-8} and 5.5×10^{-8} mm³ /N m, respectively. The former under a normal load of 10 N and the latter under a normal load of 50 N for 6 h or 2160 m dry sliding. The reduction in specific wear rate seems to be abetted by the formation of a transfer layer on the counter-layer, because of structural transformations triggered by the normal load applied during the sliding. Among these structural effects, the re-crystallisation process becomes very active at the contact interface in such a way that, due to the reciprocating sliding, a re-orientation of the re-crystallised layers brings the basal planes parallel to the top surface of the coating with the consequent reduction in the wearing rate [2]. Specifically, the sliding-induced localised annealing at the contact asperities, likely causes a gradual destabilization of the carbon-hydrogen bond in the sp³ tetrahedral structure and as a result, a transformation of this sp³ structure into a graphite-like sp² structure takes place [3]. These changes in the chemical behaviour of the near-surface structure of the worn coatings were characterized by Raman spectroscopy and are shown in Fig. 3. The spectrum taken from the wear tracks of the high frequency peaks (G) have shifted to a higher frequency nearing the graphite frequency. Particularly, if it is considered that hydrogenated DLC Raman spectra are commonly composed of the high and low frequency peaks oscillating at 1540 cm⁻¹ for the graphite-like sp²-bonded carbon and 1360 cm⁻¹ for the sp³-bonded phase [9]. There is also an increase in the intensity of the low frequency peak due to D band graphite contributions, since the ID/IG ratio is also proportional to sp²/sp³ ratio.

Therefore, the wear track H-DLC surface undergoes certain amount of changes in the chemical behaviour due to the strain-stress state of the sliding surfaces and the chemical reactions with ambient atmospheric contamination, leading to graphitization/amorphization to some extent.

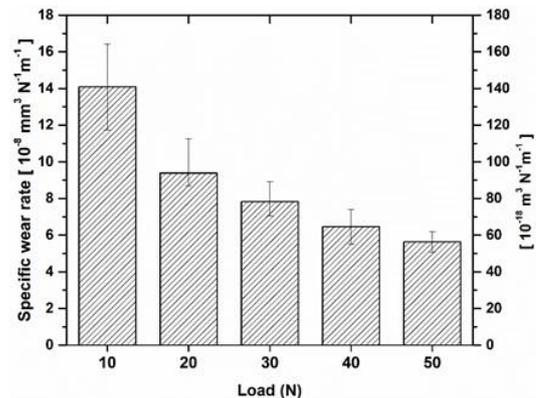


Figure 2 Dimensional wear coefficients of the H-DLC assessed at several loads. Error bars are the standard deviation from the average values of three weight measurements.

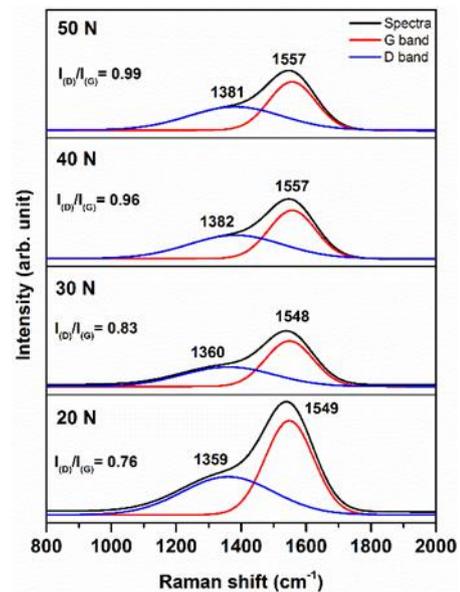


Figure 3 Raman spectroscopy taken from wear track zones of the coated plate after testing, and for different applied loads.

As expected, under dry conditions, the aforementioned graphite-like sp² structure contributed to the transfer of C from H-DLC to the steel pin with a consequent reduction in the adhesion and friction due to the fact that the contact was carbon-on-carbon rather than carbon-on-steel. This was verified, firstly, by measuring the wear depth of the H-DLC coating at the end of the sliding tests. The coating presented DLC after the rubbing and also there was no transferred material from the steel pin to the coated. The top of the a-

C:H was partially worn holding approximately 0.6 μm thickness with carbon and tungsten to a lesser extent. The Cr interlayer remained intact for all applied loads. And secondly, Raman analyses were carried out on the wear surfaces of the plates (Fig. 3), these appeared to have a tendency to a graphitic character, which clearly indicates the carbon nature of the tribo-layer formation at the contact. Secondly, by analysing the transfer layer on the wear scars on the AISI 52100 steel pins. Raman spectroscopy was utilised to identify the tribolayer formations on these counterparts. The spectra were measured on the several zones of the wear scars and a representative spectrum of two different loads is shown in Fig. 4. Evidently the signals are dissimilar to those taken on the wear tracks of the coated plates (Fig. 3). This is because the quantities of transferred carbon to the steel pin are much lower than those present in the deposited bulk carbon film on the steel plate, and therefore, the thickness of transferred material appears to be non-homogeneous as can be seen in the inset picture of the wear scar on the steel pin in Fig. 4. In the same inset image, it is observed that dark-grey transfer layers are present on the wear scar and along the sliding direction in the shape of long stripes. It also can be corroborated from the signals depicted in the same Fig. 4, as the intensities were very much lower than those for the plate worn tracks, which suggests that the amount of graphite formed was rather limited. In addition, the Raman spectra of the transferred layer exhibited two broad and strong peaks with wave numbers oscillating at 1589-1609 cm⁻¹ and 1328-1358 cm⁻¹. These peaks are close to the G and D band peaks of the natural graphite and their shapes resembles that of highly disordered graphite [4]. Therefore, the surface of the coating wear track and the tribolayer formations on the pin wear scars appeared to have a graphitic character, confirming the carbon-carbon contact.

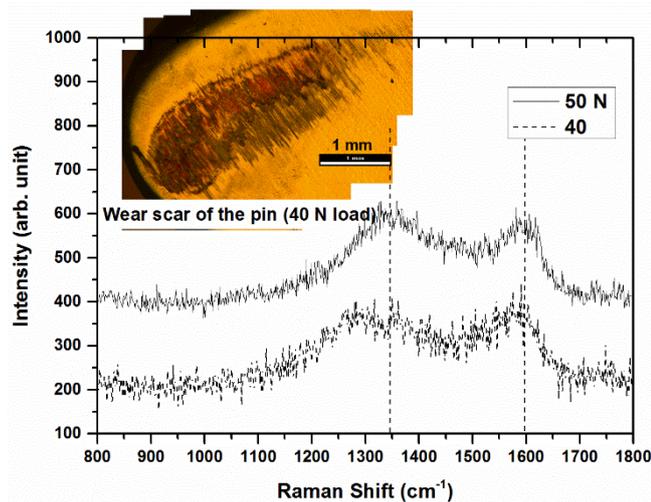


Figure 4. Selected Raman spectra of the steel pins wear scars after sliding against H-DLC coating. Tribotest conditions were: 2300 m sliding distance in humid air (45 ± 5 % RH) and sliding velocity of 0.1 m s⁻¹. The inset image shows the wear scar on the steel pin for a 40 N applied load.

3.1. Phase transition analysis

There is a strong indication of DLC coating graphitisation from prior observations as well as from the correlations between friction and wear behaviours. Under dry sliding conditions, temperature and high contact stresses appear to be central in the breakdown of the hydrogenated DLC coating [5]. The rationale comes out of the pressure induced temperature at the sliding contact; the hydrogen atoms are unbound from the diamond-like matrix and as a result, feebly hydrogen-depleted sites turn out. This weak surface is then deformed by the high contact stresses turning into a graphitic structure (from sp³ bonded carbon to sp² bonded carbon) which favours a reduction of friction [6]. The carbon transition temperature for hydrogen desorption mostly depends on the initial hydrogen content and the sliding contact pressure. As a qualitative account on the transition observed in this study, the Clapeyron law [7] can be used for the present discussion. It states that, the increase of Hertzian contact pressure leads to a decrease in the graphitisation temperature as long as the specific volume of hydrogenated coatings is higher than the dehydrogenated coatings, which can be mathematically expressed by the following relationship:

$$\frac{dP}{dT} = \frac{L}{T(v_f - v_i)} \text{-----} (1)$$

Note that $v_i > v_f$ because if the density of a hydrogenated film decreases when the hydrogen content increases, then $dP/dT < 0$.

Where L is the transition phase energy of diamond (15.6 x 10⁴ J/kg) [7], v_i is the hydrogenated film specific volume (from $v_i = 0.294 \times 10^{-3}$ to 0.416×10^{-3} m³/kg, depending on the amount of hydrogen incorporated in the film), v_f is the dehydrogenated film specific volume ($v_f = 0.284 \times 10^{-3}$ m³/kg) [8] and T is the transition temperature of coating in vacuum (around 400 °C [9]). The solution of the differential equation (1) is given by the following equation:

$$T = T_c \exp\left(\frac{v_f - v_i}{L} \Delta P\right) \text{ with } \Delta P = P_{\max} - P_a \text{-----} (2)$$

Where P_{max} is the Hertzian contact pressure given by and

$$P_{\max} = \frac{1}{\pi} \left(\frac{6FE^2}{R^2}\right)^{\frac{1}{3}} \text{ } P_a \text{ is the atmospheric pressure (0.1 MPa). F is the applied load, R is the radius of the pin (R =$$

$$110 \text{ mm) and } E = \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}\right)^{-1}, \text{ } E_1 = \text{Elastic moduli}$$

of the steel pin (~160 GPa), $E_2 =$ Elastic moduli of the H-DLC (180 GPa), $\nu_1 =$ Poisson ratio of the steel pin (0.3) and $\nu_2 =$ Poisson ratio of the coating (0.28).

When all the above parameters for the present study are used in Eq. (2), it can be shown that the phase transition temperature of the H-DLC coating decreases with an increase of contact stress but also decreases abruptly with an increase of hydrogenated coating specific volume, as

illustrated in Fig. 5. Specifically, if it is taken into account that the mass density of H-DLC oscillates from 1.9-3.0 g/cm³ [10], it can then be considered a density of 2.5 g/cm³ (0.4 x 10⁻³ m³/kg) for the actual coating. In the process, the transition temperature can be decreased to 300 - 325 °C, for contact stresses ranging from 0.1 - 0.2 GPa, i.e., when the applied normal loads vary between 10 and 50 N.

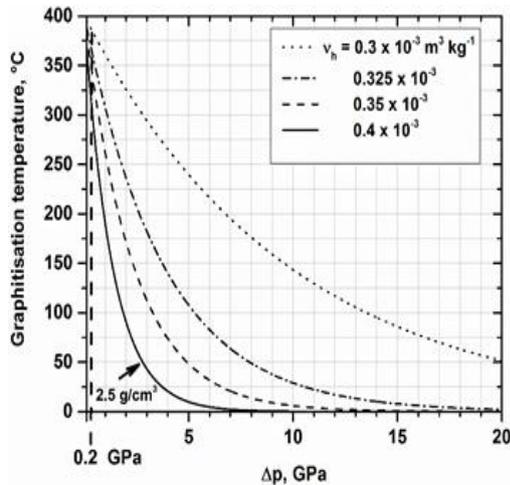


Figure 5 Graphitisation temperature of the H-DLC coating as a function of specific volume of hydrogenated coating and contact pressure. Plots are obtained from Eq. (2).

In order to determine if the surface temperature of the two sliding bodies in contact is sufficiently high as to reach the graphitisation temperature, the following flash temperature relationship [3] can be used to estimate an approximate of the induced temperature rise due to the frictional heat at the contact area.

$$\Delta T = \mu P v / 4J(K_1 + K_2)a \quad \text{with } a = \left(\frac{P}{\pi H} \right)^{\frac{1}{2}} \quad \text{-----(3)}$$

where μ is the coefficient of friction, P is the applied load, v is the sliding velocity, K_1 and K_2 , are the thermal conductivities of the coating and the steel pin, J is the Joule's constant ($J = 1$), a is the contact radius of the real contact area, and H is the measured hardness of the H-DLC coating. Using Eq. (3) and the actual experimental data, the calculated surface temperature rise when the applied load varies are enumerated in Table 1.

Table 1. Estimated flash temperature.

Constants	P (N)	a (μm)	μ^b	ΔT
^a K_1 (W/mK)Steel	17 ^a	10	11.8	0.21 221
^a K_2 (W/mK)H-DLC	3 ^a	20	16.6	0.21 315.6
H (GPa)	23	30	20.4	0.19 349.7
v (m/s)	0.1	40	23.5	0.17 361.3
		50	26.3	0.15 356.4

^aRef. [11], ^b μ ~ initial at 240 m sliding distance.

The calculated flash temperatures eased the graphitisation process for the applied loads of 30 - 50 N, due to the fact that exceeded the phase transition temperatures (~325 °C). This result appears to agree with the frictional behaviour, since for such loads the very initial values of CoF exhibited a slowly decrease to almost constant value during the following sliding distance, which could be an indication of an early graphitisation degree of the H-DLC surface layer. In the case of the loads 10 and 20 N, the calculated temperature rise at contact asperities was lower than the calculated graphitisation temperature. These results also seemed to agree with the frictional tendencies for such loads, since the CoF slowly increase to a maximum and eventually decrease to almost constant value. The estimated flash temperature is high enough to change the state of the contact interfases in the way of desorbed hydrogen. Therefore, the edge sites multiply themselves and there is an increase in the adhesion of the tribopair. This may explain that increasing values of CoF. As the sliding continue and since there is hydrogen on the friction track, hydrogen desorption from the surface is also progressive generating inactive sites and in consequence CoF reduces. The extremely unstable carbon atoms from the active sites may attempt to form more stable structures, but because of the contact stress, the active surface can be dislocated facilitating the transformation of the sp² structure on the surface of the coating. In addition, it has been analysed in previous research [12] that the presence of wear debris in the tribopair's interface can promote the graphitisation of amorphous hydrocarbon molecules, by virtue of a rise in the Hertzian contact pressure at surface asperities, which brings down the transition temperature.

4. Conclusions

A hydrogenated Diamond-like Carbon has been characterised both prior to, and following tribological testing. Wear behaviour under dry unlubricated conditions of a H-DLC/steel contact has been assessed for different normal loads in ambient atmosphere. At the levelled off stage, coefficients of friction decrease with the increase of the applied normal load. This is because, depending on this increase in the normal load, the chemical composition of the coating can be seen to alter in the form of a graphitized wear surface and a degree of transfer layer formation also takes place, as revealed by the Raman analyses. Specific wear rate of the H-DLC/steel tribocouple behaves as the degree of graphitisation does, which, in turn, is governed by the severity of the applied load. Hence, in this study, the specific wear rate decreased with the increase in normal load. The formation of a protective transferred layer on the counterpart made carbon-carbon contact conditions with a consequent reduction in wear of both mating surfaces. The maximum wear rate value for the H-DLC coatings was $14 \times 10^{-8} \text{ mm}^3/\text{N m}$ under a normal load of 10 N and $5.5 \times 10^{-8} \text{ mm}^3/\text{N m}$ under a normal load of 50 N, following 2160 m of dry

sliding. According to the outcomes from the present research, the H-DLC coating could be useful for wide range of industrial applications such as automotive, aircraft and machine components.

Acknowledgments

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