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Scratch resistance and tribological properties of DLC coatings under dry and lubrication conditions

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ABSTRACT

Scratch resistance and tribological properties of hydrogenated and hydrogen free diamond like carbon (DLC) coatings were investigated in ambient atmosphere under unlubricated and lubricated conditions using layers of oleic ($C_{18}H_{34}O_2$) and linoleic acid ($C_{18}H_{32}O_2$). Scratch resistance property improved in hydrogenated DLC while using linoelic and oleic acids compared to unlubricated condition. Coefficient of friction (CoF) was found to decrease under ambient dry conditions, while under lubrication condition, it was found to increase with normal load. At low load of 1 N, hydrogenated and hydrogen-free coatings show a super low CoF of 0.001 and high wear resistance with oleic acid.

1. Introduction

The diamond like carbon coatings have been explored extensively in recent years due to their low friction, high wear resistance properties and adhesive protection [1]. However, their low surface energy limits them to have any physical and chemical interaction with conventional lubricants and additives. Thus the influence of lubricants, lubricant additives and lubrication process on the friction and wear properties of these coatings needs to be investigated. When sliding occurs under unlubricated atmospheric conditions, two solid surfaces in contact produce surface layer of chemisorbed or physisorbed molecules, or a capillary condensed liquid bridge, between them. Each of these effects can drastically modify their response to adhesion and friction. Adhesion usually decreases, but in the case of capillary condensation, the additional Laplace pressure, or attractive capillary force between the surfaces, may further enhance the adhesion [2]. However, in lubricated sliding contact conditions, the molecules at the interface relax and/or rearrange to form a new equilibrium configuration that is distinctly different from the ones that prevail when the surface is kept in isolation. These rearrangements may involve simple positional and orientational changes of the surface molecules. In a complex condition, new molecular groups that are previously buried below the surfaces can re-appear and intermix with the interface. This behavior commonly occurs with surfaces whose molecules have both polar and nonpolar groups [3]. All these effects act to enhance the adhesion between the contacting surfaces. Shear stress is also an important factor which can convert the amorphous structure of liquids into crystalline ones when the liquid is confined at high pressure. Applying the critical stress liquid can lead to the formation of a monolayer ($\sim$10 atomic layers). In this case, the viscosity of the liquid is very high which can cause to freeze the sliding hence strong adhesion acts [2,4]. Crystalline structure of a liquid can also have freezing behavior due to rapid rise in viscosity. Adhesion and friction become low if the viscosity is normal and the behavior of liquid emulates that of a crystalline medium. It can easily shear and provide slippage induced movement. In amorphous state, when the stress is below a critical value needed for transition, the liquid molecule sticks and hinders shearing which raises adhesion and friction. Adhesion and friction are related to slip induced movement and viscosity enhancement. These parameters depend on the structure and bonding fraction of materials participating in a sliding contact.

DLC coatings consist of a fractional combination of sp^2 and sp^3 bonded carbon atoms with a considerable amount of hydrogen. If hydrogen content is about 40 at%, it is called as a hydrogenated DLC and if it is less than 1 at%, it is known as a hydrogen free DLC [5]. Depending upon sp^2/sp^3 ratio and content of hydrogen, different kinds of DLCs with different properties can be synthesized [6,7]. DLC coatings are called inert coatings because of their low surface energy [8,9]. Therefore, they do not react with various lubricants, oil additives as these coatings do not attract the polar groups from these oils and additives. There are conventional lubrication mechanisms for steels and other metals [10–13]. Most of the mechanical systems work under lubricated conditions. As DLC coatings exist in a wide variety possessing different properties, there

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is a huge demand for these coatings in various mechanical systems like, bearings [14], gears [15], piston rings and pins [16,17], direct-injection fuel systems [18], cutting and forming tools [19,20]. In computer industry, these coatings have application as head–disk interface [21–24]. These coatings also find applications in orthopedic applications in medical industry [25,26]. To reduce the severity of the contact conditions, some of the above performance driven systems are to be operated under lubricated conditions [27,28]. Thus it is necessary to investigate mechanism of lubrication of these coatings. In this regard, some of the important studies have been carried out to address physical and chemical interaction of lubricants, oils and additives with DLC coatings in sliding contact conditions [29–36].

In the present study, the lubricating mechanisms and their influence on the scratch resistance and tribological properties of DLC coatings are investigated. Two types of diamond like carbon coatings, a hydrogen free amorphous carbon (a-C) and a hydrogenated amorphous carbon (a-C:H), were investigated under different loading conditions in the presence of unlubricated and lubricating layer of fatty acids.

2. Experimental

In the present study, we designate commercial name of Graphit (hydrogen free) and Dymon (hydrogenated) coatings as G1 and D1, respectively. The G1 coating was deposited by closed field unbalanced magnetron sputter ion plating from the carbon target in a closed field arrangement [37]. Coating D1 was deposited by plasma enhanced chemical vapor deposition using a hydrocarbon gas precursor. Hydrogen content entrained in solid matrix during the deposition of D1 coating in CH_4/Ar plasma amounts to 2%. The bias voltage applied to the substrate was pulsed direct current (PDC) and the plasma was further enhanced by the use of additional radio frequency (RF) electrodes [38,39]. Both these coatings are single layered deposited on a steel substrate. Adhesive strength of the coating was tested by using a commercial scratch tester (CSM Instruments, Switzerland) fitted with a Rockwell spherical diamond indenter (tip radius of 200 μm). Scratch-tests were performed using progressive loads from 1 to 40 N for a transverse scratch length of 3 mm in dry unlubricated and lubricated (linoleic and oleic acids) conditions. The scratch tester is equipped with an acoustic emission monitoring sensor which detects acoustic energy in the range of 20–80 kHz. To detect the failure of the coating, the scratches were examined using Scanning Electron Microscope (SEM) and correlated with the acoustic emission peaks. Tribological tests were performed using a ball on disk microtribometer (CSM Instruments, Switzerland) in linear reciprocating mode. A spherical steel ball (100Cr6 SS) of diameter 6 mm with a surface roughness 0.06 μm was used as a sliding body to measure the CoF. Tests were carried out at 1, 4 and 8 N loads with constant sliding speed of 2 cm/s and a stroke length of 3 mm in ambient dry and lubricated conditions with a relative humidity of 58%. For this purpose oleic and linoleic acids were used as lubricating media for the contacting surfaces. Wear dimension was measured using a Dektak 6 M stylus profiler (Veeco, USA). Friction coefficient was found to be reproducible in couple of tests carried out under similar conditions. Calculated wear rate was also found to be more or less similar. A nano-hardness tester (CSM, Switzerland) was used for extracting surface hardness of D1 and G1 samples at a constant load of 2 mN with a Berkovich diamond indenter. Load–displacement curves were generated and resulting curves were analyzed using the Oliver and Pharr method to obtain nano-hardness of the samples. Five indentations were performed on each sample. Raman measurements, using a 5 mW laser power and 514 nm wavelength, were performed to record the local chemical structure present at the coating surface as well as in the wear tracks. Raman measurements in the wear tracks were performed while stopping the test after each sliding distance. These locations are indicated as d1, d2 and d3. X-ray photoelectron spectroscopy (XPS) was used to study the chemical state of constituents comprising this coating. Prior to acquisition of XPS spectra the specimen was sputtered to remove surface contaminants. An Ar^+ ion beam sputtering of specimen surface was carried out for a duration of 3 min. Energy dispersive X-ray (EDX) was carried out to obtain the elemental analysis of the coating surface and the scratched region.

3. Results and discussion

3.1. XPS of coatings surface

The sp^3 and sp^2 fractions of DLC films are deduced from XPS fitting for C (1s) core level peak. These peaks comprise of contribution from C–C (sp^3) at a binding energy of 285.3 eV, graphite C–C (sp^2) at 284.8 eV and C–O at 286.3 eV. Broad FWHM of C (1s) peak points to presence of carbon with several distinct local bonding environments. The C (1s) XPS in Fig. 1(D1) depicts these contributions. Since the area under each peak is directly related to the concentration of the corresponding phase, the sp^3 content is estimated by taking the ratio of diamond peak area

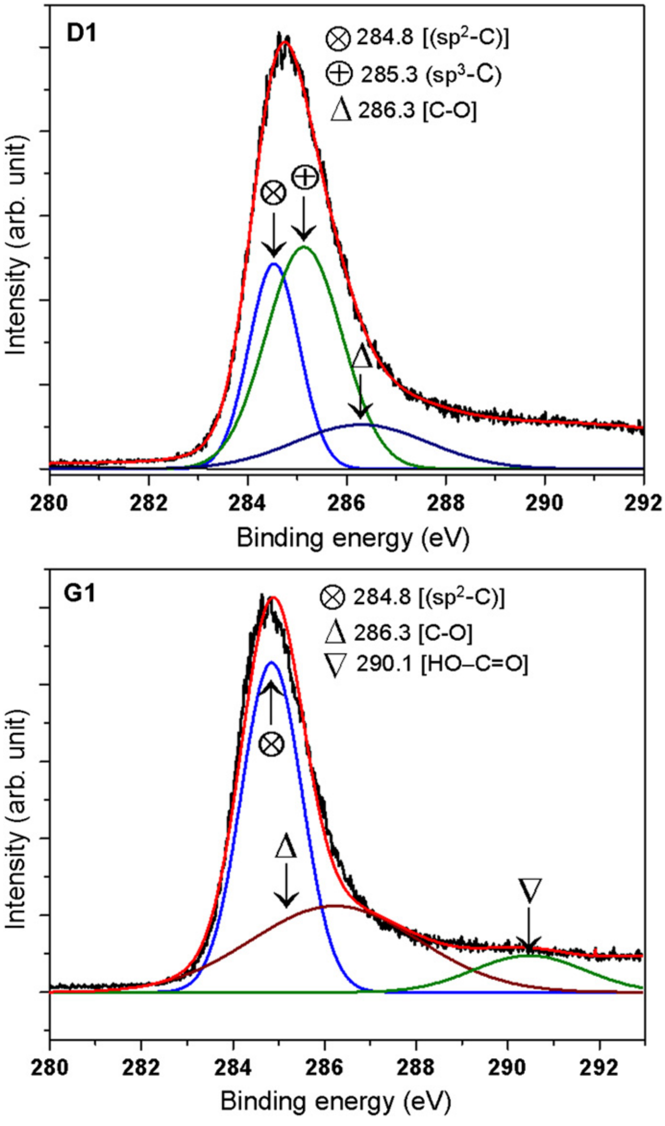

Fig. 1. XPS of coating surface (D1) hydrogenated and (G1) hydrogen free.