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Structure and tribological behavior of diamond-like carbon coatings deposited on the martensitic stainless steel: The influence of gas composition and temperature

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ABSTRACT

The relationship between the tribological behavior and inherent features of the DLC coatings (i.e. structural and mechanical properties) as a consequence of deposition conditions was investigated. Hence, a plasma nitrocarburising process as pretreatment followed by Diamond-Like Carbon (DLC) deposition by pulsed DC Plasma Assisted Chemical Vapor Deposition (PACVD) method, was utilized. Although a remarkable reduction in the friction coefficient of coated samples was observed, almost the same friction coefficient was measured for the DLC coatings (i.e. 0.2), regardless of their diverse intrinsic properties. As the H/C ratio in feeding gas and temperature increased up to certain values, the hardness and elastic modulus increased while the wear rate decreased. Therefore, the DLC coating deposited with the highest Hydrogen fraction at 160 °C, exhibited the highest hardness and elastic modulus (i.e. 25.4 GPa and 177.4 GPa, respectively), as well as the lowest wear rate of 5.9×10^{-06} $mm^3/N{\cdot}m$.

1. Introduction

Over the last few years, diamond-like carbon (DLC) coating has attracted extensive attention owing to its excellent properties such as high hardness, exalted wear resistance, low coefficient of friction and superior surface finish [1–5]. Because of its remarkable tribological properties, as well as reasonable deposition cost, this type of coating has been demanded extensively for various engineering applications [6,7]. Currently, this type of coating can be deposited on the metallic substrates by many methods including ion-beam assisted deposition, magnetron sputtering, laser ablation and several kinds of physical and chemical vapor deposition (PVD and CVD) systems [6,8–10]. These various deposition methods lead to a wide range of mechanical and tribological behaviors which can be modified and altered by means of selecting the appropriate combinations of deposition parameters [6,10,11]. It is worth to mention that the possibility of wide range of alteration is not practical for other hard coatings including crystalline diamond or transition metal nitride and carbide films. Hence, this modification has been made DLC as a unique coating which can be formulated in many ways for diverse applications [6].

Based on the deposition method, parameters and carbon sources, the content of hydrogen can be varied from zero (i.e. hydrogen free DLC) to > 40% (i.e. highly hydrogenated DLC) [6,10,11]. Moreover, the different relative ratios of sp^2/sp^3 bonded carbon are present in the DLC coatings. Although all the DLC coatings are amorphous, the mentioned differences along with the test conditions lead to completely distinct tribological properties among the DLC coatings which reveal a wide range of friction coefficient from 0.003 to 0.7 and a variety of wear rates [6,9,12]. In fact, this significant dissimilarity in friction and wear properties can be attributed to the intrinsic and extrinsic elements which affect the tribological behavior of the DLC coatings. Intrinsic elements comprise chemical composition (i.e. concentration of hydrogen and other doping elements), structural state (i.e. ratio of sp^2 versus sp^3 bonding), physical and mechanical properties (i.e. hardness and Young's modulus) which all can be manipulated by variation of deposition parameters such as feed gas composition (i.e. various H/C ratios), deposition temperature and plasma parameters. On the other hand, extrinsic elements are directly related to the test conditions and environmental effects which significantly influence the tribological behavior [6,8–12].

In general, the adhesion of DLC coatings on carbide- and silicide forming substrates (like Si, Ti, W and Cr) are sufficient and satisfying. However, their adhesion to the metallic substrates is not good enough which cause the delamination in sliding and restriction of their

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application [1,3,13,14]. In order to enhance the adhesion of DLC on the metallic substrates, some of the researchers have utilized an initial treatment on substrate prior to the DLC deposition such as the thermochemical process [1,13–15]. This process provides a hard layer consists of carbides and nitrides which promote the load-bearing capacity along with strong bonding between the DLC coating and metallic substrates. Therefore, delamination and failure of coating as a consequence of the substrate plastic deformation, would diminish extremely [1,16].

The present project aims to study the relationship between the tribological and the inherent properties of hydrogenated DLC coatings (i.e. structural and mechanical features) deposited by means of D.C. Pulsed Plasma Assisted Chemical Vapor Deposition (PACVD) method on martensitic stainless steel by changing the feeding gas compositions (i.e. diverse C/H ratios) and deposition temperature. In the first step, the duplex treatment consisting of plasma nitrocarburising process followed by deposition of DLC coating was utilized in order to enhance the adhesion quality of DLC coating. Next, the friction and wear data, mechanical and structural properties as well as the tribological properties and wear mechanisms were evaluated. Therefore, the better understanding of wear mechanism and tribological properties of the hydrogenated DLC coatings as consequence of intrinsic and extrinsic elements was achieved. In addition, the suitable set of temperature and feeding gas composition for deposition of DLC coating on the martensitic stainless steel were determined which can be used in selecting the appropriate deposition conditions for achieving better DLC coatings and tribological performance for this stainless steel type. It is worth to mention that the advantage of the mentioned duplex treatment is the low cost of operation due to the use of the conventional plasma nitriding plant for whole treatment which made it distinctive from other studies.

2. Materials and methods

In this project, the specimens were cut in dimensions of 20 mm × 8 mm (diameter × thickness) from a 410 martensitic stainless steel which its composition is mentioned in Table 1.

The samples were made of as-annealed steel bar with approximate hardness of 20 HRC which in the next step, were austenised at 980 °C for 45 min, oil quenched and tempered at 600 °C for 30 min to the hardness of 35 HRC.

The surface of samples or substrates was mechanically grounded by various grades of SiC emery papers to a surface roughness of approximately $R_a = 0.1$ μm, and finally cleaned in acetone.

After cleaning the substrates, they were mounted on the holder in a Pulsed Direct Current Plasma Assisted Chemical Vapor Deposition (DC Pulsed PACVD) chamber in order to accomplish the plasma nitrocarburising process as pretreatment for DLC deposition. The holder in the DC pulsed PACVD system which acted as cathode and thermocouple support, was biased by a unipolar pulsed DC source, consisting of variable negative pulse with peak amplitude ranging from 0 to −650 V at 10 KHz and variable pulse duration. Moreover, the evacuation of deposition chamber was accomplished by means of a rotary vacuum pump which equipped with a ball valve. Hence, the total pressure could be adjusted independently of gas flow by regulating the ball valve. Furthermore, by adjusting the voltage and current between the cathode and anode (i.e. the deposition chamber), the substrate temperature (i.e. deposition temperature) could be controlled and modified. Therefore, the deposition current was changed in order to achieve the proper deposition temperature for intended coating.

Table 1
Chemical composition of AISI 410 stainless steel.

Element	C	Mn	Si	Cr	P	S
Wt%	0.15	1.00	1.00	11.5–13.5	0.04	0.03

Table 2
DLC deposition parameters.

Specimen no.	Gas composition (CH_4:Ar:H_2)	H/C ratio	Time (min.)	Temperature (°C)	Frequency (KHz)
H10T160	3:6:10	10.7	120	160	10
H10T180	3:6:10	10.7	120	180	10
H12T160	3:4:12	12	120	160	10
H12T180	3:4:12	12	120	180	10

After evacuation of chamber to 10^{-2} mbar, the substrates were further cleaned by bombarding with a mixture of argon and hydrogen ions for about 2 h at pressure of 3 mbar and 10 kHz frequency, in order to eliminate the native oxide layer and enhance the subsequent layer's adhesion. Moreover, the mentioned bombardment induces heating of substrates to desired temperature (550 °C) which prepares them for plasma nitrocarburising process. The plasma nitrocarburising treatment was carried out in a gas mixture of methane, hydrogen and nitrogen with the 1:5:15 ratio of flow rates for 3 h at 550 °C and pressure of 4 mbar. Finally, the nitrocarburised substrates were maintained in vacuum to reach room temperature.

The DLC deposition on the treated substrates was conducted in the same system in which the plasma nitrocarburising process occurred. With intent to acquire proper feeding gas composition for DLC deposition, a wide range of gas mixtures consisting of methane, hydrogen and argon were evaluated. Eventually, merely two sets of gas mixtures led to appropriate DLC coating (without delamination), which is indicated in Table 2.

In this study, one of the nitrocarburised substrates and one of the bare specimens were assigned as PNC (Plasma Nitrocarburised specimen) and BM (Bare Metal), respectively in order to conduct comparison with other DLC-coated substrates. It is worth mentioning that the BM specimen is referred to quenched-tempered AISI 410 martensitic stainless steel substrates.

Prior to the DLC deposition, the substrates were subjected to the argon and hydrogen ions-etched for 1 h. This ion bombardment led to heating the substrate up to the desired temperature. In subsequent step, the DLC deposition took place by admitting the gas mixture into the chamber which its parameters are clarified in Table 2. During coating process, the chamber pressure was sustained at 5 mbar and the deposition proceeded for 2 h.

The evaluation of microstructure and nitride phases in nitrocarburised substrates was done by means of X-ray diffraction (XRD) test, using a conventional Philips X-Pert diffractometer operating with Cu-Kα radiation and 2θ angle scanning from 0 to 120°.

The study of chemical bonding nature of DLC coating was performed using Horiba Yvon Xplora Raman spectroscopy with an excitation light of 532 nm and a laser power of 40 mW in ambient condition. The Raman spectra were analyzed by deconvolution of them into two components (G and D peaks) using fitting to two Gaussian functions in order to achieve I_D/I_G ratio of their intensities, the G peak position (ω_G) on the frequency scale, and its full width at half maximum (FWHM). Moreover, after wear test, wear tracks examined by micro-Raman spectroscopy in the same manner stated earlier to investigate the chemical alteration which was occurred due to wear test.

Hardness and young's modulus measurement of the DLC coating was carried out in five random spots on the surface, utilizing a TriboScope system (Hysitron Inc. USA), equipped with a Cube corner type indenter tip. In order to eliminate the substrate influence, the final displacement of indenter was restricted to a depth of $< 1/10$th of the coating thickness and the hardness and elastic modulus were determined using the Oliver–Pharr method [17,18]. The results were statistically analyzed by Minitab 17 software (Minitab Inc., State College, USA) using Student's *t*-test and the data were expressed as the mean ± standard