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Optimization of pulsed DC PACVD parameters: Toward reducing wear rate of the DLC films

Mansoureh Ebrahimi[a], Farzad Mahboubi[a,*], M. Reza Naimi-Jamal[b]

[a] Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, P.O. Box 1875-4413, Tehran, Iran
[b] Research Laboratory of Green Organic Synthesis and Polymers, Department of Chemistry, Iran University of Science and Technology, P.O. Box 16846, Tehran, Iran

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ABSTRACT

The effect of pulsed direct current (DC) plasma-assisted chemical vapor deposition (PACVD) parameters such as temperature, duty cycle, hydrogen flow, and argon/CH_4 flow ratio on the wear behavior and wear durability of the diamond-like carbon (DLC) films was studied by using response surface methodology (RSM). DLC films were deposited on nitrocarburized AISI 4140 steel. Wear rate and wear durability of the DLC films were examined with the pin-on-disk method. Field emission scanning electron microscopy, Raman spectroscopy, and nanoindentation techniques were used for studying wear mechanisms, chemical structure, and hardness of the DLC films. RSM results show that duty cycle is one of the important parameters that affect the wear rate of the DLC samples. The wear rate of the samples deposited with a duty cycle of >75% decreases with an increase in the argon/CH4 ratio. In contrast, for a duty cycle of <65%, the wear rate increases with an increase in the argon/CH_4 ratio. The wear durability of the DLC samples increases with an increase in the duty cycle, hydrogen flow, and argon/CH_4 flow ratio at the deposition temperature between 85 °C and 110 °C. Oxidation, fatigue, abrasive wear, and graphitization are the wear mechanisms observed on the wear scar of the DLC samples deposited with the optimum deposition conditions.

1. Introduction

Diamond-like carbon (DLC) coatings have found a wide range of applications, especially in the field of tribology, because of their good mechanical and tribological properties [1]. Plasma-assisted chemical vapor deposition (PACVD) is one of the typical and useful techniques used for DLC deposition [2–4]. This method has different varieties such as radiofrequency (RF) PACVD, bipolar PACVD, glow-discharged PACVD, and pulsed direct current (DC) PACVD. It is well known that the DLC properties are affected by the deposition methods [5–8]. Pulsed DC PACVD is the simplest, cheapest, and novel method, and hence can be easily used at the industrial scale [7]. The effect of different deposition method parameters such as those of the RF PACVD method on the properties of the DLC films has been already investigated [9–11]. For example, Jeong et al. deposited DLC films on nitrided steel using the RF PACVD method. They reported that surface roughness of the nitrided steel increases with an increase in the deposition duty factor, and the adhesion of the DLC films decreases with an increase in the surface roughness of the nitrided steel [10]. Beake et al. also investigated the effect of RF PACVD power on the failure mechanisms of the DLC films. They reported that failure time decreases with an increase in the RF power [11]. V.J. Trava-Airoldi et al. deposited DLC films using RF PACVD, IBAD, and bipolar pulsed DC PACVD methods and reported that the DLC films deposited by the bipolar pulsed DC PACVD method showed the highest adherence, the lowest friction coefficient, and the lowest stress [8]. However, there has been no study conducted to determine the effect of the pulsed DC PACVD method parameters, especially the duty cycle, on the properties and wear behavior of the DLC films. This brings in the need to understand the effect of the duty cycle in addition to the effect of the deposition atmosphere (H_2 flow and argon/CH_4 flow ratio) and deposition temperature on the mechanical properties of the DLC films.

The purpose of this study is to investigate the effect of pulsed DC PACVD parameters such as duty cycle, hydrogen and argon/CH_4 flow, and deposition temperature on the wear behavior and wear durability of the DLC films. In addition, wear mechanisms of the DLC sample deposited with the optimum conditions are studied.

* Corresponding author.
E-mail address: mahboubi@aut.ac.ir (F. Mahboubi).

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Table 1
Design point combinations and the corresponding experimental responses.

DLC number	Hydrogen flow (sccm)	Argon/CH_4	Deposition temperature (°C)	Duty cycle (%)	Wear rate ($\times10^{-14}$ m^3/Nm)	Wear durability (m)	Hardness (GPa)
23	10	2	150	80	3.2	430	20.3
17	50	0	130	50	1.7	3100	18.9
5	40	0	60	80	291	500	8.7
7	20	1	90	50	4.2	1800	12.6
8	50	2	90	80	0.07	5500	30
22	50	0.5	150	80	1.8	1500	17.33
13	30	1	110	70	0.918	2000	17.4
20	10	0	150	60	1.51	800	14
6	0	1	60	80	88.3	300	10.6
19	30	2	150	50	941	15	19.5
12	0	2	110	60	52	3000	16.3
4	20	2	60	70	273	140	10
10	30	1	110	60	346	3500	22.05
18	0	1	150	50	0.78	4400	19
11	0	2	110	60	2.5	2800	20.13
16	0	0	110	80	7.9	300	10.56
2	50	2	60	50	717	220	11
3	50	0.5	60	60	50	90	7.5
15	30	1	110	70	0.8	1800	15.8
1	0	0	60	50	138	400	6.51
9	30	1	110	60	84	100	18.6
14	30	1	110	70	0.86	2100	18.6
21	50	2	150	60	280	150	13

2. Experimental method

To determine the optimal deposition conditions for the DLC films, response surface methodology (RSM) was used. In RSM, the response is influenced by several variables (deposition temperature, hydrogen flow, argon/CH_4 flow, and duty cycle[1] in this study) and the objective is to optimize the wear rate and wear durability of the DLC films. By using the RSM, the effects of individual parameters and the interaction of parameters on each response can be estimated [12,13]. In this study, Design-Expert 8.0.7 software was used for statistical analysis. The upper and lower limits of the deposition temperature, hydrogen flow, argon/CH_4 flow, and duty cycle were established after preliminary DLC deposition trials. The arrangements of all the design point combinations and their corresponding responses are shown in Table 1. Standard deviations for the hardness, wear rate, and wear durability were $15 \times E^{-3}$ GPa, $83 \times E^{-7}$ mm^3/Nm, and 862.4 m, respectively.

The substrates were nitrocarburized AISI 4140 steel in the form of 2-cm disks with 6 mm thickness. The samples were plasma nitrocarburized for 3 h at 550 °C in a gas mixture of nitrogen, hydrogen, and methane. Plasma nitrocarburizing substrate preparation is described in detail in our previous work [14]. As shown in Table 1, the DLC films were deposited on the nitrocarburized samples by using the pulsed DC PACVD method. Deposition frequency was kept constant at 8.5 kHz, and the applied voltage was changed from 320 to 450 V according to deposition temperature. In this study, deposition temperature was changed from 60 °C to 150 °C.

Atomic force microscopy (AFM) was used for studying roughness of the DLC samples. Chemical structure of the DLC films was characterized by micro-Raman spectroscopy using a Horiba system equipped with a 534-nm laser. The spectra were recorded at room temperature over a range of 0–3000 cm^{-1}. The typical D and G peaks in the Raman spectra of the DLC films were fitted to Gaussian curves using LabSpec 6 software to verify any changes in the local bonding structures. After fitting the Raman spectra with Gaussian function, the intensities of the G and D peaks were determined using Labspec6 software. Donnete et al. suggested that the ratio of the intensity of D peak to the intensity of G peak is related to the sp^2/sp^3 ratio [5]. Hydrogen content of the DLC films was calculated according to equation (1) [5]:

$$H\,[at\%] = 21.7 + 16.6\log(m/I_G\,[\mu m]) \quad (1)$$

Hardness of the DLC samples was calculated using a TriboScope system (Hysitron Inc., USA), equipped with a Cube corner-type indenter tip. The calibrated contact area function was achieved from indentation tests conducted on a fused quartz standard specimen. Five indentations were made on each DLC sample at random locations, and their average number was reported. The adhesion of the DLC films to the substrates was evaluated using Rockwell C indentation according to the VDI 3198 standard [15].

Wear rate of the DLC samples was analyzed using the pin-on-disk method. The pin was 5-mm-diameter AISI 52100 steel with a semispherical end of 3.1 mm radius. Unlubricated wear tests were performed with a normal load of 5 N, sliding speed of 0.1 m s^{-1}, and wear track radius of 6 mm at room temperature (30 °C) and relative humidity of about 35%. To study the wear behavior of the optimum DLC sample, the wear test was performed with a 10 N normal load by using a silicon carbide pin. This test was performed with a sliding speed of 0.13 m s^{-1}, sliding distance of 1000 m, and wear track radius of 8 mm at room temperature (30 °C) and relative humidity of about 35%. The wear durability was defined as the sliding distance after which the friction coefficient of the DLC films exceeded the value of friction coefficient of the plasma nitrocarburized layer (~0.7). Before each sliding process, both the treated samples and pin were cleaned with acetone to remove impurities. The wear volume and wear rate of the samples were calculated according to the ASTM G 99-04 standard [16].

3. Results and discussion

3.1. Wear rate

Fig. 1 a–c show plots of the effect of the A/C flow ratio and deposition temperature on the wear rate of the DLC films at different duty cycles and constant hydrogen flow. The figures show that the wear rate of the DLC samples decreased with an increase in the temperature from 60 °C to 110 °C and increased with a further increase in the deposition temperature from 110 °C to 150 °C. Wear rate of the materials depends not only on wear test condi-

[1] Duty cycle = $t_{on}/(t_{on} + t_{off}) \times 100\%$.