



Surface modification of 6150 steel substrates for the deposition of thick and adherent diamond-like carbon coatings

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ABSTRACT

Because of the high residual compressive stress normally accompanying the growth of diamond-like carbon (DLC) coatings and the large mismatch in the thermal expansion coefficient between DLC and steel, it is difficult to grow DLC coatings much thicker than 0.25 μm on steels. This paper describes our attempt to overcome this thickness limitation by a sequence of carbonitriding, carburizing and equilibration pre-treatments of the steel surface, followed by DLC coating deposition, all conducted within the same deposition system without breaking vacuum. These pre-treatments resulted in a surface with a graded composition and hardness profile. Such a graded interface is expected to reduce the interfacial energy, decrease thermal mismatch between the coating and the substrate, and thus improve coating adhesion. X-ray diffraction revealed the formation of various hard carbide and nitride phases. Raman spectroscopy showed that the modified steel surface just before DLC deposition exhibits local carbon bonding characteristics similar to DLC. Pulsed dc plasma-enhanced chemical vapor deposition was used to deposit one-micron thick DLC on these steel surfaces. The coating hardness was $\sim 18\text{--}19$ GPa. Its adhesion on the steel substrate was measured by scratch testing and was found to be comparable to thick, adherent DLC coatings deposited by other methods.

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1. Introduction

Diamond-like carbon (DLC) coatings have been widely studied in the last few decades due to their interesting properties such as high hardness, wear resistance, and low friction. Application examples include self-lubricating components [1], microelectromechanical devices [2], hard disks and read-write heads [3,4], and biomedical prosthetic implants [5]. DLC coatings can be produced by a variety of deposition methods, viz., magnetron sputtering [6], various forms of ion-assisted deposition, and chemical vapor deposition [7]. One problem with DLC is its high residual compressive stress on the order of several GPa [8–10]. Another problem is the difference in the thermal expansion coefficients of DLC ($\sim 1 \times 10^{-6}/\text{K}$) and steel ($\sim 11.8 \times 10^{-6} - 14.7 \times 10^{-6}/\text{K}$). These two factors limit the maximum coating thickness that can be grown on steels. Previous studies showed that the maximum DLC coating thickness is less than 0.25 μm on untreated steel surfaces [11]. Other studies demonstrated that thicker DLC coatings could be synthesized by incorporating inter-layers [12–15].

In this paper, we present results of our attempt to overcome this thickness limitation by subjecting the steel substrate to a series of pre-treatments prior to DLC deposition [16]. The intent of the pre-treatment is to produce a graded interface, beginning with the steel substrate, followed by a carbonitrided layer, then a carburized layer, and the final DLC coating. Such a graded interface decreases the interfacial free energy [17], thereby increasing the work of delamination and improving DLC coating adhesion [14]. In addition, the gradual transition from steel to DLC through an intermediate carbon-containing region reduces the thermal expansion coefficient mismatch at the DLC-substrate interface and thus the thermal stress. We therefore expect these pre-treatments to increase the thickness of DLC that can be grown on steels. A side benefit of the pre-treatment process is to produce a harder substrate, which increases the load-carrying capacity [18]. The major advantage of our approach is that all pre-treatment steps and coating deposition are conducted in the same chamber without breaking vacuum. In this work, we used a pulsed DC plasma-enhanced chemical vapor deposition system to perform the pre-treatments and DLC coating deposition.

2. Experimental

SAE 6150 steels after normalizing heat treatment were used as substrates for this work. The alloy composition is shown in Table 1. According to the manufacturer, the tensile strength of this steel after the normalizing heat treatment is 1.4 GPa. They were polished using

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Table 1
Chemical composition of the steel substrate (SAE 6150).

Element	C	Mn	P	S	Si	Cr	V
wt.%	0.48–0.55	0.65–0.9	<0.04	<0.04	0.20–0.35	0.50–1.10	0.1–0.15

standard metallographic techniques down to one-micron diamond paste and then degreased in an ultrasonic bath before introduction into the deposition chamber. All *in situ* surface pre-treatments and depositions were performed in a pulsed DC plasma-enhanced chemical vapor deposition system. The substrate was mounted on a water-cooled 50 mm diameter cathode, which was biased by an asymmetrical bipolar pulsed DC source, consisting of fixed positive pulse amplitude of 30 V followed by a variable negative pulse with peak amplitude ranging from -250 to -900 V at 20 kHz [7,13]. The substrate was first cleaned in an argon discharge for ten minutes. The surface treatment prior to DLC deposition involved four steps:

- (1) We subjected the steel substrate to a *carbonitriding* plasma treatment, in a 250 Pa mixture of methane, hydrogen and nitrogen (flow rate ratio of 5:15:80) at 475 °C for 2 h. The steel sample after this step will be labeled as CN1.
- (2) While keeping the total pressure and temperature constant, the relative flow rates were changed to methane:hydrogen:nitrogen = 15:5:80 (i.e., increasing the methane content at the expense of hydrogen). This step continued for 1 hour. The steel sample after these two steps will be labeled as CN2.
- (3) The gas mixture was changed to methane and hydrogen (flow rate ratio of 60:40), thus changing this to a *carburizing* treatment. This step was performed at 250 Pa and 475 °C for 0.5 h. The steel sample after these three steps will be labeled as CNC.
- (4) The total pressure and temperature were reduced to 40 Pa and 150 °C respectively, while keeping the methane/hydrogen ratio constant. This step continued for 1 h to thermally equilibrate the system. The steel sample after these three steps will be labeled as CNCE.

At the end of these four steps, DLC deposition followed, operating with pure methane at 40 Pa and 150 °C for 1.5 h. Pulsed DC power was applied throughout the four steps of surface treatment and coating deposition.

We used the Renishaw 2000 Raman system with an Ar-ion laser (wavelength = 514 nm) in the backscatter geometry to obtain Raman spectra of the surface after various surface treatments and deposition [19–21]. Spectral fitting of the G and D bands was performed using two Gaussian functions to obtain the I_D/I_G intensity ratio. X-ray diffraction (Philips PW1840) was used to analyze the carbide and nitride phases [18] formed by different surface pre-treatments. Hardness profiles perpendicular to the steel surface were obtained by micro- (UMIS) and nano-indentation (Hysitron Triboscope). Microstructure and chemical composition were obtained by scanning electron microscopy and energy-dispersive X-ray analysis (Hitachi S-3400 VP-SEM) respectively. The adhesion of the DLC coating was qualitatively determined by a scratch test (Micro Materials). In this test, a diamond Berkovich tip (radius of 8.8 μm) was slid across the sample at 1 $\mu\text{m/s}$. The load was increased at 1 mN/s until 300 mN and was kept at this maximum load for the remainder of the scratch. The onset of delamination and the length of the scratch track were determined by optical microscopy examination of the scratched surface. The vertical position of the tip and the friction coefficient were measured at the same time. The length of the scratch track and the load at which the tip undergoes sudden downward displacement due to coating delamination provide two estimates of the critical load for delamination, which is used as a relative measure of coating adhesion.

3. Results and discussion

3.1. X-ray diffraction and carbon concentration profile

Fig. 1 shows a series of X-ray diffraction patterns obtained from the as-received steel substrate, the same substrate subjected to the three pre-treatments described above, and after the deposition of a one-micron thick DLC coating. The as-received steel substrate shows the expected diffraction peaks at 44.6° and 64.9° [10]. Based on the comparison with standard powder diffraction patterns, one can conclude that various new phases, $(\text{Cr, Fe})_7\text{C}_3$, Fe_{2-3}N and Fe_5C_2 , emerge as a result of the carbonitriding and carburizing pre-treatments [7,22,23]. Fig. 2 shows the carbon concentration profile of the steel sample after the four pre-treatment steps and DLC coating deposition using cross-sectioned energy-dispersive X-ray analysis. Note the extent of carbon diffusion into the steel substrate – the carbon concentration is 3 wt.% at about 35 μm from the surface. Compared with the bulk carbon concentration of SAE 6150 steel (0.5 wt.%), this indicates the extensive carbon diffusion as a result of the pre-treatments.

3.2. Hardness profiles and diffusion

It is known that steels can be hardened by the addition of carbon or nitrogen [22,24]. To determine the effect on the hardness of the steel as a result of all these treatments, we performed a series of cross-sectioned hardness indentation measurements to determine the hardness profile. Fig. 3 shows the close-up of one such indent in the vicinity of the DLC coating. The result of these hardness measurements is shown in Fig. 4. The hardness varies from about 11 GPa just below the coating to about 5 GPa at 80 μm from the coating-substrate interface (compared with the substrate hardness of ~4 GPa). This hardening is likely due to the incorporation of carbon and nitrogen interstitials and the formation of hard phases such as Fe_{2-3}N , Fe_5C_2 , and $(\text{Cr, Fe})_7\text{C}_3$ as shown by X-ray diffraction.

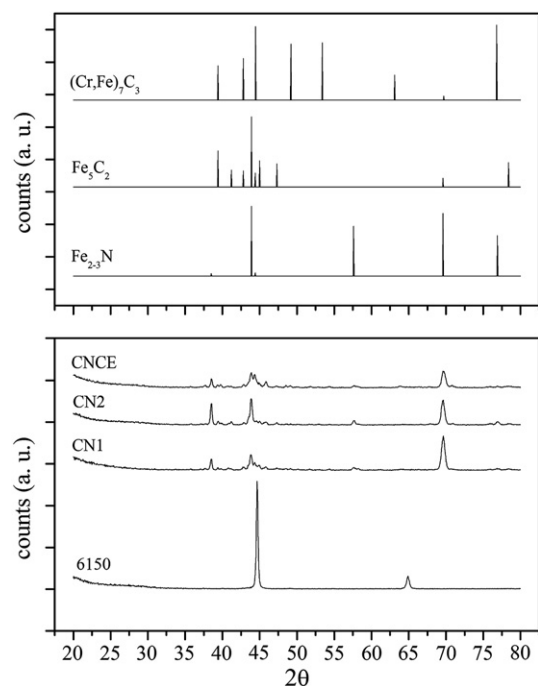


Fig. 1. X-ray diffraction patterns obtained from the as-received steel substrate, the same substrate subjected to three pre-treatments as described in the text, and after the deposition of a one-micron thick DLC coating, along with patterns from reference materials.

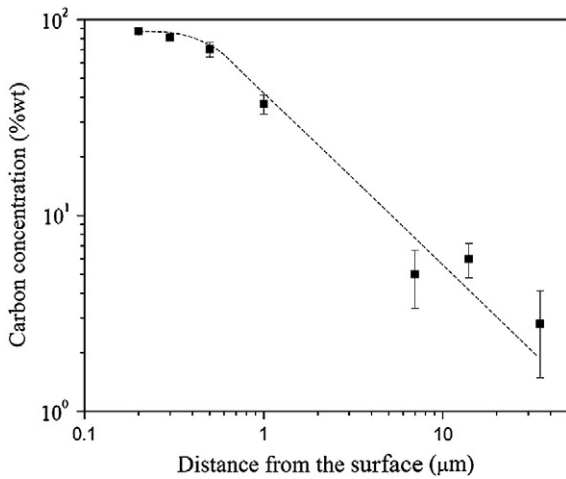


Fig. 2. Carbon concentration profile obtained by energy-dispersive X-ray analysis from the DLC-coated steel sample.

The extent of carbon diffusion can be corroborated by estimating the carbon diffusion distance at the pre-treatment temperature of 475 °C (748 °K) for 3.5 h. Here, we ignore carbon diffusion at the subsequent lower processing temperature of 150 °C. We write the diffusivity D in the standard form $D = D_0 \exp(-E/kT)$, where all symbols have their usual meanings. For carbon diffusing in bcc iron in our temperature range of interest, $D_0 = 6.2 \times 10^{-7} \text{ m}^2/\text{s}$ and $E = 8 \times 10^4 \text{ J/mol}$ [25]. At $T = 748^\circ\text{K}$, the diffusivity of carbon in bcc iron can be computed to be $1.59 \times 10^{-12} \text{ m}^2/\text{s}$. The diffusion distance ($=\sqrt{2Dt}$) after a diffusion time of 3.5 h ($= 1.26 \times 10^4 \text{ sec}$) is equal to $2.0 \times 10^{-4} \text{ m}$, or 200 μm . This is within a factor of 2–2.5 of the thickness of the hardened surface layer.

Fig. 5 shows the hardness of the untreated steel substrate, the same substrate after the second carbonitriding pre-treatment (CN2), and after equilibration (CNCE) at indentation loads from 50 to 150 mN. The steel substrate has a hardness of ~4 GPa (consistent with its tensile strength of 1.36 GPa). After the second carbonitriding pre-treatment (CN2), the hardness increases to ~11 GPa. The sample after equilibration (CNCE) has gone through the process of carbon and nitrogen diffusion and an equilibration step, resulting in the likely deposition of a thin transition DLC layer. The latter is inferred from the hardness variation as a function of indentation load, from 16 GPa at 50 mN to 12 GPa at 150 mN. As a reference, the hardness of the DLC coating was measured to be $18.4 \pm 1.6 \text{ GPa}$ after averaging over 20 indents, at applied loads between 0.3 and 2.0 mN, with contact depth equal to or less than 0.1 μm (10% coating thickness) [26–29].

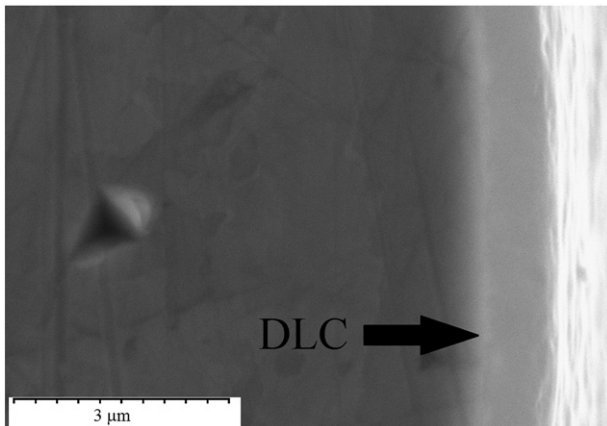


Fig. 3. SEM image showing an indent near the DLC-substrate interface.

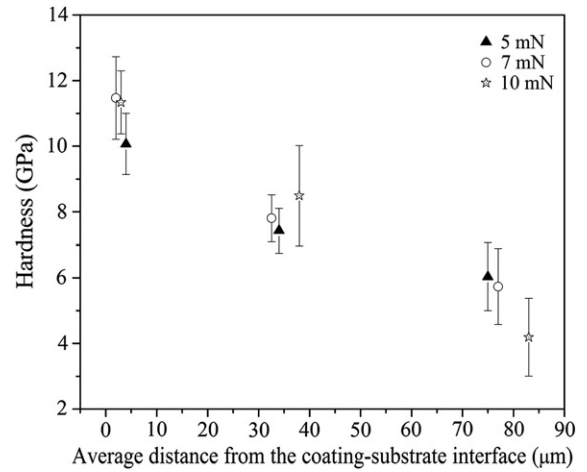


Fig. 4. Hardness profile of the DLC-coated steel sample.

3.3. Raman spectroscopy

Fig. 6 shows Raman spectra obtained from DLC and the steel sample after carbonitriding (CN1 and CN2) and after equilibration (CNCE). Table 2 compares the various characteristics associated with the D and G bands obtained from three steel samples and DLC. As the pre-treatment progresses, the D and G characteristics approach those of DLC. For example, the I_D/I_G ratio is 0.64 for sample CNCE, compared with 0.61 for DLC. This indicates that as a result of these pretreatments, the carbon bonding state evolves from one that is very different from DLC to one that is similar just prior to DLC deposition. This similarity may be an important factor in enhanced coating adhesion.

3.4. Scratch testing

Fig. 7 shows a SEM image of the scratch track from the initial point of scratch to the beginning of the delamination. The length of the scratch track was measured to be $119 \pm 6 \mu\text{m}$, corresponding to a critical load of $119 \pm 6 \text{ mN}$, since the experiment was performed at a sliding rate of 1 $\mu\text{m/s}$ and loading rate of 1 mN/s. Fig. 8 shows the diamond indenter depth, friction force, and friction coefficient during scratching. Both the indenter depth and friction force vary smoothly until the onset of delamination, at which a sudden downward displacement of the indenter occurs. The critical load was measured

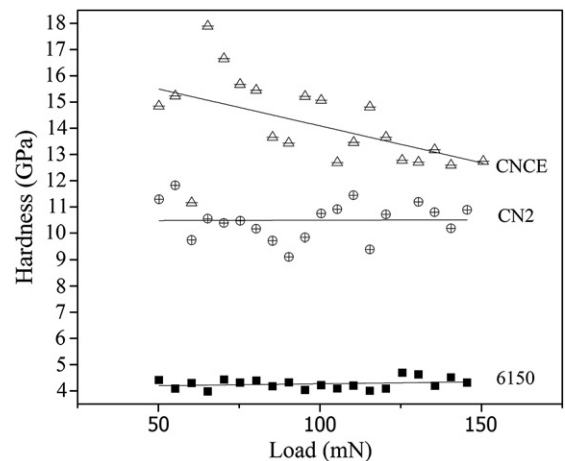


Fig. 5. Hardness of the untreated 6150 steel substrate, the same substrate after the second carbonitriding pre-treatment (CN2), and after equilibration (CNCE) as a function of indentation load.

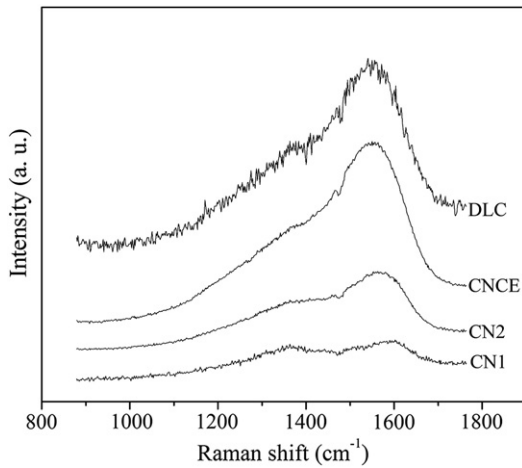


Fig. 6. Raman spectra obtained from the steel sample after carbonitriding (CN1 and CN2) and after equilibration (CNCE) and the DLC-coated steel.

to be 126 ± 6 mN, consistent with the scratch length measurement. The scratch experiment was repeated three times, and the average critical load for delamination was found to be 121 ± 6 mN. Assuming Hertzian contact and an elastic modulus of 180 GPa for the DLC coating, the shear and tensile stresses at this critical delamination load are ~ 6.3 and 2.7 GPa respectively. As a comparison, in the work of Mori and Tachikawa [16] using surface pre-treatment steps lasting more than 35 h, their three-micron thick DLC coating had a critical load of 50 N using a diamond indenter with 200-micron radius. The corresponding shear and tensile stresses at the critical delamination load can be shown to be ~ 5.9 and 2.5 GPa respectively. This indicates that the extensive pre-treatment process adopted by Mori and Tachikawa [16] produced DLC coatings with adhesion on steels similar to ours.

4. Conclusions

In an effort to increase the thickness of DLC coating that can be deposited on steels, we used a series of carbonitriding and carburizing steps to modify the composition of 6150 steel substrates, followed by DLC coating deposition. These pre-treatment steps resulted in a surface with a graded composition and hardness profile. X-ray diffraction showed the formation of various hard carbide and nitride phases due to such pre-treatments. The composition profile is consistent with the extent of carbon and nitrogen diffusion in bcc iron at the pre-treatment temperature. Raman spectroscopy showed that the modified steel surface just before DLC deposition exhibits local carbon bonding characteristics similar to DLC, thus promoting adhesion. Subsequent DLC deposition by the pulsed dc plasma chemical vapor deposition technique resulted in a one-micron thick coating with hardness ~ 18 – 19 GPa. The major advantage of our approach is that all pre-treatment steps and coating deposition are conducted in the same chamber without breaking vacuum. Adhesion of DLC coatings on 6150 steel deposited by this technique was measured by scratch testing and was found to be comparable to that

Table 2
Comparison of the D and G band characteristics between steel samples after different pre-treatments and DLC.

Sample	Band position (cm^{-1})		FWHM (cm^{-1})		I_D/I_G
	D	G	D	G	
CN1	1373.9	1586.4	269.2	122.0	1.02
CN2	1403.1	1573.6	329.0	125.2	0.85
CNCE	1392.8	1558.3	322.3	147.4	0.64
DLC	1391.7	1559.1	308.7	151.3	0.61

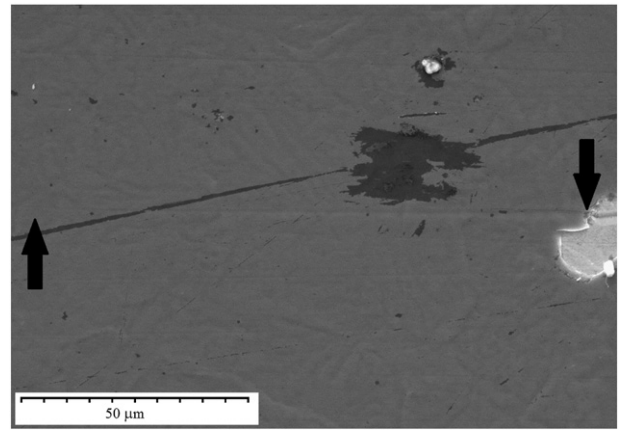


Fig. 7. SEM micrograph of a typical scratch track from the beginning to the onset of DLC coating delamination.

of other thick, adherent DLC coatings deposited via more extensive pre-treatments.

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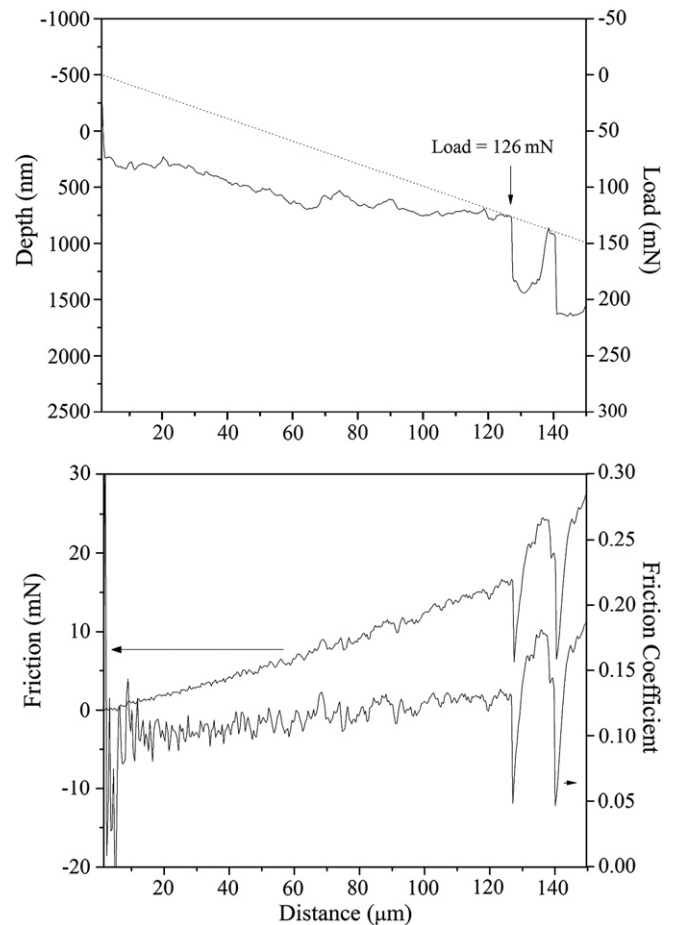


Fig. 8. Indenter depth, applied force, friction force, and friction coefficient during diamond scratch testing of one-micron thick DLC-coated steel. These plots correspond to the scratch shown in Fig. 7.

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