Impact of Thickness and Modulus on Adhesion of Diamond-like Carbon Coatings

PURDUE MATERIALS ENGINEERING

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Diamond-like carbon (DLC) coatings are a new environmentally friendly form of low-friction, high wear resistant, and self-lubricating solid material which could eliminate the need for grease-based lubrication in some applications. Certain DLC coatings can often adhere poorly to various substrates, so interlayers are sometimes used, such as silicon. However, some substrates still have poor adhesion to DLC at micron-level coating thicknesses even with the interlayer. The ratio of modulus to hardness, sp^2/sp^3 hybridization of the carbon in the coating, and surface morphology have all been found to be factors affecting adhesion.

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Project Background

DLC Background

- Hydrogenated Diamond-like carbon (DLC) consists of an amorphous carbon matrix of diamond-like sp^3 orbitals and graphite-like sp^2 orbitals, and includes hydrogen bonds embedded within the matrix.

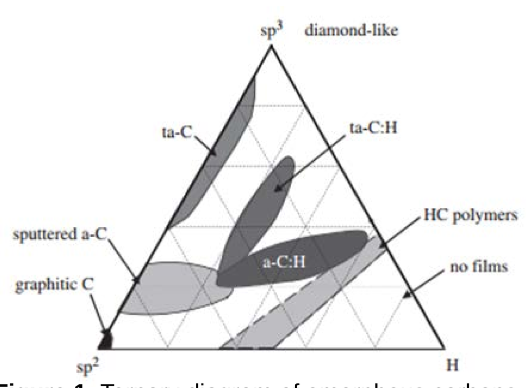

Figure 1. Ternary diagram of amorphous carbons

- DLC coatings are grown onto materials through Plasma Assisted Chemical Vapor Deposition (PACVD). The material was put into a vacuum chamber where it was sputter cleaned, nitrided and then coated with a silicon interlayer. Finally a carbon-rich gas was introduced into the chamber and ignited into a plasma to deposit a DLC coating.

Objective

- To investigate the relationships between coating thickness, modulus, hardness, hybridization, and surface morphology to DLC adhesion

Experimental Procedure

Samples

- Four thicknesses of DLC coating were grown onto five different substrates with a silicon interlayer. These five substrates included 17-4PH steel, 13-8PH steel, I-718, D2 and P20. The thicknesses were analyzed to determine an optimal DLC coating process.

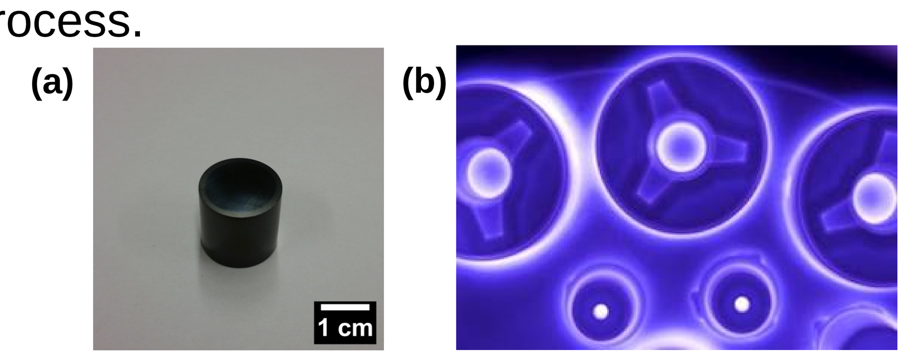

Figure 2. Images of **(a)** the 17-4PH DLC coated sample and **(b)** an IBC product glowing during PACVD process

Raman Spectroscopy (HORIBA Scientific T64000)

- 514nm laser centered at 1400nm
- Raman shift collected at the range 1164 -1614 cm^{-1}

AFM (Dimension 5000)

- Surface roughness and morphology analyzed

Scratch Testing (Hysitron TI-950 TriboIndenter)

- Adhesion failure identified through inconsistencies in the scratch graphs and quantified through micrographs of the scratches
- 3 distance controlled scratches of length 10 μm for each substrate
- 5 μm conical tip with a high load head

Nanoindentation (Hysitron TI-950 TriboIndenter)

- Nine indents performed on each sample with a Birkovich diamond tip attached to a high-load head
- Partial loading and unloading program used to penetrate to a maximum depth of 500 nm Beta 1 samples and 1500 nm for Beta 2-4 samples

Results & Discussion

Raman Spectroscopy

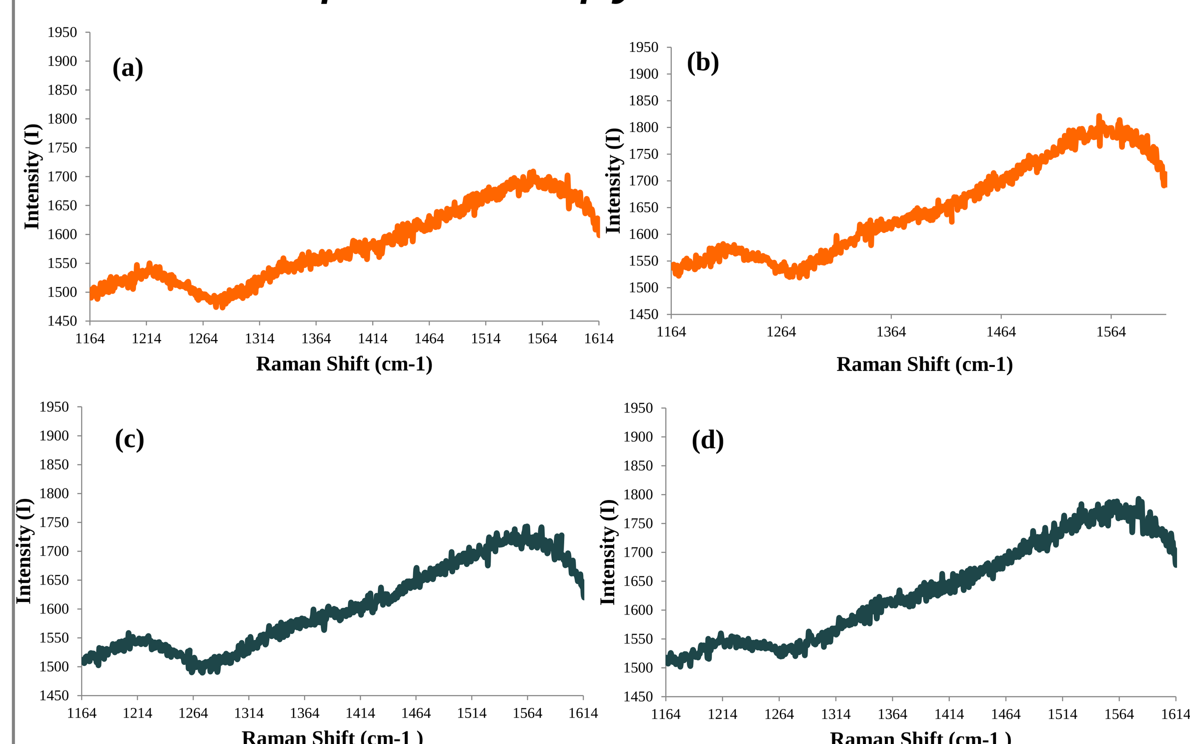

Figure 3. Raman Spectra data from **(a)** Beta-1 17-4PH) and **(b)** Beta-4(17-4PH) **(c)** Beta-1 (13-8PH) **(d)** Beta-4 (13-8PH) steel. The sp^3 diamond content decreased with increasing coating thickness from Beta 1 to 4

Raman spectrum of two DLC samples (17-4PH & 13-8PH) indicates a compositional range of 35-45% for the sp^3 content using the peaks intensities ratio I(D)/I(G). Limitations in the Raman shift range in the T64000 during scanning are reflected in data collection as only differences between spectrums were considered with I(D)/I(G) of 0.86 indicating higher Sp^3 content than (0.9). High-low designation is applied. In Figure 3 increased Beta 4 coating thicknesses in both (b) and (d) compared to Beta 1 in (a) and (c) indicates a lower sp^3 content and higher G dispersion as can be seen in Table 1. Beta 2 samples overall have the highest diamond content and 13-8PH have higher sp^3 content in both Beta 2 and Beta 3 thicknesses.

Table 1. I(D)/I(G) intensity ratios of 17-4PH & 13-8PH samples using limited spectra Raman shift where H designate high sp^3 content and L lower Sp^3 content

I(D)/I(G)				
Sample	Beta 1	Beta 2	Beta 3	Beta 4
17-4PH	0.9 (L)	0.87	0.9 (L)	0.88
13-8PH	0.9 (L)	0.86 (H)	0.88	0.88

Atomic Force Microscopy (AFM)

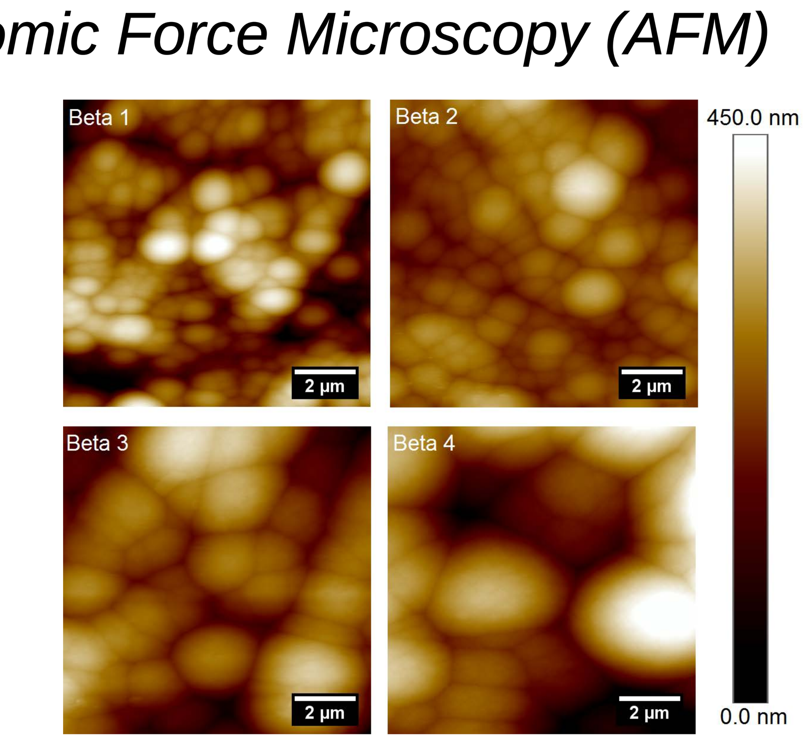

Figure 4. Representative AFM images from all 13-8PH samples. Images have been edited to remove streaking

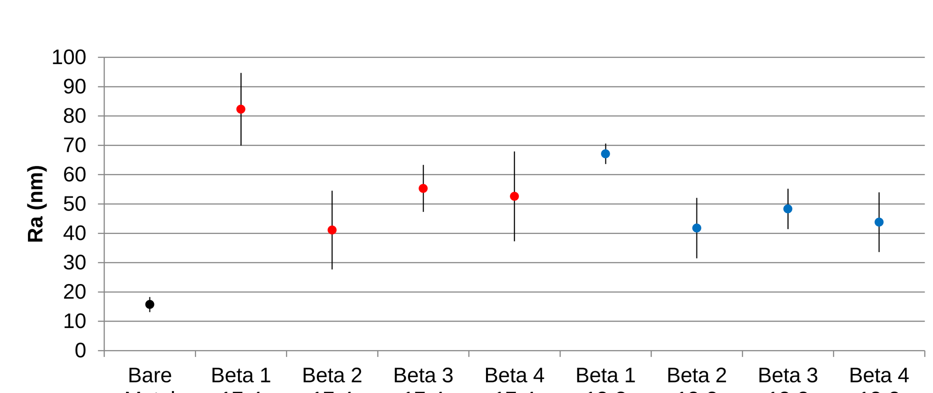

Figure 5. Average Ra values for a delaminated surface, 17-4PH, and 13-8PH samples with a 95% confidence interval (n=10 for delaminated surface, n=8 for 17-4PH and 13-8PH)

As the thickness of the coating increased, the diameters of nodules on the sample surface also increased as shown in Figure 4. Both 17-4PH and 13-8PH followed the same trends. As the DLC nucleates on the surface, it undergoes the Stranksi-Krastanov (S-K) growth mode. The coating begins as a layer, then builds up into islands that coalesce when more DLC is added. This coalescence is seen particularly in the Beta 4 samples. It was also found that the smallest coating thickness resulted in the roughest samples (highest Ra value). The trends found from the Ra values match those of the Raman spectroscopy, though there are larger variations in the Ra data due to surface finish.

Scratch Adhesion

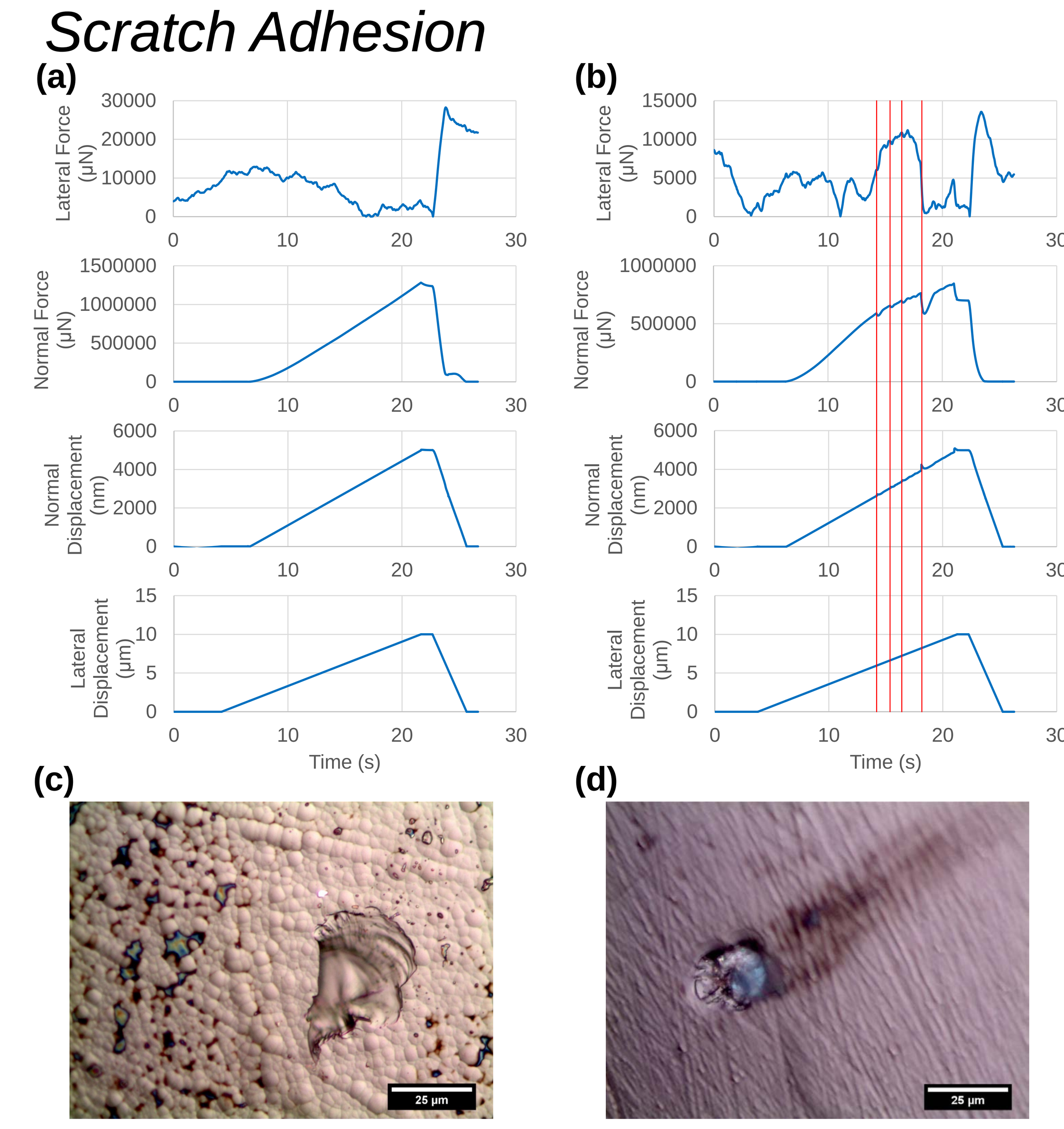

Figure 6. Scratch adhesion data from Steel 17-4PH **(a)** Beta 4 and **(b)** Beta 2, along with their corresponding micrographs **(c)** and **(d)**, respectively. Red lines were placed to quantify adhesion failures through inconsistencies in the data set.

Scratch tests were performed in a displacement controlled function instead of load control due to nonlinear load control during testing. Because of the programming in the machine during the displacement controlled function, the tip went to the desired displacement and then quickly retreated to the start point causing partial delamination. Therefore, adhesion failure will mainly be quantified through inconsistencies within the graphs before the tip starts to retreat. Beta 1 and 2 showed signs of adhesion failure, while 3 and 4 did not. Red lines were placed on Beta 2 data set in Figure 6.b to highlight concurrent inconsistencies throughout the graphs.

Nanoindentation

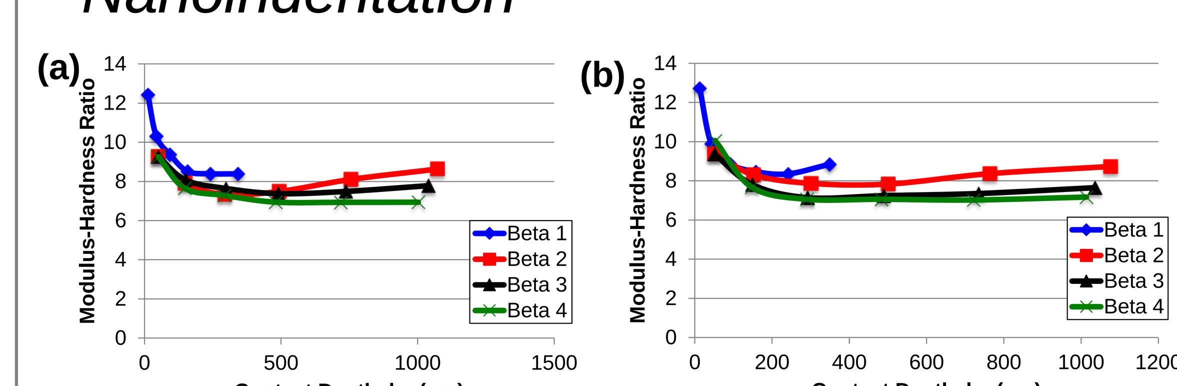

Figure 7. Nanoindentation data from **(a)** 17-4PH steel and **(b)** 13-8PH steel. The modulus and hardness ratios decrease with increasing coating thickness.

Table 2. Modulus of samples from nanoindentation testing with a 95% confidence interval

Modulus (GPa)				
Sample	Beta 1	Beta 2	Beta 3	Beta 4
17-4PH	92±13.5	95.9±4.4	90±3.2	74±4.5
13-8PH	92.8±14.1	96.4±6.4	86.1±4.4	81.2±4.3

Table 3. Hardness of samples from nanoindentation testing with a 95% confidence interval

Hardness (GPa)				
Sample	Beta 1	Beta 2	Beta 3	Beta 4
17-4PH	10.8±1.3	11.8±0.9	11.6±0.4	10.7±1.1
13-8PH	10.9±2.2	11.5±1.2	11.2±1.2	11.3±1.1

The values for modulus and hardness followed the same trend as the thickness increased. Both increased from Beta 1 to Beta 2 but then decreased in Beta 3 and Beta 4 as shown in the modulus and hardness tables. The values used in Tables 2 and 3 were taken at a depth that was 10% of the coating thickness. The modulus to hardness ratio also increased and then decreased as illustrated in Figure 7a and 7b. The lower values in higher thickness coatings are due to the lower sp^3 content found through Raman spectroscopy. More sp^2 content appeared in the coating during the growth process which is shown through the large nodule sizes in thicker coatings from AFM testing. That sp^2 content contributes to lower modulus and hardness values in the Beta 3 and Beta 4 samples.

Conclusion & Recommendations

Beta 3 coatings are the best candidate for dry lubricant applications due to their lack of failure during scratch adhesion and intermediate roughness and sp^3 content. Beta 2 has the highest sp^3 content and hardness, but Beta 3 adheres better to the substrates. In the future, we recommend investigating a set with a thickness range of 7-10 μm to achieve the best properties of both coatings. We also recommend using XPS to confirm hybridization and REELS to confirm hydrogen content. It would be beneficial to cut cross-sections of the samples and analyze any interlayer interactions along with quantifying the actual thickness of the DLC coating as well. Curvature measurements should be taken before and after the PACVD process to measure residual stress. If scratch adhesion is performed again, longer scratches should be made.

References

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