Technical Bulletin

Issue Date: January, 2008

The Hard Carbon Coating

Subject: Carbon Raptor® PACVD vs. PVD film properties

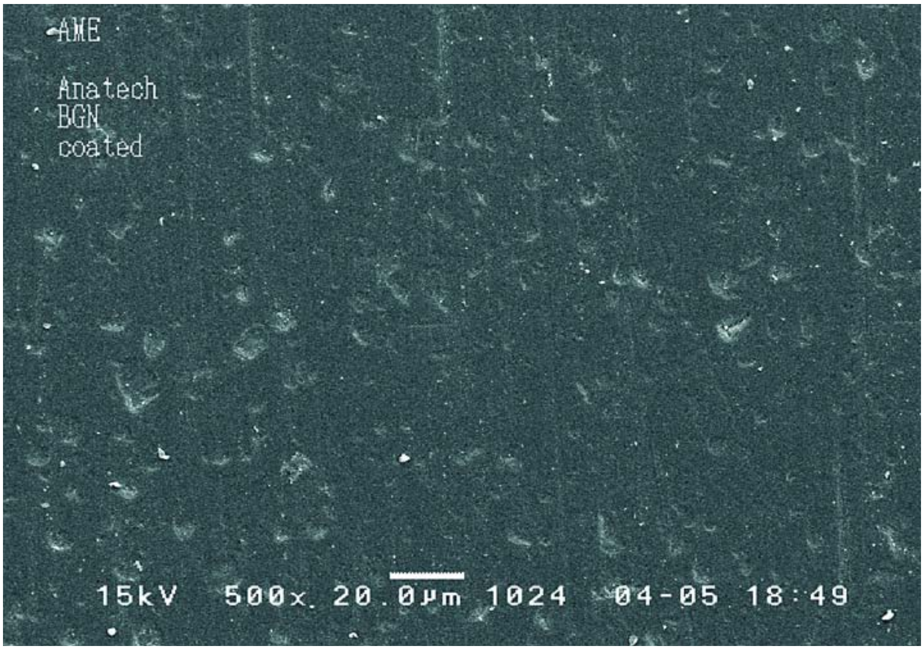

Figure 1. Carbon Raptor on the Nationwide^{tm} sample at 500x. Carbon Raptor is very smooth over much of the area and shows pits and some scratches due to use of the part in an engine over 1100 miles. This is typical of a PACVD film. Carbon Raptor's even wear is attributed to its lack of grain structure, since there are no grains to pull out of the film during use. The film is characterized by tightly chemically and energetically bonded orthogonal Carbon.

Overview of the Process:

There are several technologies that can be used to deposit thin films. Within these technologies, there are ranges of recipes that result in different films with different properties. This bulletin describes the film properties for Anatech's Carbon Raptor and a DLC PVD coating. Differences in results between the two technologies are evidenced here.

Carbon Raptor is deposited by Plasma Assisted Chemical Vapor Deposition (PACVD). PACVD is a vacuum based process. Precursor gases are introduced to a vacuum chamber in which they are cracked into a plasma, the fourth state of matter, which are condensed into a solid onto the substrate surface with an assist by a plasma bias and by a temperature differential between the substrate surface and the plasma. Adherence to the substrate is a function of chemical and mechanical bonding. Energy at the surface of the substrate is closely controlled with plasma assist.

The other coating is deposited by Physical Vapor Deposition, or PVD. PVD is a vacuum based process. Gas is introduced into a vacuum chamber which is ionized into a plasma. This plasma contains energetic ions which have enough energy to physically dislodge solid particles of a target material and accelerate these particles toward a substrate. Particles arrive with varying energies, which are not controlled as precisely as with PACVD resulting in inclusion formation and loosely adhered particles. Furthermore, PVD is characterized by columnar growth, that is, particles form in islands that then grow vertically. It is a challenge to join columns to get uniform film growth without cracks and voids.

Anatech Ltd. has over 5,000 PVD systems in the field. Some are very technically sophisticated, however, the company believes that film growth for best performance in DLC applications is with PACVD technology, as PVD shortcomings cannot all be overcome with such a light element as Carbon.

Background:

Analyses of Anatech's Carbon Raptor were performed on a steel Nationwide^{tm} wrist pin that had seen 1100 miles of use, and on a new, unused wrist pin. Analyses of the other film were done on the barrel of a new, unused flat tappet lifter. A third party independent laboratory that specializes in surface, interface, thin film, coating and other materials evaluations performed all testing and analysis, which include X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). This bulletin reports excerpts from those analyses.

Anatech's Cabron Raptor® on a used Nationwide^{tm} wrist pin

X-ray Photoelectron Spectroscopy (XPS) Analysis:

Depth profiles indicate that Carbon Raptor consists of three similar layers. The innermost layer is approximately 30% Silicon and 70% Carbon. Silicon is used to chemically bond to the substrate, as Silicon has an affinity for most materials. The intermediate layer is approximately 10% Silicon and 90% Carbon. The outermost layer is nearly 100% Carbon.

Carbon Raptor is characterized by tightly chemically and energetically bonded orthogonal Carbon.

Wear characteristics occur when force on the film is great enough to overcome chemical and energetic bonds, and planes of Carbon slip from adjacent planes. This structure explains why Carbon Raptor is an excellent heat transfer medium.

Scanning Electron Microscopy [SEM] Analysis:

The Carbon Raptor coating on the Nationwide sample is relatively smooth at lower magnification, except where worn, as shown in Figure 1. Some light scratching in the direction of the cylinder length is also visible. Both the pits and the scratches are due to the use of this part in an engine for 1100 miles.

Higher magnification reveals the size and irregular shape of the pits, and further that the pits seem to contain some additional debris, as seen in Figure 2. However, no grain structure such as that seen in the PVD DLC sample was present in the Nationwide sample, as between pits and scratches the surface remained smooth in appearance, even at 7000x magnification. The grain size is exceedingly small, so there is little long-range order in the Carbon Raptor DLC.

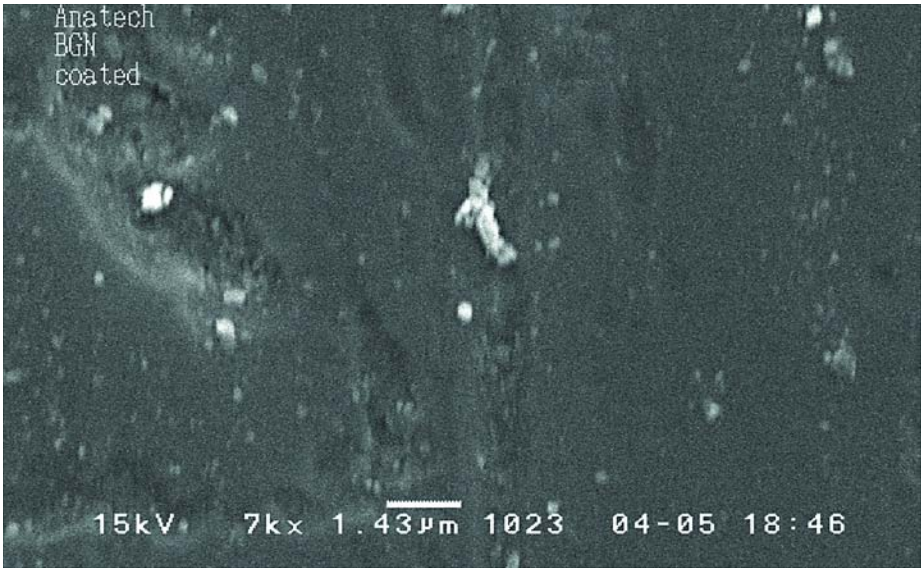

Figure 2. Carbon Raptor on the Nationwide sample at 7000x. Pits are irregular in shape, and there is debris present in and around the pits. Carbon Raptor is very smooth over much of the area and shows pits and some scratches due to use of the part in an engine over 1100 miles. The surface is otherwise smooth as contrasted with the PVD DLC.

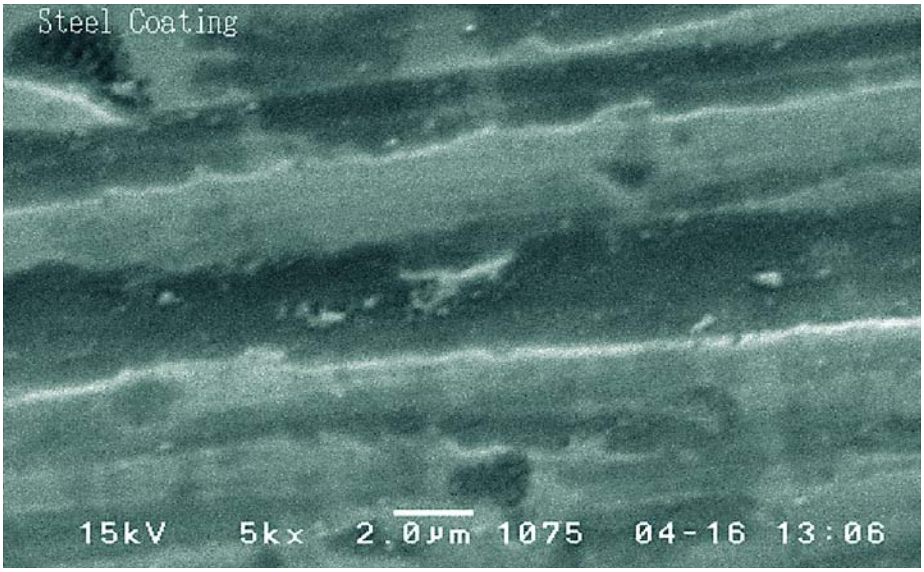

Figure 3. Carbon Raptor on a new, unused steel sample at 5000x. Edges of the scratches are rounded, showing that they exist in the substrate surface, and that Carbon Raptor covers them conformally. Conformal coverage is typical of a PACVD deposited film. No grain structure such as that seen in the PVD DLC is present here. This is an attribute of Carbon Raptor's microcrystalline graphite with C–H bonding, that is, tightly chemically and energetically bonded, laterally overlaid, orthogonal Carbon.

PVD DLC on a new, unused flat tappet lifter barrel

Depth profiles reveal a five layer system of dissimilar layers. The inner layers are oxides, nitrides and carbides. The outer layer is DLC. This structure explains why the PVD DLC film is an excellent heat barrier. The morphology of this surface includes many peaks and valleys of changing size.

These features translate through the depth of the film, as large grains of DLC, up to 1.6 microns, distributed unevenly along the edges of peaks and valley and edges of circumferential cracks. These grains sometimes extended the full depth of the coating, leading to a potential defect situation where an entire grain could be pulled from the coating, leaving a substantial hole.

As we shall see below in Scanning Electron Microscopy (SEM) Analysis, this film formation has shortcomings due to differential cooling of layers, which can propagate cracks radially through the entire depth of the film, and due to growth plate defects, a typical PVD process attribute. Wear char-acteristics occur when force on the film is great enough to overcome chemical and energetic bonds, and grains pull from the film.

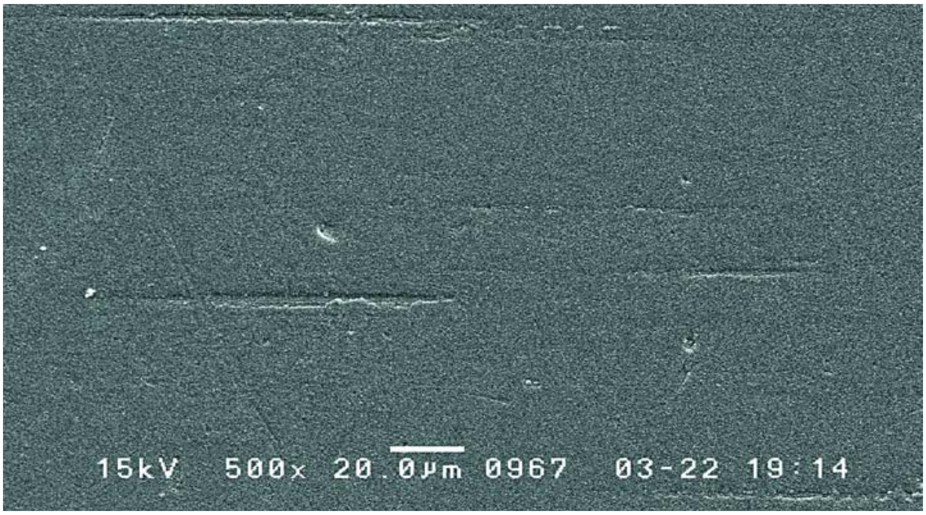

Figure 4. PVD DLC at 500x on a new, unused lifter, seems relatively smooth, with some radial cracks and a few pits. The origin of the cracks may be due to differential cooling of dissimilar layers that have different coefficients of expansion.

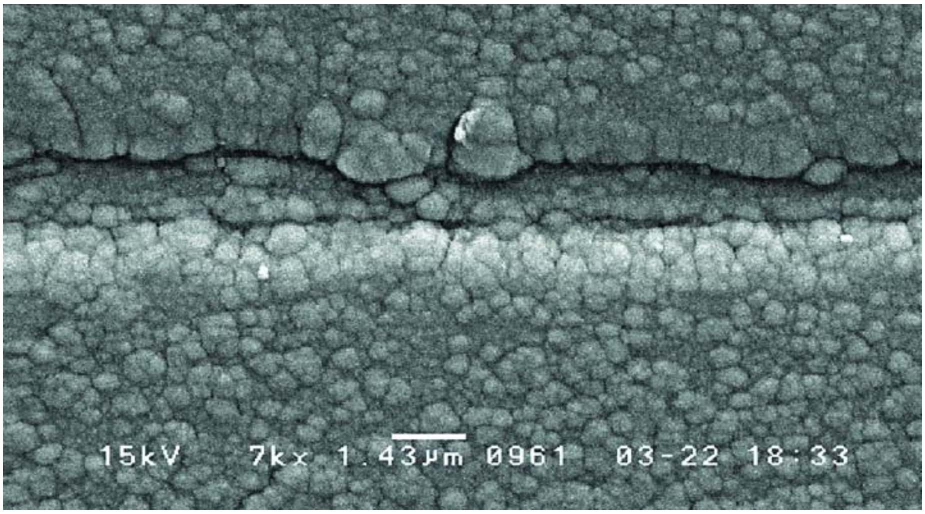

Figure 5. PVD DLC at 7000x. Crystalline grain structures ranging from 0.1-1.6 mm are present on the surface. The crack is caused by growth plate defects formed during coating, as grains are seen on the exposed walls of the crack. This can be a typical PVD shortcoming. When a 1.6 mm grain rips from a 2 to a 4 mm thick film during use, it will look as though the film was gouged at that point and down the path of applied force.

Examples of the PVD DLC surface are shown below. The coating appears to be relatively smooth at lower magnification, as shown in Figure 4, however, some radial cracks and a few pits are visible. Higher magnification reveals a significant amount of structure as seen in Figure 5. Grain structure is visible at 7000x and consists of grains ranging in size from roughly 0.1 mm to 1.6 mm in diameter lateral to the surface and elongated by a measure of columnar growth, as judged by the grains at the crack edges. Cracks are related to growth plate defects formed during coating, a typical Physical Vapor Deposition (PVD) shortcoming. Support for the growth plate conclusion comes from the fact that additional crystalline growth is apparent inside the cracks, possibly from previously formed layers, such as a seed layer. Some cracks may be due to differential cooling of dissimilar layers that have different coefficients of expansion. Support for the differential cooling conclusion is presented in the topographical cross section micrographs, where it is shown that at least some cracks extend from the coating surface fully through the coating to the metal interface.

Tangential cross section views of the PVD DLC sample are shown in Figure 6 and Figure 7. A change in texture from the area close to the metal/DLC interface to the coating surface suggests a transition within the coating that probably plays a role in the bonding of the coating to the substrate. The substrate surface is still clearly delineated, however.

Radial cracks seen in the surface Scanning Electron Microscope (SEM) images, probably associated with differential cooling, can be seen in Figure 7 to extend through the full thickness of the coating to the metal surface.

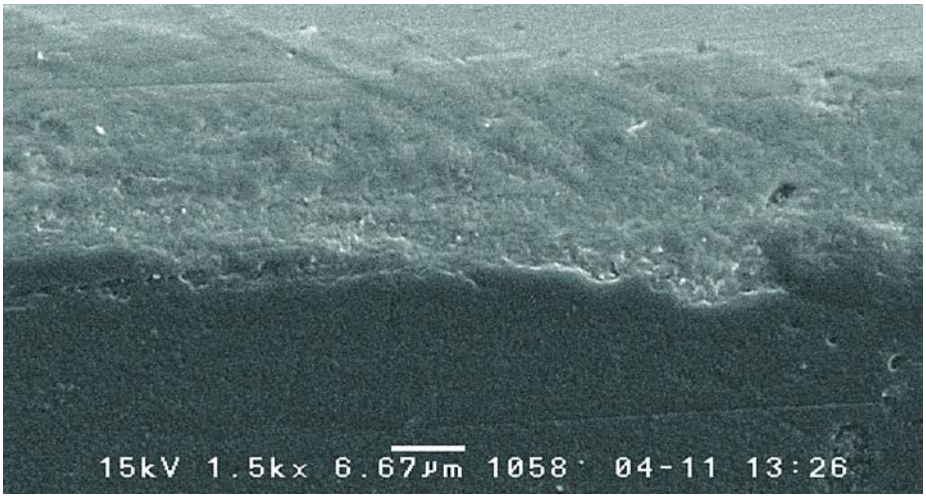

Figure 6. Tangential Cross Section (TCS) view of the PVD DLC coating. A change in texture occurs between the substrate /coating interface and the coating surface. The unpolished coating surface is at the bottom of the image. The center band is the polished coating, and the polished substrate is at the top. The thinner outer part of the coating in cross section has a different texture compared to the inner part.

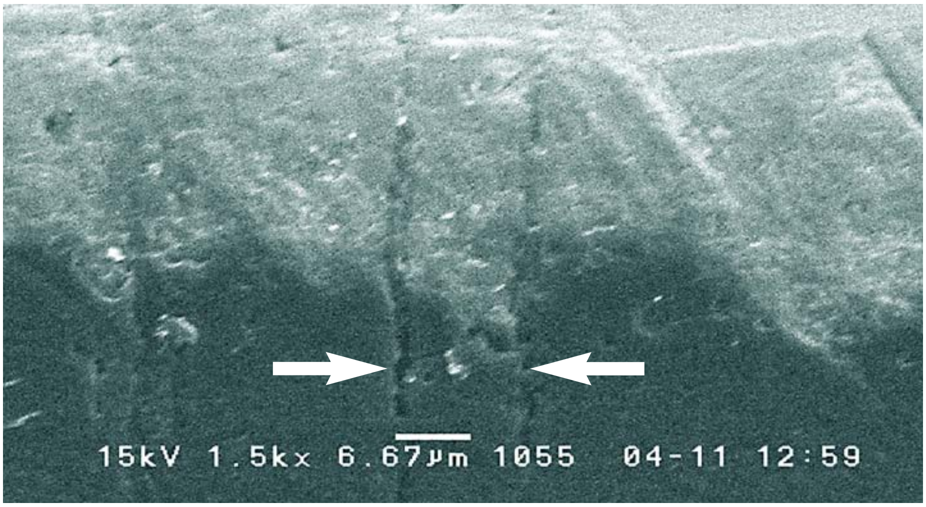

Figure 7. Cracks seen in the surface of the PVD coating (at bottom) extend through the full thickness to the substrate interface (cracks are indicated by arrows). Radial cracks are associated with differential layer cooling, as they extend through the full thickness of the coating to the metal surface and have no grains deposited within them.

Conclusions:

Homogeneity:

Carbon Raptor® DLC forms in conformal, continuous, tightly chemically and energetically bonded, similar layers. The PVD DLC is formed in dissimilar layers with varying textures and grain sizes. Only the top layer is DLC. The balance of the film is nitrides and carbides.

Cracks:

Carbon Raptor DLC has none. The PVD film cracks between layers, from the top of the coating to the substrate, and along the top layer.

Wear:

Carbon Raptor wears in a planar fashion, hexagonal layer by hexagonal layer, forming shallow pits. The PVD film wears by eroding the columnar structure of the PVD deposited film, pulling particles as large as 1.6 microns from the film.

Thermal:

Carbon Raptor is a heat transfer film. The PVD DLC is a heat barrier.

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