

Investigation of PVD-DLC Thin Films Manufactured Using HIPIMS Etch / Unbalanced Magnetron Sputter (UBM) Deposition and Secondary Mechano-Chemical Modification

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PVD diamond-like-carbon (DLC) coatings are finding increasing industrial acceptance in automotive, aerospace and medical applications due to their reduced friction and low wear coefficient. Very recently, High Power Impulse Magnetron Sputter (HIPIMS) sources have been shown to produce fluxes with very high metal ion fractions similar to those produced by arc evaporation sources, without showing excessive heating and droplet formation characteristics. These new source properties now enable industrial-scale low temperature operation, low roughness and high efficiency etching of the substrate prior to deposition to deliver enhanced adhesion. In this paper, we report on the properties and performance of HIPIMS-etched titanium-containing DLC (Me-DLC) and metal-free (graphite-based) C-DLC films deposited at temperatures below 160°C.

Keywords: *Diamond-like carbon, high-power impulse magnetron sputtering, mechano-chemical surface modification*

Introduction

First examinations into the deposition and characterization of diamond-like-carbon (DLC) coatings were published by various European universities and corporate research institutions during the 1980s and both commercial and academic investigations continue to the present day.¹⁻⁶ The principal reasons for the use of DLC films stems from their superior tribological performance through excellent sliding wear coefficients, very low friction coefficients and the ability to be deposited at relatively low substrate temperatures. Industrial applications include cutting and forming tools, bearings, gears, fuel injectors, medical and dental components, as well as decorative finishes. For automotive and aerospace applications, DLC films may be utilized to reduce frictional forces. This allows component weight to be reduced while enhancing the wear resistance of the surface, leading to wider application of lighter materials such as titanium and aluminum alloys. Such films

enable smaller dimensional designs, lowered energy consumption, increased component lifetime and the use of cheaper substrate materials.

Several types of hydrogen-containing DLC films are in existence today. Metal-containing DLC films (also known through the acronyms Me-DLC or a-C:H:Me coatings) are most commonly produced through sputter deposition in high flow reactive gas atmospheres, comprised of inert and hydrocarbon gases where poisoning of a metal or metal carbide target surface is utilized.^{7,8} More recently, sputtered DLC coatings without metal content (known as C-DLC or a-C:H) have been introduced where metal targets are typically replaced by graphite.⁹ Such films can exhibit significantly higher coating hardness over Me-DLC films and hence improved sliding wear behavior may be coupled with increased residual stress and significantly reduced adhesion and cohesion.

The use of energetic metal ion bombardment of a surface, causing shallow ion implantation into the near-surface region of the substrate, has been shown to improve the adhesion of PVD films significantly, and at elevated temperatures, promote localized epitaxial film growth.¹⁰⁻¹² In this article, we present results which characterize the properties and deposition conditions of production scale, low temperature reactive unbalanced magnetron sputtered Me-DLC and C-DLC films deposited on steel substrates which

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have been *in-situ* metal ion etched prior to deposition using a novel chromium HIPIMS cathode at low temperature and without excessive surface roughening.

The surface of Me-DLC films have been further modified by a secondary mechano-chemical method. Mechanical processing using high pressure and high shear deformation ball milling can be used to create surface films or change the atomic structure of existing layers.^{13,14} We have used such a novel approach to deposit multi-functional secondary carbon-based lubricant surface layers. Mechano-chemical processing of DLC-coated specimens in an oxygen-free environment is discussed. Variation of critical process parameters has been undertaken to provide differing impact forces and shear angles for mechanical processing.

Experimental

Me-DLC and C-DLC films were deposited in a commercially available industrial scale combined HIPIMS / UBM sputter chamber (Fig. 1). The 1250-mm diameter chamber was equipped with three vertically mounted rectangular targets for unbalanced magnetron (UBM) sputtering and one rectangular target used for HIPIMS. Permanent magnet arrays, fitted with a motorized drive to enable stable control of the cathode voltage by variation of the magnet withdrawal distance as a function of target life, were located behind each cathode. Unbalancing and closed field linking was attained by adjustment of the current to coils surrounding each permanent array. All UBM cathodes were powered by individual DC supplies capable of delivering up to 30 kW. The HIPIMS source utilized an Advanced Converters HMP 2/4 unit with peak power capability up to 8 MW at 2 kV with arc suppression. Within the chamber, a

three-fold rotation substrate table capable of holding a maximum substrate load of 800 kg could be DC-biased with voltage from 0 to 1200 V. In the center of the chamber, a cylindrical anode over 1.0 m in length, was located, capable of independent positive biasing to a maximum of +200V for enhancement of the plasma density at the substrate. High rate chamber pumping was accomplished with three 1600 L/sec turbomolecular pumps, backed by a rotary vane and Roots pump. Radiant heater arrays within both doors could be used to elevate the substrate temperature and remove water vapor ($T_{\max} = 200^{\circ}\text{C}$) in combination with a Meissner cold trap. The base pressure of the system was below 1×10^{-5} mbar.

The target arrangements used to produce both Me-DLC and C-DLC films are shown in Fig. 2.

Etching was carried out in an inert atmosphere (argon). Sputter deposition was carried out in a mixed inert gas + reactive gas discharge using N_2 or C_2H_2 and varying the reactive gas flow while maintaining constant working gas flow. The substrates chosen for the experiments were ground and polished M42 high speed steel coupons and 304 austenitic stainless steel sections, each cleaned in a series of aqueous and acetone baths with ultrasonic agitation.

Following substrate heating and outgassing, all targets were sputter-cleaned in an inert gas atmosphere behind shutters to prevent contamination of the substrate surfaces. Following target cleaning, the substrates were sputter-cleaned by unbalanced magnetron enhanced glow discharge etching with high substrate bias voltage maintained for 20 min. HIPIMS etching was initiated following glow-discharge etch and prior to coating using chromium as the metal source at a constant frequency of 500 Hz, a discharge power of 5 kW, a 100 μsec pulse duration, a bias voltage of -1000 V and a pressure of 1.8×10^{-3} mbar.



Figure 1—Me-DLC and C-DLC coating chamber line at the Richter Precision Inc, East Petersburg, Pennsylvania facility.

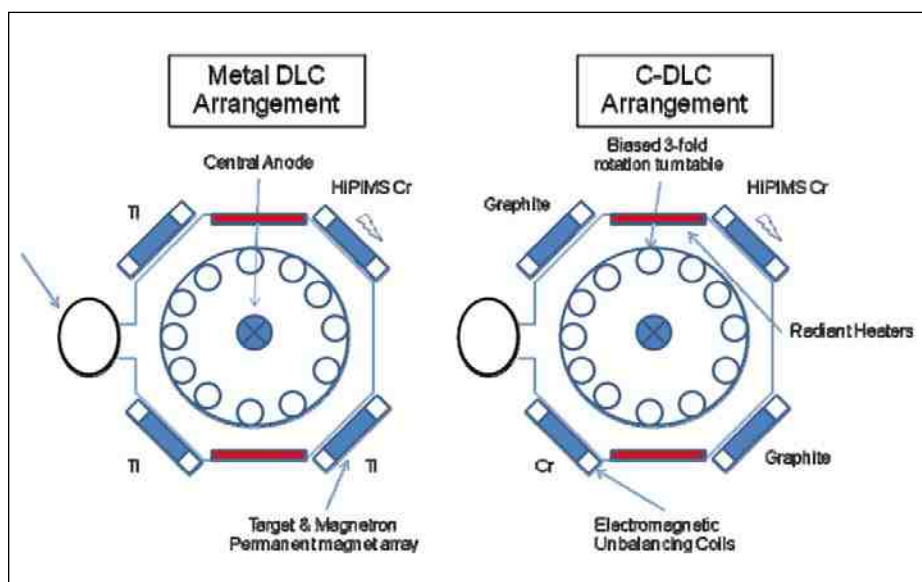


Figure 2—Schematic diagram of the chamber arrangement for etch and DLC film deposition.

Me-DLC film architecture (Fig. 3a) consisted of an adhesion promoting layer followed by a wear-resistant Ti_xC_y intermediate layer generated through the introduction of acetylene gas. Towards the end of the coating cycle, the C_2H_2 flow rate was further increased to produce greater target poisoning and strongly increase the C:Me ratio within the film. The temperature during coating was typically held at 160°C .

The C-DLC film architecture (Fig. 3b) consisted of a simultaneous UBM/HIPIMS sputtered pure chromium metal adhesion layer followed by the ramped introduction of nitrogen reactive gas to the plasma to generate a dense CrN interlayer. Once the initial interlayer deposition was completed, the HIPIMS cathode was switched off and shuttered. The third stage of the architecture was comprised of a high bias C-Cr secondary interlayer where power to a chromium cathode was ramped down while the power on the opposing UBM graphite targets was simultaneously increased in a pure argon atmosphere. Upon completion of the chromium target power

ramp down, the target was shuttered. Graphite targets continued to be sputtered while a reduced flow of C_2H_2 gas was introduced into the plasma, bias voltage was raised and coil current was increased to provide higher plasma density at the substrate. The temperature during carbon deposition was typically 140°C .

Mechano-chemical coating deposition was carried out using a specially designed vibratory ball mill with an adjustable vial amplitude of 0 to 4 mm at a frequency of 50 Hz. The ball mill vials used for the modification process were specially designed for this project. The vials had a volume of 100 mL and were filled with steel ball bearings with a distribution of diameters in the range of 2 to 10 mm and 8 to 15 mm. Selection of the correct ball size distribution was found to be important for process optimization, and was carried out using a special procedure. Me-DLC coated substrates were placed in the vials and filled to 66% of the total volume for ball loading. Mechano-chemical treatment of the coated substrates was carried out in specially selected organic solvent medium in order to prevent oxidation and chemical changes in the composition of Me-DLC layers. The duration of the mechano-chemical treatment was based on our preliminary experience and was about one hour. A schematic diagram of mechano-chemical processing is shown in Fig. 4. The process operates at low temperature and is flexible, easy to perform, needs no expensive equipment and be controlled by the process parameters outlined in Fig. 4.

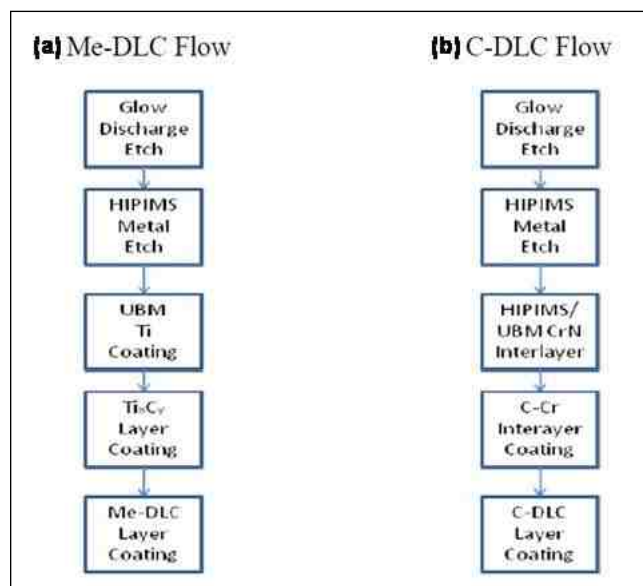


Figure 3—Etch and deposition process flows.

Evaluation techniques

The coating microstructure and analysis of the elemental state of the coating-substrate interface was undertaken using cross-sectional scanning transmission electron microscopy (XSTEM) with energy dispersive x-ray (EDX) analysis (JEOL EM-2010F operated at 200 kV with an EDAX x-ray detector) with a stationary electron beam diameter of approximately 1.0 nm during interface analysis, giving approximately ± 2.0 nm EDX resolution and an ultimate resolution of 0.2 nm during high resolution imaging.

Conventional XTEM images were obtained with a Philips EM420T operated at 120 kV and a JEOL EM-2010 operated at 200 kV. Surface morphology was examined using tilted cross-sectional scanning electron microscopy (XSEM) (Amray 1850 Field Emission system).

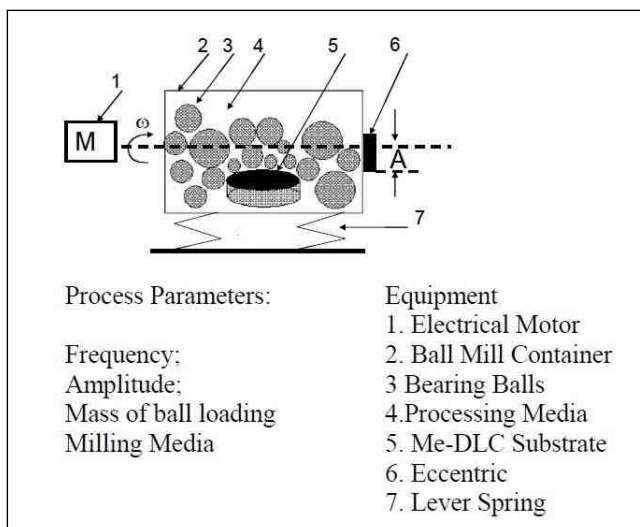


Figure 4—Schematic diagram of the mechano-chemical treatment equipment and key process parameters.

The coating hardness and elastic modulus were recorded using a CSM Instruments NHT-TX nano-hardness indentation tester, applying a maximum end load of 3.0 mN. Coating adhesion was tested using a combination of Rockwell-C indentation and dynamic scratch adhesion testing system (independently tested by CSM instruments with Revetest) using both optical and acoustic emission detection to define LC1 and LC2 critical loads. The friction and sliding wear coefficients were determined using a CSM instruments pin-on-disc tester (5 N load, dry sliding, 1000 m distance, 5.0 cm/sec sliding speed).

Phase composition was examined using visible and ultra-violet wavelength Raman microscopy (Renishaw 2000).

Results and discussion

As-deposited DLC coating properties

Table 1 summarizes the mechanical, physical and tribological properties of as-deposited Me-DLC and C-DLC films on high speed steel substrates which were etched prior to coating using a single chromium HIPIMS source.

Table 1
As-deposited DLC film properties

Sample →	Me-DLC	C-DLC
Thickness, μm	3.5	2.5
Rockwell C adhesion class	1	1
Critical Load LC1, N	60	59
Critical Load LC2, N	160	90
Hardness, HV	1,000	3,400
Elastic Modulus, GPa	110	230
Friction Coefficient (against 100Cr6)	0.15	0.06
Sliding Wear Coefficient, $\text{mm}^3/\text{N}\cdot\text{m}$	9×10^{-8}	7×10^{-8}

Both types of DLC films exhibited excellent levels of coating adhesion and high interfacial strength with Me-DLC coatings, typically demonstrating as much as 100 N load separation between the point of first failure and final delamination of the film from the substrate. Me-DLC films delivered modest hardness values coupled with low levels of friction and sliding wear rate against 100Cr6 steel pins. By contrast, C-DLC showed a three- to fourfold increase in hardness, increased stiffness and a 150% reduction in friction coefficient as compared to Me-DLC films while maintaining similar adhesion characteristics. Equivalent Me-DLC films, where only argon glow discharge etching was utilized as a reference, delivered a strong reduction in LC1 value to approximately 35 N and LC2 value to 41 N.

Figure 5 elucidates how the steel interface was modified by chromium HIPIMS metal ion etching to enable the improved adhesion. Glow discharge-etched coupons exhibited a relatively abrupt interface with well defined boundaries. Between the titanium interlayer and the steel substrate, no evidence of enhanced chromium signals could be detected. The interface was found to be clean and contained no foreign or amorphous contamination phases.

XSTEM imaging of HIPIMS-treated coupons showed a 10 to 15 nm-wide disturbed region, below the UBM-deposited pure titanium interlayer, with contrast and brightness similar to that of the austenitic stainless steel substrate grains. This band is the result of high energy ion bombardment, where contrast variation is related to lattice strain caused by radiation damage-induced metal ion implantation. EDX examination of the interfacial region defines the coating-substrate interface, *i.e.*, the point at which the Fe-K α signal begins to rise from its minimum value while the Ti-K α signal remains high. Superposition of the Cr-K α x-ray intensity as a function of probe position on the Fe and Ti traces shows a peak in Cr x-ray intensity to the right of the interface. The Cr peak is fully within the steel substrate region with a shape characteristic of an implanted zone, with maximum intensity at 4.0 nm depth and signal decay to steady-state Cr-K α intensities of that stainless steel beyond depths of 10 nm. Such stopping ranges and implantation zones fit well with Monte-Carlo simulation studies.

Figure 6 defines the typical coating morphology of both Me-DLC and C-DLC films while the XSTEM selected area electron diffraction patterns illustrate a gradual transition from polycrystalline (spot pattern at a thickness of 0.3 μm) to amorphous (halo at a thickness of 2.5 μm) structure with increasing distance from the coating-substrate interface (Me-DLC).

Me-DLC and C-DLC film interlayers appeared dense and fine grain columnar-structured. In the case of the Me-DLC coatings, competitive columnar growth remained present throughout the full thickness of the coating despite strongly increasing C_2H_2 gas flow and increasing target “poisoning” towards the end of the deposition process. Conversely, the amorphous top 1.0- μm thick surface region of the metal-free C-DLC films showed no evidence of columnar structure. Both cohesion between the individual film layers and adhesion to the steel substrate appear excellent.

Closer examination of the upper amorphous region of the Me-DLC films showed a pronounced fine multi-layering of the coating structure with a period of about 20 nm, due to variation in the Me: C ratio as the substrates passed each cathode during the three-fold rotation (Fig. 7).

Figure 8 illustrates the typical Raman signatures of Me-DLC and C-DLC films under visible (green laser wavelength, 514 nm) and ultraviolet stimulation (325 nm). In the case of Me-DLC Raman spectra recorded using visible light excitation, all films showed the typical DLC feature of a broad peak in the 1000 to 1700 cm^{-1} region, with well separated first order phonon modes, namely disorder (D) and graphite (G) peaks lying at about 1390 and 1560 cm^{-1} , respectively.

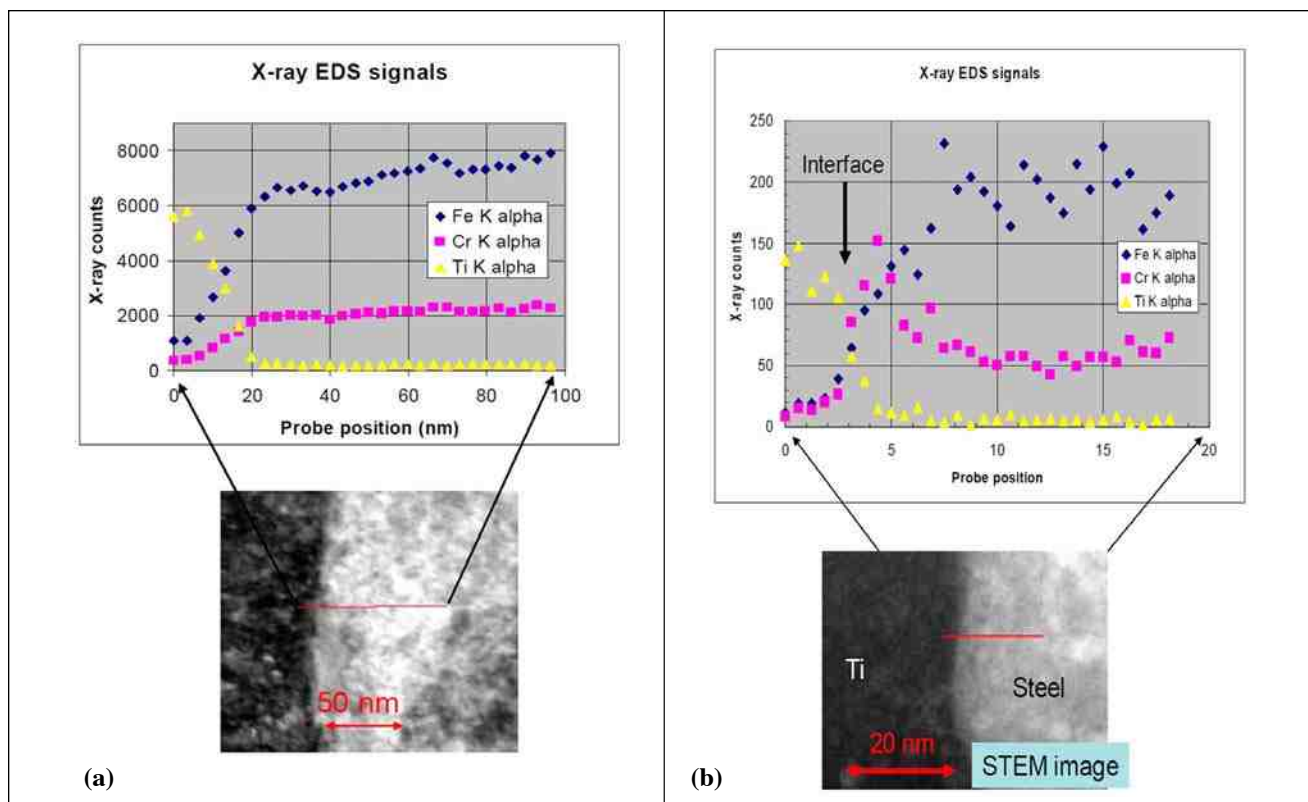


Figure 5—XSTEM and EDX interface analysis of (a) argon glow-treated and (b) HIPIMS steel coupons.

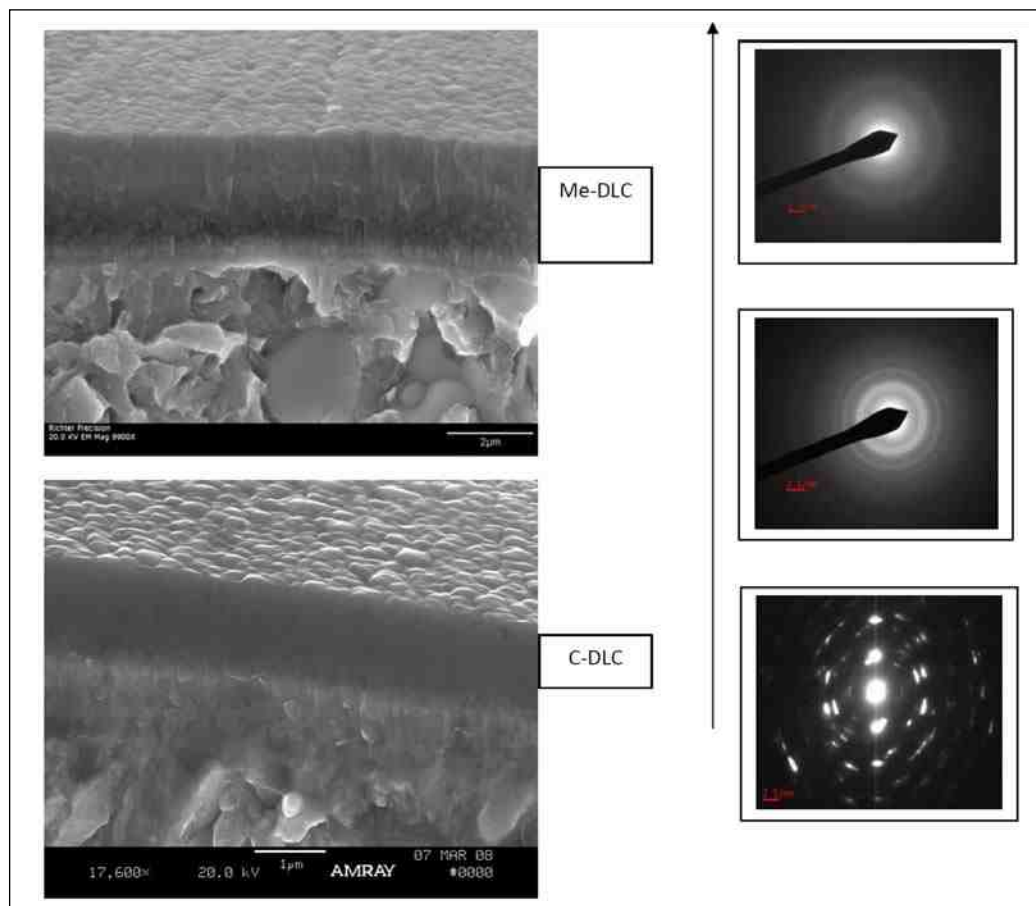


Figure 6—DLC coating architecture and structure.

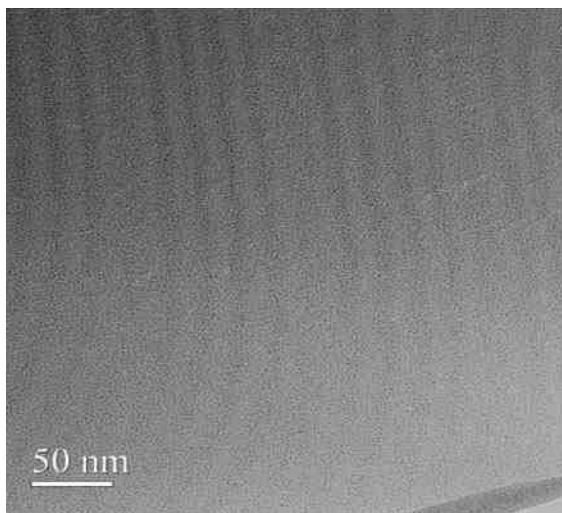


Figure 7—XSTEM image of an amorphous carbon multi-layer structure in Me-DLC.

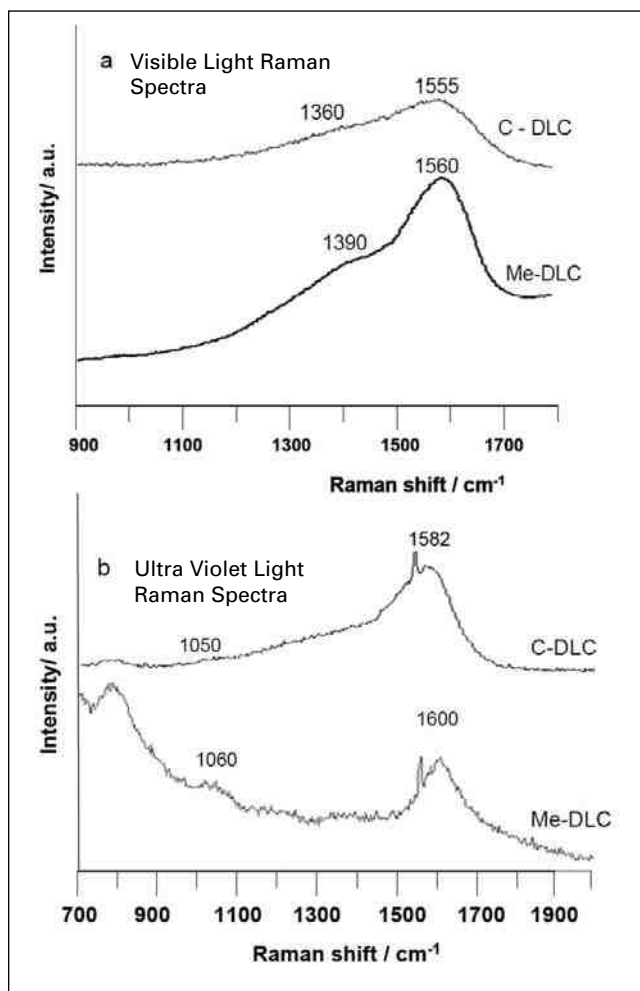


Figure 8—Plots of Me-DLC and C-DLC Raman spectra: (a) visible light and (b) UV.

By taking the ratio between the slope, m , of the fitted linear background and the intensity of the G-peak, $m/I(G)$, we may empirically derive the bonded hydrogen contribution as shown in Table 2. Accordingly HIPIMS-etched Me-DLC exhibited a hydrogen content 18 to 20% higher than that of the C-DLC films, where the film exhibited a hydrogen atomic concentration significantly less than 15%.

Analysis of the G-peak position and its dispersion was used to examine the sp^3 hybrid orbital content of the Me-DLC films. For all films investigated, the G-peak position showed an increase in Raman shift as the excitation wavelength was reduced from 514 to 325 nm. We have calculated the change in the value of the G-peak position and dispersion according to Ferrari, *et al.*¹⁵ The sp^3 composition of the Me-DLC films was found to be approximately 30%. Sharp peaks exhibited on the ultraviolet Raman spectra at 1570 cm^{-1} are attributed to atmospheric oxygen during spectral acquisition. The sp^3 composition of the films may also be defined through the existence of broad, low intensity T-peaks (approximately 1060 cm^{-1}) seen only within the UV Raman spectra.¹⁶ We have calculated and tabulated the $I(T)/I(G)$ intensity ratio as T-peaks are sensitive in hydrogenated films only to C-C sp^3 bonding. Comparison confirms similar sp^3 tendencies to those observed using G-peaks.

The sp^3 hybrid orbital content of the C-DLC films was also evaluated based on visible and UV Raman spectra. From an analysis of the G-peak position and its dispersion, we evaluated the sp^3 content at 70%. The T-peak position was typically found at 1050 cm^{-1} , corresponding to approximately 72% sp^3 content in the film. Calculation of the sp^3 content based on peak intensity ratio described similar values at 75%, indicating a sp^3 fraction approaching that of ta-C films (tetrahedral amorphous carbide, typically 80 to 85% sp^3) and levels more than double those of Me-DLC films. Calculation of the elastic modulus, based on correlation with the FWHM of peaks in the Raman spectra, was found to be 220 GPa and in excellent agreement with measured values of 230 GPa taken through nano-indentation testing.

Mechano-chemically treated Me-DLC films

Mechano-chemical processing techniques are novel methods used to deposit various kinds of coatings and modify metallic surfaces. The technique combines the characteristics of mechano-chemistry (mechanical alloying) and shot peening.^{13,14} The method is based on the principle of *in situ* mechanical activation and physio-chemical transformation processing of the metallic surface in the presence of different gaseous, liquid and powdered media to form the desired compounds on the surface, or change the microstructure of the surface in a directed and controlled fashion. The purpose

Table 2
Raman microscopy phase composition analysis

	Me-DLC	C-DLC
H content	18 to 20%	< 15%
Sp3 content Based on G peak Shift	30%	72%
Sp3 content based on I(T)/I(G) ratio	26%	75%

of the present study was to establish whether mechano-chemical processing can improve the hardness and tribological characteristics of sputter-deposited Me-DLC films by changing their surface morphology and microstructure.

Figure 9 illustrates the coating morphology of a Me-DLC coating after mechano-chemical modification. By comparing the surface morphology and cross sectional structure of the mechano-chemically modified layer with the morphology and cross section of the as-deposited coating (Fig. 6), the following evident changes can be seen:

1. Because of mechano-chemical treatment, the surface roughness of the as-deposited films was decreased.
2. The coating structure and chemical composition as a function of depth within the coating became more uniform and the transition zone, clearly visible between the metal-rich sub-layer and carbon-rich top-layer of the as-deposited films (Fig. 6), was no longer visible on the SEM image of the modified coating.
3. The columnar structure of the coating after mechanical processing became more pronounced.

Table 3 compares the hardness, Young's modulus and friction coefficient of as-deposited and one-hour mechano-chemically processed Me-DLC coatings. The second result row presents the data obtained after processing the as-deposited Me-DLC coating with the ball bearings having size distribution in the range of 2 to 10 mm. In the third row, the same data is given for ball bearings having a size distribution in the range of 8 to 15 mm. Comparison with the as-deposited data indicates that both hardness and Young modulus of the coating was increased after mechano-chemical treatment. The hardness was increased by approximately 28 to 40% and the Young's modulus in the range 20 to 60%, respectively. No significant changes were observed in friction and adhesion behavior of the films.

The principles and mechanisms by which mechanical impact initiates and accelerates physical and chemical transformations in the solid phase have been and remain the subject of extensive studies.^{16,17} The tremendous intensification of diffusion, creation and motion of dislocations, local heating and propagation of shock waves are several examples of the processes initiated by the mechanical processing of solids. Under our experimental conditions, we believe that the changes observed in the morphology, hardness and elastic modulus of Me-DLC films are taking place

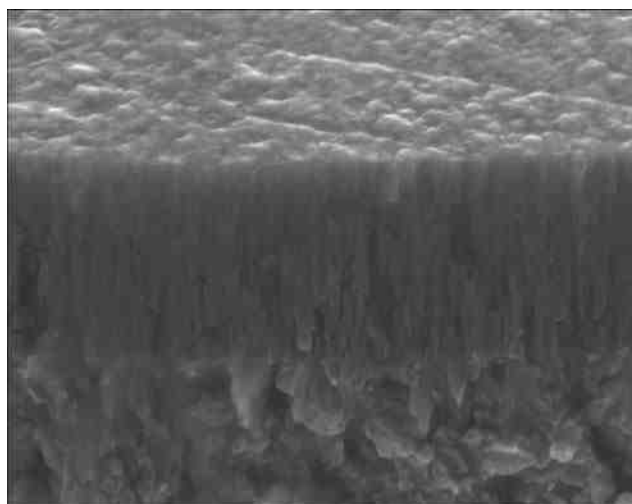


Figure 9—XSEM micrograph of Me-DLC films after mechano-chemical modification.

by the simultaneous influence of accelerated diffusion, dislocation hardening and sp²-to-sp³ transitions induced by shock waves generated by ball-substrate collisions. All of these approaches were discussed in detail in our earlier paper.¹⁸ We assume that the surface of the coating bombarded by ball bearings induces localized plastic deformation at the site of impact. Provided complete coverage is achieved, the entire near-surface region is placed in a state of compressive stress. Dislocation hardening is accompanied by accelerated diffusion between the Me-rich sub-layer and the carbon-rich top-layer of the Me-DLC coating. As a result, the coating becomes more uniform as a function of depth and becomes compacted under compressive stress. We observe both of these phenomena in our mechano-chemically modified coatings. Along with dislocation hardening, we assume that over each “ball-coating” collision event, a shock wave may propagate in the region near to the impact area. By this mechanism, part of the mechanical energy undergoes adiabatic transformation into the pressure and heat within a microscopic volume localized in the vicinity of the corresponding impact area. Due to high pressure and temperature release, some part of sp²-bonded amorphous carbon could be transformed into

Table 3

Vickers hardness, elastic modulus and friction coefficient of as-deposited and one-hour mechano-chemically processed Me-DLC coatings

Sample	Hardness (HV)	Elastic Modulus (GPa)	Friction Coeff. (against 100Cr6)
As-deposited Me-DLC	1000	110 - 150	0.15
Mechano-chemically modified Me-DLC coating ^(a)	1280	160	0.15
Mechano-chemically modified Me-DLC coating ^(b)	1450	180	0.14 - 0.15
(a) The diameter of the used balls was in the range of 2 to 10 mm. (b) The diameter of the used balls was in the range of 8 to 15 mm.			

sp³-bonded carbon, thus increasing the hardness and Young's modulus of the films. This suggestion is also supported by the fact that hardness and Young's modulus of the DLC films are directly related to the sp³ content of the films.¹⁵ Our experimental results are in agreement with this approach, since the hardness and elastic modulus of the modified films are higher when the diameters (consequently the energy of impact) of the ball bearings is greater, as we can see by comparing the second and third rows of Table 3. The detailed mechanisms of hardening of the as-deposited coating will be the object of our future studies.

Applications

Both Me-DLC and C-DLC films, with optional secondary mechano-chemical processing, are being routinely applied to various industrial products. Some examples are shown in Fig. 10.

Conclusions

Industrial scale HIPIMS chromium metal ion etching can be used to cause significant modification of the near-surface region of steel substrates prior to coating.

HIPIMS chromium metal etching provides significant improvement in the adhesion of DLC films on steel substrates in comparison to glow discharge etching. Adhesion is promoted through shallow metal ion implantation into the near-surface region of the steel substrate prior to deposition.

Sputtered Me-DLC films were found to be relatively soft due to the use of a high acetylene gas flow rate and a high C:Me ratio. They also had a low friction coefficient, demonstrated excellent sliding wear resistance, were highly adherent and had a nano-layered, columnar microstructure. The film architecture was comprised of a gradual transition from micro-crystalline to amorphous layers at increasing distances from the coating-substrate interface.



Figure 10—Typical industrial applications of Me- and C-DLC films.

Sputtered C-DLC films were found to be very hard, remained adherent, exhibited significantly improved sliding wear coefficient and lower friction coefficient than Me-DLC films and showed a column-free microstructure with a higher sp³ content than Me-DLC films, approaching levels found for tetrahedral amorphous carbide.

Mechano-chemical techniques have been applied to modify Me-DLC coatings deposited by the combined HIPIMS / UBM sputtering method.

It has been shown that mechano-chemical modification significantly improves the surface quality, hardness and elastic modulus of HIPIMS deposited Me-DLC films without compromising frictional behavior.

It was established that the hardness of a Me-DLC coating could be increased by up to 40% and Young's modulus up to 60% for some selected parameters of mechano-chemical processing.

The process could be controlled by varying a series of key process parameters. Since the method suggested is a flexible, low temperature technique, easy to perform and does not need expensive equipment, it could find potential application to modify any DLC-containing film for improving tribological performance.

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