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 find increasing industrial acceptance in automotive, aerospace and medical applications due to 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 fraction similar to that produced by arc evaporation sources, without showing excessive heating and droplet formation characteristics. These new source properties now enable industrial scale low temperature, low roughness and high efficiency etching of the substrate prior to deposition to deliver enhanced adhesion. 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 temperature below 160°C. Prior to deposition, the coating-substrate interface was engineered using high substrate bias voltage closed field unbalanced magnetron enhanced Ar etch followed by metal ion etch using a single Cr HIPIMS source. The mechanical, tribological and physical properties of the coatings have been investigated using XTEM, dynamic micro-hardness, Scratch and Rockwell-C Adhesion, Raman microscopy and pin-on-disc tribological testing. 3.5µm as-deposited Me-DLC films showed hardness around 1000HV, friction coefficient 0.15 and excellent adhesion (LC1~60N, LC2>140N). 2.5µm thick as-deposited C-DLC coatings exhibited significantly increased hardness to 3400 HV, extremely low friction coefficient (0.06), a shift in phase composition to high sp3 percentage, whilst maintaining very good adhesion following HIPIMS etch. XSTEM & EDX analysis across the coating-substrate interface showed distinct modification of the substrate through the use of a HIPIMS source. After deposition, selected Me-DLC coatings have been treated by secondary surface modification using a novel mechano-chemical method. SEM and nano-indentation investigations established that by applying mechano-chemical processing it is possible to change the microstructure of Me-DLC coating, increases hardness and decrease surface roughness without compromising friction or adhesion behavior. In particular a significant change in the film morphology has been observed and as a result the hardness of the films may be increased by up to 40%.

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1.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 1980's and both commercial and academic investigations continue to the present day (1-6). The principal reasons for the use of DLC films stems from superior tribological performance through excellent sliding wear coefficient, very low friction coefficient and the ability to be deposited at relatively low substrate temperature. 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 allowing component weight to be reduced whilst enhancing the wear resistance of a surface allows wider application of lighter materials such as Ti and Al 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 comprising 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, hence improved sliding wear behavior, but may 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 significantly improve the adhesion of PVD films and at elevated temperature promote localized epitaxial film growth (10-12). In this article, we present results characterizing 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 have been in-situ metal ion etched prior to deposition using a novel Cr HIPIMS cathode at low temperature and without excessive surface roughening.

The surface of Me-DLC films has 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 oxygen free environment is discussed. Variation of critical process parameters has been undertaken providing differing impact forces and shear angles at mechanical processing.

2.Experimental.

Me-DLC and C-DLC films were deposited in a commercially available industrial scale combined HIPIMS / UBM sputter chamber.



Fig 1 Me-DLC & C-DLC Coating Chamber Line, Richter Precision Inc, East Petersburg, PA Facility

The 1250mm diameter chamber was equipped with 3 vertically mounted rectangular targets for unbalanced magnetron sputtering and 1 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 d.c supplies capable to deliver upto 30KW, whilst the HIPIMS source utilised an Advanced Converters HMP 2/4 unit with peak power capability upto 8MW at 2KV with arc suppression. Within the chamber, a 3-fold rotation substrate table capable of holding a maximum substrate load of 800Kg could be d.c biased with voltage from 0-1200V. In the centre of the chamber, a greater than 1m long cylindrical anode was located, capable of independent positive biasing to maximum +200V for enhancement of plasma density at the substrate. High rate chamber pumping was undertaken using three 1600ls⁻¹ turbo molecular pumps backed by a rotary vane and Roots pump. Radiant heater arrays within both doors could be used to elevate substrate temperature and remove water

vapour (Tmax=200°C) in combination with a Meissner cold trap. The base pressure of the system was below $1x10^{-5}$ mbar.

The following target arrangements were used:



Fig 2 Schematic of chamber arrangement for etch and DLC film deposition.

Etching was carried out in an inert atmosphere (Ar) whilst sputter deposition was carried out in a mixed inert gas + reactive gas discharges using N_2 or C_2H_2 and varying reactive gas flow whilst maintaining constant working gas flow. 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 out-gassing, all targets were sputter cleaned in an inert gas atmosphere behind shutters to prevent contamination of the substrate surfaces. Following target clean, substrates were sputter cleaned by unbalanced magnetron enhanced glow discharge etching with high substrate bias voltage maintained for 20mins. HIPIMS etching was initiated following glow-discharge etch and prior to coating using Cr as metal source at constant frequency 500Hz, discharge power 5KW, 100 μ S pulse duration, bias voltage -1000V and pressure 1.8x10⁻³mbar.

Me-DLC film architecture consisted of an adhesion promoting layer followed a wear resistant Ti_xC_y intermediate layer generated through 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 ratio of C:Me ratio within the film. The temperature during coating was held at typically 160°C.

The C-DLC film architecture consisted of a simultaneous UBM/HIPIMS sputtered Cr pure 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 comprised a high bias C-Cr secondary interlayer where power to a Cr cathode was ramped down whilst power on opposing UBM graphite targets was simultaneously increased in pure Ar atmosphere. On completion of the Cr target power ramp down the target was shuttered. Graphite targets continued to be sputtered whilst low flows of C_2H_2 gas was introduced into the plasma, bias voltage was raised and coil current increased to provide higher plasma density at the substrate. The temperature during carbon deposition was typically 140°C.



Fig 3. Etch & Deposition Process Flows

Mechano-chemical coating deposition was carried out using a specially designed vibratory ball mill with adjustable vial amplitude (0-4 mm) at frequency of 50Hz. The ball mill vials used for the modification process were specially designed for this project. The vials had volume of 100ml and were filled with steel bearing balls with a distribution of diameters in the range of 2-

10 mm and 8-15mm. Selection of the correct ball size distribution was found to be important for optimization of the process, 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 by ball loading. Mechano-chemical treatment of the coated substrates were carried out in the medium of specially selected organic solvent in order to prevent oxidation and chemical changes in the composition of Me-DLC layers. The duration of mechano-chemical treatment has been selected based on our preliminary experience and was equal at about 1hour in our experiments. The schematic of mechano-chemical processing is shown on fig.4



Frequency; Amplitude; Mass of ball loading Milling Media

Process Parameters:

Equipment 1. Electrical Motor 2. Ball Mill Container 3 Bearing Balls 4.Processing Media 5. Me-DLC Substrate 6. Eccentric 7. Lever Spring

Fig 4. Schematic of mechano-chemical treatment equipment and key process parameters.

The process of mechano-chemical treatment is low temperature and flexible, easy to perform, does not need expansive equipment and could be controlled by process parameters outlined in fig.4.

3. 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 stationery electron beam diameter approximately 1nm during interface analysis giving approximately $\pm 2nm$ EDX resolution and ultimate resolution 0.2nm during high resolution imaging.

Conventional XTEM images were recorded on 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) using an Amray 1850 Field Emission system.

Coating hardness and elastic modulus was recorded using a CSM instruments NHT-TX nanohardness indentation tester applying maximum end load 3mN.

Coating adhesion was tested using a combination of Rockwell-C indentation testing and dynamic scratch adhesion testing (independently tested by CSM instruments with Revetest) utilising both optical and acoustic emission detection to define Lc1 and Lc2 critical loads.

Friction coefficient and sliding wear coefficient were determined using a CSM instruments pinon-disc tester (5N load, dry sliding, 1000m distance, 5cms⁻¹ sliding speed).

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

4. Results & Discussion.

4.1 As-Deposited DLC Coating Properties.

Table no.1 summarises 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 Cr HIPIMS source.

| Sample | Thickness (µm) | Rockwell-C Adhesion Class | Critical Load LC1 (N) | Critical Load LC2 (N) | Hardness (HV) | Elastic Modulus (GPa) | Friction Coefficient (against 100Cr6) | Sliding Wear Coefficient (mm ³ N ⁻¹ m ⁻¹) |
|--------|-------------------|---------------------------------|--------------------------------|--------------------------------|------------------|-----------------------------|--|---|
| Me-DLC | 3.5 | 1 | 60 | 160 | 1000 | 110 | 0.15 | 9x10 ⁻⁸ |
| C-DLC | 2.5 | 1 | 59 | 90 | 3400 | 230 | 0.06 | 7x10 ⁻⁸ |

Table no.1 As-deposited DLC film properties.

Both types of DLC film exhibited excellent levels of coating adhesion and high interface strength with Me-DLC coatings typically demonstrating as much as 100N 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. In contrast C-DLC showed a factor 3-4 increase in hardness, increased stiffness and a reduction in friction coefficient by 150% in comparison to Me-DLC films whilst maintaining similar adhesion characteristics. Equivalent Me-DLC films, where only Ar glow

discharge etching was utilized as a reference, delivered a strong reduction in LC1 value to approximately 35N and LC2 value to 41N.

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







Figure 5 XSTEM & EDX interface analysis of HIPIMS and Ar Glow treated steel coupons.

XSTEM imaging of HIPIMS treated coupons showed a 10-15nm 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 due to lattice strain caused by radiation damage induced metal ion implantation. EDX examination of the interface region defines, at the point at which the Fe-Ka signal begins to rise from its minimum value whilst the Ti-Ka signal remains high, the coatingsubstrate interface. Superposition of the Cr-Ka 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 shape characteristic of an implanted zone, with maximum intensity at 4nm depth and signal decay to steady-state Cr-Ka intensities of that stainless steel beyond depths of 10nm. Such stopping ranges and implantation zones fit well to Monte-Carlo simulation studies. Figure 6 defines the typical coating morphology of both Me-DLC and C-DLC films whilst XSTEM selected area electron diffraction patterns illustrate a gradual transition from polycrystalline (spot pattern at thickness 0.3μ m) to amorphous (halo at thickness 2.5μ m) structure with increasing distance from the coating-substrate interface (Me-DLC).



Figure 6 DLC Coating Architecture & Structure

Me-DLC and C-DLC film interlayers appeared dense and fine grain columnar structured. In the case of 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 1µm thick surface region of metal free C-DLC films showed no evidence of columnar structure. Both cohesion between the individual film layers and adhesion to the steel substrate appears excellent.

Closer examination of the upper amorphous region of Me-DLC films showed a pronounced fine multi-layering of the coating structure at period ~20nm due to variation in the Me:C ratio as the substrates pass each cathode during 3-fold rotation (fig 7).



Figure 7 XSTEM Image of amorphous carbon multi-layer structure in Me-DLC.

Figure 8 illustrates the typical Raman signatures of Me-DLC and C-DLC films under visible (green laser wavelength 514nm) and ultra-violet stimulation (325nm). 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 1000-1700cm⁻¹ region with well separated first order phonon modes, namely disorder (D) and graphite (G) peaks lying at about 1390cm⁻¹ and 1560cm⁻¹ respectively.



Figure 8 Plot of Me-DLC and C-DLC Raman spectra (U.V & visible light).

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

Table no.2 Raman Microscopy Phase Composition Analysis.

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 no.2. Accordingly HIPIMS etched Me-DLC exhibited hydrogen content of 18-20%, higher than C-DLC films, where the film demonstrates hydrogen atomic concentration significantly less than 15%. Analysis of the G-peak position and its dispersion has been used to examine the sp³ content of the Me-DLC films. For all films investigated, G-peak position showed an increase in Raman shift as the excitation wavelength was reduced from 514nm-325nm. We have calculated the change in the value of the G-peak position and dispersion according to Ferrari et al (15). The sp³ composition of Me-DLC films were found to be approximately 30%. Sharp peaks exhibited on ultraviolet Raman spectra at 1570cm⁻¹ are attributed to atmospheric oxygen during spectral acquisition. The sp³ composition of the films may also be defined through the existence of broad, low intensity T-peaks (approximately 1060cm⁻¹) seen only within the ultraviolet 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 sp³ bonding. Comparison confirms similar sp³ tendencies to that observed using G-peaks.

The sp3 content of C-DLC films has also been evaluated based on visible and U.V Raman spectra. From analysis of the G-peak position and its dispersion we evaluated the sp³ content at 70%. T-peak position was typically found at 1050cm⁻¹, corresponding to approximately 72% sp³ content in the film. Calculation of sp³ content based on peak intensity ratio described similar values at 75%, indicating sp³ fraction approaching that of ta-C films (typically 80-85% sp³) and levels more than double that of Me-DLC films. Calculation of elastic modulus, based on correlation with the FWHM of peaks in the Raman spectra, was found to be 220GPa and in excellent agreement with measured values of 230GPa taken through nano-indentation testing.

4.2. Mechano-chemically treated Me-DLC films.

Mechano-chemical processing techniques are novel methods 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 in order to form the desired compounds on the surface or change the microstructure of the surface in a directed and controlled fashion. The purpose of the present study was to establish whether mechano-chemical processing is able to improve the hardness and tribological characteristics of sputter deposited Me-DLC films by changing it surface morphology and microstructure.



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

Figure 9 defines the coating morphology of an Me-DLC coating after mechano-chemical modification. By comparing 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:

(i) Because of mechano-chemical treatment the surface roughness of as deposited films was decreased.

- (ii) The coating structure and chemical composition as a function of depth within the coating becomes more uniform and the transition zone, clearly visible between the metal rich sub-layer and carbon rich top-layer of as deposited films (fig.6), is no longer visible on the SEM image of the modified coating.
- (iii) The columnar structure of coating after mechanical processing becomes more pronounced.

Table no.3 compares 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 as deposited Me-DLC coating with the balls having size distribution in range between 2-10mm and in the third row the same data for the balls having size distribution in range between 8-15mm. Comparison with as-deposited data indicates both hardness and Young modulus of the coating have been increased after mechano-chemical treatment. The hardness was increased by approximately 28- 40% and the Young's modulus in the range 20- 60% respectively. No significant changes were observed in friction and ahdesion behavior of the films.

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



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 at mechanical processing of solids. In our conditions of experiment we believe that the changes observed in the morphology, hardness and elastic modulus of Me-DLC films are taking place by simultaneous influence of accelerated diffusion, dislocation hardening and sp²-sp³ transitions induced by shock waves generated at ball-substrate collision. All of these approaches in detail were discussed in our earlier paper [18]. We assume that the surface of coating bombarded by bearing balls 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 Me-rich sub-layer and carbon rich top-layer of Me DLC coating. As a result the coating becomes more uniform as a function of depth and becomes compacted under compressive stress. Both of these phenomena we observe 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 sp^2 bonded amorphous carbon could be transformed into sp³ bonded, thus increasing the hardness and Young modulus of the films. This suggestion is supported also by the fact that hardness and young modulus of DLC films directly related to 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 bearing balls is greater, as we can see by comparing second and third rows of the table 3. The detailed mechanisms of hardening of as deposited coating will be the object of our further investigations.

4.3 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 figure 10.



Figure 10 Typical Industrial Applications of Me & C-DLC film.

5. Conclusions

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

HIPIMS Cr 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 high acetylene gas flow rate and high C:Me ratio, had low friction coefficient, demonstrated excellent sliding wear resistance, were highly adherent and had nano-layered, columnar microstructure. Film architecture comprised gradual transition from micro-crystalline to amorphous layers at increasing distance from the coating-substrate interface.

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 column-free microstructure with higher sp³ content than Me-DLC films approaching levels found for ta-C.

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

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

It was established that the hardness of Me-DLC coating could be increased 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 flexible, low temperature technique, easy to perform and does not need expansive equipment it could find potential application to modify any DLC containing film for improving it tribological performance.

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