Synthesis, structure, and tribological behavior of nanocomposite DLC based thin films

Varshni Singh
Louisiana State University and Agricultural and Mechanical College, vsingh2@lsu.edu

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Part of the Engineering Science and Materials Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_dissertations/3379
SYNTHESIS, STRUCTURE, AND TRIBOLOGICAL BEHAVIOR OF NANOCOMPOSITE DLC BASED THIN FILMS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Interdepartmental Program in Engineering Science

by
Varshni Singh
B. Tech., Indian Institute of Technology-Kanpur, India, 1990
M. Tech., Indian Institute of Technology-Kanpur, India, 1993
December 2004
ACKNOWLEDGEMENTS

The author would like to express his sincere appreciation to his major professor Dr. E.I. Meletis for his excellent guidance and constant encouragement throughout this work. He would also like to thank Dr. A. Srivastava, Dr. W.J. Meng, Dr. E. Woldesenbet and Dr. Jeffrey Nunn for valuable suggestions and participation in this research work as members of his examination committee.

He also wishes to thank Pankaj Gupta, Dean Guidry, Summer D. Jhonson, Yohannes Desta, Tracy Moris, Amit Varma, Fengli Wang, Dr. Qi Chu Chang, Dr. V. Palshin, Dr. R. Tittsworth, Dr. P. Schilling, Dr. J. C. Jiang, Dr. Cindy Henkstrom, Dr. X. Xie and Dr. X. Nie for their help and fruitful discussions. Further, the author would like to mention the various LSU labs that had helped in this research, MCC, SEM facility of Life Sciences, WDS facility of Geological Science and Center for Advanced Microstructures and Devices (CAMD).

The author also wishes to express his sincere appreciation to his wife, children, parents, sisters, brothers-in-law and other relatives for their constant support and encouragement.

The author would like to acknowledge the support by Army Research Office grant DAAG55-98-1-0279 and Louisiana Board of Regents to perform this study.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................... ii

LIST OF TABLES .................................................................................................................. v

LIST OF FIGURES ............................................................................................................... vi

ABSTRACT ............................................................................................................................ x

I. INTRODUCTION ................................................................................................................. 1

II. OBJECTIVES ..................................................................................................................... 5

III. STATE-OF-THE-ART ................................................................................................... 6

A. DLC Coatings .................................................................................................................... 6
   1. Synthesis and Deposition Techniques ........................................................................ 6
   2. Structure, Properties and Proposed Models ................................................................. 8
   3. Tribological Behavior and Wear Mechanism ................................................................. 22

B. Me-DLC Coatings .......................................................................................................... 25
   1. Synthesis and Deposition Methods ............................................................................ 25
   2. Microstructure and Composition .............................................................................. 26
   3. Mechanical Properties ............................................................................................... 29
   4. Tribological Behavior ................................................................................................. 32

C. Me/DLC Multilayered Films ......................................................................................... 37
   1. Synthesis and Processing ............................................................................................ 41
   2. Mechanical Properties and Tribological Behavior ......................................................... 41

D. Functional Coatings and Nano Inter Layers ................................................................. 45
   1. Structure, Properties and Tribological Behavior ........................................................... 49

IV. EXPERIMENTAL DESIGN AND PROCEDURES ......................................................... 51

A. IPAP Processing System ................................................................................................. 52

B. Nitriding of 4340-Steel and Chromium Ion Plating ..................................................... 55

C. Deposition of Nanocomposite DLC and Chromium Interlayers .................................. 56
   1. Nanocomposite Cr-DLC Films .................................................................................... 57
   2. Multilayered Cr/DLC Films ......................................................................................... 59

D. Characterization of Nanocomposite Cr-DLC, Cr/DLC Multilayers and Functional
   Coatings .......................................................................................................................... 60
   1. Wavelength Dispersive Spectroscopy ........................................................................ 60
   2. Nuclear Reaction Analysis ......................................................................................... 61
   3. X-Ray Diffraction ....................................................................................................... 61
   4. Transmission Electron Microscopy ............................................................................ 61
   5. X-Ray Absorption Spectroscopy .............................................................................. 62
   6. X-ray Photoelectron Spectroscopy ............................................................................ 63
   7. Nano- and Micro-Indentation .................................................................................... 64
8. Corrosion Testing ................................................................. 65
9. Tribological Experiments ................................................... 65
10. Scanning Electron Microscopy ......................................... 66

V. RESULTS AND DISCUSSION .................................................. 67
A. Functional Layers ............................................................... 67
1. Processing, Microstructure and Properties ....................... 67
2. Tribological Behavior ....................................................... 76
B. Nanocomposite Cr-DLC Films ........................................... 79
1. Film Composition .......................................................... 79
2. XRD Analysis ................................................................. 82
3. TEM Studies ................................................................. 84
4. X-ray Absorption Spectroscopy Studies ......................... 88
5. X-ray Photoelectron Spectroscopy Studies ..................... 100
6. Nanoindentation Studies .................................................. 103
7. Thermal Stability .......................................................... 105
8. Electrochemical Behavior ............................................... 108
9. Tribological Behavior ..................................................... 108
C. Cr/DLC Multilayer Films .................................................. 115
1. Microstructural Characteristics of Layers ....................... 115
2. Mechanical Behavior ..................................................... 118
3. Tribological Behavior ..................................................... 122

VI. SUMMARY .............................................................................. 126

REFERENCES ............................................................................. 129

VITA ..............................................................
LIST OF TABLES

Table 1: Deposition processes for DLC films [28]..............................................................8
Table 2: Properties of Carbon containing materials [1].................................................11
Table 3: Mechanical properties of ceramic and multilayered films.................................42
Table 4: Processing parameters for IPAP nitriding 4340 steel and ion plating of Cr layers..............................................................68
Table 5: Nominal composition of medium carbon low alloy 4340 steel......................69
Table 6: Processing parameters for deposition of Cr-DLC films......................................80
Table 7: Composition of Cr-DLC films, combining results from WDS and NRA........80
Table 8: Results of the linear combination XANES fitting over the energy range of 5985-6040 eV..............................................................93
Table 9: Structural parameters obtained from curve fitting of Cr-DLC films and pure Cr3C2 powder..............................................................93
Table 10: Open circuit potential of nanocomposite DLC films in 3.5% NaCl solution [161]........................................................................................................108
Table 11: Processing parameters for deposition of Cr coating, Cr(N) coating and Cr/DLC layers........................................................................................................115
LIST OF FIGURES

Figure 1: $\sigma$ and $\pi$ bonds in $sp^3$, $sp^2$ and $sp$ configuration of carbon atoms……………...9

Figure 2: (a) A typical FTIR spectrum of DLC film (b) The deconvoluted peaks for the C-H stretch vibrational absorption region [33]………………………………………………..12

Figure 3: Raman spectra of as-deposited and laser treated DLC films at different laser fluences [35]…………………………………………………………………..13

Figure 4: (a) C 1s and Ti 2p XPS spectra of Ti-containing DLC films………………..15

Figure 4: (b) Valence band XPS spectra, before (left) and after (right) correction for inelastic losses of diamond, microcrystalline graphite, crystalline graphite and glassy carbon [40]……………………………………………………………..16

Figure 5: Typical AES spectra of (a) diamond, graphite, amorphous carbon and (b) DLC [41]…………………………………………………………………..17

Figure 6: Two dimensional representation of clusters consisting of 91 rings with 7 carbon vacancies (a) $sp^2$- coordination and (b) $sp^3$- coordination [58]…………….22

Figure 7: Variation of friction of DLC-coated 440C discs, arrows 24 indicate the initiation of the steady-state stage [64]…………………………………………………..24

Figure 8: X-ray diffraction pattern of Ta-DLC with varying at% Ta. [5]……………….27

Figure 9: XPS-spectra of (a) DLC and Ta-DLC with 25 at% Ta [5] and (b) typical C 1s showing deconvolution of the observed spectrum [78]…………………..28

Figure 10: Dark field micrograph of (a) W-DLC with 9.7 at% W [77] and (b) Ti-DLC with 2.5 at% Ti [79]…………………………………………………………………..29

Figure 11: Model for Si-DLC structure [80]……………………………………………..30

Figure 12: (a) Hardness and (b) Young’s Modulus of W- and Ta-DLC films as a function of volume % MeC [5]………………………………………………………..31

Figure 13: Friction of Ta-DLC as a function of at% Ta [5]……………………………..33

Figure 14: Load dependence of friction of W-DLC with 12 at% W [5]…………………33

Figure 15: Friction of W-DLC in low and high humidity nitrogen environment as a function of ratio of W/C [5]………………………………………………………..34
Figure 16: Abrasive wear rate of Me-DLC as a function of at% metal [5], ‘Calo-Test’ apparatus was used with aqueous suspensions of 5 µm Al₂O₃ particles……35

Figure 17: Flow stress as a function of interlamellar spacing in Al/Al₂O₃ composites (Hall-Petch plot) [99]…………………………………………………………………………43

Figure 18: Mechanism for toughness of multilayers [89]……………………………………44

Figure 19: Schematic illustration of the FGI concept…………………………………………………46

Figure 20: (a) Nanoparticle composite, (b) multilayered nanocomposite and (c) functional interlayer………………………………………………………………………51

Figure 21: Schematic of the IPAP system with triode configuration……………………………………52

Figure 22: XTEM of Cr layers deposited on Si with bias voltage (a) -100 V, (b) -400 V and (c) high resolution image of (b)……………………………………………………70

Figure 23: Zone structural model depicting coating morphology of metals magnetron sputter deposited [131]……………………………………………………………70

Figure 24: X-sectional scanning electron micrograph showing the ion-plated Cr layer...72

Figure 25: Microhardness profile and the microstructures as a function of depth of IPAP nitrided tempered 4340 steel……………………………………………………………………73

Figure 26: Surface microhardness of tempered, IPAP nitrided and duplex treated 4340 steel…………………………………………………………………………………………75

Figure 27: Corrosion behavior of IPAP nitrided and tempered 4340 steel …………………75

Figure 28: (a) Wear rate, (b) friction vs sliding distance of IPAP nitrided and annealed 4340 steel………………………………………………………………………77

Figure 29: Surface morphology of wear tracks for (a) ion plated Cr (b) IPAP nitrided 4340 steel………………………………………………………………………………78

Figure 30: NRA results of hydrogen content in Cr-DLC films…………………………………81

Figure 31: (a) XRD of DLC film and Cr-DLC films deposited at –200 V and –1,000 V bias [139] and (b) grazing angle XRD of Cr-DLC films with 1.5, 4.8 and 11.8 at% Cr [148]………………………………………………………………………83

Figure 32: HRTEM of Cr-DLC films (~5 at% Cr) deposited at a bias of (a) –200 V and (b) –1,000 V [139]……………………………………………………………………84

Figure 33: SAED pattern of Cr-DLC films (~5 at% Cr) deposited at a bias of (a) –200 V and (b) -1,000 V [139]……………………………………………………………………85
Figure 34: HRTEM image of interfacial structure between Si substrate and Cr-DLC films (~9 at% Cr) deposited at a bias of (a) −200V and (b) −1,000V [139]........87

Figure 35: X-sectional TEM showing self grown multilayer structure of Cr-DLC film...88

Figure 36: X-ray absorption near edge structure spectra of Cr-DLC Films, Cr and Cr3C2 (a) Normalized and spectra (b) normalized and translated along the y-axis (intensity).................................................................90

Figure 37: Best fit of XANES spectrum of sample Cr-DLC 4 by linear combination of Cr3C2 and Cr-DLC 1 spectra.................................................................93

Figure 38: (a) EXAFS of Cr-DLC films and pure Cr3C2 powder and (b) their Fourier transform.................................................................95

Figure 39: A typical example of a fit obtained for Cr-DLC film with 11.8 at% Cr using FEFFIT.................................................................97

Figure 40: XPS (a) General spectrum, (b) high resolution Cr 2p peak for Cr-DLC films, pure Cr and Cr3C2 target, (c) high resolution C 1s peak for Cr-DLC films and pure Cr3C2 target, (d) deconvoluted C 1s peak of Cr3C2 target, (e) deconvoluted C 1s peak of Cr-DLC9 and (f) deconvoluted C 1s peak of Cr-DLC38.................................................................101

Figure 41: (a) Hardness, (b) reduced elastic modulus and (c) hardness to reduced modulus ratio vs Cr/C atomic content ratio of Cr-DLC films........................................104

Figure 42: Heat absorbed as a function of temperature by DLC film..................106

Figure 43: Thermal stability results for Cr-DLC films.......................................106

Figure 44: (a) Coefficient of friction and wear rate of Cr-DLC films as a function of Cr/C ratio and (b) coefficient of friction as a function of the sliding distance for Cr-DLC films [139].................................................................109

Figure 45: Wear track 3-D profile of Cr-DLC films containing (a) 1.5 at% Cr, (b) 4.8 at% Cr, (c) 11.8 at% Cr and (d) 17.5 at% Cr........................................111

Figure 46: Typical wear track 3-D profile of a DLC film....................................112

Figure 47: Scanning electron micrograph of wear track region in Cr-DLC film with 11.8 at% Cr.................................................................112

Figure 48: Scanning electron micrograph of wear debris, from Cr-DLC film with 4.8 at% Cr sliding against (a) 440C steel ball and (b) alumina ball.......................113

Figure 49: XRD pattern of (a) bulk and PVD Cr and (b) PVD Cr and Cr(N) [163]......116
Figure 50: XTEM micrograph of Cr/DLC (200/20) (a) overview and (b) high-resolution image of the Cr/DLC interface [163].................................................................117

Figure 51: Nanoindentation results of Cr/DLC multilayers (a) hardness and (b) reduced elastic modulus, $E/(1-\nu^2)$ [163].................................................................118

Figure 52: (a) Microhardness of Cr, Cr(N), DLC and Cr/DLC multilayers and (b) hardness vs grain size [163].................................................................121

Figure 53: Wear behavior of Cr/DLC multilayers, DLC, Cr and Cr(N) [163].........123
ABSTRACT

Diamond-like carbon (DLC) films possess a combination of attractive properties and have been largely employed to modify the tribological behavior of materials. Nanocomposite, metal-containing DLC films are the new generation of these coatings providing tremendous potential to modify and tailor their properties expanding their applications in the field of nanotechnology. The present study investigates nanoscale effects on the tribological behavior of composite nanostructured DLC-based films and functional coatings. Three aspects were studied: (i) effect of Cr interlayer on a functionally gradient substrate; (ii) nanoparticulate Cr-containing DLC (Cr-DLC) films; and (iii) nanocomposite multilayered Cr/DLC coatings.

Intensified plasma assisted nitriding produced a functionally graded interface and Cr layers exhibited best tribological behavior in their presence validating the theoretical concept. Nanocomposite Cr-DLC films were synthesized with Cr content in the range of about 0.1 at% to about 17 at%, on Si_{100} substrate. TEM studies showed defect free, dense and continuous film containing crystalline nanoclusters embedded in amorphous matrix. X-ray absorption spectroscopy showed that the chemical state and environment around Cr in films with ≥1.5 at% Cr is similar to that in Cr-carbide. However, the environment around Cr in films with Cr ≤0.4 at% is distinctly different with atomic clusters of Cr dissolved in the DLC matrix. Nanoindentation experiments showed that Cr-DLC films possess high hardness. Also, Cr-DLC films exhibit low friction (up to 12 at% Cr) and excellent wear resistance (up to ~5 at% Cr) with a low stable wear rate (10^{-7} \text{ mm}^3/\text{N-m}). In the multilayered nanocomposite films, DLC layers were found to be amorphous whereas Cr layers exhibit a nanocrystalline structure. Cr/DLC interfaces were found to be
dense and continuous. Presence of DLC and a decrease of Cr layer thickness increases the hardness. This behavior was found to be consistent with the Hall-Petch formalism. Multilayered nanocomposite films with a significant volume fraction of DLC were found to possess low friction and low wear rate (10^{-7} \text{mm}^3/\text{N-m}). A common wear mechanism was found on both nanocomposite and multilayered systems. These nanocomposite and multilayered systems exhibited wear and friction properties comparable to those of DLC films, thereby expanding their scope in the field of nanotechnology.
I. INTRODUCTION

Nanostructured materials can exhibit unique mechanical, chemical and electronic properties and thus, possess great potential for applications in tribology, electronics, biotechnology and information technology. The tribological behavior is mainly dependent on the materials surface characteristics. Nanocomposite films have tremendous potential to modify and tailor the surface state and optimize the materials wear and frictional behavior, while maintaining desirable bulk material properties, such as strength and toughness.

In the past, diamond-like carbon (DLC or a-C:H) films, possessing a combination of attractive properties, were largely employed to modify the surface and enhance the behavior of materials addressing to friction, wear, corrosion, fretting fatigue, biocompatibility, etc. In this aspect, DLC, amorphous hydrogenated carbon, films have been extensively studied in the last two decades and have found a large number of applications [1]. However, further utilization is limited due to their low thermal stability (above 350°C) and low toughness and adhesion [2,3]. It has been observed that above 400°C graphitization of DLC film occurs by conversion of $sp^3$ carbon bonding to graphitic $sp^2$ bonding. Such temperatures can very well be reached during wear at asperity contacts and lead to ‘wear induced graphitization’ of DLC films, as has been previously proposed by Liu and Meletis [4]. Therefore, efforts have been initiated in the area of metal containing DLC (Me-DLC) films to improve wear resistance, thermal stability, toughness, and adhesion. Previous work has been carried out on non-carbide formers such as Cu, Ag, Au and carbide formers Si, Mo, Nb, Ti, Ta and W incorporated into DLC and has been reviewed by Klages and Memming [5]. Most of the previous
emphasis has been on carbide formers [5-8]. Generally, it has been reported that compared to DLC, Me-DLC films, show inferior wear resistance though lower compressive stresses and better adhesion to substrates such as steels [9]. Nevertheless, controversy exists regarding the differences in the wear resistance between DLC and Me-DLC films. In this aspect, Si-DLC has shown the potential to slow down the kinetics of wear-induced graphitization [10] and improve thermal stability by 100°C [11,12]. Also, very few studies have been published on the fracture toughness of Me-DLC films [8], which can help develop the basic understanding of the wear and frictional behavior of these films. Therefore, further in-depth studies on Me-DLC films are needed to develop the fundamental understanding of their tribological behavior. In spite of the fact that Cr is an excellent carbide former and possesses attractive combination of other properties (corrosion resistance, wear resistance, etc.) no in-depth study has been reported on Cr-DLC films. Klages and Memmming [5] reported abrasive wear rate of Cr-DLC films (greater than or equal to $9.5 \times 10^{-4}$ mm$^3$/min). Wang et al [8] studied the delaminating mechanism of Cr-DLC film with the help of a cylinder on disc setup. Weissmantel et al [13] reported decreasing hardness and Young’s modulus values for Cr-DLC films. Koduri and Sunkara group reported electrochemical behavior in acidic medium and TEM results of Cr-DLC films [14-16].

Another drawback of DLC films is that they tend to delaminate or peel off when deposited above certain thickness, due to large inherent residual stresses present [17], thereby, limiting their applications (involving high contact stresses) and deposition thickness. DLC/DLC (multilayer) nanocomposites offer a great promise in that direction. In this respect, Sheeja et al [18] had used amorphous diamond and hydrogenated DLC
film as individual layers in a multilayer coating in an effort to improve wear resistance, adhesion and toughness. Studies have also been conducted on multilayer DLC/DLC coatings in our laboratory [19]. Since, DLC films are known for their high hardness and low friction and metals typically possess high toughness, multilayers combining a metal and DLC have high potential of impacting significantly on tribological behavior. Cr layers are well known for good adhesion to metal substrates and have been used successfully as electroplated coatings for corrosion, fatigue and wear resistance. To the best of our knowledge no work has been reported up-to-date on multilayered Cr/DLC nanocomposites. Therefore, such a study would have a lot to offer to understanding the tribological behavior of Cr/DLC nanocomposite coatings.

As noted earlier, a key issue in the tribological behavior of DLC coatings is the adhesion to the substrate. Previous work in our laboratory has shown that this behavior can be significantly improved by DLC deposited on a functionally gradient (hardness gradient) substrate obtained by intensified plasma-assisted nitriding [20,21]. An aspect that was not investigated in that previous study is the possible role of an adherent nano-interlayer (e.g. Cr) between the functionally gradient substrate and the DLC or Me–DLC coating. Contact stress analysis showed that the main failure mechanism in these systems is strain concentration (deformation) at the discrete substrate/film interface followed by delamination. It is evident that an adherent interlayer (< 200 nm) has the potential of accommodating deformation at the interface, thus having a significant impact on the fundamental failure mechanism improving coating performance and longevity. Therefore, a functional coating system can be produced by introducing a metallic interlayer, compatible to both substrate and top coating (i.e. between the DLC film and the plasma
nitrided substrate). Cr is known for its high adhesion, hardness and compatibility to DLC as well as various types of substrates, for example stainless steel [22], thus, offering a great opportunity to modify the failure mechanism and significantly improve coating longevity.

Therefore, a detailed study is needed to develop the fundamental understanding of nanoscale effects on the tribological behavior of nanocomposite coatings involving Cr-DLC nanoparticulate coatings, Cr/DLC multilayered coatings and DLC/Cr (nanointerlayer)/nitrided substrate functionalized coatings.
II. OBJECTIVES

The overall objective of the present study is the development of a better fundamental understanding of nanoscale effects on the tribological behavior of composite nanostructured films and functional coatings that will allow their optimization and design of future systems for a number of advanced engineering applications.

The specific objectives of this research, based on a synthesis-structure-property relationship route, are:

To increase our scientific understanding of the wear mechanism and the frictional behavior of

(1) Cr-DLC nanoparticle composite films;
(2) Multilayered Cr/DLC nanocomposite films; and
(3) Functionally gradient systems with nanostructured Cr layer.
III. STATE-OF-THE-ART

A. DLC Coatings

DLC (a-C) films were first reported in early 1970’s by Aisenberg and Chabot [23]. They used carbon ion beams to deposit these films with electrically insulating, hard, scratch and corrosion resistant properties showing good adherence to silicon substrate. DLC films have been the subject of expanding technological interest for the past two decades due to their attractive properties such as low friction coefficient, high hardness, thermal conductivity and wear resistance; optical transparency, no wetting, chemical inertness and biocompatibility. DLC films, are characterized as amorphous and consist of a mixture of diamond-like and graphite-like domains and usually referred to as a-C:H films. The diamond-like character that gives high hardness to DLC films, comes from the $sp^3$ bonding of C atoms, whereas the $sp^2$ bonding gives the graphite-like behavior, such as low coefficient of friction. The major drawbacks with these films are their low toughness and thermal stability above 350°C (graphitization of DLC due to conversion of $sp^3$ to $sp^2$) [11], along with inadequate adhesion on soft metallic substrates, such as steels, Ti alloys and Al alloys.

1. Synthesis and Deposition Techniques

DLC films are synthesized mainly by two different techniques, high temperature CVD and low temperature plasma assisted deposition [1]. The former is based on the chemical decomposition of a carbon bearing gas phase on the substrate while high temperatures of the order of 900°C are maintained. In the latter technique, processing takes place typically from room temperature to 400°C. Plasma-assisted deposition of DLC films can be performed by using either solid phase or vapor phase carbon sources.
Plasma-assisted deposition using a solid source for carbon, generally employs a graphite target which is sputtered by using a magnetron gun, ion beam, electron beam or laser beam. Here, carbon is deposited onto the substrate as neutral atoms and/or ions. The mixture of ions and neutrals is extracted by applying an appropriate bias voltage to the substrate. In ion beam sputtering, a beam of $\text{Ar}^+$ is used to sputter the graphite target to create the carbon flux \[23,24\]. In sputtering dual-beam method \[25\], a second $\text{Ar}^+$ beam is used to bombard the growing film, to increase the density of the film and the $sp^3$ bonding. In magnetron sputtering \[26\], the graphite target is bombarded by ions to produce neutrals as well as ions. In electron beam, the focused electron beam interacting with the graphite target produces a carbon ion and neutral flux. In laser beam, highly energetic photons impact the target producing the flux of carbon ions and neutrals. Additional $\text{H}_2$ gas can be fed to the deposition atmosphere or ion source to produce a-C:H.

The techniques involving a gaseous source for carbon typically use a hydrocarbon gas, for example methane, ethane, acetylene, etc. The ion beam method of DLC film deposition utilizes a beam containing medium energy (typically $<1000$ eV) carbon or hydrocarbon ions. It is the impact of the ions on the growing film that induces the $sp^3$ bonding \[27\]. In this method, hydrogen is always incorporated in the films and the plasma is generated either by radio frequency (rf) source, micro-wave (mw) source, direct current (dc) source, or pulsed dc source. The substrate is bombarded by various ionized hydrocarbon molecules, neutrals, and inert ions ($\text{Ar}^+$) with ion energies typically below 1 keV. The deposition process is generally dependent on gas pressure, power density, bias voltage, etc.
<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Process from hydrocarbon gases</th>
<th>IBAD (hydrocarbon liquid)</th>
<th>Process from solid C</th>
<th>Sputtering</th>
<th>Ion beam sputtering</th>
<th>Laser ablation</th>
<th>Vacuum arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 – 0.5</td>
<td>PACVD Direct ion beam 0.1 10^{-5}</td>
<td>Ion plating 10^{-5}</td>
<td>Ion beam sputtering 5 \times 10^{-3}</td>
<td>10^{-3}</td>
<td>&lt; 10^{-6}</td>
<td>&lt; 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Gases</td>
<td>CH_{4}, C_{2}H_{2}, C_{6}H_{6}, C_{4}H_{10}</td>
<td>CH_{4}, C_{2}H_{2}, C_{6}H_{6}, Ar, CO, CO_{2}</td>
<td>C_{6}H_{6} Polyphenyl-ether + N</td>
<td>Ar, Ar + H_{2}, Ar + CH_{4}</td>
<td>Ar, Ar + H_{2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid Target</td>
<td>-</td>
<td>-</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
</tr>
<tr>
<td>Impurity source</td>
<td>Reactor walls Filament, walls, gas Grid, walls, gas Liquid, gas</td>
<td>Gas, target, walls</td>
<td>Gas, target, walls</td>
<td>Powder, walls</td>
<td>Target</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen content (at%)</td>
<td>10 – 40 (soft); 40 – 65 (hard)</td>
<td>0 - 30</td>
<td>~ 1</td>
<td>5 - 30</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Some of these processes are summarized in Table 1 [28]. The hydrogen content in the films can vary from 0% to 65%. Most of the deposition processes also use ion bombardment of the coating during deposition, which affects film density and structure. The mechanical properties of the films depend on both of these factors.

2. Structure, Properties and Proposed Models

DLC films mainly consist of carbon, which exists in nature in different allotropic forms, namely graphite, diamond and polymers. Graphite, the stable phase, has hexagonal crystal structure and density of 2.6 g cm^{-3}. The planes in which hexagonal rings are present are weakly bonded to each other by Van der Waals bonds. Therefore, they can slide on each other with very minimal force, giving graphite extraordinary lubricating properties. It is soft, optically opaque, electrically conductive and chemically active. Its electrical conductivity is relatively high in crystallographic directions parallel to the
hexagonal sheets. Diamond has the largest bulk modulus of any solid, the highest atomic density, the largest room temperature thermal conductivity and very small thermal expansion coefficient. It is a metastable phase and exhibits the diamond cubic crystal structure, i.e. face centered cubic structure with two atoms at every lattice point with the second atom displaced by \(\frac{1}{4}\) distance from the lattice point position. It is the hardest natural material, transparent from far ultraviolet to far infrared, electrically insulating, chemically inactive and has a density 3.5 g cm\(^{-3}\). Carbon, with the addition of hydrogen, forms various types of polymers as well.

DLC, a novel material, forms by combining the above-discussed allotropic forms of carbon. Carbon forms a variety of crystalline and amorphous structures because it is able to exist in three different hybridizations, namely \(sp^3\), \(sp^2\) and \(sp^1\), as shown in Figure 1. In the \(sp^3\) configuration, present in diamond, each of the four valence electrons of each carbon atom are assigned to a tetrahedral directed \(sp^3\) orbital. This makes strong \(\sigma\) bonds to all four adjacent atoms. In the \(sp^2\) configuration, present in graphite, three of the four valence electrons of each carbon atom form trigonally directed \(sp^2\) orbitals, which make \(\sigma\) bonds in a plane. The fourth electron of the \(sp^2\) atom lies in a \(\pi\) orbital, which lies normal to the \(\sigma\) bonding plane. This \(\pi\) orbital forms a weaker \(\pi\) bond with a \(\pi\) orbital of one or

\[
\begin{align*}
\text{sp}\textsuperscript{3} & \quad \text{sp}\textsuperscript{2} & \quad \text{sp}\textsuperscript{1}
\end{align*}
\]

Figure 1: \(\sigma\) and \(\pi\) bonds in \(sp^3\), \(sp^2\) and \(sp\) configuration of carbon atoms [1].
more neighboring atoms. In the \( sp^1 \) configuration, two of the four valence electrons of the carbon atom form \( \sigma \) orbital, each forming \( \sigma \) bond directed along the \( \pm x \)-axis, and the other two electrons form \( p\pi \) orbital in the \( y \) and \( z \) directions.

Generally, the surface atoms of a covalent solid have broken or dangling bonds that cost energy, thereby increasing the surface energy. In order to minimize the surface energy, the surface reconstructs or restructures, reducing the number of dangling bonds. For Si (111), surface reconstructs in such a way that the dangling bonds move to nearest neighbor atoms and bond to each other. Similar reconstruction occurs on the diamond (111) surface. In the DLC, dangling bonds are very few or almost non-existent due to the hydrogen atoms bonding to them. Therefore, none or very minimal restructuring of surface takes place in DLC. The surface energy of DLC is lower than that of non-hydrogenated DLC [29]. The hydrogen in DLC matrix plays an important role in altering the film structure not only internally, but also on the surface as well as its properties. The total hydrogen content (including both bound and unbound) in the DLC matrix is mainly dependent upon the incident energy of the ions and radicals forming the film, and also on the type of precursor, ratio of the gases present in the chamber and deposition technique.

Overall, DLC is an amorphous structure with domains of \( sp^2 \)-bonded carbon atoms and \( sp^3 \)-bonded carbon atoms. The \( sp^3/sp^2 \) ratio of DLC films depends on the deposition conditions and technique, hydrogen concentration and other elements in the film. The \( sp^3/sp^2 \) ratio affects merely all the properties of the film. Typical properties of the different forms of DLC are compared to diamond and graphite in Table 2. In general, a higher ratio gives a more diamond-like character (higher hardness) [30]. Typically, the relative fraction of \( sp^3 \) and \( sp^2 \) bonding configuration of carbon atoms may vary from
Table 2: Properties of Carbon containing materials [1].

<table>
<thead>
<tr>
<th></th>
<th>$sp^3$ (%)</th>
<th>H (at.%)</th>
<th>Density (g/cm$^3$)</th>
<th>Friction Coefficient ($\mu$)</th>
<th>Chemical resistance</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>100</td>
<td>0</td>
<td>3.517</td>
<td>0.1</td>
<td>High</td>
<td>100</td>
</tr>
<tr>
<td>Graphite</td>
<td>0</td>
<td>0</td>
<td>2.267</td>
<td>-</td>
<td>Good</td>
<td>-</td>
</tr>
<tr>
<td>a:C-H hard</td>
<td>40</td>
<td>30-40</td>
<td>1.6-2.2</td>
<td>0.1-0.2</td>
<td>High</td>
<td>10-20</td>
</tr>
<tr>
<td>a:C-H soft</td>
<td>60</td>
<td>40-50</td>
<td>1.2-1.6</td>
<td>0.1-0.2</td>
<td>High</td>
<td>&lt;10</td>
</tr>
<tr>
<td>ta:C-H</td>
<td>70</td>
<td>30</td>
<td>2.0-2.5</td>
<td>0.1-0.2</td>
<td>High</td>
<td>50</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>100</td>
<td>67</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
</tr>
</tbody>
</table>

30% to 70%. The two limiting cases are diamond-like and polymer-like hydrogenated amorphous carbon films. A variety of tools have been used to estimate values of $sp^3 / sp^2$ ratio, namely, electron spin resonance (ESR), Raman spectroscopy, electron diffraction, optical spectroscopy, infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), X-ray excited auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), nuclear magnetic resonance (NMR), etc. Each of these techniques has its own merits and demerits, and the measurements obtained from them are sensitive to changes in the film structure. Some of the techniques are briefly discussed below.

Fourier Transmission Infrared (FTIR) Spectroscopy- is the study of the interaction of electromagnetic radiation with a chemical substance. When the radiation passes through the material, certain frequencies of the radiation are absorbed. The wavenumber (cm$^{-1}$), is popularly used to measure the position of an infrared absorption. FTIR spectroscopy is often used to obtain quantitative information on the $sp^2$ and $sp^3$ hybridization in DLC films by analyzing the FTIR spectra in the region 2700 to 3400 cm$^{-1}$. The C-H bonds have their stretch vibrations at different wavenumbers depending upon
the configuration of carbon atom. Curve fitting of the peaks obtained allows
differentiation between different kinds of electron hybridizations [31,32]. The $sp^3/sp^2$
ratio obtained by this technique may not be necessarily the actual ratio of the DLC film.
This is so because this technique does not give much quantitative information about C-C
bonds, though qualitative information can be obtained [33]. Typical FTIR spectra of DLC
film are displayed in Figure 2 [33].

![Figure 2: (a) A typical FTIR spectrum of DLC film (b) The deconvoluted peaks for the
C-H stretch vibrational absorption region [33].](image)

Figure 2: (a) A typical FTIR spectrum of DLC film (b) The deconvoluted peaks for the
C-H stretch vibrational absorption region [33].
Figure 3: Raman spectra of as-deposited and laser treated DLC films at different laser fluences [35].

Raman Spectroscopy- is based on the inelastic scattering of photons in the optical range of lattice vibrations. Raman spectra are sensitive to changes in translational symmetry and can be used to study disorder, formation of crystallites, or changes in structure of DLC films. Laser beams utilized in this technique can penetrate only a thin layer of carbon (20 - 50 nm), thereby limiting the information to the near surface of DLC films. The first order Raman spectrum for diamond consists of a single line at 1332 cm$^{-1}$ and that of graphite is a line at about 1580 cm$^{-1}$, G-band, [33,34]. In disordered graphite, which does not have the long-range translational symmetry, crystal momentum is no longer conserved and this causes significant changes in the spectrum. The most
pronounced effect is that in addition to G band, another disorder or “D” broad line appears at about 1535 cm\(^{-1}\), which is also associated with in-plane vibrations [33]. Typical Raman spectra of the as-deposited and laser treated DLC films are displayed in Figure 3 [35]. The spectrum of the as-deposited film shows an asymmetric broad band near 1570 cm\(^{-1}\). In the spectra of the laser-irradiated films, an additional feature appears in the region 1320-1350 cm\(^{-1}\). With increasing laser fluence, both the G- and D- lines become narrower and their relative intensities are changed. This fact has been interpreted as a development of graphitization induced by the irradiation of laser beam.

X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy- these are powerful non-destructive surface characterization techniques (electrons come from first few atomic layers of the surface) and are generally combined with ion milling to obtain information from subsurface layers. Both techniques can be exploited to obtain the chemical composition of the film and also the chemical state in which the elements are present [36]. Both techniques can also be utilized to analyze the \(sp^3\) and \(sp^2\) content of the carbon atoms in the film [1,37,38]. The different coordination in \(sp^3\) and \(sp^2\) bonded carbon atoms produces substantial differences in their chemical bonding energies and an advantage of XPS is that both \(sp^2\) and \(sp^3\) regions are seen and their weighting is the same [1].

The binding energy of C1s and Ti 2p obtained from XPS spectra of Ti containing DLC film is shown in Figure 4(a) [39]. And High resolution valence band XPS spectra of diamond, graphite and glassy carbon, are presented in Figure 4(b). Three distinct spectral regions can be observed in the valence-band spectra [40]. For diamond, region I has a peak between 16 and 21 eV binding energy (zero is the top of the valence band) and
arises from s-like bands. Region II has a peak between 10 and 15 eV with a strong mixture of s- and p- character. Region III has a broad peak between 5 and 10 eV that is attributed to the p- bands. For graphite, peak III can hardly be distinguished from the slope of peak II. The spectra of microcrystalline graphite and glassy carbon are similar to that of graphite.

In AES the derivative of electron energy distribution, dN(E)/dE is used for analysis. Auger peaks are relatively sharp features on a slowly varying background, and

![Figure 4 (a): C 1s and Ti 2p XPS spectra of Ti-containing DLC films.](image-url)
Figure 4 (b): Valence band XPS spectra, before (left) and after (right) correction for inelastic losses of diamond, microcrystalline graphite, crystalline graphite and glassy carbon [36].
they appear more prominently on dN/dE spectra. Figure 5 [41] shows AES of different carbon allotropes, that can be observed from the changes in the line shape of carbon Auger signals from diamond, graphite and amorphous carbon. The Auger peak for the DLC lies somewhere between those of the graphite and natural diamond. The observable difference between DLC and graphite can be clearly seen from Figure 5 (a) and (b). The peak at 255 eV shown by diamond is present in the DLC film spectrum whereas not in that of graphite. Further the shoulder in DLC film spectrum, around 260 eV, is not as pronounced as that in the graphite spectrum. Mirtich et al [42], had reported that the spectrum for natural diamond shows no shoulder and the main peak is shifted to higher energies. This can be caused due to the charging effect. They have also reported that after sputtering, the spectra from the carbon film and natural diamond become identical with that from graphite. It is thus difficult to distinguish the mixed phases such as graphite, diamond and amorphous carbon in the material.
Hydrogen Content: increase in DLC has a positive impact on its diamond-like mechanical properties and tribological behavior. The hydrogen content of DLC can be measured by NMR, nuclear reaction analysis (NRA), elastic recoil detection (ERD), combustion, hydrogen evolution or FTIR spectroscopy. Nuclear methods require special facilities but are widely used. They have the advantage that if used to determine the areal density of both H and C, then the desired H:C ratio can be derived without a measurement of the film thickness. The determination of H content by NMR requires the use of proton decoupling to separate the carbon bonded to C and H [43,44]. This method is rarely used because of the effort involved. NRA technique was used to analyze the amount of hydrogen in DLC films [45,46]. The following nuclear reaction takes place

\[
^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \text{gamma-ray}
\]

This reaction has a large cross section at the resonance energy of 6.385 MeV laboratory energy; yielding an alpha particle and a characteristic 4.43 MeV \(\gamma\) ray. The sample is bombarded with \(^{15}\text{N}\) with energy at or above the resonant energy and the yield of characteristic 4.43 MeV \(\gamma\) ray is measured by NaI scintillation detector. Hydrogen content at the surface is directly proportional to the \(\gamma\) ray yield when bombarded with \(^{15}\text{N}\) at the resonant energy. The NRA technique can also be used to carry out the depth hydrogen profiling of a material. For this, \(^{15}\text{N}\) with energy higher than the resonant energy is bombarded on to the sample. The reactions at the surface are negligible as the energy is higher than the resonant energy. As \(^{15}\text{N}\) penetrates the surface, it slows down and its energy reaches resonant energy at a certain depth. Now the yield of \(\gamma\) ray is proportional to the hydrogen at that depth. Hence, measuring the \(\gamma\) ray yield as a function of energy of beam, the H concentration as a function of depth can be determined.
X-ray and electron diffraction- these techniques are commonly employed to study the structure of films. X-ray diffractogram of DLC films, by wide angle method will show an overall amorphous nature of these films, whereas low angle method can show the presence of the nanocrystalline domains. Though, electron diffraction studies by TEM, are more sensitive on the scale of short inter-atomic distances, and more suitable for studying the short-range structure. Electron diffraction patterns of DLC films usually demonstrate wide, diffuse diffraction rings, suggesting a very small domain size and the overall amorphous nature of the films [33,47]. Liu and Meletis [4] had observed two diffuse diffraction rings with $d_{111} = 0.21$ nm and $d_{220} = 0.12$ nm, suggesting the presence of a short-range cubic diamond structure ($sp^3$). Evaluation of bright and dark field TEM images showed a three-dimensional network structure. These techniques are limited to study the (nano) crystalline nature of the DLC films and cannot be employed to explore amorphous DLC films as well as the local structure around the carbon atom and its coordination number. Whereas, X-ray absorption spectroscopy (XAS) has the advantage to study both the short range order and coordination number of the C atom.

X-ray Absorption Spectroscopy- X-ray absorption at the carbon K-edge depends principally on the atomic number and consequently the cross-section is independent of the carbon atom coordination. The $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ resonances in $sp^2$ carbon and $1s \rightarrow \sigma^*$ resonance in $sp^3$ carbon present a distinguishable difference in energy and a simple identification of each contribution can be made. X-ray absorption near edge structure (XANES) spectroscopy has been used in the past to study the amorphous and nanostructured carbon films [48,49].
Structure- Several structural models have been proposed for amorphous DLC, none of which has been generally accepted. The simplest model consistent with the observed H/C and $sp^3/sp^2$ bonding ratio, would be a covalent bond network consisting of diamond-like, graphitic and polymeric components, tetrahedrally and trigonally coordinated atoms with some bonds being terminated by hydrogen [50]. McKenzie et al [51], suggested a noncrystalline two-phase structure consisting of polycyclic aromatic hydrocarbon regions interconnected by tetrahedral carbon. They reported the nature of the as-prepared films as that of carbon network containing many hydrocarbon groups and that after heat treatment at 500°C in vacuum, the films would stabilize and their properties would resemble more to those of glassy carbon. Bredas et al. [52], proposed only a fused ring aromatic structure, interruption of which by any other component leads to localization of the electronic excitations on the graphitic parts. The connection between local coordination and macroscopic properties is made through the concept of random covalent network (RCN). Two types of RCN treatments have been applied to DLC (i) the theory of optimally constrained networks described by Thorpe [53], which defines the minimal degree of network connectivity required to achieve macroscopic rigidity, with the constraint that network can be continuously deformed, and (ii) the treatment of over constrained networks, in which the degree of over constraints is connected to macroscopic elastic properties by a simple empirical relationship [54].

The modified form of the RCN model coincides well with the NMR measurements indicating that graphitic clusters are present in DLC. These are locked in a slightly over constrained network that defines its mechanical properties. Although formally rigid, optimally constrained networks cannot be macroscopically hard. It must
be confirmed that the small degree of over constraint is sufficient to account for the observed hardness of DLC. He and Thorpe [54], treated an over constrained RCN in a simulation, in which bonds were randomly deleted from a diamond lattice and the resulting elastic properties calculated as a function of the average constraint in the remaining network.

Thus, it is seen that the hard and rigid mechanical nature of the films must arise from the structure of the matrix that makes up the bulk of the film. Angus and Jansen [55], modeled the dense, diamond-like hydrocarbon films (class of amorphous solid with extreme properties) as a fully constrained non-crystalline network (FCN model), using the constraint counting arguments of Phillips [56], Thorpe and Dohler [53,57]. The predictions of $sp^3/sp^2$ ratio and the average coordination number are in general agreement within the available experimental observations, particularly at the upper end of the hydrogen composition range. The model, as originally derived, predicts a range of compositions, from 0.17 to 0.62 atom fraction hydrogen, over which a fully constrained network comprising $sp^3/sp^2$ coordinated carbon atoms and hydrogen atoms can exist. The predicted stability range is in agreement with the observations.

Tamor et al [58], has proposed a defective graphite model for the structure of the diamond-like hydrocarbon. In this model, removing carbon atoms and saturating the resulting dangling bonds with hydrogen modify an initially perfect graphite crystal. Percolation theory is used to predict the upper and lower limits of hydrogen concentration. The defective graphite model predicts an existence range of diamond like hydrocarbons from 0.2 to 0.6 atom fraction hydrogen. The authors have reported that this approach is in variance to that of RCN models, but many properties expected of DLC are
reproduced in the very simple DG model, for which there is significant experimental support. Figure 6 shows the proposed two-dimensional model of DLC matrix.

Miyagawa et al [59], used dynamic Monte Carlo simulations with the binary collision approximation for synthesis of DLC film by plasma based ion implantation. They reported that the energy of the impinging ion plays a crucial role for the film structure and thereby, its mechanical, electrical, and optical properties. The $sp^3$ fraction of the film was reported to be highest till 100eV energy. Above that, it was observed and calculated to decrease.

3. Tribological Behavior and Wear Mechanism

DLC films are known for their low coefficient of friction ($\mu$) and wear rate. The $\mu$ values are generally reported in the range 0.05 to 0.2 and wear rates $10^{-6}$ to $10^{-8}$ mm$^3$/Nm. This subject has been recently reviewed by Donnet [9], Grill [29] and Erdemir and Donnet [60]. Donnet summarized the tribological behavior of DLC films by noting that high compressive stress (up to 3 GPa) results in poor adhesion to most substrates,
requiring adhesion-promoting interlayer and transfer layer builds up followed by easy-shear within the interfacial material. Whereas, Grill summarizes the review by concluding that tribological behavior of DLC, in all environments, is controlled by an interfacial transfer layer formed during friction. This transfer layer is formed by a friction-induced transformation of the top layer of the DLC film into a material of low shear strength, caused by friction induced annealing (as was proposed by Liu and Meletis [4]). Furthermore, he explains the low friction and ultra-low wear of DLC and counterparts by the low shear strength of the transfer layer. And Erdemir and Donnet summed their review by noting that tribological behavior of DLC coatings is strongly dependent on the nature of the films controlled by the deposition process and the parameters employed in wear testing of the films.

Erdemir et al [61] observed that hydrogen is essential to obtain low friction and high wear resistance in DLC films. They suggested that hydrogen passivates the dangling surface bonds of carbon atoms, which significantly reduces the adhesion component of friction. These results are supported by those of Paulmier et al [62], hydrogen terminated surfaces have lower friction compared to that which is terminated or contaminated by water or oxygen. Therefore, hydrogen content of precursor material and of the overall gas plays an important role in tribological properties of DLC films.

Tribological behavior of DLC film also depends on its structure. As mentioned earlier the ratio of $sp^2$ and $sp^3$ C-C bonds and hydrogen content and structure of the DLC films, depends on the deposition and process conditions. For example, the friction and wear properties of DLC films have been correlated to the energy of the hydrocarbon ions striking the growing substrate [59]. Zhang et al [63] reported that with increase in
substrate bias voltage, $sp^3$ C and H content decreased. This decreases the hardness and intrinsic stress along with wear resistance of the DLC film, though critical load increases and friction shows little variation.

Detailed studies of the friction characteristics conducted by Liu et al. [4,20,21,64], showed that the tribological behavior of DLC films exhibits three distinct friction regimes as follows. Initially, a break-in period with continuous decreasing friction coefficient exists, followed by an intermediate constant friction plateau of a relatively short duration which is preceding a low friction ($f_{-0.05}$) steady-state stage, Figure 7. The initial reduction in the friction coefficient during the break-in stage is attributed to the gradual release of hydrogen from the DLC structure at ‘hot spots’ producing a low-shear strength layer. The intermediate constant friction plateau is related to the transfer layer formation with possibly some small scale graphitization, whereas the steady-state stage was a result of extensive graphitization in the tribolayer [64]. The latter aspect was confirmed by
direct TEM from the tribolayer and constituted the basis for the ‘wear-induced graphitization’ mechanism. One important aspect of the aforementioned mechanism is the formation of a graphitic layer that in ceramic cases is also evidenced as a transfer layer. This is also supported by the recent results of Erdemir et al [65].

The potential applications of DLC films can be expanded by incorporating other elements, which can modify the properties of the DLC films while maintaining their tribological behavior. For example, DLC in itself, is only mildly hydrophobic. Therefore, different elements such as N, F, O and Si are usually incorporated into the coating to improve its hydrophobic property [66]. Furthermore, metal additions have the potential to modify the tribological behavior by slowing down graphitization kinetics and increasing thermal stability and mechanical properties.

B. Me-DLC Coatings

Synthesis of Me-DLC films was first reported as early as in 1980s. In 1985, Dimigen et al [67] reported work on nanocomposite Me-DLC, with metals as carbide formers (heavy transition elements) in DLC. In the 1980s, research in the area of Me-DLC was initiated using various metals Au, Cu, Ag, Cr, Ti, W, Ta, and Ru. Klages and Memming [5] had reviewed the subject of nanocomposite Me-DLC films.

1. Synthesis and Deposition Methods

Me-DLC films have been synthesized by different deposition methods, thereby providing a wide range of different film properties. Synthesis of hydrogenated amorphous silicon carbon (a-Si_{1-x}C_x:H) alloy films using glow-discharge (GD) decomposition of silane and a hydrocarbon, like methane or ethylene, has been reported since 1970s [68-70]. Saito [71] and Basa and Smith [72] had studied a-Si_{1-x}C_x:H alloy films prepared by
RF diode magnetron sputtering of silicon in methane-argon gas mixtures. Varying the partial pressure of methane with respect to the total gas pressure varied the carbon content and the properties of the films. These films were also synthesized using the electron cyclotron resonance plasma CVD method [73]. The Si-DLC films were also prepared by using energetic Ar\(^+\) ion beam and a vapor-deposited precursor material: tetraphenyl-tetramethyl-trisiloxane [10]. Tin containing DLC films were prepared from a tin foil in an Ar/ethylene atmosphere at 26 Pa using an inductively coupled glow discharge process [74]. Roy and colleagues, co-sputtered metal/polymer to prepare composites containing platinum, gold and copper [75,76]. Ti-and W-containing DLC films have been synthesized by glow discharge reactive magnetron sputter deposition in an Ar/CH\(_4\) mixture [77]. Deposition of Me-DLC films, by applying negative bias on substrate has positive impact on the film properties compared to that of neutral or positive bias [5].

2. Microstructure and Composition

Me-DLC films prepared by incorporating various metals and using different techniques, such as simultaneous evaporation of metal and carbon, or metal sputtering in the presence of hydrocarbon and argon gas mixture, will exhibit a range of microstructures and composition. Several techniques have been employed in the past to investigate the chemical composition and structure of Me-DLC films, such as XRD, XPS, AES, TEM and extended X-ray absorption fine structure spectroscopy (EXAFS).

The microstructure of Me-DLC is considerably different from that of DLC. When a carbide forming metal is used above a certain level, XRD investigations show small crystalline metal carbide clusters embedded in the DLC matrix. For example XRD of Ta-
Figure 8: X-ray diffraction pattern of Ta-DLC with varying at% Ta. [5].

DLC, exhibiting cubic TaC peaks, intensity of which varies with Ta content is shown in Figure 8. Similar results were obtained with other carbide forming metals such as Ti, V, W, Mo, Nb, whereas non-carbide formers Au and Ag resulted into metal clusters distributed within the DLC matrix [5]. They also reported particulate sizes between 1 and few 10s nm depending on the type of metal and its concentration. 2 nm of cluster size was obtained for Ta-DLC with 22 at% Ta.

Benndorf et al. [78] studied the structural properties of Nb-DLC films. From the diffraction line broadening they reported increase in particulate diameter from 2 to 4 nm with Nb content 20 to 40 at%. Meng and Gillispie [77] from their XRD results on Ti- and
Figure 9: XPS-spectra of (a) DLC and Ta-DLC with 25 at% Ta[5] and (b) typical C1s showing deconvolution of the observed spectrum [78].

W-DLC reported 3.5 and 1.2 nm cubic metal carbide precipitates, respectively. They also reported the increasing carbide precipitate size with increase in metal content in DLC films. A detailed analysis of the XPS spectra, for Ta and Ti-DLC, over a large metal content range has shown, that the spectra could only be deconvoluted keeping the carbon binding energies and the half width of each line within each phase constant, if a third phase (pseudocarbidic) is assumed as presented in Figure 9 (a) [5]. XPS results of Benndorf et al. showed both carbidic as well as polymer like carbon and with increase in Nb content polymer like carbon decreases and above 50 at% only carbidically bonded C is seen. A typical 1s C XPS spectrum for carbide forming metal incorporated in DLC is
Figure 10: Dark field micrograph of (a) W-DLC with 9.7 at% W [77] and (b) Ti-DLC with 2.5 at% Ti [79].

shown in Figure 9 (b). TEM results by Meng and Gillispie for W-DLC, Figure 10 (a), and Meng et al for Ti-DLC, Figure 10 (b), showed that nanocrystalline precipitates are uniformly dispersed in DLC matrix. XAS was used by Meng et al [79] to study the atomic bonding environment around the Ti in Ti-DLC films. Also, by combining XAS and TEM results it was determined that the dissolution limit of Ti in Ti-DLC is between 0.9 and 2.5 at%. Vadim et al used XAS to investigate the coordination and chemical environment around Si in Si-DLC [80] and constructed a model of Si-DLC structure. The resulting amorphous network is shown in Figure 11. Incorporation of Si in DLC shows that Si-DLC films are thermally more stable than DLC films [81], while maintaining or even improving tribological behavior.

3. Mechanical Properties

Kalges and Memming [5] summarized the hardness response of Me-DLC films by noting that differences in hardness as found with films containing different metals, are most probably due to hydrocarbon used for deposition: acetylene, ethylene and methane
Figure 11: Model for Si-DLC structure [80].

were used for preparing films containing W, Ta and Ti, respectively. The W and Ta-DLC hardness results as a function of volume fraction of segregated carbide, are shown in Figure 12 (a). It was asserted that qualitatively similar results with hardness values, 15 to 18 GPa, were obtained for Ti-DLC films containing up to 30 vol% TiC. They explained that the invariant hardness values below a critical fraction of segregated hard phase was due to yield behavior of the Me-DLC same as that of matrix, whereas the increase in hardness for larger volume fractions was due to formation of large extended clusters of carbide particulates. Further, they asserted that increase of the H/C ratio in the precursor gas leads to decreasing film hardness. Incorporation of non-carbide former metals Al, Cu, Ag, Ni and Au decreased film hardness. In contrast to hardness, Young’s modulus increased with carbide volume fraction even for small metal contents, Figure 12 (b).

Benndorf et al [78] had reported uniform increase in the compressive stress of Nb-DLC with increase in Nb content. Their films exhibited nearly constant hardness (~13 GPa) up to a volume fraction of ~ 50% NbC. Whereas, the Young’s modulus of the films
Figure 12: (a) Hardness and (b) Young’s Modulus of W- and Ta-DLC films as a function of volume % MeC [5].
deposited at low pressure increased immediately with increase in carbide volume fraction. Those of the films deposited at higher pressure showed nearly constant value (~100 GPa) up to 50 vol.% NbC. Baia Neto et al [82] showed that incorporation of Si into DLC reduced the residual stresses, while maintaining the hardness of the films up to about 50 at% Si. They attributed this to the increased density of voids in the films.

Ti-DLC films studied by Meng et al [7] exhibited a decrease in the elastic modulus and hardness with the incorporation of Ti up to 5 at%. The basic reason of this behavior is to be investigated. The above results are at variance to those reported by Meng and Gillispie [77] where the monotonic increase of hardness and elastic modulus with Me content was observed. Furthermore, hydrogen content in the Me-DLC films affect their mechanical properties though the fundamental understanding is still lacking [7].

4. Tribological Behavior

The main points from the review of tribological properties of Me-DLC films by Klages and Memming [5] are as follows. Low friction was observed for Me-DLC provided that the carbide forming metal is present at low levels (~0.15 at%), Figure 13. Qualitatively similar friction results were obtained for other carbide forming metals. Dependence of friction on load applied was observed for W-DLC containing 12 at% W. Friction decreased with increase in load, Figure 14. Similar to DLC films, dependence of friction on humidity was observed for W-DLC films. In dry nitrogen (R.H. < 0.1%) very low values, 0.02, were obtained for compositions <13 at% W. Whereas, in humid nitrogen values increased significantly as shown in Figure 15. Reversal of influence of humidity on friction values was noted for higher metal contents. Qualitatively similar
Figure 13: Friction of Ta-DLC as a function of at% Ta [5].

Figure 14: Load dependence of friction of W-DLC with 12 at% W [5].
Figure 15: Friction of W-DLC in low and high humidity nitrogen environment as a function of ratio of W/C [5].

results were obtained for Fe-DLC films. The low friction for DLC and Me-DLC in vacuum was explained by transfer layer phenomena. Under high humidity conditions, this phenomenon was not observed. Abrasive wear rates of various Me-DLC films is presented in Figure 16. The width of the wear rate curves increased from Ti (subgroup IVa of periodic table) over Mo and W (Va) to Nb and Ta (VIa). Within one subgroup, the minimum wear rate decreases with increasing atomic mass, for example compare Nb and Ta. Adhesive wear rates of W-DLC (12 at% W), in pin-on-disc configuration, were more than an order lower than those of TiN and TiAlN. The excellent tribological behavior of W-DLC is even more pronounced, compared to that of nitrides, if the wear of uncoated
Figure 16: Abrasive wear rate of Me-DLC as a function of at% metal [5], ‘Calo-Test’ apparatus was used with aqueous suspensions of 5 µm Al₂O₃ particles.

ball is considered. Finally they compared tribological properties of Me-DLC with their mechanical properties, however, found no relation between abrasive properties and hardness of the films. They suggested that since these properties are not yet understood, further investigations are required.

Recently, Donnet [9] reviewed the tribological properties of Me-DLC films. Si incorporation in DLC structure affected most of the films properties, such as decrease of surface energy and internal stress, and tribological behavior. Friction reduces significantly (< 0.1) compared to conventional DLC in ambient air, with comparable wear resistance. This was observed for low contact pressures, < 1 GPa. At higher contact
pressures wear rate of conventional DLC films were superior. Further he asserted that generally, metal incorporation reduces compressive residual stress compared to pure DLC. Ambient air tribological tests exhibited steady-state friction in the range of 0.1 – 0.2, with slight dependence on the humidity, load and metal content. Interesting optimum wear rates may be obtained for each type of metal, with a concentration that seems to depend on its nature. The tribological behavior of Me-DLC films was explained by a combination of ceramic-like properties (high hardness, H) and polymer-like properties (high elasticity, E, and low surface energy, S), thus leading to high H/E values and low S/H values.

Bewilogua et al [83] has reported that all the Me (Ti, W, Nb)-DLC films in their study show adhesive wear and among the three Me-DLCs, Nb–DLC shows the lowest coefficient and intermediate wear resistance. They also reported that all the three Me-DLC films show low wear rate, though all of them have lower wear resistance than pure DLC film. Su et al [84] also studied the Ti-DLC system and discussed the transfer layer formation on the counter body (1045 steel cylinder) under unlubricated conditions. They have also reported that the wear mechanism, for the Cr_{30}/Ti_{30}-DLC film and 1045 steel cylinder system, is adhesive and tribo-oxidative wear. Further, Meng et al. [79] had reported monotonic increase of the coefficient of friction with the increase in content of Ti in Ti-DLC films in the unlubricated condition and found that it does not follow the pattern of the hardness of the films. In another study on the same system, Cao et al [85] found that the wear rate as well as the coefficient of friction of Ti-DLC, was independent of the Ti content up to 20 at. % and was reported to be \( \sim 5 \times 10^{-7} \) mm\(^3\)/N-m and 0.1, respectively. From 20 to 30 at% Ti, it increased with the Ti content and after 30 at% of Ti
it again became constant at \( \sim 4 \times 10^{-6} \text{ mm}^3/\text{N-m} \) and 0.28. The exact mechanism is not clear and needs to be investigated further.

In brief, previous experimental studies show that the incorporation of Me into DLC films changes the microstructure of the DLC films and modifies their tribological properties. The friction coefficient of metal containing DLC films can be comparable to that of DLC films whereas the wear resistance is inferior. However, the mechanism behind the tribological behavior of the Me-DLC films is not yet completely understood. Since the Me-DLC films are not yet studied and explored in depth, therefore potential of further optimization of wear properties of Me-DLC films still exists. In spite of the interesting properties exhibited by Cr, little work has been reported on Cr-DLC films. More importantly, to the best knowledge of the author, no systematic study has been performed to understand the fundamental wear mechanism of Cr-DLC films and the effect of Cr content on their microstructure and wear mechanism.

**C. Me/DLC Multilayered Films**

In the recent past, multilayer coatings have been attracting considerable research interest due to their high potential for engineering applications. This is so because these have the capability of combining the interesting properties of different materials to meet specific performance requirements that cannot be achieved by a monolithic layer. For example, the multilayers can have strength well above that of the monolithic layers involved. Furthermore, the nanoscale effects that can significantly enhance the mechanical properties of the material can be incorporated in the multilayer by modulating the thickness of the individual layers.
A multilayered structure that resisted the deformation and was not susceptible to brittle fracture was first proposed by Koehler [86]. According to Koehler’s theory, a structure comprised of alternating layers of two suitable materials can exhibit a resistance to plastic deformation greater than that expected from a homogeneous material of the two constituents. A requirement for the two selected materials is that their dislocation self-energies should be appreciably different, leading to an energy barrier effect that can be further enhanced by interfacial dislocations, misfit elastic strains, and mismatch of glide systems. Further strengthening can be produced by suppressing the generation of dislocations within the layers by reducing the layer thickness. Such strengthening effects have been experimentally verified [87]. Following Koehler’s model there were many theoretical and experimental studies on multilayers. At present, there are several application areas of multilayers, including [88]:

(i) The use of single or several interlayers to enhance the adhesion of coatings. The interlayers are essentially used to minimize the differences between coatings and substrate with respect to mechanical, chemical, or thermal properties;

(ii) Multilayers with monolithic layers of nanoscale thickness that inhibit dislocation motion, and thereby possess extremely high strength;

(iii) The use of ductile and tough and hard and brittle alternate layers to avoid the significant stress concentrations that may occur with thick hard coatings;

(iv) Employing the alternating layers that can improve the fracture toughness either by introducing layer interfaces to stop the propagation of cracks or by providing a relatively tough medium through which propagation of cracks is prohibited;
(v) The use of multilayered structures to minimize the residual strain (residual stress) within coatings, mainly to enhance the effective adhesion and strength;

(vi) Using the individual layers that can provide distinct physical or electrical properties, such as diffusion, thermal, or insulating barriers.

The multifunctional character of the multilayer coatings along with moderate residual stresses, good hardness-to-toughness ratio, low friction coefficients and good adherence to substrates provides them broad scope of applications and makes them suitable as a composite exposed to complex service conditions [89]. Additionally they can have a combination of layer materials with different functional characteristics and their structure inhibits the growth of columnar structure. Further, a fine-grained multiphase structure with large number of interfaces often improves the crack propagation resistance and thus the toughness of the brittle ceramic bulk materials. The hard coatings performance can also be improved similar to those of brittle ceramics. Along with high hardness, high toughness is also important for high performance. This is so because cracks, fractures, or poor adhesion due to high stresses can lead to early coating failure. The large amount of interfaces in the coating by the formation of nanocrystalline or multilayer films should help to overcome these problems. It is well known from fundamental studies on the relations between wear and material properties that abrasive wear, fatigue strength, and fracture of materials are dependent on the proper toughness-to-strength ratio [90]. The large number of interfaces in multilayer coatings are also sites of energy dissipation and crack deflection, leading to a toughening of the layer material. Therefore, in designing a multilayer coating, we have to consider a structural and functional design. The functional design can be used to combine different materials
with different strength, toughness, and wear properties in the coatings, and the structural
design can be used to adjust the grain size, the shape of the grains, the amount and
constitution of interfaces, the thickness of the individual layers. This provides us the
opportunity to tailor the properties such as the hardness-to-toughness ratio, or the strength
at higher temperatures for specialized applications [89].

The hardening mechanisms were explained by a combination of two effects that
inhibited dislocation motion across the layers, Shinn et al [91]. The primary hardness
enhancement was related to the difference in dislocation line energies in the TiN and
NbN layers. A secondary reason was related to coherency strains. The maximum
hardness occurred where the layers were too thin for coherency-strain relaxation or
dislocation motion, but thick enough that the NbN layer provided effective “potential
wells” so that dislocations and interdiffusion did not significantly reduce the composition
modulation amplitude. Similar effects were found in another single-crystal TiN/VN
strained-layer superlattice system by Helmersson et al [92].

With the help of highly advanced deposition techniques, individual layer
thickness of nanometer size can be deposited with high precision. The coating materials
for wear protection can be classified according to chemical bonding character: metallic,
covalent or ionic hard material. Examples of covalent bonded materials are DLC, AlN,
SiC, etc. These are difficult materials to coat as single layers because of their poor
adherence to metallic substrates. However, when deposited as layers on other covalent or
metallic layer by sputtering, exhibit a better bonding. DLC films are known to have
adhesion problems when deposited on steels, titanium, etc. The intrinsic compressive
stresses in the DLC films further restrict their area of applications. Recently, multilayers
with alternate DLC and ceramic layers are being explored [93] due to the potential of reducing the internal stress and improving the adhesion to substrate, and exhibiting tribological properties comparable to those of DLC. However, one is struck by the very limited work performed in the area of DLC multilayers.

1. Synthesis and Processing

Multilayer coatings can be deposited by using PVD and/or CVD and PECVD techniques. Coatings synthesized by CVD are deposited at relatively high temperatures, thus the interfaces between the layers are not very sharp owing to the inter-diffusion of the elements involved. Whereas, the coatings synthesized by PVD are deposited at relatively low temperatures. Also, PVD processes have an advantage in terms of flexibility in controlling the thickness of each layer, and the deposition rate is much faster than that obtained in the CVD process. Magnetron sputtering is one of the most promising methods for deposition of multilayers and normally a sequential magnetron sputtering system is employed [94]. Magnetron sputtering in the presence of reactive gases can also deposit ceramic coatings. Using these techniques, a range of metals and ceramic layers of desired thickness, down-to nanometer size can be deposited onto any substrate.

2. Mechanical Properties and Tribological Behavior

A number of ceramic/ceramic and metal/ceramic systems involving metal nitride (TiN, AlN), carbide (TiC, CrC, B₄C) and boride (TiB₂) films or TiₓAlₓN, Ti (C,N), Ti-B-N or Al₂O₃ and sputtered carbon have been investigated and work in this area has been recently reviewed by Munz [95]. The advantage of these systems is that nanoscale multilayered hard coatings can be manufactured in the hardness range between 25 GPa
Table 3: Mechanical properties of ceramic and multilayered films

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film</th>
<th>Hardness (GPa)</th>
<th>Scratch (Lc/N)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiAlN-ZrN</td>
<td>41</td>
<td>55</td>
<td>Donohue et al.</td>
</tr>
<tr>
<td>2</td>
<td>TiAlN-TiNbN</td>
<td>26</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TiN-W&lt;sub&gt;2&lt;/sub&gt;N</td>
<td>30</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt; (dep at 100°C)</td>
<td>39</td>
<td></td>
<td>Mollart et al.</td>
</tr>
<tr>
<td>5</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt; (dep at 400°C)</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>TiN</td>
<td>20</td>
<td></td>
<td>Zhou et al.</td>
</tr>
<tr>
<td>10</td>
<td>CrN</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>TiN-CrN</td>
<td>30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and 55 GPa by modulating the thickness and choice of the individual layers. Table 3 shows the mechanical properties of some of the multilayer coatings [96]. Mollart et al [97] reported that the hardness and young’s modulus of TiB<sub>2</sub>N<sub>x</sub> (some reported in Table 3) decrease continuously with increase of nitrogen content due to the increased proportion of the soft BN phase. Zhou et al [98] showed significant increase in hardness of the TiN/CrN multilayer deposited with modulation period of 21 nm, compared to the individual components, TiN and CrN, Table 3. Alpas et al [99] reported on Al/Al<sub>2</sub>O<sub>3</sub> system that by modulating the thickness of the monolayer the strength of the film can be tailored as desired. Their results are summarized in Figure 17.

Ziegler et al [100], have reported hardness and Young’s modulus for metal-carbon multilayer films. They measured 27 GPa hardness and 270 GPa Young’s modulus for Ti-C multilayer and <20 GPa hardness and ~200 GPa Young’s modulus for Al-C multilayer. Furthermore, hardness tests showed that Ti-C multilayer coatings adhesion to substrate was poor whereas that of Al-C multilayer coatings was good. They suggested that cracks caused by the indenter were much better deflected by Al interlayer than by Ti interlayer,
Figure 17: Flow stress as a function of interlamellar spacing in Al/Al₂O₃ composites (Hall-Petch plot) [99].

therefore, ductility of Al resulted into better toughness to hardness ratio. In both studies, friction and wear properties were not studied.

Zhang et al [101] have studied the wear behavior of TiC-TiN multilayer coated system and have suggested that the wear of these coatings occurs by the removal of the material layer by layer. They have reported that multilayer coating performed better than the single layer coating and both were better than uncoated steel. Lyubimov et al [102] based on their mathematical model and calculations on PVD TiN and titanium layers on stainless steel substrates, have suggested improved adhesion, reduction of stresses in multilayers, along with reduction of defects and imperfections at the interfaces. A
Inhibition of grain growth
(crack splitting, interface toughening, stress relaxation)

Crack deflection
(reduced crack propagation)

Interface ‘opening’ or delamination
(reduced stress concentration)

‘Nanoplasticity’
(energy dissipation, reduced crack propagation, stress relaxation)

Figure 18: Mechanism for toughness of multilayers [89].

A multilayer system that has attracted the attention in recent past consists of TiN/ carbon layer. This has a very low coefficient of friction, in addition to a high wear resistance. The amorphous carbon layer provides the lower friction coefficient, and the presence of interfaces due to the alternating layers of amorphous carbon and TiN imparts additional toughness by arresting crack growth. The mechanism of improvement in toughness in the multilayer system is shown in Figure 18 [89]. It has been proposed that the cracks are deflected by the interfaces, which toughen the entire matrix. Koskinen et al [103] has vindicated this mechanism by experiments. They reported lower friction coefficient for TiN and DLC multilayers than that of pure DLC films. However, the wear rate of the multilayer film increased slightly and that of counter surface increased about ten fold. A
multilayer system consisting of WC and DLC [93] improved the adhesion of the upper DLC layer to steel substrate while maintaining its low friction coefficient.

In spite of the potential shown by the carbide forming metals as a layer along with DLC, to the best of our knowledge no work has been performed in the area of multilayers using metal and DLC layers. Thus, a study to develop a fundamental understanding of the tribological behavior of nanocomposite multilayer coating of a carbide forming metal and DLC would have a lot to offer in advancing the field in this direction.

D. Functional Coatings and Nano Inter Layers

As mentioned previously a major drawback of the DLC coatings, preventing their widespread use in tribological systems, is the interface problem that can adversely affect the adhesion and thus, their durability. One of the principal reasons is the significant difference in the mechanical behavior between the hard DLC coating and underlying metallic substrate (elastic and/or plastic strain mismatch). These effects are more pronounced when the coatings are applied to relatively soft substrates, such as steels, Ti and Al alloys. An innovative approach that can provide a promising solution to these limitations is the design of novel functional coating systems with functionally graded interfaces (FGI), Figure 19. For example, a surface hardening treatment can be first performed producing a FGI layer that can serve as a precursor to coating deposition, achieving improved strain accommodation resulting in enhanced adherence and coating support. Meletis et al. [104] studied this concept in Ti-6Al-4V alloys and demonstrated that development of a FGI by plasma nitriding (hardness gradient) prior to DLC deposition, produced a three-fold increase in the coating lifetime. Liu et al [4,20,21] performed a detailed study on the same system utilizing the same concept. An important
result of this study was that the DLC coatings, during wear experiments using higher loads, failed when yielding in the substrate reached the interface of substrate and hard DLC coating. Therefore, a complimentary route, to further improve the interface of the substrate and DLC coating proposed here would be to introduce a functional interlayer, which is compatible to both the nitrided substrate and the hard DLC coating. Koskinen et al [105] have studied the effect of adding a nano-layered molybdenum/ titanium intermediate layer in between the DLC coating and steel substrates in terms of the mechanical properties and the bond strength, which was evaluated using scratch indentation testing. Although the Mo/Ti layer had poor adhesion to the substrate, it showed improvement in the hardness and elasticity of the multi-layer system. Cr, a hard carbide former metal has potential to form strong bond with C, is soluble in Fe and has good compatibility to steels as they both are known to have bcc structure and their atomic radius has a less than 1% difference. PVD technique, such as magnetron sputtering can be
exploited to deposit very hard and tough nanocrystalline Cr interlayer on plasma nitrided steels prior to DLC deposition.

Intensified Plasma Assisted Processing (IPAP), a novel nitriding technique, was developed in the recent past in our laboratory [106,107]. In the IPAP technique a glow discharge is employed in a triode configuration. Here, in the triode configuration a positive electrode and a hot filament (for thermionic emission of electrons) were introduced in an innovative manner to intensify the glow discharge. Intensification of glow discharge can also be achieved by other methods including electron emitter, RF fields and magnetic fields. However, one of the most effective methods is thermionic emission process [108,109]. The novelty of this process is that it is conducted at relatively low pressures compared to conventional (diode) plasma processing. In IPAP nitriding the current density can be modulated independently of other processing parameters: chamber pressure and substrate bias voltage. Furthermore, this technique is characterized by a high degree of ionization, thereby, greatly improving the throwing power of the plasma, achieving low-temperature diffusion treatments and synthesis of a range of advanced compounds.

In the past, IPAP nitriding has been used successfully to process many different and difficult systems, for example, austenitic stainless steels [108,110], Ti and Ti alloy [111,112] and Al alloys [113]. Stainless steel nitrided by IPAP demonstrated the presence of a single-phase layer [114] on the top surface with hardness several times that of the substrate, followed by a nitrogen diffusion zone. Plasma nitriding mechanism details have been discussed in details elsewhere [115]. In brief, N$_2^+$ ions undergo charge exchange and dissociation processes at very short (~5-6Å) distances from the surface of
the substrate, and strike the surface as mainly neutral nitrogen atoms. According to the collision dissociation mechanism, energetic ions collide with nitrogen molecules which dissociate and produce active nitrogen atoms. These active nitrogen atoms react with a substrate forming the nitride layer. An alternate view supported by other researchers is that nitrogen ions are the species responsible for the nitride layer formation. The surface layer along with a thin layer below it can act as a source for vacancies and interstitials, was suggested by Shockley [116]. Hudis [117] study on ion nitriding in nitrogen-hydrogen - argon atmosphere concluded that ion nitriding is not a gas absorption process and that it requires ionic bombardment. Therefore, in spite of controversy regarding the nitriding mechanism, the crucial thing that produced nitriding was bombardment of the substrate by the energetic particles (neutrals or ions) generated by plasma.

The enhanced ionization concept has also been previously utilized in ion plating. The beneficial effects of ion bombardment or enhanced ionization are mainly producing an equiaxed coating microstructure (refinement) at low bulk temperatures and atomic mixing at the substrate/coating interface impacting on adhesion. Ion plating utilizes concurrent or periodic bombardment of the depositing film by atomic-sized energetic particles, to modify and control the properties of the depositing film. Here, the energy, flux and mass of the bombarding species along with the ratio of bombarding particles to depositing particles are important processing variables. The energetic particles used for bombardment are usually ions of an inert or reactive gas, or in some cases, ions of the condensing film material. Ion plating can provide hard and dense nanostructured metal coatings. Deposition of Cr by PVD [118,119,120] is an environmentally clean alternative to electroplating that is hazardous (produces toxic Cr^{+6}).
1. Structure, Properties and Tribological Behavior

An in-depth study on duplex system was performed in our laboratory by Liu [20], where tribological behavior of DLC deposited on IPAP nitried Ti alloy was studied. The important results of the study are given below in brief:

The DLC films synthesized by IBD technique exhibited dense, amorphous structure and possessed high hardness, low coefficient of friction, 0.06-0.08 and low wear rate, $1.6 \times 10^{-9} \text{ mm}^3/\text{Nm}$. The low friction and wear rate were attributed to the low shear strength of the hexagonal graphite planes.

The graded interface produced by surface hardening using plasma nitriding reduced the size of the yield zone compared with the original substrate. The size and growth rate of the yielding zone increases with increasing contact stress, and the critical contact stress for the onset of yielding increases with coating thickness. As the friction coefficient increases, the initial yield location moves towards the coating substrate interface along the sliding direction, meanwhile the normalized size of plastic zone increases. A higher coating/substrate modulus ratio brings the initial yield location toward the coating/substrate interface and increases the size of plastic zone. Theoretical analysis showed that a multilayer system with a gradient in modulus is expected to result in a reduction of the maximum equivalent stress on the contact surface and in the substrate. This concept presents high promise and needs to be studied experimentally.

At low external loading, the FGI had a small effect on durability of DLC because the interfacial region of the coating/substrate system is mainly in the elastic regime. In this case, the lifetime of the DLC coating is determined by the wear process, that is gradually consuming the film. At higher loading levels, the presence of the FGI resulted
in a progressively more significant effect that reaches an improvement of about 80% in durability for the loading levels applied in the study. These positive effects are attributed to the reduction of the plastic zone size developed in the substrate and the prevention of yielding from reaching the coating/substrate interface. Interlayers are expected to strengthen the substrate/coating interface and thus impact on adhesion.
IV. EXPERIMENTAL DESIGN AND PROCEDURES

The three different types of coatings, with high potential for advanced tribological systems, synthesized and characterized in the present study are schematically shown in, Figure 20. All the different coatings and plasma treatments were performed in our laboratory utilizing a multi-purpose surface modification system, Figure 21. The capabilities of the system include: intensified plasma nitriding, dual magnetron co-sputter deposition, ion-beam deposition and ion-beam and plasma- assisted deposition.

Figure 20: (a) Nanoparticle composite, (b) multilayered nanocomposite and (c) functional interlayer.
Figure 21: Schematic of the IPAP system with triode configuration.

A. IPAP Processing System

The surface modification system designed and constructed in our laboratory allows three different modes of operation, such as conventional (diode) and intensified (triode) plasma assisted processing, ion beam assisted deposition/treatment, and magnetron sputter deposition. A schematic of the system is shown in Figure 21. It stands 0.56 m high and has a diameter of 0.45 m. The system consists of a base plate, holding two planar magnetrons; ion beam gun; thickness monitor, connected to the mechanical and diffusion pumps, a cylindrical stainless steel chamber and a top plate supporting the
specimen holder. All three components of the system have ports to accommodate electrical and mechanical feedthroughs.

A filamentless broad beam ion source, 3 cm in diameter, by Anatech Ltd. is attached to the bottom plate and is connected to electrical and gas feedthroughs through the bottom plate ports. The ion source is powered by IS-3000 Anatech power supply and is capable of delivering energetic particles in the energy range of 5 eV to 1200 eV. The ion gun is mounted on a swivel collar mount allowing height, tilt and rotational motion.

Two D.C. magnetron guns (Torus 2C), capable of sputtering from 2” diameter 0.25” or 0.125” thickness target, are also attached to the bottom plate. Both magnetrons, facing upwards, are flexible in terms of angle of deposition and can be adjusted so as to deposit at the required angle on the substrate. One of the magnetrons is powered by a MDX 500 power supply and the other by a MDX 1k power supply, with maximum sputtering power of 0.5 kW and 1 kW, respectively. A MDX SPARC-LE 20 unit is connected in the latter magnetron allowing pulse mode operation and deposition of ceramic coatings. A thickness monitor, Leybold Inficon, is also installed on the bottom plate to determine the in-situ growth rate and thickness of depositing thin films. The sensor is positioned close to the sample in line of view from the two magnetrons and ion beam source, and regulated by a deposition monitor (L.H. Inficon model XTM/2) that displays the deposition rate, thickness and elapsed time. A motor driven shutter, controlled by a relay timer has also been placed between the two magnetrons that can be used to cover either of the two magnetrons. The relay timer can control the predetermined time for the shutter to stay on the magnetrons.
The intensification of the plasma in the system is achieved by a thermionic emission filament and a positive electrode. The filament is made from 0.5 mm diameter tungsten wire (R.D. Mathis company). An austenitic (non-magnetic) stainless steel plate (8 cm X 6 cm) is used as the positive electrode and is positioned diametrically opposite to the filament. The positive plate is operated by a 250 W low current HCR power supply (model 150-2-110). The thermionically emitted electrons from the filament are attracted by the positive bias applied to the positive plate. In their path, electrons interact with gas ions and neutrals present in the plasma, especially in the vicinity of the sample, thereby, intensifying the plasma. This allows independent control of the cathode current density on the sample and obtaining relatively high current densities at low pressures.

A high voltage cathode assembly capable of providing rotational motion to the sample ensures uniform intensified plasma-processing conditions (nitriding or film deposition) for the whole sample. A 2000 V Hewlett Packard 6522A high voltage, low current power supply, powers the cathode.

Various gases can be introduced into the chamber. The flow rate is controlled individually for each gas by MKS mass-flow meters (Type 1159). The latter are controlled by a MKS controller type 247C 4-channel readout that has also the capability to control ratio of gases admitted into the chamber. Vacuum level in the chamber is monitored by a MKS baratron type 122A absolute pressure gauge powered by a MKS type PDR-D-1 power supply with digital readout. In the lower region of the system below the base plate, there are two thermocouple vacuum gauges to monitor pressure in the fore-line to the diffusion pump and the bottom of the chamber. Vacuum in this system is maintained by a Varian VHS-4 diffusion pump filled with DOW Corning 704 oil and an
Alcatel 2033 mechanical pump, filled with mechanical pump oil # 19, capable of pumping 765 lit/min. (27 CFM). The baratron vacuum gauge can be used down to 1 mtorr. Pressure below this level is monitored by an ionization gauge (bayerd alpert tube) connected to Perkin-Elmer, Digital Gauge Control-III.

**B. Nitriding of 4340-Steel and Chromium Ion Plating**

4340-steel samples were polished down to 1µm size alumina powder. Subsequently, the samples were ultrasonically cleaned with acetone as solvent, dried in air and mounted inside the chamber. The samples were received in annealed conditions and were tempered before nitriding. The annealed material has a hardness of 96 HRB (HK 231). Tempering of the samples was performed by heating to 800°C for 65 minutes, followed by quenching in oil and then, tempering at 500°C for 3 hrs. This will produce a final hardness of 38 HRC (HK 380).

The IPAP nitrided steel samples were ion plated with Cr by magnetron sputter deposition in the presence of argon gas at pressures around 10-12 mtorr. A preliminary study was conducted on magnetron sputter deposition of Cr and it was observed that a stable plasma of magnetron was obtained around 10-12 mtorr pressure. In the present system pressures below 10 mtorr made the magnetron plasma unstable. Further, higher pressures are not preferred due to decrease in deposition rate. Generally, at pressures higher than 5 mtorr the sputtered ions/neutrals are thermalized before they reach the substrate. Thermalization is the energy reduction of high-energy particles to the energy of the ambient gas due to collisions, as the particle moves through the gas. The optimal conditions for obtaining dense, adherent and strong ion plating of Cr was obtained by carrying the depositions on Si and analyzing them by TEM and performing...
microhardness measurements. The substrate was mounted inside the chamber and after attaining a base pressure of the order of $10^{-6}$ or lower, the chamber was flushed with argon gas several times. Subsequently, the steel substrate was sputter cleaned for 20 minutes or less at a substrate bias of -1000 V and pressure 100 mtorr, with Ar flowing at a rate of 20 sccm. Then, the substrate was covered by the shutter and the magnetron target was sputter cleaned for 5 minutes, at a power of 50 W, keeping the same flow rate of Ar as above and pressure at 20 mtorr. The base pressure of $1 \times 10^{-5}$ or lower was maintained throughout the duration of the experiment.

Magnetron sputtering has long been available as a physical vapor deposition technique. Here, the sputtering rate of the target is a function of the total chamber pressure and magnetron current, voltage or power, based on the mode it is working in-current, voltage or power, respectively. When the magnetron is operating in the current mode, generally the sputtering rate of the target increases with magnetron current. This is so because with increase in magnetron current, the flux of electrons that sputters the target increases. Therefore, there is a larger flux of ions and neutrals generated from the target. This can lead to increase in the deposition rate and change in the structure of the coating. However, when reactive gases are used, the scenario is much more complicated and the flux of ions/neutrals of target reaching substrate will also depend on the amount of target poisoning. Increasing the pressure can have much worse affect due to increased poisoning of the target.

C. Deposition of Nanocomposite DLC and Chromium Interlayers

The nanocomposite Cr-DLC and multilayered Cr/DLC films were deposited on single crystal (100) Si wafer. Samples, of ~5 cm (2”) diameter or square pieces of 15 X
15 mm cut from the ~10 cm (4”) diameter wafer, were cleaned ultrasonically with acetone as solvent, dried in air and then mounted inside the chamber. The wafer was masked in two places (diametrically opposite) at the edge while mounting to prevent deposition. These areas were later used to measure the film thickness. The silicon substrate was sputter cleaned at a pressure of 25 mtorr and substrate bias –1500 V, for about 20 minutes.

1. Nanocomposite Cr-DLC Films

DLC film was deposited by using dc plasma (diode configuration), generated between the negatively biased substrate and the grounded chamber. The deposition rate depends on the chamber pressure, ratio of argon to methane, and substrate bias, and it was calibrated to produce a layer of desired thickness by using the thickness monitor.

Cr-DLC films were synthesized, by incorporating the metallic element (Cr) into the DLC via magnetron sputtering of pure Cr target by an argon and methane gas mixture. Such a process results in co-deposition of Cr and DLC. The substrate was mounted and sputter cleaned using the same process as noted earlier. Methane was introduced into the chamber after cleaning the magnetron target and the flow rates of argon and methane adjusted to the predetermined values. Initially, the magnetron current (or power) was kept low and then was slowly increased to the desired level. This was followed by applying the required bias to the substrate and moving away the shutter to initiate the deposition. A negative bias was applied to the substrate in order to enhance reactivity, and promote bonding between the chromium and the carbon network in DLC and also to improve adhesion of the coating to the substrate. The Cr content to be incorporated in the DLC was controlled, by controlling the magnetron current, processing
pressure and substrate bias. A broad range of Cr content was investigated starting from less than 0.1 at% to more than 17 at%. A preliminary calibration study was performed to correlate current density to Cr content for the given deposition conditions. A set of deposition experiments were conducted to vary the Cr content from less than 1 at% to more than 15 at% Cr in the Cr-DLC film.

The produced Cr-DLC coatings were characterized by HRTEM in terms of structure, size and distribution of nanoparticulates. Also, short-range order characterization was accomplished by XAS measurements and subsequent analysis/modeling. Improvement in thermal stability of DLC was previously observed by incorporation of Si [11]. In the present study, thermal stability of the modified DLC coatings was investigated by conducting thermal annealing experiments at 300°C and 350°C. Microhardness of the coatings was studied as a function of annealing temperature keeping the time constant (30 min.). Graphitization is accompanied by a sharp decrease in hardness and thus is indicative of the transformation of the $sp^3$ C bonding.

The tribological behavior of the Cr-DLC coatings was investigated by conducting pin-on-disc experiments to obtain and study the frictional response as a function of Cr content. As discussed earlier, two surfaces come into contact at asperities. And during friction, the interaction between two surfaces can create a temperature rise on the contacting regions, which may induce microstructural changes and phase transformations. Dealing with thin films and given the small material volume involved in the contacting asperities, it is evident that these changes occurring at asperities play a fundamental role in the tribological behavior. Besides nature of contacting surfaces, the principal value of temperature rise is mainly related to external load and sliding velocity
due to friction-induced heat [121]. Thus, in the present wear experiments, different loading levels were chosen to investigate its effect on the tribological behavior of Cr-DLC coated surfaces. Also, the interaction of Me-DLC film with metal and ceramic was investigated by using two different pin materials, 440C steel and alumina. Following testing, wear tracks were characterized by using an optical profiler to determine their morphology, surface roughness, wear rate and maximum penetration depth. The wear scar of the pin was studied and quantified using a metallurgical optical microscope. Characterization of the wear track region was also performed by using other analytical techniques (SEM for morphology and wear debris, energy dispersive spectroscopy (EDS) for chemical composition) in order to help us identify structural or compositional changes occurring during wear that can infer important mechanistic information useful in determining wear mechanism.

2. Multilayered Cr/DLC Films

A series of Cr/DLC nanolaminates were developed by varying the interlamellar spacing and then characterized by various complimentary techniques. It has been documented that strength in these multilayered coatings in general increases by decreasing the interlamellar spacing, Figure 17 [99]. The objective was to produce hard coatings with minimal internal stress, improved adhesive behavior and tribological properties close to those of the DLC coating. It may be noted that alternating layers were deposited with various layer thicknesses, within the Hall-Petch region but also in the vicinity of critical level (level below which Frank-Read dislocation source will not be able to operate). The critical thickness \( (t) \) for Cr can be calculated by using the relationship given below [99]:

\[
t = \frac{1}{\kappa} \left( \frac{E}{\sigma} \right)^{1/2}
\]
\[ t < \frac{32\pi \times b_A}{\left( \frac{\mu_B + \mu_A}{\mu_B - \mu_A} \right)} \]  

where, \( b_A \) is Burgers vector in layer A and \( \mu_A \) and \( \mu_B \) is the modulus of rigidity of A and B, respectively and units of \( t \) are in nanometers. The critical thickness for Cr is \(~55\) nm.

Deposition of these multilayered nanocomposites was accomplished by \( \text{Ar}^+ \) sputtering of Cr metal target using magnetron sputtering, whereas for DLC, methane and argon mixture dc plasma was used. In view of the nanosize of the individual layers, the appropriate calibration studies were conducted to maintain control of the deposition rates since layer thickness is of utmost importance.

Pin-on-disc experiments were conducted on multilayered coatings in order to study their tribological behavior and effect of reduction in thickness of nanosized Cr layers on friction and wear properties. Following testing, wear tracks were characterized in order to develop a better fundamental understanding of the tribological behavior of these multilayered coatings as a function of layer thickness.

D. Characterization of Nanocomposite Cr-DLC, Cr/DLC Multilayers and Functional Coatings

The films/coatings to be synthesized were characterized by employing various complementary techniques as follows:

1. Wavelength Dispersive Spectroscopy

Coating composition was obtained by WDS utilizing a JEOL JXA 733 super electron probe microscope at 15 keV accelerated voltage and 10 nA beam current. Appropriate standards were employed for instrument calibration. This technique cannot provide H content and thus, the results are reported in terms of Cr/C ratio or Cr content based on Cr and C.
2. Nuclear Reaction Analysis

The hydrogen content of selected few films was measured using NRA technique. The area of sample analyzed is approximately 0.75 cm X 0.75 cm. Thus, a good average of the hydrogen content was obtained. The experiments were performed at the Ion Beam Laboratory, SUNY (Albany, NY) using a nitrogen-15 ion (15N) beam from an accelerator to react with protons [122]. The depth profile of hydrogen content in the Cr-DLC films was obtained by increasing the 15N beam energy from 6.38 MeV to 7 MeV in steps of 100 KeV. The results obtained from the accelerator were analyzed using a software and from this the hydrogen content as a function of depth of film was obtained. The depth of the sample penetrated by the beam is proportional to the density of the film. Penetration depth was calibrated by taking the density of graphite (since density of film was not known) as a standard. However, it does not affect the overall hydrogen content in the film.

3. X-Ray Diffraction

Cr-DLC and functionalized coatings on steel were studied by using wide angle XRD mode on Rigaku Miniflex. Low angle XRD mode was also employed, on a state-of-the-art Phillips X'pert XRD equipment, to study the Cr-DLC films.

4. Transmission Electron Microscopy

High-resolution TEM of Cr-DLC films was performed using a JEOL JEM 2010 electron microscope operated at 200 keV with a point-to-point resolution of 2.3 Å. Cross-sectional slices were obtained by cutting the samples along a direction normal to the coating surface and then gluing, face to face, the two coating surfaces. Cross-sectional specimens for TEM observations were prepared by mechanical grinding, polishing, and
dimpling followed by Ar+ milling using a Gatan Precision Ion Polishing System (PIPS™, Model 691) at 4.5 keV at an angle of 5°. The structure of the Cr-DLC films was studied by selected area electron diffraction (SAED) patterns.

5. X-Ray Absorption Spectroscopy

The Center for Advanced Microstructures and Devices (CAMD) synchrotron facility at Louisiana State University was utilized to conduct X-ray absorption spectroscopy (XAS) experiments on the Cr-DLC films. XAS data at the K edge of Cr (5989 eV) were collected using bending magnet radiation at the DCM1 beamline. The monochromatic X-ray beam was obtained from a fixed exit double crystal monochromator, operating with Si (111) crystals providing an energy resolution of approximately 1.0 eV at 6000 eV. The incident beam intensity (I₀) was monitored with an ionization chamber. XAS spectra were recorded in fluorescence mode for the Cr-DLC films using a 13 element germanium detector. EXAFS signal is the oscillatory variation in X-ray absorption as a function of photon energy just above an absorption edge. This structure may extend as far as 1 keV beyond the edge, with amplitude typically 1-20% of the edge jump. It results from interference effects caused by scattering of the outgoing photoelectron from neighboring atoms [124]. EXAFS spectra were recorded over an energy range of 5700 – 6970 eV with 1 eV steps and XANES spectra were recorded from 5910 – 6400 eV with 0.2 eV steps in the near edge region. Data for pure Cr foil and Cr₃C₂ powder (standards) were recorded in transmission detection mode.

XANES data were fitted with a linear pre-edge for background removal and normalized to the 6300 - 6400 eV post-edge regions of the spectra using the WinXAS software package [123]. The EXAFS data analysis is discussed here in brief. The details
can be found elsewhere [115,124]. The first step is to deglitch the collected data. Glitches may sometimes appear in the experimental spectra due to spurious reflections from the monochromator crystal, rather than by X-ray absorption by the sample. Then, alignment of the energy is performed. The EXAFS data were extracted and analyzed utilizing the UWXAFS software package [125]. Background removal and normalization were performed using the AUTOBK routine in the UWXAFS package. \( E_0 \) was set at the first inflection point of the Cr spectrum, and the extracted EXAFS signal was Fourier transformed over the region of 2.0 Å\(^{-1}\) to 11 Å\(^{-1}\), using a Hanning window function. Refined structural parameters were obtained from nonlinear least square fitting in R-space over a range of 1.2 Å to 3.0 Å, encompassing the first two peaks representing Cr…C and Cr…Cr, in the single scattering approximation. Theoretical phase and amplitude functions were calculated using FEFF8, a computer program for \textit{ab initio} calculation of EXAFS and XANES spectra using multiple-scattering theory [126]. The amplitude reduction factor \( S^2_0 \) was determined by fitting the EXAFS data of the Cr\(_3\)C\(_2\) powder standard yielding a value of 0.72.

6. X-ray Photoelectron Spectroscopy

XPS of the coating surface was performed on an AXIS 165 Kratos Analytical system, also equipped with AES. Cr-DLC film specimens cut to the required size were mounted on the studs and introduced inside the chamber under high vacuum. Since these techniques are truly limited to the surface up to a depth of 50 Å, initially a surface analysis was performed, even though the atmosphere contaminated the surfaces. This served as a reference and provided useful information for analysis of the films. Subsequently, the surfaces were Ar ion sputtered and analysis was performed after each
step of sputtering to characterize the chemical state of the elements present in the coatings.

XPS was used to analyze the state of Cr in selected Cr-DLC films, pure Cr and Cr$_3$C$_2$ target and state of C in selected Cr-DLC films and pure Cr$_3$C$_2$ target. Also, it was used to estimate the $sp^3$ and $sp^2$ content of Cr-DLC films.

7. Nano- and Micro-Indentation

Nanoindentation experiments were performed using a Hysitron Triboscope ® instrumented nanoindentation/ nanoscratch device incorporated on a Digital Instrument Dimension 3100 atomic force microscope. The Triboscope ® allows AFM imaging of surfaces prior to, and after indentation. A three-sided, Berkovich-type pyramidal indenter was employed to carry out nanoindentation measurements of pure DLC and various Cr-DLC films (thickness > 1200 nm). The indenter shape function is obtained, assuming an indenter contact depth independent modulus, using fused silica as the calibration standard. Multiple indentations were performed at two different loads and at least three indentations were made at each loading level, to obtain an average value. The hardness, $H$, is calculated using the equation:

$$H = \frac{P}{A}$$

(2)

$$A = kh_p^2$$

(3)

where $P$ is the maximum load applied, $k$ is a constant (~24.5 for Berkovich tip geometry), $A$ is the contact area and $h_p$ is the depth of plastic deformation. Reduced elastic modulus ($E_r$), was also obtained from the nanoindentation experiments.

$$E_r = \frac{E}{1 - \nu^2}$$

(4)
where $E_r$ is reduced elastic modulus, $E$ elastic modulus and $\nu$ is Poisson’s ratio of the film. It was calculated from the relatively straight portion of the unloading curve, load versus displacement, between 90% and 40% of the maximum load. The contact depth for the maximum load was kept below 10% of the coating thickness to avoid any substrate effect.

Micro hardness measurements of the chrome plated and IPAP nitrided steel, DLC and Cr-DLC films were taken using micro indentation with a Knoop indenter and 100, 50, 25 and 10 gf load. The reported values are the average of at least five measurements.

8. Corrosion Testing

The variation in the open circuit potential as a function of time was measured for Cr-DLC, IPAP nitrided and tempered 4340 steel, using an EG&G computer-controlled Corrosion Measurement System (Model 273). The baseline, tempered sample was prepared by using SiC grinding paper of 600 grit size, and the IPAP nitrided sample was used in the as-processed condition. The corrosion behavior was assessed using an aqueous solution of 0.6 N (3.5 wt%) NaCl (pH = 6.9) exposed to laboratory environment. All corrosion potentials were measured with respect to a saturated calomel electrode (SCE).

9. Tribological Experiments

Pin-on-disc experiments (ISC-200 tribometer), were conducted on deposited films to characterize their tribological behavior. The pin used in these experiments was Al$_2$O$_3$ or 440C stainless-steel ball of 9.5 mm diameter. The wear tests were performed in laboratory air. The coefficient of friction ($\mu$) was monitored continuously during the experiments by a linear variable-displacement transducer and recorded on a dedicated,
data acquisition computer. The wear rate was calculated from the trace of the surface profile (average of four traces), taken across the wear track by optical profilometry.

A state-of-the-art optical profiler, Wyko NT1100 and/or NT3300, was used for measuring the surface roughness and the wear rates of the films. The surface roughness was measured in the PSI (phase shift interferometry) mode, when it is less than 150 nm. Whereas, if it is more than 150 nm, the VSI (vertical shift interferometry) mode was employed to obtain accurate results. The wear rate measurements were performed, by measuring the depth (in PSI mode if step-height less than 150 nm, else, VSI mode), and width of the wear track. The average wear depth was calculated by averaging over 4 measurements. Wear volume was measured by multiplying the average depth with average width and length of the wear track. Further, the wear rate was calculated by dividing the calculated wear volume (mm³) with the load applied (N) on the pin and the total sliding distance (meters).

10. Scanning Electron Microscopy

Hitachi 4500-II and S-3600 SEM’s, with EDS detector, along with Cambridge Stereoscan 260 SEM were used in this study to investigate the surface morphology of all the films and the IPAP nitrided steel. These were also utilized to study the structure of the IPAP nitrided steel. The cross-section of the nitrided and Cr ion plated samples was also studied using the SEM. Cross-sections of specimens were prepared by cutting them and mounting in epoxy. The mounted specimens were polished down to 1 µm alumina powder. The samples were etched in 2% nital solution to differentiate the nitrided layer thickness from the steel substrate. SEM was also employed to study the wear track morphology and wear debris of the samples.
V. RESULTS AND DISCUSSION

As mentioned earlier, Cr has been found to exhibit good compatibility and adhesion with Fe-based alloys. Furthermore, Cr has an affinity for carbon by forming carbides. Thus, Cr has been selected as a functional component either as an interlayer or as a modifier of DLC films. The first part of the study is concerned with the role of Cr as an interlayer between a surface hardened substrate and a low friction DLC film.

A. Functional Layers

In an earlier study in our laboratory, the fundamentals of the IPAP technique have been studied to allow full exploitation of this technique [127]. In the present study, the IPAP technique was utilized to develop functionally gradient substrates (with respect to hardness) for subsequent Cr layer deposition. IPAP nitriding of 4340 steel was performed to obtain a functionally gradient surface layer followed by deposition of a dense Cr interlayer. On these IPAP nitrided steels, relatively thick Cr layers were deposited using ion plating, with the aim to study their microhardness response, tribological properties and corrosion behavior. The study followed the route of processing-microstructure-property relationship.

1. Processing, Microstructure and Properties

Table 4 shows the processing parameters employed for IPAP nitriding of 4340 steel and the subsequent ion plating of Cr layers. The nominal composition of this medium carbon low-alloy and high-strength steel is given in Table 5. The nitriding parameters shown in Table 4 were selected after analyzing the results of previous studies of IPAP nitriding and conducting a new study on AISI 316 austenitic stainless steel [110]. This subject has been recently reviewed by Meletis [128]. The low-pressure
Table 4: Processing parameters for IPAP nitriding 4340 steel and ion plating of Cr layers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Processing Time (min)</th>
<th>Substrate Bias (V)</th>
<th>Flow rate Ar:N₂ (sccm*/sccm)</th>
<th>Chamber Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4340 tempered + IPAP Nitriding</td>
<td>180</td>
<td>-1000</td>
<td>4:16</td>
<td>6.67</td>
</tr>
<tr>
<td>4340 tempered + IPAP Nitrided + Cr ion plating</td>
<td>300</td>
<td>-400</td>
<td>10:0</td>
<td>1.33</td>
</tr>
</tbody>
</table>

* sccm = standard cubic centimeter per minute
substrate current density (IPAP Nitriding) = 0.75 mA/cm²

nitriding of AISI 304 austenitic stainless steel [108] showed that the most effective nitriding could be achieved in a discharge with an Ar:N₂ ratio of 1:4 and temperatures lower than 500°C. Lower nitrogen concentration in the plasma resulted in a lower nitrogen flux and shallow nitrogen profile producing lower hardness. Addition of Ar to a pure nitrogen plasma was found to significantly increase the hardness. Presence of Ar produces higher concentration of excited and ionized N and a higher density of vacancies and defects at the near surface region thus enhancing diffusion [108,128]. Furthermore, nitriding at low temperatures (< 500°C) is required to avoid formation of Cr nitrides that are causing depletion of Cr and are detrimental to corrosion properties. Low-temperature nitriding has been found to produce either extended solid solutions or hard metastable phases [128] while maintaining a uniform Cr distribution in the steel.

In a new study conducted in our laboratory on AISI 316 steel [110] it was found that effective nitriding can be achieved at a low cathode current density such as 0.75 mA/cm³, 6.7 Pa pressure and 1:4 Ar:N₂ ratio. It should be noted that the various processing parameters are interrelated. Thus, the above optimum parameters should be considered as the compromise between opposite effects. High pressures reduce the
Table 5: Nominal Composition of AISI 4340 Steel

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>0.37 – 0.43</td>
<td>0.7 – 0.9</td>
<td>0.6 – 0.85</td>
<td>0.2 - 0.3</td>
<td>1.83</td>
<td>&lt; 0.23</td>
<td>&lt; 0.035</td>
<td>&lt; 0.04</td>
<td>Balance</td>
</tr>
</tbody>
</table>

energy of the impinging species and low pressures reduce the concentration of N in the plasma. High current densities may rise surface temperature while low current densities may not have sufficient energetic species. Therefore, nitriding of 4340 steel in present study was performed at 6.67 Pa pressure, current density of 0.75 mA/cm² and an Ar:N₂ ratio of 1:4. Nitriding under these processing conditions for 3 hours produced a hardness gradient and a four fold increase in the surface hardness without adversely affecting the other properties of the steel. Thus, the same nitriding parameters were adopted in the present study.

Subsequent to nitriding, the specimens were ion plated in the same system by operating the magnetron source. The ion plating of Cr was performed in Ar atmosphere at a substrate bias of -400 V to enhance the plasma and a chamber pressure of 1.33 Pa. In an earlier study in which Cr was deposited on silicon keeping other processing parameters constant, a lower substrate bias (-100 V) produced coarse columnar microstructure, compared to Cr deposited at higher bias (-400 V), Figure 22. High-resolution TEM examinations of ion-plated Cr layers at -400V showed the presence of a dense and defect-free coating structure, Figure 22(c). Apparently, a higher bias causes plasma enhancement and resputtering effects resulting in a finer and denser coating microstructure. Such beneficial effects of plasma intensification has been well documented in the literature [128,129].
Figure 22: XTEM of Cr layers deposited on Si with bias voltage (a) -100 V, (b) -400 V and (c) high resolution image of (b).

Figure 23: Zone structural model depicting coating morphology of metals magnetron sputter deposited [131].
A zone diagram for metal films prepared by magnetron sputtering has been proposed by Movchan and Demchishin [130] and extended by Thornton [131]. Even though it is not well understood, the diagram shown in Figure 23 illustrating the microstructure of single-element films magnetron sputter deposited, is worth discussing in view of the present ion plating Cr layers. The diagram shows that the morphology of the coating is dependent on two parameters $T/T_m$ ($T$ temperature of the substrate/film and $T_m$ melting point of the element being deposited) and processing pressure. Three zones exist based on first parameter Zone-1 $T/T_m < 0.3$, Zone-2 $0.3 < T/T_m < 0.45$ and Zone-3 $T/T_m > 0.45$. It should be noted that under the present conditions plasma enhancement results in energetic bombardment that raises surface temperature significantly. Also, the densification and grain size reduction of the film with decreasing pressure is related to the ion bombardment phenomenon. Based on this phenomenon, Thornton introduced a new zone (Zone-T) between Zone-1 and Zone-2. Films deposited in this zone are much denser and have smoother morphology. The choice of processing pressure was made based on Thornton’s zone structure model and given that at pressures lower than 1.33 Pa the magnetron gun was unstable. Thus, a relatively low deposition pressure and plasma intensification by biasing the substrate resulted in Cr coating densification and a desirable microstructure consistent with the Thornton model. Figure 24 is a cross-sectional SEM micrograph showing the ion plated Cr layer on IPAP nitrided 4340 steel. It is evident that the ion plating parameters employed produced a defect-free interface between the substrate and the Cr layer. Adhesion tests showed that the Cr layer possesses an adhesion $> 80$ MPa (the strength of the polymeric glue on the testing stubs). It is noted that plasma enhancement can result in implantation and surface mixing from resputtering that are
Figure 24: X-sectional scanning electron micrograph showing the ion-plated Cr layer. Expected to affect film adhesion [128,132]. Figure 25 presents the microhardness profile along with the resulting microstructures of tempered 4340 steel IPAP nitrided for 3 hours at a substrate current density of 0.75 mA/cm². It is evident that the IPAP nitriding treatment produces a functionally-gradient layer in terms of hardness (highest hardness at the surface followed by a gradual decrease). This is due to the formation of thin layer of high nitrides followed by a diffusion controlled layer of about 50µm. The significant N penetration obtained in just 3 hrs of processing clearly attests to the enhanced N diffusion kinetics produced from the plasma intensification during IPAP [108]. Further, from the microstructures shown in the Figure 25 it is evident that the top surface of the nitrided steel has completely different microstructure compared to that of the bulk 4340 steel (tempered martensite). It may be noted, that no cracks are discernible in the nitrided region. The microstructure in the diffusion zone exhibits a mixture of the microstructure
Figure 25: Microhardness profile and the microstructures as a function of depth of IPAP nitrided tempered 4340 steel.
of IPAP nitrided and tempered steel. This suggests that incorporation of nitrogen into the tempered steel beyond a certain amount results in, microstructure modification. The exact mechanism of this process of modification of the microstructure is presently not known but is expected to involve N incorporation and structure modification under the high strains introduced into the lattice. A similar hardness gradient profile was obtained for AISI 316 steel, but the diffusion layer thickness was much smaller, about 10 µm [110]. The presence of alloying element Ni and the denser FCC structure of AISI 316 steel are responsible for slowing down the nitriding kinetics. In the past, plasma nitriding of Ni based superalloys has revealed slow nitriding kinetics due to significant Ni content in these alloys [133].

Surface roughness (R_{a}, root mean square) was measured on ion plated Cr, tempered and 1 hr and 3 hrs nitrided steel. Roughness of the as-polished tempered steel was measured to be 15 nm. Plasma nitriding is expected to increase the surface roughness of the substrate due to the ion bombardment. Specimens nitrided for 1 and 3 hours exhibited a roughness of ~300 nm and ~1000 nm, respectively. Cr ion plating produced a surface roughness of ~20 nm (measured on a Cr layer of a few hundred nm thick).

The surface microhardness of tempered 4340 steel and various processed conditions is presented in Figure 26. An interesting observation is that the IPAP nitriding treatment can be used as a tool for tailoring the surface hardness of the substrate to the desired level. It is evident that the microhardness of the substrate nitrided using the same conditions though processed for different time, 1 hr and 3 hrs, is very different. This suggests that the variation of the processing time for IPAP nitriding the substrate can provide the desired functionally gradient layer with an excellent control on the surface
Figure 26: Surface microhardness of tempered, IPAP nitrided and duplex treated 4340 steel.

Figure 27: Corrosion behavior of IPAP nitrided and tempered 4340 steel.
hardness. The highest hardness was shown by the 3 hrs nitrided sample. It may be noted that the indentation using low load (25 g) did not produce clear and sharp indents. This is so due to the high difference between peak to valley (of the order of few µm) on the surface producing high roughness. This could have introduced errors in measuring hardness for low load. However, the trend is similar when comparing the hardness of all samples at different loads. The duplex treated sample was IPAP nitrided for 1 hour before ion plating Cr.

Figure 27 shows the corrosion behavior of tempered 4340 steel and IPAP nitrided (3 hrs) steel. It is evident that the nitriding treatment enhances the corrosion resistance of the steel. The tempered 4340 steel shows a continuous reduction of the open circuit potential (activity) while that of the nitrided steel stabilized at about -460 mV. This could be attributed to the incorporation of N into the steel structure and acting as an inhibitor. These results are similar to those reported in the past for austenitic stainless steel [110] and even Ti alloys [128]. It has been proposed that N at the near-surface region oxidizes providing a passive layer inhibiting further reaction, with the steel. Therefore, besides hardening, nitriding would further improve the corrosion resistance of the substrate. DLC films are known for pinhole porosities [134] and can lead to pitting of the substrate. Therefore, the functional coatings with a Cr interlayer can have another beneficial effect on the substrate, i.e. improvement in the corrosion resistance.

2. Tribological Behavior

Wear and friction behavior of tempered 4340-steel and various processed conditions is presented in Figures 28(a) and (b), respectively. It is clear that tempered 4340 steel shows a wear rate of the order of $10^{-5} \text{mm}^3/\text{N-m}$, typical of engineering
Figure 28: (a) Wear rate, (b) friction vs sliding distance of IPAP nitrided and annealed 4340 steel.
materials possessing good wear resistance. Ion plating of 4340 steel with Cr significantly improves its wear behavior. Traditionally, Cr coatings have been used for wear reduction. It is important to note that IPAP nitriding further improved the wear resistance of the substrate. However, the duplex coating produced by combining the ion plating of Cr with IPAP nitriding exhibited the lowest wear rate. Indeed, the wear rate of $\sim 2 \times 10^{-6}$ mm$^3$/N-m is considered very low and approaches that of DLC coatings. The variation of the friction coefficient as a function of sliding distance for tempered, Cr ion-plated and duplex treated 4340 steel is shown in Figure 28(b). All treatments exhibit a similar steady-state behavior. In spite of the similar friction characteristics exhibited by the duplex treated, Cr ion-plated and tempered steel, the wear rate of each of them is different and in ascending order. The surface morphology of the wear track on ion-plated Cr deposited on tempered 4340 steel and that of IPAP nitrided steel is shown in Figure 29. The pin material used in this study was 440C steel. It can be observed that the surface in the wear track region for both surfaces shows signs of adhesive wear. This can be attributed to the adhering tendency of pin to both surfaces. Therefore, the reason for observed relatively high
friction is that the mode of wear for both surfaces is predominantly adhesive and the wear rate is controlled by the hardness of the substrate surface.

The duplex treatment exhibited low wear rate as a result of the effect of the gradient layer. It is known that Cr has good compatibility to both steel and DLC. Therefore, by depositing DLC on top of steel with a thin Cr interlayer is expected to further enhance the tribological behavior of these high strength low alloy steels. A study was performed in our laboratory to improve our understanding of the tribological behavior exhibited by DLC films deposited on thin Cr film acting as an interlayer with silicon as substrate [135]. The study showed that the tribological behavior was not adversely affected by the Cr interlayer. Since, the compatibility of Cr with steel is much better than that with silicon, it is clear that in view of the present findings deposition of DLC on nitrided steel with Cr interlayer can result in an excellent adhesion of DLC and enhanced tribological behavior.

B. Nanocomposite Cr-DLC Films

Cr-DLC films were synthesized using dc magnetron sputtering of Cr target in plasma discharge of Ar and CH₄ gas. The variation of the magnetron current allowed deposition of Cr-DLC films with a variation in the Cr content. The range of Cr content varied from < 0.1 at % to ~ 18 at %.

1. Film Composition

Table 6 presents the processing parameters utilized for synthesizing the present Cr-DLC films. Table 7 presents the Cr, C and H content of the various Cr-DLC films. It may be noted that the composition of the Cr-DLC films presented in Table 7 is obtained by combining the results of WDS and NRA. The NRA method was used to measure the
Table 6: Processing parameters for deposition of Cr-DLC films.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Processing time (hrs)</th>
<th>Bias Voltage (V)</th>
<th>Magnetron Current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-200</td>
<td>215</td>
</tr>
<tr>
<td>2*</td>
<td>3</td>
<td>-1000</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-1000</td>
<td>160</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>-1000</td>
<td>171</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>-1000</td>
<td>230</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>-1000</td>
<td>260</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>-1000</td>
<td>320</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>-1000</td>
<td>360</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>-1000</td>
<td>180</td>
</tr>
<tr>
<td>10*</td>
<td>3</td>
<td>-1000</td>
<td>135</td>
</tr>
</tbody>
</table>

Pressure=2.66 Pa (20 mTorr),
*Pressure= ~ 4 Pa (30 mtorr),
Ar:CH\(_4\) = 5.33:1

Table 7: Composition of Cr-DLC films, combining results from WDS and NRA.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cr (at%)</th>
<th>C (at%)</th>
<th>H (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.9*</td>
<td>90.1*</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>52.97</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>54.9</td>
<td>43.6</td>
</tr>
<tr>
<td>4</td>
<td>2.8</td>
<td>53.5</td>
<td>43.7</td>
</tr>
<tr>
<td>5</td>
<td>4.8</td>
<td>48.7</td>
<td>46.5</td>
</tr>
<tr>
<td>6*</td>
<td>11*</td>
<td>89*</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>11.8</td>
<td>50.5</td>
<td>37.7</td>
</tr>
<tr>
<td>8</td>
<td>17.5</td>
<td>48.2</td>
<td>34.3</td>
</tr>
<tr>
<td>9</td>
<td>0.4</td>
<td>52.9</td>
<td>46.8</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
<td>52.4</td>
<td>47.5</td>
</tr>
</tbody>
</table>

* Cr and C at% is as obtained from WDS, considering Cr+C = 100
hydrogen content depth profile of selected Cr-DLC films with Cr content ranging from <0.1 at% to ~18 at%. The NRA results are presented in Figure 30. For all films analyzed, hydrogen exhibits a sharp increase initially at the surface and then remains relatively stable with depth. The initial increase is due to the moisture content present on the surface. The depth to which the $^{15}$N beam penetrates the surface is a function of the density of the film. It was difficult to have a precise value of the density of the films due to their complex structure. So, the depth of hydrogen analysis does not represent the exact depth of penetration but gives a fair representation. Table 7 shows the average hydrogen content present in the films. In general the hydrogen content decreases with increasing metal content [136]. This trend has been observed previously in other Me-DLC system [137]. Recently, this trend has also been observed in Co-DLC films in our laboratory [138]. Keeping the other processing parameters constant (Ar/CH$_4$ ratio, bias voltage,
higher magnetron current causes more sputtering of the Cr (or Me) target increasing its content in the film. In all probability, the mechanistic aspect of the decrease of hydrogen with increase in Cr content in the present study is that as a larger number of Cr ions/neutrals are reaching the substrate accelerated by the high bias voltage (-1,000V) they sputter away hydrogen atoms from the top layer of the film. In addition, a higher current is expected to cause more break-down of the hydrocarbon molecules that is typically realized by removal of hydrogen.

2. XRD Analysis

XRD patterns of DLC and Cr-DLC films, with different Cr contents, deposited at bias voltage –200V and –1,000V are shown in Figure 31(a) [139]. Besides the peaks arising from the Si substrate, a very broad peak at around 2θ = 40° is present in all films indicating an overall amorphous structure of the films containing up to ~18 at% Cr. The thickness of the films used in the present study was of the order of a micron. The present results are surprising considering that in the past, other researchers have observed crystalline carbide precipitates for the metal content down to <5 at% [5]. Therefore, low angle XRD (LAXRD) experiments were preformed for Cr-DLC films with 1.5, 4.8 and 11.8 at% Cr, deposited at –1,000 V substrate bias. Figure 31(b) [148] presents LAXRD patterns obtained from these three Cr-DLC films. The area scanned had several wear tracks present and the wear experiments were run using an alumina ball. The sharp peaks observed in the region of 56 to 60° in the XRD patterns are a contribution from the crystalline phase, orthorhombic Al₂O₃. It is possible that few Cr carbide peaks are superimposed on these sharp peaks, however it is difficult to resolve them. Further, a very broad peak at around 2θ = 40° was observed in all these films and its intensity
Figure 31: (a) XRD of DLC and Cr-DLC deposited at –200 V and –1,000 V bias [139] and (b) grazing angle XRD of Cr-DLC films with 1.5, 4.8 and 11.8 at% Cr [148].
increased with increasing Cr content. This is more than likely the superimposed amorphous carbon peak along with several small and broad peaks of chromium carbide present between 2θ of 32° and 50°. The latter would be consistent with the increase in intensity by increasing Cr content. Typically, the second phase forming in these systems is in the nanoscale. Thus, XRD (Cu radiation used with λ=1.542 Å) is not the most appropriate probe to study such structures. Electron diffraction is a much better tool with much higher resolution. These studies are presented next.

3. TEM Studies

Figure 32(a) shows a high-resolution TEM image of the film with ~5 at% Cr deposited at low bias (-200V). The micrograph shows dark contrast nanoclusters (NCs) with a size of 1-5 nm in diameter. Figure 32(b) shows a high-resolution TEM image of the film with 4.8 at% Cr deposited at high bias (-1,000V). This micrograph also shows dark contrast NCs encapsulated by the amorphous matrix. The NCs are crystalline in nature as is evident from the lattice fringe pattern. The NCs in this film were found to

Figure 32: HRTEM of Cr-DLC films (~5 at% Cr) deposited at a bias of (a) –200 V and (b) –1,000 V [139].
have a size of 3-6 nm in diameter. Thus, for these Cr content levels, the Cr-DLC structure can be described as ‘nanocomposite’, i.e., crystalline NCs encapsulated by an amorphous “diamondlike” hydrocarbon matrix.

Figures 33(a) and (b) [139] show two SAED patterns of the Cr-DLC films shown in Figure 32 deposited at a substrate bias voltage of –200 V and –1,000 V, respectively. The central diffuse halo in Figure 33 corresponds to \( (002) \) \( sp^2 \)-graphite reflection produced by the amorphous matrix. Also, two diffuse rings corresponding to \( (111) \) and \( (220) \) diamond reflections more than likely are overlapping with relatively more intense and sharp rings showing the presence of another phase. These results are typical for amorphous DLC films as has been previously reported [4,35,68], which in the present study corresponds to the amorphous matrix around the NCs.

The three rings in Figure 33(a) can be identified to be the \( (110) \), \( (200) \) and \( (211) \) reflections of the body-centered cubic (bcc) Cr structure. Whereas, the diffraction rings in Figure 33(b) can be identified to be the \( (111) \), \( (200) \), \( (220) \) and \( (311) \) reflections of the face-centered cubic (FCC) chromium carbide structure, with a lattice parameter of 0.4038 nm. Commonly, three carbides of chromium are reported in the literature, a complex FCC
structure $\text{Cr}_2\text{C}_6$ with a lattice parameter 1.0659 nm and two orthorhombic structures $\text{Cr}_3\text{C}_2$ ($a=0.553$, $b=0.2827$, $c=1.148$ nm) and $\text{Cr}_7\text{C}_3$ ($a=0.7929$, $b=2.4326$, $c=0.71$) [140]. Though relatively rare another phase, FCC CrC (metastable) has been reported in the past. Bewilogua et al [141] reported a B1 structure Cr carbide with 0.41 nm lattice parameter, in thin films prepared by ion plating. He proposed a mechanism of formation of this phase. Due to high ion energies (2,000 eV) an increased number of C atoms could be incorporated into internal voids of the dense random packing structure producing large compressive stresses in the films. A transformation into a crystalline phase occurs, reducing these stresses by densification of the film material. Further, he suggested as a result of the rapid quenching rates in the ion bombarded surface regions of the growing deposits, the metastable phase was frozen and the transformation could not be continued into a stable carbide phase. Fujihana et al [142] also reported this metastable structure by ion implantation of C into chromium. The atomic ratio of carbon to chromium is about 0.6, therefore C implantation into Cr should basically cause the amorphization as suggested by Hohmuth et al [143]. Fujihana et al reported the formation of FCC carbide at doses $> 5 \times 10^{17}$ ion/cm$^3$ and attributed this to a martensitic transformation from BCC Cr to FCC carbide induced by carbon implantation. More recently, the FCC structure of carbide has been reported by Cekada et al [144] in hard coatings deposited using an Ar-$\text{C}_2\text{H}_2$-$\text{N}_2$ plasma. Therefore, from the present results, it can be concluded that the dark contrast NCs in the micrograph shown in Figure 32(a) correspond to metallic Cr whereas, the ones in the micrograph shown in Figure 32(b) correspond to FCC Cr carbide. These results suggest that the energetic conditions at $-1,000$ V bias favor the bonding between Cr and C whereas, at lower energy level (-200 V), Cr due to fast cooling rate freezes or is
trapped and deposited in the metallic state.

Figures 34(a) and (b) [139] show high-resolution TEM images of the interfacial structure of the Cr-DLC/Si deposited at relatively low and high bias, respectively. It is evident that in both Cr-DLC samples there are no defects and complete atomic continuity exists at the interface. Also, in both cases, due to Ar⁺ bombardment during the sputter cleaning process, an amorphous phase forms first on the Si substrate surface followed by Cr-DLC deposition.

Another interesting observation is the self-assembled multilayer structure of Cr-DLC films deposited at high bias. This formulation of self-assembled alternate layer structure was also observed by Wu et al [145] in other metal containing DLC films, Ni, Cu and Pt and was reported to enhance the fracture toughness of these films. Also, Co-DLC self-assembled alternate layers were recently observed in our laboratory [158]. Figure 35 shows a typical self grown multilayer structure of Cr-DLC film (4.8 at% Cr). The exact mechanism of the formation of multilayer is not clear. EDS measurements of the alternating layers of dark and bright contrast showed significant variation in the Cr content. The periodicity of the Me-rich and DLC-rich layers observed indicates that the
source of this self-assembling process is a periodic process. Thus, most likely the formation mechanism of multilayer involves deposition of Cr alternately from clean and poisoned Cr target (methane gas contamination).

As the hydrocarbon molecules dissociated by the magnetron plasma reach the target, they gradually poison the Cr target and a lower density of Cr is resulting in the deposited film. This poisoning of the target makes it less conductive and causes voltage rise in order to maintain the constant current (current control characteristic) and most likely causes a burst of the poisoned target layer leaving behind a clear Cr surface. The process is repeated causing deposition of periodic layers with graded Cr content.

4. X-ray Absorption Spectroscopy Studies

XANES spectra obtained from selected Cr-DLC films with Cr content ~0.1 at%, ~0.4 at%, 1.5 at%, 2.8 at% and 11.8 at% along with pure Cr, Cr-III oxide (Cr₂O₃) and Cr
carbide (Cr$_3$C$_2$) samples are shown in Figure 36(a). In order to accommodate the comparison, the spectra were translated along the intensity (y) axis by arbitrary amounts and shown in Figure 36(b). The chemical state of the absorbing atom determines the white line intensity and the position of the absorption edge, $E_0$ (5,989 eV for Cr). This is usually defined as the first inflection point in the absorption spectrum and other features of the white line. The intensity of the peak is proportional to the original intensity and the thickness $X$ (for transmission mode):

$$\frac{I}{I_0} = e^{-\mu(E)\mu X}$$

(5)

where $I$ is the intensity recorded, $I_0$ original intensity and $\mu$ is the linear absorption coefficient (is a function of the energy of light) of the material through which light has traveled. For fluorescence mode the equation is:

$$\mu(E) \propto \frac{F}{I_0}$$

(6)

where $F$ is the fluorescence recorded from the material.

Cr is in a neutral state in metallic Cr, in the Cr (III) oxidation state in Cr$_2$O$_3$ and probably between (II) and (III) in Cr$_3$C$_2$ based on the stoichiometric composition. Therefore, as expected Figure 36(a) shows that the chemical state of the absorbing atom Cr is different in metallic Cr, Cr$_3$C$_2$ and Cr$_2$O$_3$. These results are in agreement with those reported by Pantelouris et al [146]. Further, it may be noted that the Cr$_2$O$_3$ spectrum has significantly different pre-edge features and higher amplitude of white line compared to the other two (Figure 36). It also has two peaks compared to one in Cr, Cr$_3$C$_2$ and Cr-DLC films. The increase in amplitude of the white line suggests a reduced electron density around the absorber atom [80,147]. Therefore, the electron density around Cr is
Figure 36: X-ray absorption near edge structure spectra of Cr-DLC Films, Cr and Cr$_3$C$_2$ (a) Normalized spectra and (b) normalized and translated along the y axis (intensity).
lowest in Cr$_2$O$_3$ and nearly the same in Cr (metal) and Cr$_3$C$_2$. The white line of the Cr-DLC films does not show any feature that is present in the spectrum of Cr$_2$O$_3$. Further, on a closer look, Figure 36(b), the pre-edge peak and the shape of the white line and its peak for the Cr-DLC films show that these have features similar to those observed in Cr$_3$C$_2$ (but not in Cr). This suggests that the Cr present in these films has a chemical state similar to that of Cr in Cr$_3$C$_2$. These results are in agreement with the TEM and low angle XRD observations [148]. Another interesting aspect of the present results is that Cr in the film is stable and protected by the surrounding amorphous matrix.

The analysis of the XANES spectra of the Cr-DLC films shows that the chemical state and the local environment around the absorber Cr atoms remains essentially the same in the films with Cr content $\geq$ 1.5 at%. However, the films with lower Cr content (0.4 and 0.1 at%) show a different local environment compared to that in the rest of the Cr-DLC films and Cr$_3$C$_2$, as is evident from the portion of the spectra after the white line peak, Figure 36(b). It was also observed that the amplitude of the white line increases with diminishing Cr content in the films. It may be noted that the change in amplitude of the white line for films with Cr content 11.8, 2.8 and 1.5 at% is less than that for films with Cr content $\sim$0.4 and $\sim$0.1 at%.

These observations can be explained by using the NCs size effect approach. The reduction in size of NCs with decreasing metal content has been observed and reported earlier in similar systems, Co-DLC [147], Co-C [149] and Ti-DLC [150]. The increase in the amplitude of the white line suggests a decrease in the electron density around the absorber atom. This effect can be attributed to the sharing of electrons by the Cr atoms, present on the interface of NCs with the hydrogenated carbon in the matrix. The NCs size
is expected to decrease with decreasing the Cr content resulting in an increase in the surface to volume Cr atom ratio. For example, for 5 nm size NCs the fraction of atoms associated with the surface is as much as 50% [151]. This ratio increases rapidly as the size of the NCs decreases. The Cr atoms present on the surface has different local environment compared to those present in the interior of the NCs and therefore produce distinctly different XANES spectra.

At this point, one can extrapolate this logic and assume that at very low concentrations, the majority of Cr atoms in the sample will exist as isolated atoms incorporated into the carbon matrix and very small precipitates of Cr carbide NCs with very high surface to volume ratio. Therefore, the XAS spectra of the samples with low Cr content will be dominated by these Cr species, while at higher concentrations the spectra should resemble that of Cr$_3$C$_2$ due to the increased contribution from the core of the nanoparticles. A similar approach was successfully used in a recent study of Co-C nanocomposite thin films [149]. If this assumption is valid it should be possible to obtain at least a rough reproduction of the spectra of the larger NCs by linear superposition of the bulk Cr$_3$C$_2$ spectrum, representing inner particle contribution, and the 0.1 at% Cr spectrum, representing a surface-dominated state with only a small inner particle contribution (if at all). Therefore, the simulations were performed using the WinXAS program and the XANES spectra of Cr-DLC films were reproduced as linear combinations of the spectrum of Cr$_3$C$_2$ powder and film with 0.1 at% Cr. As shown in Figure 37 and Table 8, these linear combinations produced satisfactory results, especially for samples 3 and 4 which have intermediate Cr contents. The best fit value of the Cr$_3$C$_2$ contribution gradually decreased with Cr content from 81.4% in sample 5 to 15.6% in
Figure 37: Best fit of XANES spectrum of sample Cr-DLC 4 by linear combination of Cr$_3$C$_2$ and Cr-DLC 10 spectra.

Table 8: Results of the linear combination XANES fitting over the energy range of 5985-6040 eV.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Cr$_3$C$_2$ fraction, %</th>
<th>Cr-DLC 10 fraction, %</th>
<th>Residual</th>
<th>$\chi^2$ *10$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Cr-DLC 9</td>
<td>15.6±0.7</td>
<td>82.6±0.9</td>
<td>2.16</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>Cr-DLC 3</td>
<td>61.2±0.3</td>
<td>38.2±0.3</td>
<td>1.37</td>
<td>5.7</td>
</tr>
<tr>
<td>4</td>
<td>Cr-DLC 4</td>
<td>68.1±0.4</td>
<td>30.3±0.4</td>
<td>1.38</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>Cr-DLC 7</td>
<td>81.4±0.1</td>
<td>16.9±0.1</td>
<td>1.77</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Table 9: Structural Parameters for Cr-DLCs and Cr$_3$C$_2$ obtained from curve fitting.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>$N_{\text{Cr-C}}$</th>
<th>$R_{\text{Cr-C}}$ (Å)</th>
<th>$N_{\text{Cr-Cr}}$</th>
<th>$R_{\text{Cr-Cr}}$ (Å)</th>
<th>$\sigma^2_{\text{Cr-C}}$ (Å)</th>
<th>$\sigma^2_{\text{Cr-Cr}}$ (Å)</th>
<th>$\chi^2_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cr$_3$C$_2$</td>
<td>4±0.0</td>
<td>2.2±0.0</td>
<td>11±0.0</td>
<td>2.7±0.0</td>
<td>0.006±0.001</td>
<td>0.009±0.001</td>
<td>13.5</td>
</tr>
<tr>
<td>2</td>
<td>Cr-DLC 9</td>
<td>6.6±0.67</td>
<td>2.25±0.01</td>
<td>2±0.92</td>
<td>2.76±0.1</td>
<td>0.016±0.002</td>
<td>0.027±0.018</td>
<td>0.67</td>
</tr>
<tr>
<td>3</td>
<td>Cr-DLC 3</td>
<td>3.6±0.4</td>
<td>2.17±0.01</td>
<td>3.2±0.58</td>
<td>2.77±0.01</td>
<td>0.006±0.001</td>
<td>0.011±0.001</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>Cr-DLC 4</td>
<td>3.9±0.56</td>
<td>2.25±0.04</td>
<td>4.2±0.82</td>
<td>2.79±0.06</td>
<td>0.006±0.001</td>
<td>0.011±0.002</td>
<td>1.72</td>
</tr>
<tr>
<td>5</td>
<td>Cr-DLC 7</td>
<td>3.9±0.31</td>
<td>2.18±0.01</td>
<td>5±0.7</td>
<td>2.75±0.01</td>
<td>0.006±0.001</td>
<td>0.01±0.002</td>
<td>1.75</td>
</tr>
</tbody>
</table>

N – coordination number; R – bond length; $\sigma^2$ – Debye waller factor, $\chi^2_r$ – reduced $\chi^2$
sample 2. The XANES spectrum of sample 1 (0.1 at% Cr) was the dominant species for the 0.4 at% Cr sample at 82.6%, but contributed only 16.9% to the 11.8 at% Cr sample.

Table 9 and Figure 38 summarize the results of the EXAFS analysis and simulation. Figure 38(a) shows the EXAFS spectra of Cr-DLC films and Cr₃C₂ powder, obtained after normalizing, removing the background and transforming them into the k-space. EXAFS signal is obtained according to the equation

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E)}$$

where, $\Delta \mu_0(E)$ is measured jump in absorption at $E_0$, $\mu(E)$ and $\mu_0(E)$ is the absorption coefficient measured and of an isolated atom, respectively. After removing the background $\mu(E) - \mu_0(E)$, data is normalized with respect to $\Delta \mu_0(E)$. Subsequently, EXAFS signal in k space, $\chi(k)$, is obtained by converting the energy $E$ into the photoelectron wave vector $k$ according to the equation:

$$k = \sqrt{\frac{2m}{\hbar^2}} (E - E_0)$$

where, $E$ is the incident photon energy and $E_0$ is the threshold energy of the absorption edge. The maximum of oscillations is around $k = 3\text{Å}^{-1}$ and then with increasing $k$, oscillations quickly damp out. Such a behavior is characteristic of scattering from light-elements [147]. In the present case, more than likely these are carbon atoms. Also, it may be noted that as the Cr content in the film decreases, the level of noise in the EXAFS spectrum increases. This makes it difficult to extract useful information. Therefore, the EXAFS analysis performed on this data is expected to have wider error margins as the Cr content in the film decreases. Due to very high level of noise, EXAFS analysis and simulation did not provide any useful FT EXAFS for Cr-DLC 10 with ~0.1 at% Cr.
Figure 38: (a) EXAFS of Cr-DLC films and pure Cr$_3$C$_2$ powder and (b) their Fourier transform
The experimental spectrum is fitted with the EXAFS equation

$$\chi(k) = S_0^2 \sum_j N_j F_j(k) k_j^{\nu-1} e^{-2\sigma_j^2} e^{-2r_j} \frac{\sin(2k_j r_j + \phi_j(k_j))}{r_j^2}$$

(9)

where, $S_0^2$ is the amplitude reduction factor, $N_j$ and $r_j$ are the coordination number and bond distance, $\sigma_j$ the mean square deviation from the bond distance, and $\lambda_j$ the inelastic electron mean free path. The parameters (such as Cr-C, Cr-Cr bond lengths, Debye Waller factor, etc.) needed to perform the fitting of the Cr-DLC data, were obtained by performing the simulation and fitting of the Cr-carbide theoretical data to the experimental data. In order to perform quantitative data analysis, the $k^3$ weighted EXAFS spectra were Fourier transformed (FT) using the FEFFIT code part of UWXAFS software package [125] with a $k$ range between 2 and 11 Å$^{-1}$. The theoretical data required to perform the fitting of Cr-carbide, was generated using the ATOMS code part of UWXAFS software package. The data required as an input for ATOMS was obtained from Pearson’s Handbook [140] and verified from the NIST standard databank-2004 for Cr$_3$C$_2$ [152]. This phase has an orthorhombic structure and belongs to $pbnm$ space group. The lattice parameters are $a= 5.53$ Å, $b= 2.827$ Å and $c= 11.48$ Å. The fitting was performed in $R$ space using the FEFFIT code, with range of $k$ between 2 and 11 Å$^{-1}$ and that of $R$ between 1.35 and 2.8 Å. The number of variables in the fit was smaller than the number of independent data points. The parameters characterizing the fit quality, such as reduced $\chi^2$ and $R$, were typically in the range of 1 to 15 and 0.005 to 0.04, respectively.

Figure 38(a) presents the FT EXAFS spectra of Cr-carbide and Cr-DLC films. The spectra of the films with relatively higher Cr content (11.8 and 2.8 at%) show two peaks (1.5 and 2.1 Å) corresponding to the two sub-shells (Cr…C and Cr…Cr) of the
first coordination shell. No significant features were observed above 2.6 Å. This suggests a highly disordered (amorphous) structure with short-range order that is mainly limited to the first coordination shell. It may be noted that the distances shown were not phase-shift corrected. The spectrum for the Cr-carbide shows a shoulder around the same distance as the first peak of the films. This is mostly due to the contribution from Cr…C bonds. The main peak centered around 2.0 Å shows the contribution mainly from the Cr…Cr bonds. The second peak of the films with 1.5 and 0.4 at% Cr drifts to the right side and is at 2.2 and 2.5 Å, respectively. Since the Cr-Cr bond lengths are nearly the same (Table 9), this could be attributed to the artifacts introduced due to higher noise level in the EXAFS spectra of these films.

An example of typical fitting is shown in Figure 39 and the summary of the fitting results is presented in Table 9. The first sub-shell conforms to Cr…C bond contributions. The corresponding coordination number (number of nearest C neighbors) remains nearly

![Figure 39: A typical example of the fit obtained for Cr-DLC film with 11.8 at% Cr using FEFFIT.](Image)
constant (around 4) with decreasing Cr content except for the film with ~0.4 at% Cr. In the latter film, the coordination number increases significantly (becomes 6.6) indicating a breakdown of the carbide structure and dispersion of the Cr atoms in the matrix. Also, the bond length is nearly the same for all films and is similar to that of the Cr$_3$C$_2$ powder. However, the coordination number corresponding to the second sub-shell (number of nearest Cr neighbors) within the first shell decreases with diminishing Cr content. But the Cr…Cr bond length remains nearly the same as that in Cr$_3$C$_2$ powder. The lower average coordination numbers (Cr…Cr) even in the highest Cr content film can be attributed to the presence of NCs with large percentage of Cr atoms on the surface that has fewer nearest neighbors. Further, the decrease in Cr…Cr coordination number and reduced amplitude of FT features with decrease in Cr content for films with $\geq$ 1.5 at% Cr, can be correlated to the reduction in size of NCs leading to higher percentage of Cr atoms on the surface that has Cr fewer nearest neighbors. However, the increase in C nearest neighbors for the film with ~0.4 at% Cr indicates that the environment around Cr atoms has changed significantly. It suggests that Cr may be present in very small groups of atoms dissolved in the amorphous hydrogenated carbon matrix.

Very recently, Palshin et al [149] reported XAS results on nanocomposite Co-C films. They also observed that decreasing the Co concentration decreased the size of NCs, reducing the coordination number and amplitude of the FT EXAFS features. Our XAS results are in general agreement with these observations. Based on the present results, the solubility limit of Cr atoms in the DLC matrix is between 0.4 and 1.5 at%. The XAS results on Ti-DLC presented by Meng et al [150] show that the dissolution
limit of Ti atoms in DLC matrix is between 0.9 and 2.5 at% and beyond the dissolution limit cubic TiC precipitates.

The present XAS results shows a good fit with the theoretical orthorhombic model of Cr$_3$C$_2$ fitted by using the bulk Cr$_3$C$_2$ powder spectra. However, the HRTEM and SAED for Cr-DLC film containing 4.8 at% Cr suggest the presence of FCC CrC NCs. This discrepancy could be attributed to the TEM sample preparation technique. The final step of TEM sample preparation involves ion milling using 4,000 eV Ar$^+$ ions. The samples are being milled from ~100 µm thickness to perforation. Based on Bewilogua et al [141] hypothesis, due to high ion energies (~4,000 eV) during this ion milling process an increased number of C atoms could be incorporated into internal voids of the defected NCs increasing the compressive stresses. A transformation into a denser phase (FCC) could reduce these stresses. Another possibility is that indeed the Cr-carbide formed during deposition is FCC. But there is no FCC carbide standard available to confirm that possibility. In fact, FCC CrC has a very similar atomic environment around the absorbent Cr atoms and thus, expected to produce very similar spectrum specific features in terms of the edge position and the amplitudes. The amplitude is determined by the atomic number and coordination number. Since these parameters are similar (coordination number for FCC CrC is 12) no significant difference in the spectra is expected. Thus, in view of the above and the TEM evidence more than likely the Cr carbide is present as FCC carbide.

The formation of chromium carbide crystals in the present study is in general agreement with, those of Kazuya et al [153] synthesizing crystalline chromium carbide thin films by pulse laser deposition and EELS measurements reported by Fan et al [154].
Fan et al found that at high doping levels (~9 at% Cr), carbide-like Cr forms Cr-rich clusters while at low doping levels (~6 at% Cr), metallic-like Cr is uniformly distributed in the C matrix. The higher Cr solubility observed by Fan et al can be attributed to the different method used (thermal evaporation) for doping their films. However, the present results seem to be in variance to the recent XAS experiments conducted in our laboratory on Si-DLC films with ~10 at% Si [80], which show the preference for Si atoms to be incorporated into the local carbon structure rather than forming clusters. This difference is attributed due to the different technique used in synthesizing the Si-DLC films, where the precursor gas itself contained Si, as well as C and H.

5. X-ray Photoelectron Spectroscopy Studies

The Cr-DLC film with 4.8 at% Cr was analyzed by XPS and the results are summarized in Figure 40. The general survey spectrum exhibits, mainly Cr and C peaks and confirms that no oxygen is present in the film, Figure 40(a). This shows the absence of Cr oxide in the film and that the DLC environment is effective in providing protection. The high resolution Cr 2p spectrum shown in Figure 40(b) connotes no significant difference between Cr and Cr-carbide. In fact, it has been reported in the literature that there is no significant difference in the binding energy between these two states of Cr [ ]. Therefore, Cr 2p peak cannot be used effectively to differentiate between Cr and Cr carbide. However, the high resolution C 1s spectrum, Figure 40(c), showed that the spectrum for Cr-carbide is different from that of Cr-DLC films implying some differences in the chemical state of Cr. The deconvolution of C 1s peak for Cr-carbide and two films was performed to quantitatively analyze the spectra. The C 1s peak can be deconvoluted into three components with binding energies 284.3eV, 284.8eV and 283 eV.
Figure 40: XPS (a) General spectrum, (b) high resolution Cr 2p peak for Cr-DLC films, pure Cr and Cr$_3$C$_2$ target, (c) high resolution C 1s peak for Cr-DLC films and pure Cr$_3$C$_2$ target, (d) deconvoluted C 1s peak of Cr$_3$C$_2$ target, (e) deconvoluted C 1s peak of Cr-DLC 1 and (f) deconvoluted C 1s peak of Cr-DLC 5.
corresponding to $sp^2$ C-C and/or C-H, $sp^3$ C-C and/or C-H [155] and Cr carbide [156], respectively. High-resolution C 1s spectra obtained from pure DLC films synthesized in our laboratory by plasma-assisted CVD, show presence of $sp^2$ and $sp^3$ forms of C at binding energies of 284.3 eV and 284.8 eV, respectively [157]. Similar binding energies for $sp^2$ and $sp^3$ bonded C have also been observed in Co-DLC [158]. Figure 40(d), shows deconvoluted C 1s peak for the Cr-carbide target. The shoulder here seems to be the contribution from the $sp^3$ bonded C atoms. $sp^3$ bonded C atoms were present in the Cr-carbide, this is most likely due to the method used for fabricating the target. Similar peaks of C in Cr-carbide are reported by XPS international [159]. Figures 40(e) and (f), show deconvoluted C 1s peak for Cr-DLC 1 and 5 films, respectively. The deconvoluted peaks suggest that the films contain all three types of C bonding with varying percentage of $sp^3$ and Cr-carbide bonded C-atoms. Therefore, higher energetic (bias) conditions used for depositing Cr-DLC 5 film produced larger interaction among Cr and C atoms leading to larger number of $sp^3$ bonded C atoms and Cr carbide than the film processed at lower bias.

Excluding the C involved in the Cr carbide, the deconvolution analysis of the present Cr-DLC film suggests that 40% of the C exhibits $sp^3$ bonding and the remaining 60% is present as $sp^2$. At least three different binding energies of C in Cr carbide have been reported. These include 283.1, 282.94 and 282.8 eV for Cr$_3$C$_3$ [156], Cr$_3$C$_2$ [156], and Cr$_2$C$_3$ [160], respectively. All three binding energies are close to allow an unambiguous identification of the Cr carbide formed in the present study. A mass balance based on the deconvolution analysis and the Cr content of the film suggests a carbide composition close to Cr$_2$C$_3$. Detailed analysis of deconvoluted peaks show that only 25%
of Cr present in Cr-DLC 1 is bonded to C and the rest is more than likely present as metallic Cr. In view of the TEM results, it can be argued that the nature of NCs is essentially metallic Cr and only the Cr atoms present at the surface of these NCs interact with hydrogenated carbon atoms to form Cr-carbide type bonds. In contrast to this Cr-DLC 5 shows that synthesizing the films at higher energetic conditions leads to nearly all of Cr interacting with hydrogenated C and forming Cr-carbide. This speculation seems to be in agreement with the TEM, XAS and LAXRD results.

6. Nanoindentation Studies

Figure 41 presents the result from the nanoindentation experiments performed on these films. The results suggest that the hardness of the films decreases with increasing Cr content up to ~1.5 at% Cr and then hardness stabilizes around 13.5 GPa, Figure 41(a). Metal incorporation and formation of NCs in the DLC breaks up the continuity of the carbon network thus causing a lower hardness. Further more, relaxation of internal stresses can also occur as reported by Donnet [9] causing the reduction in hardness. Klages and Memming [5] have reviewed the mechanical properties of various Me-DLC films, and their nanoindentation results are in general agreement with those of the present study. With the exception of an initial deep, \( E/(1-\nu^2) \) was found to increase with increasing Cr content and stabilized around 118 GPa at ~12 at% Cr, Figure 41(b). The initial deep is probably due to stress relief by the presence of Cr. Increasing Cr content increases percentage of Cr-carbide and thus modulus due to higher E of the carbide. The \( H/E/(1-\nu^2) \) variation that is used as a criterion to assess the tribological behavior, exhibits a peak value of ~0.17 at 0.03 atomic % Cr and then gradually decreases and stabilizes to values around 0.11, Figure 41(c). Compared to other Me-DLC films, the present profile
Figure 41: (a) Hardness, (b) reduced elastic modulus and (c) hardness to reduced modulus ratio vs Cr/C atomic content ratio of Cr-DLC films.
of \( H/E/(1-\nu^2) \) for Cr-DLC exhibits this interesting region between 0.03 at% Cr and ~1.5 at% Cr. The reason for this peculiar behavior is not clear. However, based on the EXAFS findings it could be argued that Cr below the solubility limit probably modifies the network of the DLC in such a way that it significantly enhances the \( H/E/(1-\nu^2) \).

7. Thermal Stability

In the present study, TEM, XRD and XAS results show that Cr-DLC films mainly consist of Cr carbide NCs embedded in the amorphous DLC based matrix. Figure 42 presents the heat absorbing capacity of the DLC film as a function of temperature. It can be observed from the reversible and nonreversible heat flow, that a transition occurs at about 400°C. Based on previous annealing studies of a-C:H, this behavior can be attributed to the graphitization process. This process starts at about 350 °C with liberation of hydrogen and gradual conversion of \( sp^3 \) bonds into \( sp^2 \) graphitic bonds [2]. Therefore, the thermal stability studies on Cr-DLC films were conducted at temperatures \( \leq 350°C \). Figure 43 presents the thermal stability results of Cr-DLC films treated at 300 and 350°C for ~30 minutes. All samples were placed together in the furnace to heat slowly at 5°C per minute. And then, they were furnace cooled before removing them and measuring their hardness. The cooling cycle lasted about 100 min. After annealing at 300°C, no change in hardness was observed for pure DLC and Cr-DLC with 11.8 at% Cr (Cr-DLC 7). Interestingly, the hardness of the remaining Cr-DLC films, increased and the increase was inversely proportional to the Cr content. In fact, after annealing at 300°C, the hardness of Cr-DLC 2 approached that of DLC. This increase in hardness is attributed to reduction of nano-residual stresses and/or modification in Cr-C network. No change in hardness of DLC shows that bulk stresses in DLC remain unaffected. The relative
Figure 42: Heat absorbed as a function of temperature by DLC film.

Figure 43: Thermal annealing results for Cr-DLC films
contributions of these two mechanisms to the increase in hardness during the annealing treatment depend on the Cr content. One of them is the relaxation of residual stresses that may be present in the films due to quenching effects during deposition. These are generated during the deposition process due to fast cooling rates or quenching of the ions/neutrals occurring when they are deposited on a relatively cool substrate (substrate temperature did not exceed 150°C) at a relatively fast rate. Secondly, annealing encourages the reaction of the dispersed Cr clusters (from HRTEM and confirmed by XAS) with the hydrogenated carbon matrix causing a fine (atomic) distribution of precipitates. However, after annealing at 350°C, it was observed that the hardness of the Cr-DLC films with Cr content 1.5 at% or higher was reduced. This is more than likely due to the onset of the breakdown of the network of the amorphous matrix due to the oxidation of Cr present on the surface of the NCs of Cr carbide. For low Cr content (<0.5 at%, below the solubility limit), Cr is mainly present dispersed in the hydrogenated carbon matrix as concluded from XAS studies and is a part of the network. The present results seem to suggest that when Cr is essentially present within the DLC network, the network protects Cr from oxidation. These results imply the presence of synergistic effect between Cr and hydrogenated carbon network (for low Cr containing DLC films) protecting each other. Another interesting observation made here is that with increase in temperature to 350°C, the hardness drops significantly and reaches the same level for all films with ≥1.5 at% Cr that contain Cr-carbide. On the contrary, the pure DLC and the film with dissolved Cr in the DLC matrix (Cr-DLC 2) maintain their high hardness. Thus, thermal stability in terms of maintain hardness is directly associated with Cr-carbide formation. The present results show that annealing of dispersed Cr solid-solution causes
Table 10. Open circuit potential of nanocomposite DLC films in 3.5% NaCl solution [161].

<table>
<thead>
<tr>
<th>Material</th>
<th>Open Circuit Potential (mV) Vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-220</td>
</tr>
<tr>
<td>Graphite</td>
<td>340</td>
</tr>
<tr>
<td>Bulk Cr</td>
<td>-438</td>
</tr>
<tr>
<td>Soft DLC on Si</td>
<td>-97</td>
</tr>
<tr>
<td>Hard DLC on Si</td>
<td>80</td>
</tr>
<tr>
<td>Cr-DLC 5 on Si</td>
<td>-8</td>
</tr>
</tbody>
</table>

an increase in hardness through residual stress relaxation or formation of fine dispersion of the atomic scale of Cr carbide.

8. Electrochemical Behavior

Table 10 [161] present the electrochemical measurement results of Cr-DLC film along with that of DLC, Cr, graphite and Si. Compared to the hard DLC film (high $sp^3$ content), the soft DLC (high $sp^2$ content) is characterized by lower density and more pinhole formation in its structure. This is more than likely what is reflected in the lower open circuit potential (OCP), approaching that of Si, of this film compared to the hard DLC film. On the other hand, the hard DLC exhibited an OCP approaching that of graphite. The film Cr-DLC 5 with 4.8 at% Cr exhibited a significantly higher OCP compared to that of metallic Cr. These measurements are in agreement with the TEM and XAS results that show Cr in the DLC is first protected by the DLC matrix and second is present as Cr carbide, which has a significantly higher potential than that of Cr.

9. Tribological Behavior

Figure 44(a) presents the variation of friction coefficient ($\mu$) and wear rate (after 1,000 m of sliding distance) of Cr-DLC films as a function of Cr content and Figure 44(b) shows the variation of $\mu$ as a function of sliding distance. The results presented
Figure 44: (a) Coefficient of friction and wear rate of Cr-DLC films as a function of Cr/C ratio and (b) coefficient of friction as a function of the sliding distance for Cr-DLC films [139].
here refer to Cr-DLC films deposited at high bias (-1,000 V) and show that in general all these Cr-DLC films exhibit a low coefficient of friction ($\mu <0.2$) for both alumina and 440 stainless steel pins. Films deposited at low bias exhibited poor tribological behavior and failed at the early stages of wear testing. The most likely reason for this behavior of films deposited at low bias is high wear rate due to incompatibility between the metal nanoparticles and the DLC-based matrix. On the contrary, all the films deposited at high bias exhibited good adhesion to the substrate and excellent compatibility between the NCs and the DLC-based matrix, as is evident from the friction results.

It is characteristic to note that initially, there is a reduction in the friction coefficient of Cr-DLC films followed by steady state. Previous investigations on the tribological behavior of DLC show that the initial $\mu$ reduction is due to transfer film formation. The subsequently shown steady state is due to the wear-induced graphitization occurring from localized rise in temperature at asperity contacts [4,64]. As a consequence, a low shear strength graphitic interlayer (transfer layer) is formed between the pin material and the film (that may or may not transfer to the pin surface), thereby reducing friction. The friction of the nanocomposite Cr-DLC film is relatively higher than that of the DLC films synthesized and studied in our laboratory. This could be due to the presence of Cr carbide that normally has higher friction than the DLC. This behavior can also be attributed to the presence of Cr carbide NCs that can cause breakdown of the lubricating interlayer resulting in refinement of the wear debris (or lubrious interlayer).

The friction of Cr-DLC films is low for compositions up to 12 at% Cr while the wear rate is nearly constant up to ~5 at% Cr. Thus, it seems that up to a certain volume
Fraction of NCs of Cr carbide distributed within the DLC matrix, the two components of the composite (DLC and Cr carbide) act synergistically. Beyond a certain level, the amount of DLC present is not sufficient to provide the necessary lubricating action and the Cr carbide that wears out at a faster rate, dominates the wear process. This reasoning is consistent with the wear track morphology shown in Figure 45. A smooth wear track surface is discerned by the Cr-DLC film with <5 at% Cr (similar to that of DLC films, Figure 46) in contrast to rough wear track surface exhibited by the Cr-DLC film with 17.5 at% Cr, Figure 45(d). The wear track morphology for Cr-DLC film with 11.8 at% Cr shows the transition from smooth to rough, Figure 45(c). Thus, the present results suggest different wear mechanisms for Cr-DLC films containing low and high Cr content. The present friction and wear results are in general agreement with those reported by Wang et
al [162] considering differences in deposition methods and parameters used during wear testing. Very similar behavior has been observed previously for W-DLC films, with $\mu$ less than 0.18 and for W/C ratios less than 0.2 [5].

It should be noted that previous studies on Me-DLC (Me= Ti, W, Mo, Nb) films revealed a “U” shape in the abrasive wear rate, Figure 16. The deep in the wear rate is observed approximately between 4 and 10 at% metal. The present results are in general agreement with the previous reports however, they don’t show high wear rates at very low Cr content. This variation may be due to different deposition processes used in the various studies that consequently resulted in a different C-based matrix microstructure and thus properties. The reason for the “U” shaped behavior of the wear rate is presently not understood. Dimigen and Klages [6] argue that considering surface properties, Me-DLC films with low metal content, resemble polymers rather than metals or ceramics. Thus, considering the surface energy (S) to hardness ratio, Me-DLC films exhibit low S/H ratios (minimum S/H) and thus low $\mu$ and low wear rates should be expected.

Further, SEM was employed to study the wear track morphologies in the present
Figure 48: Scanning electron micrograph of wear debris, from Cr-DLC film with 4.8 at% Cr sliding against (a) 440C steel ball (b) alumina ball.

study. A typical result is shown in Figure 47. Also, the wear scar and debris on both 440C steel and alumina pins slid on the Cr-DLC film with 4.8 at% Cr, were analyzed with SEM-EDS, Figure 48. It was observed that the wear scar was much larger on the steel ball compared to that on the alumina ball. EDS analysis of the transfer layer showed that for both pin materials it was rich in chromium oxide. This suggests that at asperity contacts where temperature spikes occur, Cr oxidizes, enters the debris and subsequently finds its way to the transfer layer. Under this scenario, the presence of abrading Cr oxide particles would have been expected to increase wear, but this is not observed at low Cr content. It is possible that the carbon that was tied up to Cr as Cr carbide prior to oxidation is counteracting this process by forming lubricious \( sp^2 \) carbon. Thus, the overall behavior is a balance between these two processes producing Cr oxide (with its volume fraction depending on the Cr content) and \( sp^2 \) carbon. Apparently, at high Cr content, the Cr oxide formation dominates and high wear rates prevail. Under these conditions, the optimum metal content is expected to depend on the individual characteristics of the particular element in the DLC film.
The TEM results showed that the DLC film with 4.8 at% Cr has NCs of Cr carbide embedded in the amorphous matrix. The analysis of XAS spectra showed that the environment around the Cr atoms in Cr-DLC films with ≥ 1.5 at% Cr is similar to that of Cr$_3$C$_2$. Thus, the TEM and XAS findings suggest that Cr-DLC films with more than 1.5 at% Cr form Cr carbide NCs. Though microstructurally these Cr-DLC films at or above 1.5 at% are similar, the tribological behavior varied significantly. The present results show that films containing up to 5 at% Cr exhibit low friction and wear rate, since they slow down the graphitization process. This is attributed to fine distribution of carbide NCs that cause refinement of the transfer layer and decrease graphitization kinetics. At these low levels the transfer layer can maintain its continuity and thus lubricity. It should be noted that the coefficient of friction for Cr carbide is high, but the results show that the presence of NCs at that level has an insignificant effect. In this case, the presence of the lubricious DLC is sufficient to maintain low friction. By increasing the Cr content beyond that level, the volume fraction of carbides increases and promotes transfer layer fragmentation and inability to maintain sufficient portion of lubricious DLC. Thus, higher wear rate is observed. The microstructure at the other end of the spectrum, DLC with ≤ 0.4 at% Cr, showed a different XAS signature that connotes dissolved Cr in the DLC network rather than formation of NCs. This probably leads to the formation of C-Cr-C backbone structure that is characterized by low µ and wear rate. Thus, the present results show that if significant discontinuity is produced in the DLC network by incorporation of large fraction of carbides an adverse effect on the tribological behavior of the film is produced. A beneficial effect is observed if the Cr addition is finely distributed either in the C network or as fine carbides and present at a level that allows formation of the
lubricious transfer layer. The latter microstructure is also expected to enhance fracture toughness.

C. Cr/DLC Multilayer Films

In this part of the study, Cr and nitrogen containing Cr, Cr(N), films were deposited using magnetron sputtering in the presence of either Ar or Ar and N₂ discharge, respectively. These films were used to synthesize the Cr/DLC multilayers. Table 11 presents the deposition parameters of Cr, Cr(N) and Cr/DLC films.

1. Microstructural Characteristics of Layers

The structure of Cr and Cr(N) films was studied by XRD. Figure 49 shows XRD patterns obtained from bulk Cr, PVD Cr, and two Cr(N) films [163]. The PVD Cr shows evidence of <211> texture. Doping of Cr film with N was found to reduce the intensity and broaden and shift the Cr peaks to lower 2θ values. These observations suggest that incorporation of N into Cr leads to amorphitization of structure and introduces strain. Furthermore, N remains in the Cr lattice producing an ultra fine size of expanded BCC Cr

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer thickness (nm)</th>
<th>Deposition time Cr/DLC (min/min)</th>
<th>Flow rate Ar:N₂/Ar:CH₄ (sccm/sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>3100</td>
<td>180/0</td>
<td>20:0/0:0</td>
</tr>
<tr>
<td>Cr(N)-1</td>
<td>1900</td>
<td>90/0</td>
<td>20:2/0:0</td>
</tr>
<tr>
<td>Cr(N)-2</td>
<td>3830</td>
<td>210/0</td>
<td>20:6/0:0</td>
</tr>
<tr>
<td>Cr/DLC</td>
<td>200/20</td>
<td>10/2</td>
<td>20:0/30:8.4</td>
</tr>
<tr>
<td>Cr/DLC</td>
<td>200/200</td>
<td>10/20</td>
<td>20:0/30:8.4</td>
</tr>
<tr>
<td>Cr/DLC</td>
<td>100/200</td>
<td>5/20</td>
<td>20:0/30:8.4</td>
</tr>
<tr>
<td>Cr/DLC</td>
<td>60/200</td>
<td>3/20</td>
<td>20:0/30:8.4</td>
</tr>
<tr>
<td>Cr(N)/DLC</td>
<td>60/200</td>
<td>3/20</td>
<td>20:2/30:8.4</td>
</tr>
</tbody>
</table>

First layer in the multilayer is Cr and last is DLC; Substrate bias = -400 V (Cr(N) and Cr), -1000 V for DLC Magnetron Power= 100 W (Cr), turned off (DLC) Pressure= 10mtorr (Cr), 100 mtorr (DLC)
Figure 49: XRD pattern of (a) bulk and PVD Cr and (b) PVD Cr and Cr(N) [163].
Figure 50: XTEM micrograph of Cr/DLC (200/20) (a) overview and (b) high-resolution image of the Cr/DLC interface [163].

structure. Similar effects have been previously reported [164]. Indeed, the present results show that the present discharge conditions of relatively low bias (-400 V) and high N dilution (≤ 23 % by volume), encourage the formation of an expanded BCC Cr lattice. Cr layers deposited under these conditions were used to develop the Cr/DLC multilayers. The microstructure of the Cr/DLC (200/20 nm) multilayer was characterized by performing cross sectional TEM, as shown in Figures 50(a) and (b). The DLC layers were found to be amorphous and Cr possessed a BCC columnar structure, especially in the layers with large thickness (200 nm). It is evident from the XTEM micrograph that the DLC penetrates into the valleys of the Cr columns resulting in an interface with no visible defects, thereby providing good adhesion. Furthermore, the TEM observations showed that Cr can be nucleated on the DLC layer developing an intimate interface. The columnar structure of Cr however produces a variation in the DLC thickness, Figure 50(b). The XRD patterns suggest that the columnar structure with (211) texture is suppressed in the Cr(N) layers and judging from the broad peaks, a nanosize grain structure develops. Thus, incorporation of N in the discharge seems to modify the Cr
deposition mechanism. Since N is incorporated in the BCC lattice, renucleation of new grains is favored over growth of large columnar grains as in pure Cr. Indeed, the lattice strain energy is expected to increase with growth of large grains. Therefore, development of a fine grain size is favored. In addition, the tremendous large grain boundary volume associated with the small size grains can accommodate the strain resulting from the incorporation of N in the Cr lattice.

2. Mechanical Behavior

Figures 51(a) and (b) present the nanoindentation results of Cr/DLC multilayers of thickness 200/200, 100/200 and 60/200. The results show a hardness increase with decreasing Cr layer thickness. More specifically the hardness of the multilayers seems to follow a $\lambda^{-1/2}$ relationship where $\lambda$ is the Cr layer thickness. With respect to microstructural effects, it is known from the deformation theory that the relationship between strength and grain size of monolithic polycrystalline materials can be described by the Hall-Petch relation [165,166].
\[ \sigma = \sigma_0 + kd^{-1/2} \]  

(10)

where \( \sigma \) is the yield strength of the polycrystalline material, \( \sigma_0 \) is the flow or friction stress, \( k \) is a material constant that measures the relative hardening contribution from the grain boundaries and \( d \) is the average grain size of the polycrystalline material. The relationship between the yield strength \( (\sigma) \) and hardness \( (H) \) of a material can be approximated by [167]:

\[ \sigma \approx \frac{H}{3} \]  

(11)

Substituting the expression for \( \sigma \) from equation 6 into equation 5 gives:

\[ H = H_0 + k_1d^{-1/2} \]  

(12)

where, \( H_0 \) (MPa) is an intrinsic material parameter (internal friction) and \( k_1 \) (MPa-m\(^{1/2}\)) is a constant, which is related to hardening contribution of grain boundaries. This formalism of Hall-Petch relationship has also been used successfully in the past in predicting the strength of multilayered structures [168-171], where \( d \) (m\(^{1/2}\)) represents the layer thickness. Shih and Dove [168] reported Hall-Petch type of relationship shown by Ti/TiN, Hf/HfN and W/WN. Shinn et al [169] showed similar relationship in the TiN/NbN system. Furthermore, similar observations were made by Ding et al [170] in Al/Al\(_2\)O\(_3\) and Ti/TiN system and by Zhang et al [171] in Cu/steel system. The individual layer thickness varied from few hundred to below 20 nm.

The present results, Figure 51(a), also show a \( \lambda^{-1/2} \) relationship with hardness and are consistent with these previous reports. The hardness increase can be a combined effect of the increasing volume fraction of DLC (possessing higher hardness) as well as
contributions from scale effects from the Cr layer. Combining equation 12 and the results shown in Figure 51(a) we obtain:

\[ H(\text{MPa}) = 10785(\text{MPa}) + 1.08(\text{MPa} - m^{0.5}) \times \lambda^{-1/2} (m^{-0.5}) \]  

(13)

Recently, hardness studies in Cr/a-C multilayers have been conducted by Qi and Meletis [172]. The results of these studies are also shown in Figure 51(a) for comparison. The higher hardness of Cr/DLC multilayers can be attributed to the higher hardness of the DLC layer (17 GPa) compared to a-C layer (9 GPa). The present Cr/DLC multilayers have significantly higher hardness but it is evident that a similar slope exists in the hardness response of the two systems. The similarity in the slope between the two systems is attributed to strengthening effects by the Cr layers.

The reduced elastic modulus \((E_r)\) of multilayers is plotted as a function of inverse of square root of Cr monolayer thickness in Figure 51(b). The ratio \(E/(1-\nu^2)\) shows a slight upward trend with increasing \(\lambda^{-1/2}\) but it is likely that the change lies within the experimental scatter. The results obtained from calculations using the rule of mixtures (ROM) are also shown in Figure 51(b). The calculations were performed for elastic modulus perpendicular to the laminates configuration. The values of \(E_r\) used were measured on pure DLC and pure Cr layers \((E_{DLC} = 114 \text{ GPa}, E_{Cr} = 144 \text{ GPa})\). Comparing the results from ROM and the fact that Cr has a higher modulus than DLC, decreasing Cr layer thickness should have produced a reduction in the modulus of the multilayered coating. However, it can be argued that the decreasing Cr layer thickness reduces the columnar structure, and thus increasing density that can somewhat impact the modulus. Previous studies on Al/Al\(_2\)O\(_3\) and Ti/TiN multilayers have also reported deviations from the conventional ROM and minor changes in elastic modulus of the multilayers with
changing the volume fraction of the components [170].

Figure 52(a) presents Knoop microhardness (0.1 N) values for Cr, Cr(N), Cr/DLC and Cr(N)/DLC coatings tested in the present study. A similar trend to that shown in Figure 51(a) of increasing hardness with decreasing Cr layer thickness is also observed here. It may also be noted that for all three multilayers, the microhardness values are higher than those obtained by nanoindentation. This is attributed to the sharper nanoindenter tip (Berkovich) compared to Knoop tip used for microhardness testing. A sharper tip is expected to result in a larger contact area reducing the hardness value. The DLC hardness is significantly higher than those of the Cr layers. Multilayers possess an intermediate hardness of their two components but higher than ROM suggesting nanoscale effects. In Figure 52(b) the microhardness values of the multilayers are plotted as a function of $1/\lambda^{1/2}$, where $\lambda$ is either the single layer thickness of Cr in multilayers or the average grain size in monolithic Cr [173]. It may be noted that the three Cr/DLC films considered here had the same thickness regarding the DLC layer (200 nm), whereas
the Cr layer thickness was varied from 200 nm to 60 nm. The straight lines in Figure 52(b) for Cr/DLC multilayer and pure Cr illustrate that both of these exhibit a Hall-Petch type behavior. Both lines can be expressed in terms of equation:

\[
H(Cr/DLC) = 19275 + 3.0 \times \lambda^{1/2}
\]
\[
H(Cr) = 979.5 + 1.74 \times d^{-1/2}
\]

A clear upward trend in hardness, with decreasing Cr layer thickness, of multilayers is also shown in the graph. This effect can be attributed to two factors that are contributing to the hardness of the multilayers, i.e. the decreasing thickness of the Cr layer and the increasing volume fraction of the harder DLC layer. Indirect support for the former contribution is provided by the fact that the Cr(N)/DLC layer exhibited higher hardness than its counterpart Cr/DLC with the same layer thickness (60/200), Figure 52(a). Similarly, comparing the pure Cr curve with that shown by the multilayers is clear that a contribution of >18 GPa is provided by the DLC layer as is evident from \(H_0(Cr/DLC) = 19.3\) GPa and \(H_0(Cr) = 1\) GPa. It is interesting to note that the results may also suggest a higher slope (material constant) in the multilayer curve \([k_1(Cr/DLC)=3, \quad k_1(Cr)=1.74]\) that may be attributed to higher volume fraction of DLC with decreasing Cr layer thickness.

3. Tribological Behavior

The tribological behavior of the multilayers and the DLC, Cr and Cr(N) films is presented in Figure 53. The results show that all multilayers with high volume fraction of DLC \(V_{DLC}\), the lubricating phase, have low friction \(\mu < 0.15\) and low wear rate \((\sim 1 \times 10^{-7} \text{ mm}^3/\text{Nm})\). Compared to the multilayers, Cr films exhibited significantly higher wear rates \((>1 \times 10^{-5} \text{ mm}^3/\text{Nm})\) and \(\mu\) values. The multilayer with low \(V_{DLC}\) (Cr/DLC:
200/20) showed high wear rate compared to the rest of the multilayers but comparable $\mu$. This suggests that the presence of a thin DLC layer between the thick Cr layers, Figure 50, can still act as a lubricant but is incapable of providing wear resistance due to its low thickness. The low friction is due to the formation of a graphitic transfer layer between the disc and the pin. Whereas, the columnar structure of Cr may be detrimental to the wear resistance, since it is incapable to slow down the crack propagation and spalling and contribute effectively to the crack deflection mechanism, Figure 18. Thus, the results suggest that a critical thickness of the lubricating component along with less columnar structure is needed for improved tribological behavior.

Figure 53: Wear behavior of Cr/DLC multilayers, DLC, Cr and Cr(N) [163].
Furthermore, the tribological behavior of the Cr(N)/DLC multilayer that exhibited higher hardness than its counterpart Cr/DLC multilayer, is consistent with this premise. Stockemer et al [174] have also reported improvement in wear resistance due to presence of N in Cr layers. As the XRD results show, the presence of N in Cr causes microstructural refinement (ultra fine grain size) that in turn increases hardness based on the Hall-Petch formalism and consistent with the experimental findings, Figure 52. Thus, the present results indicate a correlation between hardness and friction and suggest that reducing the Cr layer thickness below 60 nm (as one means for obtaining higher hardness) may produce further improvements from scale effects. Based on Koehler theory, the critical thickness for Cr is ~55nm. Thus, the present results are in general, consistent with the theoretical predictions since a hardness increase was observed in the neighborhood of the critical thickness ($\lambda_{Cr} = 60$nm).

The present results of multilayered coatings show similar trend as those observed for nanoparticulate Cr-DLC films, i.e. the wear and friction behavior is comparable to the DLC coatings (~1 x 10^{-7} mm^3/N-m) when a sufficient percentage of lubricious layer is present in the coatings. When the Cr content increases beyond a certain limit (Cr-DLC > 5 at% Cr), the wear rate starts rising and eventually the friction increases accompanied with significant increase in the wear rate. For example, when Cr is present in significant amounts either as carbide in Cr-DLC (18 at% Cr) or as a thick layer in Cr/DLC (200/20) it dominates the wear process producing high wear, close to that of pure Cr film, Figure 53. In Cr-DLC films, the larger volume incorporation of Cr carbide results into fragmentation and enrichment of the transfer layer in Cr carbide and thus producing higher friction. However, in Cr/DLC coating the Cr layer does not interfere with the DLC
network and transfer layer directly. Therefore, even for larger volume fraction of Cr, for example 200/200 Cr/DLC multilayer, it can show a tribological behavior comparable to that of DLC and Cr-DLC with < 5 at% Cr. The form in which Cr is present is different, but fundamentally in both cases there is strengthening by a nanodispersion mechanism (Cr-DLC) or scale effects (Cr/DLC). However, both systems show similar wear characteristics and require the significant presence of the low friction DLC-rich (or graphite-rich) layer between the two surfaces in contact to exhibit a tribological behavior comparable to DLC films.
VI. SUMMARY

The role of Cr as an interlayer, an addition to DLC forming nanocomposites and in Cr/DLC nanoscaled multilayers was investigated. The present results showed that:

A. IPAP-treatment can be effectively used to tailor the surface properties and produce a functionally graded interface (FGI). Cr layers were found to best function in the presence of a FGI. Such a system tested for 4340 steel and Cr was found to possess significantly improved wear resistance (wear rate of the order of $10^{-6}$ mm$^3$/N-m) while at the same time improving the corrosion resistance. Therefore, a DLC coating on top of duplex treated surface is expected to further enhance the tribological behavior of the coating.

B. Multilayered nanocomposite films were synthesized with amorphous DLC layers and crystalline BCC Cr layers ranging from 200 nm to 60 nm in thickness. Cr/DLC interfaces were found to be defect-free, dense and continuous. Presence of DLC and a decrease in Cr layer thickness were found to increase hardness consistent with Hall-Petch formalism. No significant effect was observed on elastic modulus of Cr/DLC multilayers. Multilayered nanocomposite films with a significant volume fraction of DLC were found to possess low friction and low wear rate. For reduced DLC layer thickness both friction and wear increase. Therefore, the tribological mechanism was found to require the significant presence of the low friction DLC-rich (or graphite-rich) layer between the two surfaces in contact to exhibit a tribological behavior comparable to DLC films.

C. Dense and uniform nanocomposite Cr-DLC films were synthesized by reactive magnetron sputtering at high bias (-1,000 V). Low substrate bias (-200 V) was
found to favor formation of metallic Cr nanoparticles, whereas high bias (-1,000 V) produced crystalline chromium carbide (1-5 nm), both embedded in an amorphous DLC-based matrix. Thus, processing parameters were found to provide a tool for nanofabrication of desired microstructures.

D. The XAS studies showed that the chemical state of Cr and local environment around it in the Cr-DLC films is similar to that of Cr in Cr-carbide. However, a distinct change occurs in the environment around Cr in films with Cr ≤ 0.4 at%. In the latter films, Cr is present in the form of atomic clusters dissolved in the DLC matrix. The solubility limit of Cr in Cr-DLC films was found to be between 0.4 and 1.5 at%. At higher Cr content, Cr exists as defected Cr-carbide nanoparticles.

E. The XPS study showed that synthesizing the films at higher energetic conditions produces Cr-carbide whereas, in case of lower Cr is mainly metallic in nature. In view of TEM results, the limited Cr…C bonding detected is attributed to the interface effects of Cr atoms present on the surface of the NCs.

F. Nanoindentation studies showed that Cr-containing DLC films possess high hardness and the plastic index of the films peaks in the region from 0.03 to 1.5 at% Cr. In view of the XAS results, the Cr atoms below the solubility limit modify the network of the DLC such that leading to the plastic index peak.

G. The tribological study showed that the friction of Cr-DLC films is low for compositions up to 12 at% Cr while the wear rate is nearly constant up to ~5 at% Cr. Thus, up to a certain volume fraction of NCs of Cr carbide distributed within the DLC matrix, the two components of the composite (DLC and Cr carbide) act synergistically. Increasing the Cr content beyond 5 at%, the volume fraction of
carbides increases and the mechanism involves promotion of transfer layer fragmentation and inability to maintain sufficient portion of lubricious DLC. Therefore, a beneficial effect is observed if the Cr addition is finely distributed either in the C network or as fine carbides and present at a level that allows formation of the lubricious transfer layer. The optical profiler image analysis from wear tracks is also consistent with the different wear mechanisms for Cr-DLC films containing low and high Cr content.

H. The electrochemical studies showed that Cr-DLC film has good corrosion resistance approaching that of DLC showing that the DLC matrix provides adequate environmental protection for the Cr or Cr-carbide nanoparticles.

I. The present study showed that nanocomposite Cr DLC films exhibit high hardness, excellent tribological behavior and good corrosion resistance. The wear and friction properties of these are comparable to those of DLC films. Therefore, the addition of Cr can be used effectively to tailor the properties of these films and enlarge the scope of their applications. For example semi-conducting/conductive hard and wear resistant films for electronics/electrical, catalytic and MEMS applications.
REFERENCES


159. www.xpsinternational.com


VITA

Varshni Singh was born in Saharanpur, Utttar-Pradesh, India. He received his schooling in St Gabriel’s Academy at Roorkee, Uttra-Khand and St Mary’s Academy at Saharanpur, Uttar-Pradesh, India. He earned his Bachelor of Technology and Master of Technology degrees from Indian Institute of Technology- Kanpur, India. Subsequently, he worked in Indian Space Research Organization’s Liquid Propulsion Systems Center at Valiamalla, Kerala from 1993 to 1998. In fall 1998, he joined Louisiana State University’s Materials Science program with Mechanical Engineering as the host department to pursue doctoral degree. He is expected to graduate by December 2004 with the degree of Doctor of Philosophy.