Tribomechanical Studies on DLC/Ni Multilayer

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Abstract —

Tribomechanical properties of pulsed laser deposited diamond like carbon (DLC) with Ni interlayers are studied. Low coefficient of friction is found for DLC/Ni multilayer when compared to DLC/Ni bilayer. The behavior of low friction coefficient of DLC/Ni multilayer is attributed to the formation of graphitized tribofilm.

Keywords- DLC, Raman spectroscopy, Nanoindentation, Friction.
TRIBOMECHANICAL STUDIES ON DLC/Ni MULTILAYER THIN FILMS

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Diamond-like carbon (DLC)
- Primarily consists of carbon atoms
- Exists in seven structures
- Wide range of properties
- Limitation: Internal stress, poor adhesion

INTRODUCTION

AIM
- To deposit DLC/Ni multilayer and bilayer thin films on to stainless steel substrate using PLD and to study its mechanical and tribological properties.

EXPERIMENTAL TECHNIQUES
- Deposition technique: PLD (Nd: YAG laser, Wavelength = 1064 nm, Pulse width – 5 ns, laser energy-100 mJ, frequency-10 Hz)
- Targets: C, Ni
- Substrates: Si(100), SS304
- Base Pressure: 10-6 mbar
- Ts: Room temperature

RESULTS AND DISCUSSIONS

Raman Spectra
- G peak: 1550 cm⁻¹ - bond stretching mode of sp² atom in aromatic rings and olefin chains
- D peak: 1350 cm⁻¹ - breathing mode of sp² rings
- Shift in G peak of DLC/Ni multilayer - lower compressive stress compared to DLC/Ni bilayer (Table 2)

CONCLUSION

DLC/Ni multilayer is found to exhibit lower coefficient of friction compared to DLC/Ni bilayer. The shift in the G peak position towards lower wavenumber in DLC/Ni multilayer shows that the multilayer architecture reduces the internal compressive stress in the film compared to bilayer. The possibility of low friction coefficient is the formation of graphitized tribofilm in case of DLC/Ni multilayer.

REFERENCE


ACKNOWLEDGEMENT

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CONTACT: Ms. S. Gayathri, e-mail: sgayathri@ece.sastra.edu
Reduction of Internal Stress in DLC Films by Using Transition Metal Nano-Interlayer

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Abstract:

Unhydrogenated diamond-like carbon (DLC) films with different transition metal nano-interlayers (Cr, Ag, Ti, and Ni) was deposited using pulsed laser deposition technique. The motivation for the introduction of the nano-interlayer was to reduce the internal stress, which in turn improve the mechanical and tribological properties. The films were characterized by using Raman spectroscopy, photoluminescence (PL), nanoindentation and micro-tribology techniques. The thickness of the nano-interlayers was ~ 15 nm and the total thickness of the multilayer system was ~ 500 nm as measured by secondary ion mass spectroscopy. The internal stress was found to be low for the DLC films with Ni interlayer as calculated from Raman spectroscopy. The metal nano-interlayer in DLC increases the PL intensity by acting as a catalyst for the formation of sp² cluster which in turn reduces the intensity due to defect states. The increased PL intensity is a consequence of increasing domain of sp² rich clusters which create more band-tail states to generate more electron-hole pairs thus enhancing the PL intensity. Micro-Raman spectra in each wear track were recorded to study the change in local chemical structure. Change in chemical structure of the track significantly influenced sliding induced adhesion and friction. The higher intensity of G and D band in the wear track of DLC/Ni and DLC/Ti films revealed the transformation of film to a graphitized film which was reason behind for DLC/ Ni or Ti multilayer to exhibit low coefficient of friction of 0.06 and 0.08 respectively. Also the hardness values of the DLC/ (Ni, Ti) multilayer is higher than the DLC/ (Cr, Ag) multilayer due to the higher sp³ content. FE-SEM images proved the ordered alignment and compactness of interface which resisted the movement of dislocations during indentation induced shear deformation and which is an added reason for high hardness of DLC/(Ni, Ti) multilayer.

Keywords: DLC, PLD, Raman, Nanoindentation, Micro-tribology
REDUCTION OF INTERNAL STRESS IN DLC FILMS BY USING TRANSITION METAL NANO-INTERLAYER

S. Gayathri1, R. Krishnan2, N. Kumar2, T.R. Ravindran2, S. Dash2, A.K. Tyagi2, Baldev Raj2 and M. Sridharan1

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2Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam – 603 102, India

INTRODUCTION

AIM

➢ To investigate the tribomechanical properties of DLC/TM (TM = Cr, Ag, Ti, Ni) multilayer
➢ To reduce the internal stress in DLC film

EXPERIMENTAL TECHNIQUES

➢ Deposition technique: PLD (Nd: YAG laser, Wavelength = 1064 nm, Pulse width – 5 ns, laser energy-100 mJ, frequency-10 Hz)
➢ Targets: C, Ni, Ti, Ag; Substrates: Si(100), SS304; Base Pressure: 10^-6 mbar; Ts: Room temperature

RESULTS AND DISCUSSIONS

➢ Shift in G peak position – internal stress [1, 2]
➢ Raman Spectra (on surface): No significant variation in chemical structure
➢ Raman Spectra (on track): Increase in the intensity of G peak – sp3 to sp2 transformation

CONCLUSION

Interfacial scratch resistance property is significantly enhanced in DLC/Ni and DLC/Ti systems due to formation of well aligned and defect free interfaces in interlayers. Transformation of high I(D)/I(G) ratio on surface to low value of I(D)/I(G) ratio in wear tracks indicates graphitized tribofilm formation in the wear track. Therefore Ni and Ti nano interlayers reduces the internal stress and enhances the adhesion compared to Cr and Ag.

REFERENCE


ACKNOWLEDGEMENT

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CONTACT: Ms. S. Gayathri, e-mail: sgayathri@ece.sastra.edu
A Comparative Study of Microstructure And Tribological Property of Pulsed Laser Deposited DLC/Ag And DLC/Ni Multilayer

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Abstract

One of the applications oriented advanced forms of carbon based material is diamond-like carbon (DLC) known to be a stiffest and hardest polymorph. It possesses high elastic modulus, high fracture toughness, high thermal conductivity, low thermal expansion coefficient and chemical inertness. These exceptional qualities make DLC ideal for numerous surface engineering applications relevant to tribology. However, inefficient bond interlocking due to low chemical reactivity reduces interfacial adhesion of these coatings. Low chemical interaction between films and their metal substrates causes poor adhesion thus limiting their use in surface engineering. To combat these problems, functional grading, doping and multilayer structuring with metal interlayer have been widely used. There are several composition and structures attainable with metal-containing DLC coatings. Here we present the comparative study of tribological and mechanical properties of Pulsed Laser Deposited (PLD) unhydrogenated DLC/Ag and DLC/Ni multilayer. The purpose of designing a multilayer structure is to reduce the average stress and to improve film toughness. DLC films with Ni interlayer exhibited ultra low coefficient of friction value of 0.06 compared to that of 0.9 of DLC with Ag interlayer. The graphitized tribofilm is a characteristic of easy in plane sliding which provides low adhesion and friction intrinsic to DLC/Ni multilayer. Transformation of I(D)/I(G) ratio from a higher value on the surface to a lower value in the wear track of DLC /Ni multilayer indicates the formation of graphitized tribofilm during sliding. Micro-Raman spectra in wear track are recorded to study the change in local chemical structure. In addition, microstructural dependence of friction and wear is also pointed out. Change in chemical structure of the track can significantly influence sliding induced
adhesion and friction. Intensity of G and D band in the wear track of DLC/Ni is higher compared to wear tracks of DLC/Ag interlayer. Interfacial scratch resistance property is significantly enhanced in DLC/Ni system due to formation of well aligned and defect free interfaces in interlayer compared to that of DLC/Ag interlayer. Hardness of DLC/Ni interlayer system is also found to be higher compared to DLC/Ag films.

**Keywords:** Diamond-like carbon, Nanoindentation, Tribology, Raman spectroscopy
MICROSTRUCTURE AND CHEMICAL STRUCTURE ANALYSIS OF DLC WITH TRANSITION METAL NANO-INTERLAYER

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INTRODUCTION

- DLC is a network consisting of strongly cross-linked sp2 bonds and sp3 bonds.
- It exists in seven structures.
- Exhibits wide range of properties.
- Limitations: Large internal stress, Poor adhesion.

AIM

- To investigate the tribomechanical properties of DLC/TM (TM = Cr, Ag, Ti, Ni) multilayer.
- To reduce the internal stress in DLC film.

RESULTS AND DISCUSSIONS

- Shift in G peak position – internal stress [1, 2].
- Raman Spectra (on surface): No significant variation in chemical structure.
- Raman Spectra (on track): Increase in the intensity of G peak – sp3 to sp2 transformation.

CONCLUSION

- Interfacial scratch resistance property is significantly enhanced in DLC/Ni and DLC/Ti systems due to formation of well aligned and defect free interfaces in interlayers. Transformation of high I(D)/I(G) ratio on surface to low value of I(D)/I(G) ratio in wear tracks indicates graphitized tribofilm formation in the wear track. Therefore Ni and Ti nano interlayers reduces the internal stress and enhances the adhesion compared to Cr and Ag.

EXPERIMENTAL TECHNIQUES

- Deposition technique: PLD (Nd: YAG laser, Wavelength = 1064 nm, Pulse width – 5 ns, laser energy-100 mJ, frequency=10 Hz).
- Targets: C, Ni, Ti, Ag, Cr; Substrates: Si(100), SS304; Base Pressure: 10-6mbar; Ts: Room temperature.

TABLE 1

<table>
<thead>
<tr>
<th>Property Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological inertness, Chemical inertness</td>
</tr>
<tr>
<td>Medical prosthesis, Medical instrument coating</td>
</tr>
<tr>
<td>Hardness, wear resistance and low friction coefficient</td>
</tr>
<tr>
<td>Cutting tool coating, Engine piston parts, Magnetic recording coating</td>
</tr>
<tr>
<td>Optical transparency</td>
</tr>
<tr>
<td>Lens, Optical fiber coating, Infrared window transmission</td>
</tr>
</tbody>
</table>

Fig. 1. Raman spectra of DLC/TM on the film (a) on surface (b) on the track.

Fig. 2. Relation between I(D) / I(G) and μ

Fig. 3. X-FE-SEM micrograph of DLC/Ni multilayer (Inset: DLC/Ag multilayer).

Fig. 4. EDAX mapping of wear track of a) DLC/Ti b)DLC/Ag multilayer.

Fig. 5. Scratch resistance properties of DLC coatings as a function of metallic interlayer.

Fig. 6. XSEM shows well aligned interface for Ni in DLC film compared to Ag.

Table 2 Mechanical and tribological variations of DLC/TM multilayers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (GPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Wear coefficient (×1010mm/Nm)</th>
<th>Friction coefficient (μ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>3.6</td>
<td>188</td>
<td>1050</td>
<td>0.95</td>
</tr>
<tr>
<td>DLC/Ag</td>
<td>9.6</td>
<td>148</td>
<td>180</td>
<td>0.95</td>
</tr>
<tr>
<td>DLC/Cr</td>
<td>9.8</td>
<td>147</td>
<td>64</td>
<td>0.2</td>
</tr>
<tr>
<td>DLC/Ti</td>
<td>10.2</td>
<td>160</td>
<td>8.7</td>
<td>0.08</td>
</tr>
<tr>
<td>DLC/Ni</td>
<td>11.3</td>
<td>164</td>
<td>5.6</td>
<td>0.06</td>
</tr>
</tbody>
</table>

REFERENCE


ACKNOWLEDGEMENT

MS thank DST, Govt. India for the financial support (DST/SR/FTP/ETA-058/2009), MS and SG thank SASTRA University for the financial support and IGCAR for providing the necessary experimental facilities.

CONTACT: Ms. S. Gayathri, e-mail: sgayathri@ece.sastra.edu
Abstract:

Diamond–like carbon (DLC) films can exhibit high hardness (as hard as 90 GPa) and are resilient. Tribologically DLC provide some of the lowest known friction and wear coefficients. These films exhibit extraordinary optical and electrical properties which can be tailored to meet the specific requirements of a given application. These films are chemically inert and are resistant to corrosive attacks in acidic and saline media. The combination of such a wide range of properties in one material makes it useful in meeting the multifunctional application needs of advanced mechanical systems. In this paper we present the spectroscopic studies of hydrogen-free diamond-like carbon (DLC) films with transition metal (TM = Cr, Ag, Ti, Ni) interlayer (bilayer and multilayer) deposited by using pulsed laser deposition technique. Secondary ion mass spectroscopy (SIMS) confirmed that the films were hydrogen free. Raman spectroscopy under UV excitation showed the T peak at 1150 cm$^{-1}$ whereas under visible light no T peak was observed. Incorporation of chromium inter layer reduced the stress value about 3 GPa as determined by micro Raman spectroscopy. Incorporation of the TM inter layer enhanced the photoluminescence (PL) intensity as compared to the monolithic DLC films. The optical band gap determined by spectroscopic ellipsometry for DLC/TM films was found to be in the range of 1.56 – 1.67 eV. Low band gap value of 1.38 eV was obtained for DLC grown in Ar atmosphere compared to DLC grown in high vacuum condition. The DLC film grown in Argon atmosphere was found to more graphitic compared to the films deposited in high vacuum condition.

Keywords: DLC, PLD, Raman, Photoluminescence, Spectroscopic ellipsometry
STUDIES ON NANOCOMPOSITE DIAMOND-LIKE CARBON COATINGS

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E-mail: m.sridharan@ece.sastra.edu

INTRODUCTION

Diamond-like carbon (DLC)
- Primarily consists of carbon atoms
- Exists in seven structures
- Nanocomposite DLC – Metal or non metal particles embedded in the DLC matrix

To deposit DLC/TM (TM=Cr, Ag, Ti, Ni) multilayers on to AISI304 stainless steel substrate and to study its optical, mechanical and tribological properties.

AIM

EXPERIMENTAL TECHNIQUE

- Targets - C, Cr, Ni, Ag & Ti
- Substrates-Si(100), SS304
- Ultrasonically cleaned with ethanol and acetone and Si was HF etched
- Deposition technique used - PLD
  - Nd: YAG laser, Wavelength = 1064 nm, pulsewidth - 5 ns, laser energy-100 mJ, frequency-10 Hz
  - Base Pressure maintained at 10⁻⁶mbar
  - substrate temperature - Room temperature

RESULTS AND DISCUSSIONS

- The optical band gap of all DLC/TM interlayer was found to be in the range of 1.56 – 1.67 eV except for DLC grown in Ar atmosphere which has a value of 1.38 eV. Though all samples were grown in similar deposition conditions, the presence of different transition metal interlayers affect the properties of DLC film grown on them. These variation can be attributed to the difference in the sp² local configurations.

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This project is supported by Department of Science and Technology (DST), Government of India (DST/SR/FTP/ETA-058/2009).
Thanks to SASTRA University for the financial support and providing the experimental facilities.
Thanks to IGCAR for providing experimental facilities.

REFERENCES

Abstract

Diamond and diamond-like carbon (DLC) materials are commercially finding wide range of applications as protective coatings over many materials. These applications include as an antireflective coatings over glass, as mechanically hard and high wear resistant coating over steel, TiAlV9 alloys, Ultrahigh molecular weight polyethylene(UHMWPE) materials which are used mainly as medical implants. Its low friction coefficient and resistant towards abrasion again makes it a perfect protective coating over tools, engine components, hard disks and also on micro and nano electromechanical systems(MEMS/NEMS). Though DLC imprints its foot as a protective coating in almost all the areas of application, it also has a major limitation of poor adhesion to the substrate due to its large internal stress inbuilt in it, during deposition. So this present work is designed with an aim to reduce the internal stress and to enhance the adhesion to the substrate by introducing transition metal dopant into the DLC matrix. Amorphous DLC films doped with different concentration of Cr was deposited on to AISI SS304 steel substrate using pulsed laser deposition technique (PLD). Raman spectroscopy was used to calculate the internal stress of the films. It was found that with the increase in the Cr concentration from 3 to 19 at%, the internal stress significantly reduced from 3GPa to 0.9 GPa. The G peak shifts to higher waveumber indicating the reduction of compressive stress in the film with the increase in the Cr concentration in the film.

Keywords: DLC, PLD, nanocomposite, adhesion
Introduction

- Diamond-like carbon (DLC) is a network consisting of strongly cross-linked sp2 bonds and sp3 bonds.
- **Properties:** High hardness, low coefficient of friction, high wear resistance, chemically inert, low electron affinity, biocompatible, optical transparency.
- **Applications:** Medical prosthesis, medical instrument coating, engine piston parts, magnetic recording coatings, infrared anti-reflective coatings, flat display panels.
- **Limitations:** Large internal stress & Poor adhesion.
- Adding metals as dopant or interlayer reduces the internal stress and increases the adhesion to the substrate.

Experimental

- **Pulsed Laser Deposition (PLD):**
  - Laser parameters:
    - Nd: YAG laser - Wavelength - 1064 nm
    - Pulse width - 5 ns
    - Laser power density - 7 GW/cm²
    - Frequency - 10 Hz
  - Targets: Pyrolytic graphite, Chromium
  - Substrates: AISI SS304
  - Base Pressure: 10⁻⁶ mbar
  - Substrate temperature: Room temperature

Results and Discussions

- **Micro Raman Analysis:**
  - G peak shift towards lower wavenumber with reference to pure DLC indicates reduction in internal stress.
  - \[ \sigma(GPa) = 2G[1 + \nu/(1 - \nu)] \Delta \omega \]

Surface Morphology

- Increase in Cr concentration leads to increase in particle size.

Raman spectroscopy of DLC-Cr nanocomposite films

- Pure DLC: 1555 cm⁻¹, ID/I_G = 0.53, FWHM = 218 cm⁻¹
- DLC-Cr 12.5%: 1527 cm⁻¹, ID/I_G = 0.37, FWHM = 201 cm⁻¹
- DLC-Cr 25%: 1529 cm⁻¹, ID/I_G = 0.40, FWHM = 193 cm⁻¹
- DLC-Cr 37.5%: 1534 cm⁻¹, ID/I_G = 0.48, FWHM = 185 cm⁻¹
- DLC-Cr 50%: 1539 cm⁻¹, ID/I_G = 0.49, FWHM = 179 cm⁻¹

<table>
<thead>
<tr>
<th>Samples</th>
<th>G peak position (cm⁻¹)</th>
<th>ID/I_G</th>
<th>FWHM (cm⁻¹)</th>
<th>Internal stress reduction (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure DLC</td>
<td>1555</td>
<td>0.53</td>
<td>218</td>
<td>1542</td>
</tr>
<tr>
<td>DLC-Cr 12.5%</td>
<td>1527</td>
<td>0.37</td>
<td>201</td>
<td>1542</td>
</tr>
<tr>
<td>DLC-Cr 25%</td>
<td>1529</td>
<td>0.40</td>
<td>193</td>
<td>1542</td>
</tr>
<tr>
<td>DLC-Cr 37.5%</td>
<td>1534</td>
<td>0.48</td>
<td>185</td>
<td>1542</td>
</tr>
<tr>
<td>DLC-Cr 50%</td>
<td>1539</td>
<td>0.49</td>
<td>179</td>
<td>1542</td>
</tr>
</tbody>
</table>

Conclusion

DLC-Cr nanocomposite films were deposited on AISI SS304 substrates with various chromium concentration by PLD. The internal stress reduction was found to be more for lower Cr concentration and adhesion strength was more for higher Cr concentration.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cr % at%</th>
<th>Cr Wt %</th>
<th>Adhesion strength (Lc1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLC-Cr 12.5%</td>
<td>3.99</td>
<td>15.9</td>
<td>1.5</td>
</tr>
<tr>
<td>DLC-Cr 25%</td>
<td>5.85</td>
<td>28.41</td>
<td>180</td>
</tr>
<tr>
<td>DLC-Cr 37.5%</td>
<td>13.65</td>
<td>33.63</td>
<td>2.3</td>
</tr>
<tr>
<td>DLC-Cr 50%</td>
<td>19.14</td>
<td>49.76</td>
<td>2.6</td>
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</tbody>
</table>

Acknowledgment

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