Tribology Studies on Ti doped DLC coatings deposited by PECVD
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Abstract: Ti doped DLC coatings were deposited using plasma enhanced chemical vapor deposition (PECVD) integrated with Magnetron sputtering. Experiments were carried out by changing the gas composition of Ar and CH₄, pressure, biasing, deposition time and sputtering parameters of the bipolar pulsed DC power supply unit. The obtained coated samples were characterized to evaluate thickness, hardness, morphology, chemical composition, wettability, wear resistance and corrosion resistance. These results show that Ti doped DLC coatings increases hardness and decreases wettability. The tribological studies show excellent wear resistance with very low COF values and corrosion resistance in Hank’s solution. The substrates coated with Ti doped DLC samples were more reliable than bare substrates.

Keywords: Diamond like carbon (DLC), titanium, surface engineering, PECVD, corrosion, wear, tribology.

I. INTRODUCTION

There has been a remarkable surge of interest in films and coatings of “diamond–like” carbon (DLC), on account of its useful properties such as high electrical resistivity, high hardness, corrosion and wear resistance, and transparency over a large portion of the electromagnetic spectrum[2].

As carbon is the central atom in DLC film, it is beneficial to understand the structure of carbon and its allotropes, and how they form bonds. The two basic allotrope crystaline forms of carbon are graphite and diamond, as well as DLC. It is the differences in bonding structures of these substances that give rise to their unique properties [2].

Diamond-like carbon (DLC) are metastable amorphous materials that can have many properties similar to that of diamond such as extreme hardness, chemical inertness, high optically transparency and high electrical resistivity [2]. Diamond is a crystal with complete carbon to carbon (C-C) sp³ bonding. DLC is amorphous with varying degree of diamond–like character; depending on the ratio of Graphitic sp² to Diamond sp³. The family of DLC coatings is perhaps the largest and represents one of most studied among all other coatings [2]. Ti alloys is a cause for concern especially in the case of implant materials. Therefore, there is a need for modifying the surfaces of Ti implants to make them wear resistant and increase their life-time. Surface modification techniques help to improve the wear resistance of titanium and its alloys [3].

The DLC matrix does not contain a specific hybridization, but contains all three in different proportions. A phase diagram of carbon as a function of sp² and sp³ bonding, and of hydrogen content is shown in Figure 1. It presents a ternary diagram, where amorphous carbon is understood to be a mixture of the three “pure” phases. There, a-C showing disordered graphitic structure lies in the lower left hand corner, and hydrocarbon polymers are located next to the hydrogen abundant region. Sputtering and PECVD increase sp³ bonding, although later technique provides H-rich samples. High plasma density PECVD reactors are necessary to maximize sp³ bonding and simultaneously diminish hydrogen content. When the sp³ fraction reaches a high degree, a-C is denoted as tetrahedral a-C (ta-C) because tetrahedral bonding due to this hybridization is predominant. The gaps defined between the different phases comprise alloys with intermediate properties. This ensures a rich variety of a-C microstructures and properties [4].

Plasma-enhanced CVD (PECVD) is a popular technique of depositing DLC films. Plasma in a reactor is ignited between two electrodes resulting in an asymmetrical discharge. PECVD processes employ inductively coupled or capacitively coupled RF power or pulsed–DC power. The power is driven to the small electrode (cathode), where the substrate is placed on the substrate holder and the reactor walls are usually grounded (anode) [5].

![Graph showing the phase diagram of carbon as a function of sp² and sp³ bonding, and of hydrogen content.](http://www.ijettjournal.org)
Fig. 1. Ternary diagram of Different compositions of common carbon-based materials in correspondence with hardness and coefficient of friction [4]

II. Experimental details.

A) Sample preparation:
Titanium alloy β-21S (Ti–15Mo–3Al–3Nb–0.25Si) (ASTM-grade-21) was cut into samples of 2×2×0.2 cm size. The samples were ground by silicon carbide emery papers of different grit sizes to smoothen the surface and then polished to mirror-like finish using diamond polishing. The polished samples were then ultrasonically cleaned for 15 min in acetone. These samples were then loaded in the vacuum chamber for coating.

B) Vacuum
A semicircular chamber made of stainless steel 304L with front door opening was used for the combination of PECVD and magnetron sputtering. The chamber was pumped down to base vacuum of around 5×10⁻⁶ mbar to minimize contamination. The rough vacuum was created by rotary vane pump and measured by the Pirani gauge. The process gas pressure was established by the Penning gauge. The substrate holder was biased to a high negative voltage of 1100 V set by the rheostat to create an electric field between the target (cathode) and chamber (anode) to attract negative ions to the substrate from the plasma. The glow discharge (plasma) was generated by using Ar gas at high pressure created by closing the throttle valve at 100W power created by RF Source delivered in to the chamber by RF antenna. Once the glow discharge was observed, the pressure was reduced to 11µBar by adjusting the throttle valve in the backside of chamber. The samples were plasma etched using hydrogen gas for five minutes. Using the bi-polar pulsed DC power supply sputter gun was activated by giving a Pulse ON and OFF voltage values set in using Channel + and Channel – controls in the supply. Sputtering voltage was set in the range of 300V-400V, Power (0.6kW) and current (0.6A) as sputtering parameters to the sputtering source. Prior to the deposition of Ti doped DLC thin film, an interlayer coating of pure Ti was carried out for 5 minutes using Ar gas at 50W RF power. After interlayer, the process gases (Ar and CH4) were introduced into the chamber. Then, Sputtering was carried out for the deposition of Ti doped DLC films on the samples.

III. Characterization techniques:

A) Raman Spectroscopy:
Raman spectroscopy is a nondestructive optical technique used to characterize organic or inorganic materials. The Raman spectra of the coatings were obtained using Micro Raman spectrometer Labram 010 Model of ILOR-JOBIN-SPEX make. The source used was a He-Ne laser of wavelength 632 nm and 3 mW power. For DLC the Raman peaks of interest appear between 1000 cm⁻¹ to 1800 cm⁻¹ range. The visible laser Raman spectra of the polycrystalline diamond are often characterized by six peaks at 1150, 1200, 1333, 1350, 1450 and 1570 cm⁻¹. The peaks at 1350 and 1560 cm⁻¹ are understood as D-band and G-band respectively [6]. In normal case, two peaks are used to fit the Raman spectrum of DLC. However, it is recommended from micro Raman studies to fit with four Gaussian peaks in that range for better results [6]. Peaks at 1150 and 1450 cm⁻¹ have to be taken in extra with the general peaks at 1350 and 1560 cm⁻¹.

B) Corrosion studies:
Electrochemical studies on the substrate and DLC samples were conducted using CHI604D Electrochemical Workstation. The conventional three-electrode glass cell was used to carry out the electrochemical studies. The test was conducted in 200ml of Hank’s solution which is a simulated body fluid (SBF). The chemical composition of the Hank’s solution is as follows: 0.185 g CaCl₂ (1.258 mol), 0.4 g KCl (0.00536 mol), 0.06 g KH₂PO₄ (0.0004 mol), 0.1 g MgCl₂.6H₂O (0.00049 mol), 0.1 g MgSO₄.7H₂O (0.00041 mol), 8.0 g NaCl (0.137 mol), 0.35 g NaHCO₃ (0.00417 mol), 0.48 g
NaHPO₄ (0.00269 mol), and 1.00 g D-glucose in 1 L of milli-Q water [7]. The pH of the solution was adjusted with 1M HCl to 7.2-7.6 and the experiments were carried out at room temperature.

The Sample was kept as the working electrode. Pt foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The reference electrode was connected to a Luggin capillary and the tip of the Luggin capillary was kept very close to the surface of the working electrode. The samples were immersed in the Hank’s solution for an hour to establish the open circuit potential (OCP) or steady state potential.

A voltage is applied and scanned over a range at a set scan rate is 1 mV/sec. slow scan rates allow the electrochemical reactions at the sample surface to fully reach equilibrium and will allow a passive film to form on the surface. A typical fast scan rate is 1 V/min. Unless the reaction kinetics are also very fast, fast scan rates will not allow the sample surface to fully reach equilibrium and passive films may not form. The measured current–voltage data are plotted as Tafel plots in the form of potential Vs log (i/Area) plot. The corrosion potential (Ecorr) and corrosion current (Icorr) were deduced from the Tafel plot. The corrosion current was obtained using the cathodic and anodic part of the polarization [29].

The corrosion current and Tafel slopes can be combined to estimate a general corrosion rate. A passive region in the curve generally indicates the ability of a surface to form a protective coating and thus protect itself in a corrosive environment. The presence of a passive region or values of Ecorr and Icorr can be compared to other treated or untreated samples in order to determine PECVD has improved the corrosion properties of the material. 1 mmpy (metric equivalent millimeter per year) = (1/1000) inch= 39.37 mpy (mills per year).

C) Wear studies
Wear testing was done on Titanium Beta-21S substrate and Ti-doped DLC samples on a linear reciprocating ball on disc wear tester according to ASTM G 133 standards in dry conditions. An alumina ball of 6mm diameter was used as the counter surface. The ball slides against the coated samples. These specimens move relative to one another in a linear, back and forth sliding motion at room temperature. In this test method, the load is applied vertically downward through the alumina ball against the horizontally mounted flat specimen. The frequency was set at 2 Hz with stroke length of 10mm and studies were performed for 20 minutes with loads of 1 N, 2N, 5N and 7N. For reciprocating wear testing, Total Sliding distance = 2 X stroke length X frequency X time. In the present case, the sliding distance is 40 m. The wear profile was obtained by Profilometer to measure the wear track area. Optical images were taken of the wear tracks to determine the type of wear on the samples. Wear rate alone was not taken into calculation, because it was reported in ASTM G133 standard that there is no reason to assume that wear occurs at a constant rate throughout the testing period.

IV. Results and discussion
A) Raman spectroscopy
The carbon bonding in coatings was analyzed by using the Micro Raman spectroscopy. The Raman spectra of Ti doped DLC are shown in Figure 2 (a) and (b). In this study, the Raman spectra for Ti doped DLC samples are fitted with four Gaussian peaks and the ratio of the area of the D-peak (Ip) at in the range 1313 - 1374 cm⁻¹ and area of G-peak (Ip) in the range 1571 – 1600 cm⁻¹. These are taken to calculate Ip/Ip ratio to determine the degree of disorderliness of the coatings.

Fig. 2(a). Deconvoluted Raman spectrum for a sample with Ti at 10.8% and Ip/Ip=1.65.

Fig. 2(b). Deconvoluted Raman spectrum for a sample with Ti at 40% and Ip/Ip=1.16.

It is observed that increase in the Ti concentration decrease in Ip/Ip ratio. Because the area of G-peak is increasing as shown in Figure 2(a) and 2(b) with the increase in the Ti % in the coating.

B) FESEM
The FESEM images for the Ti doped DLC are obtained at different magnifications. The surface morphology at 100 KX magnification for different samples is shown in Figure 3(a) and 3(b).
Fig. 3(a). FESEM image of Ti doped DLC sample with 7.6 at % of Ti.

Fig. 3(b). FESEM image of Ti doped DLC sample with 15.6 at % of Ti.

At the lower magnification the surface looks smoother and at higher magnification the surface appears rough with nodular morphology. Roughness is observed to increase with the increase in the Ti concentration. Sample with 7.6% of Ti is observed to have a lesser particle density than with 15.6% of Ti shown in Figure 3(a) and (b) respectively.

C) X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was used to get the composition of the elements on the surface of the Ti doped DLC films. The samples considering Ti2p orbital as a prominent shell for Ti and 1s for Carbon. Figure 4 shows the wide range XPS spectra of Ti doped DLC sample with binding energy range 0-1200 eV which shows the presence of Ti and C and the oxygen.

Fig. 4. Wide range XPS Spectra of one sample (Ti doped DLC).

D) Corrosion

Potentiodynamic polarization studies show the corrosion behavior of the Ti doped DLC samples when they are exposed to Hank’s solution. The polarization studies give the Tafel plot and the electrochemical parameters known as polarization resistance ($R_p$), corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$) and corrosion rate (CR) are obtained from Tafel plot for the Ti-β21s substrate, Pure DLC and Ti doped DLC samples.

Fig. 5. Tafel plots of substrate, Pure DLC and DS-Ti-14 (24.2 Ti at %)

Figure 5 shows that $E_{corr}$ values shift from Ti-β21s, having -0.326 V to -0.197 V for pure DLC and for Ti doped DLC it is -0.172 V. It is observed that $E_{corr}$ for Ti doped DLC is shifting to a nobler values. The $I_{corr}$ value is 0.012 μA for Ti-β21S, 0.038 μA for pure DLC and 0.02, 0.006 and 0.003 μA for different concentration of Ti doped samples.
Table 1 shows the $I_{corr}$, $E_{corr}$, $R_p$ and corrosion rate values for Substrate, Pure DLC and for Ti doped DLC with different Ti concentrations. It is observed that from the Table 1 that the corrosion rate of the coated samples is very much lower than both the pure DLC and the Ti-β21s substrate. Better corrosion resistance observed when coated with Ti doped DLC on the samples.

Table 1. Corrosion parameters for different samples.

<table>
<thead>
<tr>
<th>Substrate name</th>
<th>Ti %</th>
<th>$E_{corr}$ (V)</th>
<th>$I_{corr}$ (µA/cm²)</th>
<th>$R_p$ (10⁶)</th>
<th>corrosion rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiMo Substrate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure DLC - DCA-478</td>
<td>-</td>
<td>-0.197</td>
<td>0.038</td>
<td>1.17</td>
<td>0.016</td>
</tr>
<tr>
<td>DS-Ti-12</td>
<td>0.8</td>
<td>-0.185</td>
<td>0.02</td>
<td>1.79</td>
<td>0.0095</td>
</tr>
<tr>
<td>DS-Ti-21</td>
<td>12.5</td>
<td>0.1352</td>
<td>0.006</td>
<td>1.97</td>
<td>0.0026</td>
</tr>
<tr>
<td>DS-Ti-14</td>
<td>24.2</td>
<td>0.1717</td>
<td>0.003</td>
<td>1.78</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

Figure 6 shows that the increase in the concentration of Ti% from 0.8 to 24.2 at % in the coating decreases in the $I_{corr}$ value from 0.017 to 0.003. Thus better performance in Hank’s solution is observed for Ti doped samples with increase in Ti at %.

![Fig. 6. Variation of $I_{corr}$ value with Ti at %](image)

The FESEM images of the corrosion sample are shown at 10KX magnification in Figure 7. It is clearly observed that the formation of peeled off region and surface delaminating region where it is exposed to the Hank’ solution.

![Fig. 7. FESEM images of corrosion sample at 10KX](image)

**E) Wear testing**

Wear tests were performed on stainless steel 202 (SS-202) and Ti-β21s the Ti doped DLC coated on the SS-202 samples to estimate the coefficient of friction (COF) and the wear loss of the coating at different loads 2N, 3N, 5N, 7N, 10N.

![Fig. 8(a). COF Vs Time for both substrate and coated sample at 7N load](image)

![Fig. 8(b). COF Vs Time for both Ti-β21s substrate and coated sample (DS-Ti-14) at 7N load](image)

From Figure 8(a) and 8(b) it was observed that the samples coated with Ti doped DLC had more wear resistance than bare substrate (without coating) and it was clearly seen that the coated sample reaching the substrate effect (wear testing ball reaches the sample surface after it was scratched the coating on bare substrate) in samples coated on Ti-β21s much later than that of SS-202 sample. Time taken to
reach COF value of the substrate while performing the reciprocating wear test on the coated sample for Ti-β21S substrate is more than that of SS-202.

The 2D-profile of wear track was taken by using Profilometer on each load. The curves of wear track at 5N and 7N are shown in the Figure 9(a) and 9(b) the wear rate per meter is extracted from the graph and coated sample showed a better wear resistance than substrate. Because the wear rate per meter is more for the substrate than the Ti Doped DLC sample.

![Fig. 9(a). 2D Wear track profile for Substrate at 5N.](image)

![Fig. 9(b). 2D Wear track profile for coated sample at 5N.](image)

**V. CONCLUSIONS**

Ti Doped DLC were deposited on substrates (TiMo,Si,Glass) using PECVD system Integrated with Magnetron Sputtering. The Coatings were deposited under different experimental conditions obtained by varying inert gas (Ar), precursor gas(CH₄) composition and electrical parameters from Pulsed DC-power supply, Basing Unit and deposition time.

Nano Hardness studies indicate that the increase in Ti concentration leads to increase in hardness of films. Hardness of Ti doped DLC were found to be in a range from 13.3 GPa to 28.5 GPa and Young’s Modulus was 119.7GPa to 202 GPa.

Micro Raman studies taken on the sample show that ID/IG ratio decreases with the increase in Ti concentration. The ID/IG ratio varies from 0.96 to 2.2.

FESEM images suggest that at lower magnification, the films appear smoother. With the increase in atomic percentage of Ti, more clusters are observed. Hence, it leads to roughening of the film.

Linear Reciprocating wear studies (Ball on disc) on titanium β-21S substrate, SS-202 and Ti-doped DLC samples shows that the coefficient of friction in the coated samples was very low compared to substrate. After sometime the COF value of coated samples becomes equal to that of substrate. Wear rate per meter was also found to be 0.0052 mm3/m for coated samples. The COF value was lesser on TiMo substrate than SS-202 when coated with Ti-doped DLC. Thus, the coating was found to be effective in reducing friction and providing desirable wear resistance.

Potentiodynamic polarization studies in Hank’s solution show that corrosion rate for the coated sample (24.2 at %) was very low (0.0014 mpy) when compared with the TiMo substrate (0.0052 mpy) and Ecorr value was shifting to a nobler values in case of Ti doped DLC samples. An excellent corrosion resistance observed for Ti doped DLC coatings.

**REFERENCES**