Pulsed-DC sputtered TIC/DLC nanocomposite coatings
Shaha, Kalpak Prakash

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2011

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
In this chapter, the first section concentrates on the effect of roughness of TiC/a-C coatings on tribological behavior while sliding against different counterface materials. It was observed that the ratio of hardness of the counterpart material and of the coating is crucial in determining the influence of roughness on the tribological properties of these coatings. Detailed analyses of the transfer film, sliding surfaces of the ball counterparts, and wear surfaces of the coatings are presented. The roughness evolution and the wear rates of the coatings are discussed. Furthermore, in order to obtain ultra-low friction, in the second section, mechanical, structural, chemical bonding- (sp³/sp²) and tribological properties of TiC/a-C:H coatings are presented as a function of substrate bias voltage, Ti-target current, C₂H₂ flow rate and pulse frequency. The change in chemical and phase composition influences the tribological performance where the TiC/a-C:H coatings perform better than the pure a-C:H coatings. Dense, column-free, smooth and ultra-low friction TiC/a-C:H coatings were obtained.

* This chapter is published in the following papers:
5.1 Effect of surface roughness on tribological properties

5.1.1 Introduction:

For metals, in most cases, initial surface textures are rapidly destroyed as soon as wear starts. However, under low loading conditions and/or for materials with a high hardness, wear rate is low and thus the initial surface roughness may play an important role in tribology. This is usually the case of hard protective coatings like Diamond like carbon (DLC)\(^1\). It is known that the frictional behavior of DLC based coatings is affected by their chemical structure (sp\(^2\)/sp\(^3\) content), the content of other alloying elements and the extent of chemical and physical interactions with the surrounding environment.\(^2\) The low friction of these coatings has been mainly attributed to the formation of a transfer film on the sliding surface of the counterface materials. The transfer film is believed to be formed by a friction-induced phase transformation of surface layer of DLC \(^3\), and is mainly composed of amorphous graphite-like carbon that isolates the counterface material. As a result, sliding occurs mainly between the transfer film and the DLC coating, yielding low friction.\(^4\) The presence of small amount of metal from the coating and its oxides in the transfer film in the case of the metal containing DLC are reported.\(^5\),\(^6\),\(^7\) The presence of metal carbide (TiC) nanocrystallites, at the sliding surfaces enhances the surface graphitization of the DLC matrix and promotes formation of transfer film. The density and chemical nature of the transfer film largely influence the CoF. The transfer film formation is affected by the environment, contact pressure and sliding velocity.\(^8\),\(^10\) Literature mainly focuses on its correlations with coating properties (composition, structure and mechanical) but ignores the possible effects of surface roughness on friction and wear. The substrate surface texture influences the frictional behavior of these coatings, where coatings deposited on polished substrates are usually better.\(^11\) In general, it is believed that a high surface roughness yields major frictional and wear losses mainly during the running-in period.\(^2\) However, the surface roughness may also influence the overall frictional behavior of these coatings. Moreover, the hardness of the mating materials also influences the tribological properties of DLC coatings.\(^12\) As a consequence, it is important to understand the influence of roughness on the formation of the transfer film and CoF of these coatings sliding against different counterface materials in order to underpin their tribological properties.

This section focuses on the evaluation of influence of coating surface roughness on the friction and wear behavior of the TiC/a-C nanocomposite coatings sliding against steel and Si\(_3\)N\(_4\) ball counterparts in humid air. The influence of the wear debris on the formation of the transfer film is also discussed. The effect of hardness ratio of the ball/coating tribo-pair on the transfer film formation and tribological behavior of TiC/a-C coatings exhibiting different surface roughness is described. It was observed that frictional behavior of these coatings sliding against steel was strongly influenced by the
surface roughness rather than the coating material itself and was mainly dependent on the transfer film formation. Also, in the case of rough coatings, the hardness of the counterface material plays an important role in governing their tribological performance.

5.1.2 Experimental

TiC/a-C nanocomposite coatings were deposited on smooth Si-wafer by simultaneous DC sputtering of Ti and pulsed-DC sputtering of graphite targets at 100 kHz pulse frequency in an argon atmosphere. In chapter 3, it was shown that the surface roughness of these coatings increases with increase in deposition time. Thus, TiC/a-C nanocomposite coatings having similar chemical composition and chemical structure (since the sp²/sp³ content depends upon the intensity of ion impingement which is same for a given pulse frequency) but exhibiting various surface RMS roughness viz. 1.50 ± 0.03, 4.00 ± 0.09, 6.00 ± 0.1 nm were obtained by 100 kHz p-DC sputtering by keeping the deposition conditions the same, but varying the deposition time viz. 30, 60 and 90 min respectively. The coatings with rms roughness about 1.5 and 6 nm were designated as smooth and rough coatings, respectively. The cross sectional SEM micrographs of these coatings, as discussed in chapter 3, revealed that the smooth coating exhibits weak columnar structure (column diameter ~ 55 nm) whereas the rough coating exhibits strong columnar structure (column diameter ~ 170 nm). However, no cracks were observed on wear tracks, which suggested that no rupture was occurred at the column boundaries during sliding. Thus, the frictional behavior was not affected by the columnar features, as discussed later in detail. The hardness and modulus of these coatings was 17 and 175 GPa, respectively. The tribotests on these coatings were performed using a CSM tribometer, with a ball-on-disk configuration, against Φ6 mm 100Cr6 ball at a sliding speed of 10 cm/s and normal load of 5 N and at room temperature (20-23 °C) and constant relative humidity of 50%. The hardness of the steel and Si₃N₄ balls were 7.5 and 16 GPa, respectively. Optical and confocal microscopy was used to characterize the transfer film formed on the ball counterparts after the tribotest. The thickness of the transfer film was measured on three-dimensional images (512 × 512 pixels) of the wear scar on the steel ball, captured by a Nanofocus® confocal microscope after ultrasonically removing the wear debris. The WSxM® 4.0 Develop10.2 free software was used to select the pixels having transfer film on the confocal micrograph. The average and maximum thickness of the transfer film was then calculated by considering the z values all these pixels. The surface roughness of the coatings before and after the tribotests was measured by AFM. 3D confocal micrographs of the wear tracks on the coatings were captured to measure the wear volume for calculation of wear rates of the coatings.
5.1.3 Results and discussion

5.1.3.1 TiC/a-C coatings sliding against 100Cr6 Steel ball

Figure 5.1 shows the dependence of the CoF on the surface roughness of the TiC/a-C nanocomposite coatings sliding against different ball counterparts.

![Graph showing CoF vs. Rms roughness for TiC/a-C coatings sliding against steel and Si3N4 balls](image)

Figure 5.1. Variation of coefficient of friction (averaged over 10000 laps) as a function of roughness of TiC/a-C nanocomposite coatings against 100Cr6 steel and Si3N4 balls.

For the given range of roughness, the CoF increases with increasing surface roughness above 1.5 nm, and the rough coating yields a steady state CoF of 0.18, which is twice as much as that observed for the smooth coating (0.09). This clearly reveals that the roughness affects the overall frictional behavior of these coatings. However, below 1.5 nm, the CoF was not influenced by the surface roughness. The CoF of these coatings sliding against Si3N4 was independent of the roughness and will be discussed later. The tribological properties of the smooth and rough coatings sliding against different counterface materials have been summarized in Table 5.1.

Table 5.1. Initial roughness (RMS), hardness ratio (r), CoF, wear rate (w), maximum thickness (t) of transfer film, fraction of worn material converted to transfer film (f), and factor n for smooth and rough coatings sliding against different ball material

<table>
<thead>
<tr>
<th>Coating</th>
<th>RMS (nm)</th>
<th>Ball</th>
<th>r</th>
<th>CoF ( \times 10^{-8} )</th>
<th>( w_t ) mm³/N·m</th>
<th>t (μm)</th>
<th>f (%)</th>
<th>n (laps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth</td>
<td>1.5</td>
<td>steel</td>
<td>0.41</td>
<td>0.09</td>
<td>2.94</td>
<td>3.2</td>
<td>28.5</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si3N4</td>
<td>0.94</td>
<td>0.10</td>
<td>3.89</td>
<td>7.3</td>
<td>49.9</td>
<td>213</td>
</tr>
<tr>
<td>Rough</td>
<td>6</td>
<td>steel</td>
<td>0.41</td>
<td>0.18</td>
<td>2.37</td>
<td>1.5</td>
<td>12.3</td>
<td>1066</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si3N4</td>
<td>0.94</td>
<td>0.09</td>
<td>2.89</td>
<td>7.8</td>
<td>66.8</td>
<td>504</td>
</tr>
</tbody>
</table>

Figure 5.2a and b show the surface morphology of the as-deposited smooth and rough coatings, respectively. The rough coating exhibits thick and sharp surface protrusions surrounded by network of valleys and the peak to valley distance was larger than that for smooth coating.
Figure 5.2 AFM micrographs (2×2 µm²) of as deposited TiC/a-C nanocomposite coatings: (a) smooth coating and (b) rough coating. The corresponding RMS roughness (R) is indicated.

The frictional characteristics of the smooth and rough coatings sliding against steel ball are shown in Figure 5.3a.

Figure 5.3 (a) Friction characteristics of bearing steel ball sliding against the TiC/a-C coatings having various surface roughness as indicated together with sliding against the polished surface (having rms roughness 1.9 nm) of the rough coating obtained after sliding 1500 laps. The rms roughness (in nm) of the wear tracks on the coatings at the corresponding laps is indicated in round brackets. Optical micrographs showing the wear scar of ø6mm 100Cr6 steel balls after the running-in period against the rough nanocomposite coating (b), after 10000 laps sliding against the smooth coating (c); against the polished surface with (d) and without wear debris (e); and against the rough coating (f). The sliding direction of the balls was from right to left.
In the case of the smooth coating, the CoF was low and remained stable at a value of 0.09. Optical micrograph of the wear scar on the steel ball after sliding against the smooth coating, in Figure 5.3c, revealed that significant amount of material transferred from the coating to the ball surface and a transfer film formed. The diameter of the wear scar was about 95 µm, indicating that the sliding surface of the steel ball remained almost unworn. The 3D confocal micrograph of the wear scar, in Figure 5.4a, shows that a thick transfer film formed on the steel ball. The average thickness of transfer film was 2.2 µm with a maximum of 3.5 µm. The volume of the transfer film was equal to ~30% of the volume of the worn material from the coating. The transfer film was evenly distributed and covered almost 90% of the contact area on the steel ball. Thus, the transfer film almost completely isolated the steel ball and facilitated interfacial sliding between the transfer film and the surface of the coating, rather than between the surfaces of the steel ball and the coating, yielding low CoF. Also, simultaneous wear of the coating decreased the surface roughness of the wear track mainly during the initial stages of the sliding. Under these conditions, the formation of a “stable” transfer film, which is always present during entire course of sliding and effectively isolated the ball counterpart, yielding a low steady state CoF.

In the case of the rough coating, a considerable increase in CoF to 0.27 was observed during the running-in period which gradually decreased thereafter and reached to a steady state value, as seen in Figure 5.3a. It is important to note that after the running in period, the CoF did not show a decreasing trend but remained stable at a high value of 0.18. This clearly shows that while sliding against steel, the high surface roughness not only gives a high CoF during the running-in period but also governs the overall frictional behavior of these coatings, with a high steady-state CoF. Optical micrograph of the wear scar on the steel ball after sliding against rough coating for 10000 laps is shown in Figure 5.3f. The wear scar diameter was ~230 µm. Dense and long scratches, parallel to sliding direction, were observed on the wear scar. This wear of the ball was mainly occurred...
during the running-in period since the diameter of the wear scar after the running in period (after first 1500 laps), as seen in Figure 5.3b, was ~ 200 µm. The maximum contact pressures are significantly higher for rough surfaces and are present at the surface asperities.\textsuperscript{13,14} During initial stages of sliding, due to high contact pressures, the sharp and hard protruding surface asperities of the rough coating causes considerable abrasive wear of the soft steel ball mainly by ploughing mechanism leading to high frictional and wear losses. During subsequent sliding after the running-in period, the removal of surface asperities of the rough coating, as discussed later, reduces the maximum contact pressure and resulted in less wear of the ball. The removal of surface asperities of the rough coating reduces the maximum contact pressure and resulted in less wear of the ball after the running-in period. The wear of the steel ball occurred mainly during the running in period since its wear rate at 1500 laps was equal to $6.94 \times 10^{-8}$ mm$^3$/N·m which further reduced to $6.2 \times 10^{-12}$ mm$^3$/N·m measured at the end of 10000 laps. This is consistent with the observation made by Harries et. al.\textsuperscript{15} where they have shown that abrasiveness of the coating decreases with increasing number of the laps and hence the wear rate of the steel ball decrease. The worn material from the steel ball was mainly accumulated at the front and on the sides of the wear scar as seen in Figure 5.3b and f. However, the wear debris from steel ball may oxidize to form metal oxides and incorporate into the transfer film and contribute to increase in CoF.\textsuperscript{5} At the beginning, the wear material transferred from the coating was mainly accumulated in front of the sliding ball and later the transfer film covered the main part of the load bearing contact area. The 3D confocal micrograph of the wear scar on the steel ball after removing the wear debris by ultrasonic cleaning is shown in Figure 5.4b. The transfer film was rather thin and unevenly distributed and covered only about 30% of the contact area on the steel ball. The average thickness of was 0.8 µm with a maximum up to 1.5 µm which was less than that observed for the smooth coating. The volume of the transfer film was only ~ 13 % of the volume of the worn material from the coating which indicates that most of the worn material was transformed into wear debris. The transfer film failed to isolate the sliding surface of the steel ball completely. Also, after 10000 laps, a relatively rougher wear track compared to that on the smooth coating was observed and will be discussed later. While sliding under these conditions, the transfer film becomes “unstable” due to repeated break-down and formation and it fails to cover the majority of the contact area leading to high CoF. It is known that the size of wear debris increases with increasing surface roughness.\textsuperscript{16} The comparatively larger wear debris which form during initial stages of sliding against rough coating may further impede the formation of transfer film and leads to increase in CoF as discussed later.

To comprehend the effect of surface roughness, an initial tribotest for 1500 laps was performed to polish out the surface asperities on the rough TiC/a-C coating. It was
observed that the depth of the wear track on the coating was less than 20 nm as measured by confocal microscopy. Thus, the thickness of the coating and hence the columnar structure remained almost the same, but rather a significant decrease in the surface roughness of the coating from an initial value of 6 nm to 1.9 ± 0.1 nm. This polished surface exhibited plateaux and sharp grooves. After removing the wear debris from the wear track by ultrasonic cleaning, a tribotest was performed with a new steel ball on this polished surface. This yielded a steady-state CoF of 0.10. For the same coating exhibiting strong columnar features, as the surface roughness decreased from 6 to 1.9 nm, the steady state CoF was reduced from 0.18 to 0.1. Also, the values of steady-state CoF, as seen in Figure 5.3a, for the polished surface exhibiting strong columnar structure and the smooth coating exhibiting comparatively weaker columnar structure are comparable. This further demonstrates that the CoF was largely affected by the surface roughness of the TiC/a-C coatings and independent of the columnar microstructure provided that no cracks formed along the column boundaries. The thickness of the transfer film was also comparable to that observed against the smooth coating. However, in the case of polished surface the formation of transfer film was a rather sluggish process since the steady-state CoF was reached only after 2500 laps, in comparison to the smooth coating where a transfer film formed within less than 30 laps. This indicates that the wear of initial small surface asperities of the smooth coating facilitate the transfer film formation. The wear scar on the steel ball shown in Figure 5.3d revealed that the transfer film completely covered the contact area. No noticeable wear of the ball was observed. On the other hand, the surface roughness of the wear track was further reduced from 1.9 to 0.4 ±0.1 nm. Furthermore, while sliding against this 0.4 nm smooth polished surface of the rough coating with a new steel ball the steady-state CoF (not shown) was equal to 0.1. This suggests that below a certain roughness, 1.5 nm in case of these coatings, the friction was not influenced by the surface roughness.

To understand the role of wear debris, another tribotest was performed with a new steel ball on a polished surface (rms roughness 1.9 nm) of the rough coating but without removing the wear debris. The average CoF was 0.13 in this case, as shown in Figure 5.3a. It is noteworthy that more laps were needed to reach the steady-state CoF as compared to those required in the absence of wear debris on the wear track. This indicates that the presence of hard wear debris retards the formation of the transfer film, likely serving as three body abrasive to break down the tender transfer film, as indicated by the dense fluctuations in the CoF curve at the beginning of test. The wear debris may re-circulate in and out of the contact during the running-in period as observed by Scharf et al.. The wear debris were collected by the steel ball as shown in Figure 5.3e and also were accumulated on both sides of the wear track, indicating that they were eventually removed from the sliding contact.
Figure 5.5 Wear rate of steel ball and CoF as a function of surface roughness of TiC/a-C nanocomposite coatings. The CoF and wear of the steel ball increased with increasing surface roughness above 1.5 nm.

Figure 5.5 shows the wear rate of the steel ball as a function of roughness of the TiC/a-C coatings. The wear volume of the steel balls was calculated according to the size of wear scars. The wear rate of the steel ball increased significantly with increasing surface roughness of the coatings and follows similar trend as that of CoF. Thus, the increase in CoF with increasing roughness can be correlated to the wear of the steel ball; as the contact area on the steel ball increases, its effective coverage by the transfer film is increasingly difficult.

Figure 5.6 (a) Friction characteristics of the smooth TiC/a-C coating against steel ball having rough sliding surface (obtained after sliding against rough coating and ultrasonically cleaned as shown in Figure 5.4b). The tribotest result on the same coating against new steel ball, same as in Figure 5.3a, is included for comparison. (b) Optical micrographs of the wear scar on the worn steel ball after 10000 laps.

Furthermore, to understand the effect of the contact area on the steel ball on the CoF, a worn steel ball with a wear scar of 230 µm in diameter shown in Figure 5.4 (which was obtained after removing the wear debris by ultrasonic cleaning of the steel ball in Figure 5.3f) was slid against the smooth coating. It is important to note that there was a pre-existing transfer film on this worn steel ball. Figure 5.6a shows the friction characteristic of this worn steel ball against the smooth coating. During the initial stages
of sliding the CoF was low (~ 0.09). This is due to the pre-existing transfer film on the worn steel ball since the protrusions of the pre-existing transfer film first comes into contact with the smooth coating. Also, the mean contact pressure was lower as it was distributed over a large contact area. During subsequent sliding, CoF gradually increased to 0.15 at the end of 10000 laps. This was due to simultaneous wear of the existing transfer film and of the smooth coating. As the contact between the two counterfaces was conformal, a concentrated wear of the coating was observed at the regions corresponding to the protrusions of the pre-existing transfer film. As the contact area on the steel ball increases during the sliding, the transfer film fails to cover it effectively leading to gradual increase in CoF. After 10000 laps, the transfer film shown in Figure 5.6b only partially covered the contact area on the worn steel ball. The mean CoF was 0.12 which was higher than that observed for the same coating against a new steel ball, as seen in Figure 5.6a. The small contact area on the new steel ball, in Figure 5.3c, was effectively covered by the transfer film and yielded a lower CoF. In contrast, the relatively larger contact area on the worn steel ball against the same coating was not covered effectively by the transfer film, leading to higher CoF. This clearly indicates that a large contact area on the counterpart ball hinders itself from effective coverage by the transfer film.

![Figure 5.7](image)

*Figure 5.7* (a) Friction characteristics of steel ball having initial transfer film (created by sliding against smooth coating indicated by black color), sliding against the rough TiC/a-C nanocomposite coating indicated by orange color; Optical micrographs of the steel ball having initial transfer film (b) before and (c) after sliding against the rough coating, respectively.

To reveal the effect of surface roughness on an existing transfer film, a transfer film was initially created on a steel ball by sliding it against the smooth coating for 5000 laps, and then this ball with transfer film was further slid for 10000 laps against the rough coating as shown in Figure 5.7a. After a significant increase during the running-in period,
similar to that observed in Figure 5.3a for rough coating, the CoF gradually reduced to about 0.13. Abrasive wear during the running in period yielded an increase in the size of wear scar from ~ 100 µm to ~ 175 µm as shown in Figure 5.7b and c, respectively. The mean CoF (0.13) was lower than that observed for a steel ball without having initial (existing) transfer film (0.18). It indicates that the existing transfer film was not completely removed from the steel ball during the running-in period. Also, the wear scar on the ball having existing transfer film was smaller (~ 175 µm) than that observed on steel ball (~230 µm) without having existing transfer film. This observation revealed that the existing transfer film protected the steel ball to some extent during the running-in period. It was noted that the CoF was not reaching to a steady state but rather was fluctuating and exhibited increasing trend at the end of the test as seen in Figure 5.7a. This shows that the large sliding surface of the steel ball, caused during running-in period, destabilizes the transfer film formation and eventually the transfer film fails to cover the entire contact area leading to increase in CoF.

5.1.3.2 TiC/a-C coatings sliding against Si3N4 ball

Figure 5.8 Friction characteristics of smooth and rough TiC/a-C coatings sliding against Si3N4 ball at 5 N normal load, sliding velocity 10 cm/s and relative humidity of 50% at 23 °C. The CoF was independent of the roughness of these coatings.

Figure 5.1 shows that the CoF of TiC/a-C coatings sliding against Si3N4 ball was independent of the surface roughness. The frictional characteristics of the smooth and rough coating sliding against Si3N4 ball are shown in Figure 5.8. For both the coatings, the CoF was low and remained stable at ~ 0.1, similar to that observed in the case of the smooth coating sliding against steel ball, as shown in Figure 5.3a. It is important to note that there was hardly a running-in period of high CoF observed even for the rough coating. Optical micrographs of the wear scar on the Si3N4 balls after the tribotest against smooth and rough coatings are displayed in Figure 5.9a and b, respectively.
Figure 5.9 Optical micrographs of the wear scar on Si$_3$N$_4$ ball, after 10,000 laps, sliding against TiC/a-C nanocomposite: (a) smooth coating; (b) rough coating.

Significant amount of material was transferred from the coating to the ball surface and the transfer film was formed. No wear of the Si$_3$N$_4$ ball was observed while sliding against both the coatings and the surface of the Si$_3$N$_4$ ball remained smooth.

Figure 5.10 Confocal micrographs showing three-dimensional view of wear scar and transfer film formed on Si$_3$N$_4$ ball after sliding against TiC/a-C nanocomposite: (a) smooth coating and (b) rough coating. The corresponding confocal micrographs of the wear scar after removing the wear debris by ultrasonic cleaning are shown on right side. No wear of the Si$_3$N$_4$ ball was observed in both cases.

The 3D confocal micrographs of the Si$_3$N$_4$ ball after the tribotests, in Figure 5.10a and b, show that thick transfer film formed in both cases. In the case of smooth coating,
the average thickness of transfer film was 3.25 µm with a maximum of 7.32 µm. A 50% volume of the worn coating material was transformed on the ball indicating efficient transfer film formation. The transfer film was evenly distributed and covered almost all the contact area. Similarly, in the case of rough coating, the average thickness of transfer film was 2.86 µm with a maximum up to 7.83 µm. A most efficient transfer film was formed with the transfer film volume ~ 65% of the total worn volume of the coating. In both the cases, the transfer film completely isolated the Si$_3$N$_4$ ball and facilitated interfacial sliding between the transfer film and the surface of the coating, rather than between the surfaces of the Si$_3$N$_4$ ball and the coating yielding low CoF. It was noted that the thickness of the transfer film formed on Si$_3$N$_4$ ball was more than that observed for steel ball. The right sides of Figure 5.10a and b show the Si$_3$N$_4$ ball after ultrasonic cleaning. In the case of smooth coating, no wear of the Si$_3$N$_4$ ball was observed and only portions of a thick well adhered transfer film were seen. In the case of rough coating, the transfer film was almost completely removed after the cleaning, and few wear scratches were observed on the Si$_3$N$_4$ ball. The wear of Si$_3$N$_4$ ball was negligible and hence is not reported. Also, the wear of the coatings decreases the surface roughness of wear tracks on both the coatings during the initial stages of the sliding, as discussed later. Since no wear of the ball was occurred, the contact area on the Si$_3$N$_4$ ball was small. Under these conditions, a stable transfer film form which covered almost all the contact area on the Si$_3$N$_4$ ball leading to a low steady state CoF.

5.1.3.3 Hardness ratio and sliding surfaces

In order to understand the different wear behavior of the steel ball and Si$_3$N$_4$ ball against the rough coating, mechanical properties of these materials were considered. The hardness of the steel ball, Si$_3$N$_4$ ball and the TiC/a-C nanocomposite coatings were 7, 16.5 and 17 GPa, respectively. Thus, the hardness ratio of the ball and the coating material for steel was 0.41, whereas it was 0.97 for Si$_3$N$_4$.

Figure 5.11 Schematic diagram of effect of hardness ratio on wear of abraded material against abrasive. 

\[ \text{Hardness ratio} \]
During the initial stage of sliding the protruding surface asperities of the coating causes abrasive wear of the ball counterpart mainly by ploughing mechanism. Thus, the hardness of the abrasive asperity becomes important in abrasive wear. Figure 5.11 shows that when the hardness ratio $r$ (the hardness of abraded material/the hardness of abrasive material) stays below a certain critical value $r_{c1}$ (0.5 to 0.8), abrasive wear clearly takes place. However, with the increase in hardness ratio above the critical value $r_{c1}$, wear volume of mating material decreases, and finally almost no wear is observed when $r$ is close to a critical value $r_{c2}$ (1 to 1.4). 18 In the case of steel ball, the hardness ratio is less than the critical value $r_{c1}$ and hence considerable wear occurs while sliding against rough coatings. However, the hardness ratio for Si$_3$N$_4$ ball approaches to the critical value $r_{c2}$ and almost no wear occurs. Thus, our results are consistent with the correlations of hardness ratio and abrasive wear, as described above.

The coatings experience wear during sliding. Since the CoF for steel and Si$_3$N$_4$ ball against the rough coating showed remarkable difference, the evolution of roughness of the wear track on the rough coating was considered. The evolution of surface roughness of wear track on the rough coating with increasing the number of laps against steel and Si$_3$N$_4$ ball was shown in Figure 5.12 and Figure 5.13, respectively. During the initial stages of sliding, the peaks of the surface asperities on the rough coating were truncated, resulting in a polished surface consisting of a plateaux and sharp grooves as seen clearly in the surface profiles in Figure 5.14. This leads to a decrease in the surface rms roughness of the coating from an initial value of 6 nm to ~1.9 nm against steel after 1500 laps and against Si$_3$N$_4$ ball after 500 laps. Truncation of surface asperities occurred mainly during the running-in process.
TRIBOLOGICAL BEHAVIOR OF NANOCOMPOSITE COATINGS

Figure 5.13 AFM micrographs (2×2 µm²) showing surface morphology of the wear track on rough TiC/a-C nanocomposite coating after sliding against Si₃N₄ ball for (a) 500; (b) 1500 and (c) 10000 laps. The corresponding RMS roughness (R) is indicated. The arrow indicates sliding direction of the coating. The surface of the wear tracks was cleaned to remove the loose wear debris before AFM measurements.

Figure 5.14 Surface profiles of rough TiC/a-C coating sliding against Si₃N₄ ball for the number of laps as indicated.

It is noted that the comparatively harder Si₃N₄ ball quickly removed the top of the surface asperities and reduced the roughness to ~ 1.9 nm in 500 laps which in the case of the soft steel ball required 1500 laps. During the subsequent sliding, the roughness of the wear track further reduced, yielding a surface having roughness of 1 nm against steel and 0.33 nm against Si₃N₄ ball at the end of 10000 laps as seen in Figure 5.12b and Figure 5.13c, respectively. Thus, during the entire course of sliding, the sliding surface of the rough coating against steel ball was relatively rougher that that against Si₃N₄ ball.

The plots of surface roughness as a function of number of laps for both the coatings against both ball counterparts were shown in Figure 5.15. The surface roughness shows a transition from an initial high rate of decrease during the running-in period to a steady decrease at low rate thereafter. This behavior was well fitted to an exponential decaying function.
Although the decrease of roughness in the smooth coating was modest in comparison with the rough coating, it was fitted also to the same decaying function as follows:

\[
\frac{R - R_f}{R_i - R_f} = \exp\left(\frac{-x}{n}\right)
\]

where \( R \) is the roughness of the wear track after \( x \) laps, \( R_i \) and \( R_f \) are the initial and final roughness of the wear track and \( n \) (in number of laps) can be interpreted as the difficulty to decrease the roughness (a larger value of \( n \) indicates that more laps are needed to decrease it).
transfer film formation. Thus, the lower hardness ratios in the case of steel ball (responsible also for its abrasive wear against the rough coating) are reflected in lower values of 1/n (cf. Table 5.1). Besides, having the same hardness ratio, the value of 1/n for a Si$_3$N$_4$ ball against the smooth coating was larger than sliding against the rough coating. This was caused by a comparatively faster and more efficient formation of the transfer coating on the Si$_3$N$_4$ against rough coating since the higher surface roughness promotes the formation of transfer film.

![Cross sectional profiles of the wear tracks on the smooth (left) and rough (right) TiC/a-C nanocomposite coatings against different ball counterparts as indicated. The corresponding values of width and maximum depth of the wear tracks are indicated.](image)

The wear surfaces of the coatings were studied by confocal microscopy in order to evaluate the wear volume which then converted to wear rates of the coatings. Figure 5.17 shows the cross sectional profile of the wear tracks on the smooth and rough coating against steel and Si$_3$N$_4$ ball. It clearly revealed that the width of the wear track on the rough coating against steel ball (~ 150 µm) was larger than that observed against Si$_3$N$_4$ ball (~ 70 µm). Since a little wear of Si$_3$N$_4$ ball was occurred, the width of the wear track on the rough coating was smaller. However, wear of the steel ball during the running-in period increases contact area on the steel ball which leads to a corresponding increase in the width of the wear track on the rough coating. This also explains the surface roughness evolution since sliding on a narrow and concentrated wear track facilitates quick removal
of surface asperities due to high contact pressure in the case of Si$_3$N$_4$ whereas sliding against a wide wear track reduces the contact pressure and hence a lower rate of decay and absolute value of surface roughness during running-in period and at the end of 10000 laps for steel. The widths of the wear racks on the smooth coating (~100 µm) were similar against both the ball counterparts. It was noted that the width of the wear track on the rough coating against Si$_3$N$_4$ ball was smaller than that observed on the smooth coating. It can be explained by the quick formation of transfer film on the Si$_3$N$_4$ ball since the initial roughness of the rough coating promotes the transfer film formation in the absence of the wearing of the ball. This is also reflected in the maximum thickness of transfer film which is larger in this case. As the sliding progresses, a slight increase in the width occurs with a faster deepening of the wear track. The much faster deepening of the wear track near the centre was a result of the unevenly distributed contact pressures over the contact interface, the pressure being the highest at the centre of the track.

![Figure 5.18 Wear rates of the smooth and rough TiC/a-C nanocomposite coatings sliding against steel and Si$_3$N$_4$ ball counterparts.](image)

The wear rates of the smooth and rough coatings against steel and Si$_3$N$_4$ were shown in Figure 5.18. It was noted that the wear rates of the rough coating were always lower than the smooth coating against the respective ball counterparts under the same loading conditions. It is important to note that in the case of rough coating, the high contact pressure during the initial stage of sliding causes considerable wear of the steel ball and a little wear of the coating. During subsequent sliding, since the contact area increases, the mean contact pressure decreases and hence a little wear of both the ball and the coating occurs. Thus, the wear rate of the rough coating was less mainly due to wearing of the steel ball. In the case of smooth coating, a little wear of the steel ball leads to a contact pressure distribution concentrated over a comparatively narrow wear track yielding increased wear rate of the coating. Similarly, a very little wear of the Si$_3$N$_4$ balls causes contact pressure distribution concentrated over a narrow wear tracks and yields relatively higher wear rates of the coatings. The quick formation of the transfer film on the Si$_3$N$_4$ ball against rough coating yields a lower wear rate of the rough coating than compared to
a smooth coating. The wear rates of the smooth coating against Si$_3$N$_4$ ball was little higher than that observed against steel ball. It can be explained because of higher maximum and mean contact pressure against Si$_3$N$_4$ due to its higher modulus of elasticity compared to that of steel.

The rate of reduction in roughness of the wear tracks and the wear rates of the coatings were found to be correlated since the variation of the factor $1/n$, in Figure 5.16, and the wear rates, in Figure 5.18, for different tribo-pairs follow similar trend. The parameter $1/n$ accounts for the rate of decrease of the roughness, while the wear rate accounts for the rate of removal of material of the coating. Considering that the coatings are tough (no cracks on the wear tracks), such a correlation seems logical, since the wearing takes place by gradual removal the surface asperities during sliding. Such a removal of material from top of asperities causes formation of plateaux and grooves, as seen in Figure 5.14, resulting in decrease in RMS roughness of the coating. Thus, the rate of removal of material (wear rate) and rate of decrease of RMS roughness are correlated in case of tough coating where the wear takes place by gradual polishing of the surface asperities of the coating. Thus, a low wear rate reflects in a low rate of decrease in surface roughness of the wear track. For example, the rate of decrease in roughness of the rough coating against steel was lower than that against Si$_3$N$_4$, since the wear rate of the coating against steel was lower than that observed against Si$_3$N$_4$.

5.2 Tribological performance of TiC/a-C:H coatings

In order to achieve ultra-low friction ($\mu < 0.1$) in DLC coatings, one has to reduce or eliminate the main causes of friction. One of the requirements, as discussed in the previous section, is to produce smooth coatings. However, it was observed that, below a certain roughness (1.5 nm for the TiC/a-C coatings) the friction was not influenced by the surface roughness and the atomically smooth TiC/a-C coatings gives a CoF $\sim 0.1$. To further reduce the CoF below 0.1, the surface of the coatings must have the highest degree of chemical passivity or inertness so as to reduce the adhesive interactions during sliding which may also strongly influence the friction. In these coatings, the adhesive interactions can primarily result from several types of bonding. Among others, covalent bond interactions between unoccupied or dangling $\sigma$-bonds of sliding interfaces of DLC coatings can account for a significant source of adhesion and contribute to high friction. It is known that hydrogen has a strong chemical affinity towards carbon, it bonds strongly to some of the carbon atoms and thus effectively passivates their unoccupied or free $\sigma$-bonds. Once passivated, such carbon atoms become chemically inert and cause very little adhesive interactions during sliding and lead to low friction. So efforts were made to obtain ultra low friction ($\mu < 0.1$) TiC/a-C:H nanocomposite coatings. Moreover, the effect of process parameters viz. substrate bias voltage, Ti-target current, C$_2$H$_2$ flow rate
and pulse frequency on the mechanical, structural and tribological performance of TiC/a-C:H coatings deposited by pulsed-DC magnetron sputtering of Ti-targets in Ar/C2H2 plasma was studied in detail. It was observed that the TiC/a-C:H coatings perform better than the pure a-C:H coatings. The structural and mechanical properties of these coatings are correlated to the deposition conditions. Dense, tough and ultra-low friction TiC/a-C:H nanocomposite coatings were obtained under optimized conditions.

5.2.1 Experimental

TiC/a-C:H nanocomposite coatings were deposited on Si (100) wafers by simultaneous p-DC sputtering of two Ti targets, opposite to each other, in an Ar/C2H2 atmosphere. The substrates, located at 80 mm distant from the targets, were pulsed biased at 250 kHz pulse frequency (50 % duty cycle). The base pressure of the chamber before deposition was 3-4×10⁻⁶ mbar. The substrates were first ultrasonically cleaned in acetone followed by Ar plasma etching for 15 minutes at p-DC -400 V bias voltage at 250 kHz and 87.5 % duty cycle. A CrTi interlayer, having a thickness of approximately 150 nm, was deposited to improve the interfacial adhesion. Finally, two Ti targets were sputtered in p-DC reactive mode in an Ar/C2H2 atmosphere to deposit the coatings. The substrate holder was rotated by 3 rpm. No external heating was applied to the substrates. The maximum temperature was measured at 120°C during deposition of these coatings. To study the microstructure and deposition rate as a function of pulse frequency, the coatings were deposited at 0 (DC), 200 and 350 kHz pulse frequency (70% duty cycle). In order to investigate the effect of various process parameters on the mechanical and tribological properties of 200 kHz p-DC sputtered coatings, the negative substrate bias voltage, Ti-target current, and the acetylene flow rate were varied in the range from 40 to 150 V, 0.6 to 1 A, and 8 to 12 sccm, respectively. The flow rate of Ar gas was kept constant at 12 sccm for all the depositions. Furthermore, the properties of optimized (in terms of microstructure and composition) 200 kHz and 350 kHz p-DC sputtered TiC/a-C:H coatings were compared.

5.2.2 Results and discussion

The results are presented as follows. Firstly, the microstructural and surface morphological evolutions of the TiC/a-C:H nanocomposite coatings deposited by p-DC sputtering at different pulse frequencies are presented with particular emphasis on inhibiting the column formation. Then, the effect of substrate bias voltage, phase and chemical composition on the mechanical and tribological properties of the a-C:H and TiC/a-C:H is discussed in detail. The synthesis conditions and properties of the coatings are summarized in Table 5.2. Finally, the effect of pulse frequency applied to the Ti-target on the mechanical and tribological properties of the optimized TiC/a-C:H coatings (in terms of microstructure and composition) is evaluated and compared.
5.2.2.1 Microstructural evolution

Figure 5.19 shows the cross sectional SEM micrographs of TiC/a-C:H nanocomposite coatings deposited for 120 min by DC and pulsed-DC sputtering at 200 and 350 kHz pulse frequency by keeping the current applied to Ti-targets and C₂H₂ flow rate and substrate bias voltage fixed at 1 A and 8 sccm and 40 V, respectively.

![Cross sectional SEM of TiC/a-C:H nanocomposite coatings deposited by (a) DC sputtering; and p-DC sputtering at (b) 200 kHz and (c) 350 kHz pulse frequency. (See text for detailed deposition conditions).](image)

The coating deposited by DC sputtering, as seen in Figure 5.19a, exhibited strong columnar features. However, switching from DC to pulsed-DC sputtering at 200 and 350 kHz pulse frequency the microstructure evolved from columnar to column-free, as seen in Figure 5.19b and c, respectively. Since the column boundaries are potential source of failure since they facilitate the crack initiation and propagation, a column-free microstructure is necessary for improved toughness under loading and contact sliding. The dense, column-free coatings deposited by p-DC sputtering coatings are expected to be tougher than compared to the DC sputtered coatings.

![AFM topography images of TiC/a-C:H nanocomposite coatings deposited by (a) DC sputtering; and p-DC sputtering at (b) 200 kHz and (c) 350 kHz pulse frequency. The corresponding RMS roughness (R) is indicated. (See text for detailed deposition conditions).](image)
Table 5.2: Synthesis conditions (substrate bias voltage - \( V_b \), Ti Target current – \( I_{Ti} \), \( \text{C}_2\text{H}_2 \) flow rate, pulse frequency - \( f \)), chemical composition, surface rms roughness – \( R \), Raman analysis (\( I(D)/I(G) \) ratio, Position of G peak), Mechanical properties (Hardness - \( H \), Young’s modulus - \( E^* \), \( H/E^* \) ratio), Residual stress - \( \sigma \) and tribological properties (coefficient of friction CoF and wear rate – \( W_r \times 10^{-7} \text{ mm}^3/\text{N.m} \)) of p-DC sputtered coatings.

<table>
<thead>
<tr>
<th>Bias (-V)</th>
<th>ITi (A)</th>
<th>C2H2 (sccm)</th>
<th>f (kHz)</th>
<th>Composition (at.%)</th>
<th>( R ) (nm)</th>
<th>( I(D)/I(G) )</th>
<th>G-peak position</th>
<th>H (GPa)</th>
<th>E* (GPa)</th>
<th>H/E*</th>
<th>( \sigma ) (- MPa)</th>
<th>CoF</th>
<th>Wr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>40</strong></td>
<td>1.0</td>
<td>8</td>
<td>200</td>
<td>17.31 79.80 1.37</td>
<td>1.85</td>
<td>0.91</td>
<td>1563.4</td>
<td>14.1</td>
<td>128.6</td>
<td>0.11</td>
<td>-</td>
<td>0.08</td>
<td>1.92</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>8</td>
<td>200</td>
<td>17.64 79.03 1.32</td>
<td>0.36</td>
<td>0.90</td>
<td>1562.6</td>
<td>15.8</td>
<td>142.6</td>
<td>0.11</td>
<td>-</td>
<td>0.09</td>
<td>1.60</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>17.82 78.98 1.21</td>
<td>0.23</td>
<td>0.74</td>
<td>1558.8</td>
<td>16.4</td>
<td>144.3</td>
<td>0.11</td>
<td>-</td>
<td>0.10</td>
<td>2.43</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>80</strong></td>
<td>0.6</td>
<td>8</td>
<td>200</td>
<td>12.47 84.09 1.07</td>
<td>0.61</td>
<td>0.73</td>
<td>1558.2</td>
<td>16.1</td>
<td>136.3</td>
<td>0.12</td>
<td>2158</td>
<td>0.05</td>
<td>0.66</td>
</tr>
<tr>
<td>0.75</td>
<td>1.0</td>
<td>8</td>
<td>200</td>
<td>17.64 79.03 1.32</td>
<td>0.36</td>
<td>0.90</td>
<td>1562.6</td>
<td>15.8</td>
<td>142.6</td>
<td>0.11</td>
<td>-</td>
<td>0.09</td>
<td>1.60</td>
</tr>
<tr>
<td><strong>80</strong></td>
<td>8</td>
<td>0.75</td>
<td>12</td>
<td>200</td>
<td>12.47 84.09 1.07</td>
<td>0.61</td>
<td>0.73</td>
<td>1558.2</td>
<td>16.1</td>
<td>136.3</td>
<td>0.12</td>
<td>2158</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td>0</td>
<td>96.31 0.20</td>
<td>0.69</td>
<td>0.25</td>
<td>1536.6</td>
<td>22.9</td>
<td>165.2</td>
<td>0.13</td>
<td>2418</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td></td>
<td></td>
<td>0</td>
<td>97.06 0.34</td>
<td>3.15</td>
<td>0.23</td>
<td>1534.8</td>
<td>23.8</td>
<td>168.1</td>
<td>0.14</td>
<td>2566</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>80</strong></td>
<td>0.75</td>
<td>8</td>
<td>200</td>
<td>12.47 84.09 1.07</td>
<td>0.61</td>
<td>0.73</td>
<td>1558.2</td>
<td>16.1</td>
<td>136.3</td>
<td>0.12</td>
<td>2158</td>
<td>0.05</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td></td>
<td></td>
<td>0</td>
<td>96.31 0.20</td>
<td>0.69</td>
<td>0.25</td>
<td>1536.6</td>
<td>22.9</td>
<td>165.2</td>
<td>0.13</td>
<td>2418</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Coatings marked with * and ** are repeated for clarity.
The surface morphologies of these coatings are shown in Figure 5.20. In the case of DC sputtering, as seen in Figure 5.20a, the surface showed cauliflower morphology with peaks surrounded by a network of valleys and the peak-to-valley distance was large. However, in the case of p-DC sputtering, the peak-to-valley distance considerably decreased and the surface exhibited small ripples at 200 kHz (Figure 5.20b) and nanosized bumps at 350 kHz (Figure 5.20c). Consequently, a drastic decrease in surface rms roughness, from about 8 nm for DC sputtered coatings to ~ 1.8 and 0.2 nm in the case of 200 and 350 kHz p-DC sputtered coatings, respectively, was observed. It must be noted that these coatings were deposited at 40 V. Thus, ultra-smooth coatings can be obtained by 350 kHz p-DC sputtering at low substrate bias voltage. The \( \text{Ar}^+ \) ions energy and flux delivered to the growing coating increases with increasing pulse frequency, as discussed in chapter 3, and the enhanced surface diffusion driven growth ascertains a smooth growth front and hence a column-free microstructure, as explained in chapter 4. The microstructural and surface morphological evolutions of these coatings deposited by p-DC reactive sputtering as a function of pulse frequency are similar to those observed for coatings deposited by p-DC non-reactive sputtering, as discussed in chapter 3 and 4.

It is important to note that the deposition rate of the p-DC sputtered coatings was lower than that observed for DC sputtering and depended on the pulse frequency. As compared to DC sputtering, approximately, 15 and 40% reduction in deposition rate (see Figure 5.19) was observed for p-DC sputtered TiC/a-C:H nanocomposite coatings at 200 and 350 kHz, respectively. The reduction in deposition rate was due to a combination of several factors. The average power dissipated at the target decreases with increasing pulse frequency and at the start of each pulse there is a dead time during which negligible sputtering occurs and the proportion of this dead time increases with increasing pulse frequency and so the deposition rate is lower at higher frequency.\(^ {19} \) The rate of voltage change at the target during the initial stages of the pulse-on period and the maximum negative voltage attained during the pulse-on period is significantly lower at higher frequencies\(^ {19} \). Since sputtering rate is proportional to power and sputtering yield is proportional to target voltage, both these factors tend to lower deposition rate at higher frequency. The \( \text{Ar}^+ \) ion and energy flux delivered to the substrate increases with pulse frequency. The higher ion to atom ratio at higher pulse frequencies may reduce the deposition rate by enhanced re-sputtering from the coating. Since the reduction in deposition rate at 200 kHz was low, this was an optimal choice for further studying the influence of process parameters on the mechanical and tribological properties of these coatings.
5.2.2.2 Effect of substrate bias voltage

In this section, the effect of negative substrate bias voltage in the range from 40 to 150 V on the tribological, mechanical and structural properties of 200 kHz p-DC sputtered TiC/a-C:H nanocomposite coatings is discussed. The Ti-target current and C$_2$H$_2$ flow rate were kept constant at 1 A and 8 sccm, respectively. All these coatings exhibited glassy microstructure (not shown) and hence any possible effects of the columnar features on the properties of the coatings, particularly on friction and wear, were excluded. The Ti-content in these coatings was ~ 17.5 at.% and was not affected by changing the substrate bias voltage (See Table 5.2). The grazing incidence XRD analysis (not shown) confirmed formation of TiC nanocrystallites in these coatings. The average size of the TiC nanocrystallites for the coatings deposited at 40 and 150 V was 2.2 and 2.3 nm, respectively which indicates that the size of TiC nanocrystallites was not affected by the changing substrate bias voltage.

![Figure 5.21](image-url)

*Figure 5.21 (a) Friction characteristics of 200 kHz p-DC sputtered TiC/a-C:H coatings deposited at various negative substrate bias voltage, as indicated, sliding against steel ball at 5 N normal load, sliding velocity 10 cm/s and relative humidity of 50% at 23 °C; (b) CoF (■) and Hardness (▲) and (c) Wear rate of these coatings as a function of negative substrate bias voltage.*

Figure 5.21a demonstrates the tribotest results of the four coatings deposited at different bias voltages. All the coatings show a quick drop in the coefficient of friction (CoF) during the initial stages of sliding, which was mainly attributed to the quick
formation of a transfer film on the steel ball which facilitates easy sliding at the interface
between the transfer film and the TiC/a-C:H coating. A transfer film was observed on the
steel balls after sliding against all these coatings (for e.g. as shown in Figure 5.25c after
sliding against the coating deposited at 80 V). The transfer film is mainly composed of
amorphous graphite-like carbon. The friction graphs of the coatings deposited at lower
bias voltages (40 and 80 V) were steady whereas jumps in CoF values were observed for
the coatings deposited at higher bias voltages (100 and 150 V). Figure 5.21b shows the
CoF and hardness dependence of TiC/a-C:H nanocomposite coatings as a function of
substrate bias voltage. A moderate increase in CoF from 0.08 at 40 V to 0.11 at 150 V
was observed. The hardness also showed a moderate increase from 14 GPa at 40 V to
16.5 GPa at 150 V. The wear rates of the coatings as a function of substrate bias voltage
are shown in Figure 5.21c. Although the difference in the values was small, the wear rate
was higher for coatings deposited at higher substrate bias voltage. Despite the increase in
hardness, the wear resistance of the coatings at higher bias values was reduced.
Considerable wear debris were observed in and around the wear track after the tribotest
on the coatings deposited at higher bias voltages (100 and 150 V). This also reflected in
the higher wear rates, in Figure 5.21c, observed for these coatings. Since the presence of
wear debris retards the transfer film formation, as discussed in section 6.1, it can be
expected that the harder wear debris formed during the sliding against the coatings
deposited at higher bias voltages hinder the formation of the transfer film by means of
three body abrasion. This also explains the fluctuations in CoF, as seen in Figure 5.21a,
obscerved for these coatings.

Raman analysis was carried out to understand the effect of substrate bias voltage on
the chemical structure (sp\(^3\)/sp\(^2\)) of these coatings. Figure 5.22a and b shows the Raman
spectra for the coatings deposited at 80 and 150 V substrate bias voltages. The Raman
spectra showed two distinct peaks; the so-called D peak at \(\sim 1350\) cm\(^{-1}\) and the G peak at
\(\sim 1580\) cm\(^{-1}\), which correspond to the so called “disordered” and “graphitic” structures
respectively. Ferrari and Robertson\(^{20}\) showed the possibility of acquiring information of
the hybridization states of C-C bonding from the analyses of the I(D)/I(G) ratio and the
position of the G peak. Provided that the I(D)/I(G) ratio is in the range from 0.2 to 2 and
the G peak position ranges from 1510 to 1600, a decrease in I(D)/I(G) ratio and a shift of
G peak to lower values indicate a progressive disordering of the sp\(^2\)-bonded rings and
increase of sp\(^3\) sites in the range from 0 – approximately 20%.\(^{20}\)
Figure 5.22 BWF-Lorentzian fitted Raman spectra for TiC/a-C:H nanocomposite coatings deposited by 200 kHz p-DC sputtering at negative substrate bias voltage of (a) 80 V and (b) 150 V; and (c) I(D)/I(G) ratio (●) and G peak position (▼) as a function of negative substrate bias voltage for these coatings.

Figure 5.22c shows the variation of I(D)/I(G) ratio and G peak position as a function of bias voltage. There was very little difference between the Raman spectra acquired from coatings deposited at 40 and 80 V. However, the I(D)/I(G) ratio decreased and the G peak shifted to the lower wavenumber for the coating deposited at 150 V, indicating an increase in sp³ content in the coating. The higher sp³ content led to an increase in the hardness at higher substrate bias voltage similar to that observed by Martinez-Martinez et al. in case of pure amorphous carbon coatings. Also, it is relatively difficult to form a graphite-like transfer film due to relatively lower sp² content in the coating and hence yields higher CoF. The increased ion energy delivered to the coating at higher substrate bias voltage may increase the compressive stress in the coatings, which facilitates the wear debris formation during sliding, as discussed later. Although the hydrogen content in the coatings was not measured, it may decrease with increasing substrate bias voltage, and thus contribute to higher CoF.
Moreover, a direct correlation between high friction and high roughness was not observed since the surface roughness of the coatings was not high enough. The influence of substrate bias voltage on the surface roughness of these coatings is shown in Figure 5.23. The surface rms roughness rapidly decreased from ~ 1.85 nm at 40 V to about 0.36 nm at 80 V and further reduced to about 0.23 nm at 150 V. The substrate bias voltage of 80 V was considered as optimum which yields smooth surface and also avoids the higher stress in the coating which otherwise deteriorates the tribological performance as that observed for coatings deposited at higher (100 and 150 V) substrate bias voltages.

5.2.2.3 Effect of phase and chemical composition

The composition of these coatings was varied by changing the Ti-target current, and the acetylene flow rate, independently, but keeping the substrate bias voltage and pulse frequency applied to the targets fixed at 80 V and 200 kHz, respectively. It was found that at lower target current and higher acetylene flow rate, a complete poisoning of the Ti targets by the carbonous species (formed by decomposition of acetylene gas) occurred. This obstructed the sputtering of Ti from the targets. Since no Ti was detected by EPMA, these coatings were pure a-C:H coatings instead of TiC/a-C:H nanocomposite coatings (c.f. Table 5.2). This gave an opportunity to compare the properties of pure a-C:H (single phase) and TiC/a-C:H (two phases) nanocomposite coatings deposited by 200 kHz p-DC sputtering. Coatings were deposited by varying the Ti target current from 0.6 to 1 A while keeping the substrate bias voltage and C$_2$H$_2$ flow rate constant at 80 V and 8 sccm, respectively.
Figure 5.24a and b shows the frictional characteristics and average CoF, and hardness of the coatings as a function of the current applied to the Ti-targets. The CoF decreases from 0.15 to 0.05 with increasing Ti-target current from 0.6 to 0.75 A and then increases to 0.09 at 1 A, as seen in Figure 5.24b. The coating deposited at 0.6 A was a pure a-C:H and the Ti content in the TiC/a-C:H coatings deposited at 0.75 and 1 A was approximately 12.5 and 17.5 at.%, respectively. This indicates that for the given range of Ti content, the TiC/a-C:H nanocomposite coatings exhibit lower CoF than the pure a-C:H coatings for the same load and environment conditions. This was mainly due to reduction in the stress in the coating with addition of Ti and toughening of the coating due to TiC nanocrystallites which reduces its brittleness and hence the wear debris formation. Considerable wear debris was found on and around the wear track of the pure a-C:H coating due to excessive stress in the coating. These hard wear debris cause abrasive wear of the steel ball, which results in a large wear scar of 362 µm in diameter as shown in Figure 5.25a.

Figure 5.25 Optical micrographs of the wear scar on steel balls sliding against the coatings deposited by 200 kHz p-DC sputtering at a Ti-target current of (a) 0.6 A; (b) 0.75 A and (c) 1 A, respectively. Sliding direction, of the coatings in contact, from left to right. (The area of transfer film is larger in (c) than in (b)).
As discussed in section 5.1, if the contact area on ball counterpart is large then the transfer film cannot cover the entire contact area and fails to isolate the steel ball completely and leads to higher CoF. Furthermore, the wear debris hinders the formation of a transfer film. Thus, the transfer film failed to cover the large contact area on the steel ball and yields higher CoF. A relatively little wear of the steel ball occurred against the TiC/a-C:H nanocomposite coatings deposited at a Ti-target current of 0.75 and 1 A. As seen in Figure 5.25b and c, the wear scar diameters on the steel balls were 145 and 175 µm, respectively. The transfer film effectively covered the contact area on the steel balls leading to a lower CoF. The TiC nanocrystallites present at the sliding surface enhance the surface graphitization and promote the formation of transfer film. Since the concentration of the amorphous lubricant phase determines the frictional behavior, with increasing Ti content from 12.1 to 17.5 at.%, the friction increases from 0.05 to 0.08. A 12 at.% content of Ti was considered as the optimum that gives the lowest CoF of 0.05. Many small yet asymmetric peaks were observed in the plot of CoF versus laps for the coating deposited at 0.75 A target current. It was associated with sudden rupture followed by gradual re-formation of the transfer film during sliding. Once the transfer film forms on the steel ball, the CoF cannot decrease further and therefore starts to fluctuate. It can be inferred that since the transfer film covered the sliding surface of the ball, the wear rate of the coating diminished. As a result, during further sliding the transfer film is assumed to get thinner until it breaks down, leading to a sudden rise of the CoF. Sliding at a higher CoF leads to wear of the coating which generates the necessary material for the growth of a new transfer film. Thereafter, a new cycle of the dynamic friction process is repeated. A similar frictional behavior of TiC/a-C:H nanocomposite coatings was observed in the previous work in our group. Such a behavior was not seen in the other TiC/a-C:H coating, since a partial break down of the transfer film has a little influence when its area is larger (see Figure 5.25c). The hardness of these TiC/a-C:H coatings was decreased with increasing Ti-target current. This was mainly attributed to decrease in sp$^3$ content in the coatings, as evidenced by the increase in I(D)/I(G) ratio and shift of the G peak position to higher wave number (see Table 5.2) with increasing Ti-target current.

The effect of changing the C$_2$H$_2$ flow rates from 8 to 12 sccm, by keeping all other parameters (Ti-target current at 0.75 A, and substrate bias at 80 V) constant, on the tribological properties of 200 kHz p-DC sputtered coatings was also investigated. The EPMA analysis indicated that the coating deposited at a flow rate of 8 sccm has 12.1 at.% of Ti whereas the coatings deposited at a flow rate of 10 and 12 sccm were pure a-C:H coatings due to complete poisoning of the race tracks on the Ti-targets, as explained earlier. The surface roughness of the coating increased with increasing C$_2$H$_2$ flow rate (See Table 5.2). Figure 5.26a shows the frictional characteristics of these coatings.
Chapter 5

Figure 5.26 (a) Friction characteristics of 200 kHz p-DC sputtered coatings deposited at various flow rates of C\textsubscript{2}H\textsubscript{2} in sccm, as indicated, sliding against steel ball at 5 N normal load, sliding velocity 10 cm/s and relative humidity of 50% at 23 °C; (b) CoF (■) and hardness (▲) of these coatings as a function of C\textsubscript{2}H\textsubscript{2} flow rate. Note that the coating deposited at 8 sccm was TiC/a-C:H nanocomposite whereas coatings deposited at 10 and 12 sccm were pure a-C:H coatings.

It must be noted that this TiC/a-C:H nanocomposite coating deposited at 8 sccm flow rate was the same coating that gives CoF of 0.05 discussed above. Figure 5.25b and Figure 5.27 show the optical micrographs of the steel balls after sliding against the TiC/a-C:H nanocomposite coating and the pure a-C:H coatings, respectively.

Figure 5.27 Optical micrographs of the wear scar on steel balls sliding against the pure a-C:H coatings deposited by 200 kHz p-DC sputtering at a C\textsubscript{2}H\textsubscript{2} flow rate of (a) 10 and (b) 12 sccm, respectively. Sliding direction, of the coatings in contact, from left to right.

A considerable abrasive wear while sliding against the pure a-C:H coatings increased the contact area on the steel ball, which obstructed effective isolation of the steel ball by the transfer film and hence led to higher CoF, as explained before. These observations were consistent with the observations in the previous section where TiC/a-C:H nanocomposite gives lower CoF than the pure a-C:H coatings and can be explained likewise. In the case of the pure a-C:H coatings, a higher CoF was observed at 12 sccm than that compared to 10 sccm. The wear scar diameter in the former case was ~ 558 µm, whereas it was ~ 427 µm in the latter case. The relatively larger contact area on the steel ball was increasingly difficult to be covered by the transfer film in case of the coating.
deposited at 12 sccm and hence leads to higher CoF. A large amount of wear debris was observed on and around the wear track on both these coatings after the tribotest. The wear debris also contribute to higher CoF, as discussed earlier. Figure 5.26b shows the CoF and hardness dependence of these coatings as a function of C$_2$H$_2$ flow rate. The CoF increases from 0.05 at 8 sccm to 0.14 at 12 sccm. The hardness increased from 16 GPa for the TiC/a-C:H coating deposited at 8 sccm to approximately 23 GPa and remained almost the same for the pure a-C:H coatings deposited at 10 and 12 sccm. Figure 5.28a-c show the Raman spectra of these coatings. There was very little difference between the Raman spectra acquired from the coatings deposited at 10 and 12 sccm. The TiC/a-C:H nanocomposite coating, in Figure 5.28a, showed a pronounced D peak compared to the pure a-C:H coatings, as seen in Figure 5.28b and c. These observations indicate that incorporation of Ti into a-C:H matrix increases the sp$^2$ content in the coatings.

![Figure 5.28](image-url)

Figure 5.28 BWF-Lorentzian fitted Raman spectra of 200 kHz p-DC sputtered coatings deposited at C$_2$H$_2$ flow rate of (a) 8 sccm; (b) 10 sccm and (c) 12 sccm; and (d) I(D)/I(G) ratio (●) and G peak position (▼) as a function of C$_2$H$_2$ flow rate for these coatings.

Figure 5.28d shows the variation of I(D)/I(G) ratio and G peak position as a function of C$_2$H$_2$ flow rate. The I(D)/I(G) ratio decreased and the G peak shifted to lower wavenumber at higher C$_2$H$_2$ flow rate. Both parameters indicate a progressive amorphisation of the sixfold sp$^2$–bonded rings and increased presence of sp$^3$ sites in the coatings. The higher hardness of these coatings was correlated to a higher sp$^3$ content in the coating. The wear rates of the TiC/a-C:H nanocomposite coating and pure a-C:H
coating deposited at 12 sccm were $6.6 \times 10^{-8}$ and $1.07 \times 10^{-7}$ mm$^3$/N m, respectively. The harder (Hardness=23 GPa) a-C:H coatings exhibited poor wear resistance than compared to the softer (Hardness = 16 GPa) TiC/a-C:H nanocomposite coatings.

![Figure 5.29 Compressive stress as a function of C$_2$H$_2$ flow rate for 200 kHz p-DC sputtered coatings. The coating deposited at 8 sccm was TiC/a-C:H nanocomposite whereas coatings deposited at 10 and 12 sccm were pure a-C:H coatings.](image)

In order to understand this phenomenon, the compressive stress in these coatings was measured. Figure 5.29 shows that the compressive stress in these coatings increases with increase in C$_2$H$_2$ flow rate. The compressive stress in the TiC/a-C:H nanocomposite coating was less compared to that of pure a-C:H coatings. This was mainly associated with the higher sp$^2$ content in the TiC/a-C:H nanocomposite coatings since only a small increase in the sp$^2$ content is needed to account for stress release in these coatings.\(^{25}\) The increase in the stress in the pure a-C:H coatings with increasing C$_2$H$_2$ flow rate was most likely due to increase in thickness\(^{26}\) from ~ 1.2 µm at 8 sccm to ~ 1.37 µm at 12 sccm. During sliding, the formation of wear debris was promoted due to the presence of high stress in the coating. This also reflects in the high wear rates observed for the a-C:H coatings (see Table 5.2). The hard wear debris are detrimental to the tribological properties of these coatings, as discussed earlier.

**5.2.2.4 Effect of pulse frequency**

In this section, the effect of pulse frequency (200 and 350 kHz) applied to the Ti-targets on the mechanical, structural and tribological properties of the TiC/a-C:H nanocomposite coatings is discussed. The 200 kHz p-DC sputtered TiC/a-C:H nanocomposite coating deposited at 0.75 A Ti-target current, 80 V substrate bias and 8 sccm of C$_2$H$_2$ flow rate was considered optimum since it yielded an ultra-low CoF of 0.05 and a low wear rate of $6.6 \times 10^{-8}$ mm$^3$/N.m. To understand the effect of pulse frequency, a TiC/a-C:H nanocomposite coating was deposited by p-DC sputtering at 350 kHz pulse frequency and by keeping all the other parameters unchanged. The properties of these two p-DC sputtered coatings at 200 and 350 kHz were compared.
The cross sectional SEM micrographs shown in Figure 5.30 revealed that both these coatings exhibited dense and column-free microstructure. The EPMA analysis measured a Ti content of 12.5 and 12.2 at.% in the coatings deposited at 200 and 350 kHz, respectively. Although the sputtering of Ti target is less at 350 kHz than at 200 kHz, the chemical composition of these coatings was comparable within the error limits of the measurements. The energy and flux of Ar$^+$ ions was much higher at 350 kHz than at 200 kHz p-DC sputtering. The intensive Ar$^+$ ion impingement at the growing coating causes considerable re-sputtering of ad-atoms during deposition. The C atoms were preferentially re-sputtered since they are lighter than the incident Ar ions, whereas Ti atoms being heavier were less likely re-sputtered. During deposition of the 350 kHz p-DC sputtered coating, the sputtering from Ti targets was relatively lower but the re-sputtering of C atom was relatively higher and hence a similar Ti content as that observed for 200 p-DC sputtered coating was observed.

![Figure 5.30 Cross sectional SEM of TiC/a-C:H nanocomposite coatings deposited by p-DC sputtering at (a) 200 kHz and (b) 350 kHz pulse frequency.](image)

Figure 5.31 Grazing incidence XRD spectra for Si substrate and the TiC/a-C:H nanocomposite coatings deposited at the indicated pulse frequency. Dashed lines indicate the peaks from the Si substrate.

![Figure 5.31 Grazing incidence XRD spectra](image)
Chapter 5

Figure 5.31 shows the grazing incidence XRD spectra which confirmed the presence of TiC nanocrystallites in these coatings. The average size of the TiC nanocrystallites was 1.9 and 1.8 nm for the coatings deposited at 200 and 350 kHz respectively. Several peaks from the Si substrates (dashed lines) were observed in the case of the coating deposited at 200 kHz. Moreover these peaks from the Si substrates were shifted to higher 2θ values due to stress in the coating and is consistent with the observations made by Zhang et al.23 during deposition of DLC on Si.

![Graph showing XRD spectra](image)

Figure 5.32 (a) Raman spectra; and (b) Frictional characteristics of the 350 kHz p-DC sputtered TiC/a-C:H nanocomposite coating sliding against steel ball (friction graph of 200 kHz p-DC sputtered TiC/a-C:H coating in blue color from Fig 5.24a was included for comparison); (c) Optical micrograph of the steel ball after the tribotest.

Figure 5.32a shows the Raman spectra acquired from the 350 kHz p-DC sputtered TiC/a-C:H nanocomposite coating. This spectra was compared with that of the 200 kHz p-DC sputtered TiC/a-C:H nanocomposite coating which is the same as shown in Figure 5.28a. The I(D)/I(G) ratio decreased from 0.74 to 0.49 and the G peak shifted from 1558.2 to a lower wave number of 1552.0 with increasing pulse frequency from 200 to 350 kHz. Both these observations indicated that the sp³ content in 350 kHz p-DC sputtered coating was relatively higher than the coating deposited at 200 kHz. The mechanism of the formation of sp³-C is modeled as “subplantation”, where energetic C ions are able to penetrate the surface layer and subsequently bond in a highly stressed tetrahedral (sp³) configuration27. For penetration to occur, the ions should overcome the
C displacement energy (25-35 eV). When the majority of C atoms are not ionized, as is the present case of p-DC magnetron sputtering, it can be inferred that more intensive Ar\(^+\) ion impingement to the growing coating would promote the formation of sp\(^3\)-C. During the deposition, some of the individual C atoms in the surface layer would be knocked-down as a consequence of the energy transfer between the incident Ar\(^+\) ions and C atoms. Since the flux and energy of Ar\(^+\) ions in the case of 350 kHz p-DC sputtering is much higher than that at 200 kHz, a higher sp\(^3\) content can be expected. The hardness of the TiC/a-C:H nanocomposite coating deposited at 350 kHz was 17.2 GPa which was higher than that observed for coating deposited at 200 kHz (16.1 GPa). It was mainly due to higher sp\(^3\) content in the 350 kHz p-DC sputtered coating. The compressive stress in the coatings was 2.15 and 2.85 GPa at 200 and 350 kHz pulse frequency, respectively.

Figure 5.32b shows the frictional behavior of both the coatings deposited at 200 and 350 kHz. A higher mean CoF of 0.07 was observed for 350 kHz p-DC sputtered coating than that of 0.05 for 200 kHz sputtered coating. Figure 5.32c and Figure 5.25b shows the optical micrographs of the wear scar on the steel balls after sliding against 350 and 200 kHz p-DC sputtered TiC/a-C:H coatings, respectively. In both the cases, a transfer film was formed on the steel ball. The higher CoF for the 350 kHz sputtered coatings can be attributed to relatively lower amount of sp\(^2\) content in the coating. Moreover, considerable wear debris were formed and around the wear track on this coating and also was collected by the steel ball as seen in Figure 5.32c. Due to high hardness of this coating, comparatively harder wear debris were formed. The hard wear debris retard the formation of the transfer film and contribute to high friction. The higher stress in the coating deposited at 350 kHz promoted the formation of wear debris during sliding. It also reflected in the higher wear rate of 8.2×10\(^{-8}\) mm\(^3\)/N.m observed for this coating compared to that of 6.6×10\(^{-8}\) mm\(^3\)/N.m observed for 200 kHz p-DC sputtered TiC/a-C:H coating.

It was noted that despite exhibiting higher residual stress compared to that of the pure a-C:H coatings, the 350 kHz p-DC sputtered TiC/a-C:H nanocomposite coating shows lower CoF and better wear resistance (see Table 5.2). This clearly indicates that incorporation of TiC nanocrystallites into the a-C:H matrix toughens (reduces its brittleness) the coating which reduces the formation of wear debris during sliding and yields lower friction by promoting surface graphitization.
Chapter 5

5.3 Conclusion

In conclusion, it was shown that smooth coatings always yield low CoF independent of the hardness of counterface materials. However, in the case of rough coatings, the hardness ratio of the ball/coating tribo-pair essentially determines the contact area on the ball counterpart which further influences the transfer film formation and hence CoF. The wear debris also retarded the formation of transfer film. Tribological behavior of TiC/a-C coatings was independent of the columnar microstructure due to excellent toughness of these coatings. The frictional characteristics were controlled to a large extent by the formation of transfer film and its coverage of the contact area. In the case of steel, the hardness ratio was 0.41 and considerable abrasive wear was occurred. The worn ball obstructs the effective transfer film formation and hence yields high CoF. However, for Si₃N₄ ball, the hardness ratio was 0.97 and a little wear of the ball occurred and a “stable” transfer film forms, which yields a low CoF. The rough coating shows better wear resistance than the smooth coating, though of the same hardness. It was shown that the surface roughness evolution of the wear tracks can be correlated to the wear rates of these coatings. Smooth surfaces of the TiC/a-C coatings are favored for obtaining a low CoF independent of the hardness of the counterface materials. Also, hydrogen effectively reduces the adhesive reactions during sliding and hence the smooth TiC/a-C:H coatings exhibit lower friction (µ ~ 0.05) than that of TiC/a-C coatings. Dense, tough, ultra-smooth TiC/a-C:H films exhibiting ultra-low friction and excellent wear resistance can be obtained by pulsed DC sputtering at higher frequencies and at low substrate bias voltage. The tribological properties of TiC/a-C:H nanocomposite films were moderately affected by the change in substrate bias voltage. The change in phase composition strongly influences the tribological performance where the TiC/a-C:H films perform better than the pure a-C:H films. In the case of TiC/a-C:H nanocomposite films, a higher sp² content and presence of TiC nanocrystallites at the sliding surface promotes formation of transfer film and yields lower CoF. The Ti content in the film also influences the tribological performance. The optimal Ti content was determined to be ~ 12 at.%. In the case of a-C:H films, a relatively higher sp³ content and residual stress promote the formation of hard wear debris during sliding, which cause abrasive wear and increases the contact area on the ball counterpart. This makes the formation of transfer film relatively difficult and leads to higher CoF. With increasing pulse frequency, the sp³ content, hardness and the residual stress in the TiC/a-C:H nanocomposite films increases due to increased intensity of ion impingement to the film. The relatively lower sp² content and higher stress in the film deposited at 350 kHz pulse frequency yields inferior tribological properties.
References
