Comparison of three types of carbon composite coatings with exceptional load-bearing capacity and high wear resistance

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Abstract

Surface coatings for high load wear applications require a combination of high hardness and toughness as well as good adhesion. Metal–carbon composite coatings have attracted special interest because of their low friction coefficients and low wear rates. Unlike the normal diamond-like carbon coatings which consist of a mixed sp2 and sp3 bonding structure and are usually highly stressed, a graphite-like carbon composite coating is reported, which demonstrates exceptionally high toughness and high wear resistance. This paper reports the preparation and characterization of three types of chromium–carbon composite coatings. The coating samples were deposited under different conditions using unbalanced magnetron sputtering of both chromium and graphite targets, and characterized with Raman spectroscopy, nanoindentation, scratch tests and pin-on-disc wear tests against alumina. A hydrocarbon gas (CH4) was also used during deposition to explore the influence of a sputter-chemical vapor deposition hybrid process on coating properties. The optimisation and the deposition parameter dependence of the coating properties as well as the sliding wear performance of the coatings are discussed. The results show that (1) the coating deposited in H2/Ar atmosphere has better low load wear performance due to its higher hardness; (2) the coating deposited in pure Ar atmosphere has exceptionally high load-bearing capacity and excellent wear resistance attributed to its excellent adhesion, high toughness and low friction coefficient; (3) the coating deposited in butane/Ar atmosphere has a higher deposition rate, blacker colour and excellent high-load wear performance.

Keywords: Carbon composite; Physical vapour deposition; Coating; Wear resistance; Load-bearing capacity

1. Introduction

Amorphous carbon coatings have been extensively studied because of their excellent tribological properties such as low friction coefficient (<0.1), high hardness (>20 GPa) and low wear rate (<10−8 mm3/Nm). They have found wide applications in optics, magnetic media, wear components and tools industries [1–5]. The methods used to produce such coatings include physical vapor deposition (PVD) and chemical vapor deposition (CVD), or their combination (PCVD). The early reported sputtered hydrogenated carbon coatings are generally described as diamond-like carbon (DLC), which is composed of both sp2 bonded graphite and sp3 coordinated diamond-like structures. Hydrogen introduced in the coating process plays an important role in determining the sp3/sp2 ratio and coating’s mechanical as well as tribological properties. Increasing the sp3/sp2 ratio leads to a higher hardness but also to a higher residual stress which causes cracking or delamination under high loading applications. Our previous work on sputtered hydrogenated DLC demonstrated that slightly doped chromium could effectively reduce the residual stress while maintaining the high hardness [6]. Recently, the research group in Teer Coatings reported sputtered unhydrogenated carbon coatings doped with chromium, which appeared to have only sp2 bond structure and also demonstrated high hardness, excellent wear resistance and exceptionally high load-bearing capacity [7,8]. These properties make it an ideal coating for high-loading wear applications.

This paper reports the preparation and characterization of such carbon composite coatings deposited under different conditions using unbalanced magnetron sputtering of both metal and graphite targets. A hydrocarbon gas (C3H10) was also used to explore the influence of a
sputter-CVD hybrid process on coating properties. To improve adhesion of the coating to substrate, a thin chromium layer (~0.2 μm) followed by a graded Cr–C transition layer was deposited. The optimisation and the deposition parameter dependence of the coating properties as well as the sliding wear performance of the coatings are discussed.

2. Experimental

Both sputtered unhydrogenated carbon and hydrogenated DLC coatings were deposited on high speed steel (HSS) discs using an Teer UDP-550 unbalanced magnetron sputtering system [6,9]. Two chromium and two carbon targets were used during sample cleaning and deposition. The targets were sputtered with DC power and the substrate holder was biased with pulsed DC power. High purity argon was used as discharge gas. Immediately after ultrasonic cleaning sequentially in three chemical solutions, the polished HSS substrates measuring 50 mm in diameter and 6 mm in thickness were mounted on a rotating sample holder and the system was pumped down to a pressure of lower than 1×10⁻³ Pa. Prior to deposition, the substrates were argon plasma-cleaned for half an hour using a pulsed DC bias voltage of 400 V with a frequency of 300 kHz. All coating samples start with a thin chromium layer, followed by a carbon doped with chromium layer. During the Cr–carbon layer deposition, only one Cr target was sputtered at a DC current of 0.1–0.2 A. The deposition conditions are summarized in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure (Pa)</td>
<td>&lt;1×10⁻³</td>
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<tr>
<td>Deposition pressure (Pa)</td>
<td>0.42</td>
</tr>
<tr>
<td>Substrate sputter-cleaning</td>
<td>PDC 400 V/300 kHz for 30 min</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Substrate bias (V)</td>
<td>PDC 60–130 V/50 kHz</td>
</tr>
<tr>
<td>Target size (mm²)</td>
<td>330×133×10</td>
</tr>
<tr>
<td>Chromium layer thickness (μm)</td>
<td>0.2</td>
</tr>
<tr>
<td>Transition layer thickness (μm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr content in the top layer (at.%)</td>
<td>5–8</td>
</tr>
<tr>
<td>Total film thickness (μm)</td>
<td>2–2.5</td>
</tr>
</tbody>
</table>

Table 1: Deposition conditions of carbon composite coatings

For samples deposited by the sputter-CVD hybrid process, butane (C₄H₁₀) was introduced after 1 h deposition of the chromium–carbon layer, as described above, and maintained for 1 h to the end of the process without changing any other deposition parameters. The gas flow rate ratio of butane to Ar was varied from 0.2 to 0.4.

The coating hardness was measured using a Nanotest 550 nanoindenter. For all the tested samples, the maximum indentation depth was set at 100 and 200 nm, respectively. The Oliver and Pharr method was used for the hardness calculations [10]. No significant difference in hardness was observed for the indentation depth of 100 and 200 nm. Adhesion strength was measured using a Teer 2200 scratch tester at a constant speed of 10 mm/min under a normal load, which linearly increased from 10 to 128 N at a constant rate of 100 N/min. Optical microscopy was used to confirm the starting point of the adhesive failure along the scratch track. Raman spectra (Rennishaw Ramanscope) were measured in the range of 800–2000/cm at room temperature with 632.8 nm excitation wavelength of a He–Ne laser to analyze the atomic bond structure of the films.

To evaluate the tribological properties of the coatings, wear tests were carried out at an air humidity of 45±10 RH% and a temperature of 24±1 °C using a pin-on-disc tribometer with the sample placed horizontally on a turntable. The tests were performed at a normal load of 10, 25 and 95 N, respectively, using alumina pins with a radius of 4.5 mm. The tests with 10 N load were performed at a linear speed of 20 cm/s for a total sliding distance of 4000 m, while the other tests were performed at a constant rotation speed of 200 rpm for a total wear duration of 1 h. The wear loss and normalized wear rate were calculated from the wear scar cross-sectional area, as measured by a Talysurf profilometer, and the wear track diameter.

3. Results and discussions

3.1. Raman spectra

Fig. 1 shows the typical Raman spectra of the three types of Cr–carbon composite coatings deposited under different atmospheres, while the substrate bias and discharge current applied to graphite and chromium targets were kept constant at PDC 70 V/kHz, DC 2.2 A/2.2 A and 0.1 A, respectively. The spectra were deconvoluted into two Gaussian peaks and a quadratic background. The fitted background curves are omitted for clarity. For each sample, a relatively sharp peak at approximately 1545/cm is accompanied by a broader peak at approximately 1370/cm, corresponding to the graphite in-plane Raman-active mode (G-band) and the disorder mode (D-band), respectively [11]. Shown also in each graph is the peak area-based D-band to G-band intensity ratio, I_D/I_G. Coatings deposited in a mixed H₂ and Ar atmosphere with H₂:Ar gas flow ratio in the range of 0.1–0.5 showed an I_D/I_G<2. A minimum value of I_D/I_G of approximately 0.5 was observed at the gas flow ratio H₂/Ar~0.3 (Fig. 1a), at which both the G-band and the D-band shifted to the lowest wave numbers (~1277/cm for D-band and 1494/cm for G-band), corresponding to the highest sp³/sp² ratio in bonding structure [6,11–13]. Coatings deposited at pure argon showed very different spectra (Fig. 1c). The I_D/I_G deposited under this condition was normally in the range of 5–9 and both the G-band (at ~1548/cm) and the
D-band (at $\sim 1380/\text{cm}$) appeared at relatively much higher positions, suggesting that the coating structure is significantly different from that deposited at a mixed gases of $\text{H}_2$ and $\text{Ar}$. In addition, unlike the $\text{H}–\text{C}$ coatings which were electrically insulating, this pure $\text{Ar}$ sputtered Cr–C coating was characterized by a high conductivity, which appeared to be graphite-like with $\text{sp}^2$ bond structure [7,8].

It is interesting to study the carbon composite deposition by sputtering graphite targets using gas mixtures of $\text{C}_6\text{H}_{10}$ and $\text{Ar}$. The gas flow ratio between $\text{C}_6\text{H}_{10}$ and $\text{Ar}$ used in this work was from 0.1 to 0.5. Fig. 1b showed a typical Raman spectrum of the coatings deposited at a gas flow ratio of 0.4, which is featured between curves (a) and (c). The $I_D/I_G$ ratio of this PVD/CVD-hybrid processed coating is in the range of 1.5–3.5, depending on the flow rate of $\text{C}_6\text{H}_{10}$ gas and the substrate bias used during the deposition. The coating showed similar mechanical and tribological properties to the pure $\text{Ar}$ deposited carbon composite coatings, as presented in the next sections, but with a much higher deposition rate due to the contributions from the gaseous $\text{C}_6\text{H}_{10}$ deposition. It is also interesting to mention that the coating is much blacker in colour compared with the other two coatings, which is desired in many applications such as IC chip pick-up nozzles for electronics packaging and for decoration.

3.2. Hardness and adhesion

The hardness and adhesion of all the three types of Cr–carbon composite coatings studied was strongly dependent on the substrate bias. As shown in Fig. 2, higher substrate bias in the range of 60–100 V significantly increased the hardness for all the three coatings. Further increasing bias to 120 V resulted in a slight decrease in hardness for both samples deposited in $\text{H}_2$/Ar gas and pure argon while the coating deposited in $\text{C}_6\text{H}_{10}$/Ar gas still showed noticeable increase in hardness. At a given bias voltage (60–120 V), the $\text{H}_2$ associated sample showed the highest hardness ($\sim 23$ GPa at 110 V), while the pure $\text{Ar}$ deposited coating was harder than $\text{C}_6\text{H}_{10}$ associated sample at lower bias ($<100$ V) but was exceeded by the latter at higher substrate bias ($>100$ V). It is believed that $\text{H}_2$ introduced in the $\text{H}–\text{C}$ deposition process effectively enhanced the $\text{sp}^3/\text{sp}^2$ ratio in the coating, resulting in a higher hardness. The pure $\text{Ar}$ sputter deposited coating has a graphite-like structure (low friction), but the hardness is comparable to that of ceramic coatings such as TiN and CrN, resulting in excellent wear resistance.

The adhesion of the coating to substrate played a decisive role in high-load wear performance. The thin chromium bond layer followed by a Cr–C graded process is essential to achieve good adhesion for all three types of carbon coatings. Fig. 3 shows the substrate bias dependence of adhesion, measured by the critical load in scratch test, at which the coatings were removed from the substrate surface. A trend roughly opposite to that of the coating hardness was observed. With increase of the substrate bias, the critical loads of all the three coatings moved downwards monotonously, with a quick drop observed above 100 V. The coating deposited in pure Ar atmosphere showed the best adhesion, which is
significantly higher than that of the coating deposited in H$_2$/Ar mixed atmosphere over the whole range of substrate bias investigated. In fact, for samples deposited at and below a substrate bias of 75 V, no scratch failure was observed even at the end point of the scratch track, as shown in Fig. 4. We simply used the end point load (128 N) to represent the coating adhesion in this case, which explains the straight line at the left side of curve (c) in Fig. 3. This apparently high adhesion may also result from the high toughness of the coating, which resulted in an exceptionally high load-bearing capacity (next section). The coating deposited with C$_4$H$_{10}$ introduction also showed high adhesion (Fig. 3b). However, it appears that C$_4$H$_{10}$ introduction has a negative effect on coating adhesion, possibly due to H–C inclusion resulting from the decomposition of C$_4$H$_{10}$.

3.3. Wear performance

Fig. 5 shows a comparison of the normalized wear rates and friction coefficients of the three types of coatings for tests at 10, 25 and 95 N. The tests with 10 N load were performed at a linear speed of 20 cm/s for a total sliding distance of 4000 m, while the other tests were performed at a constant rotation speed of 200 rpm for a total wear duration of 1 h. For the test at 10 N load, the coating (a) deposited with H$_2$ had the lowest wear rate of approximately 1×10$^{-8}$ mm$^3$/Nm, attributing to its high hardness (~21 GPa), although the friction coefficient (~0.09) was the highest among the three coatings. With a lower friction coefficient (0.07–0.08) and also a lower hardness (17 GPa), the coating (c) had a wear rate of 1.8×10$^{-8}$ mm$^3$/Nm. The coating (b) deposited with butane atmosphere had a wear rate of 3×10$^{-8}$ mm$^3$/Nm, due to its higher friction coefficient. When the wear load was increased to 25 N, the wear rate of coating (a) increased to approximately 6×10$^{-8}$ mm$^3$/Nm, although the friction coefficient was reduced to 0.07–0.08, and very often, the coating failed halfway through the test due to chipping or spalling of the coating from the substrate, indicating that the test was running at the maximum load that the sample could bear (related to its residual stress level). For coating (c), the friction coefficient was further reduced to 0.05–0.06, and the wear rate was slightly increased to approximately 3×10$^{-8}$ mm$^3$/Nm. At the load of 95 N, an immediate coating failure was always observed for coating (a), with chipping debris scattered around the wear track. In contrast, the coating (c) and also (b) demonstrated only a slight increase of the wear rate to approximately 4–5×10$^{-8}$ mm$^3$/Nm under this extremely high load (equivalent to a contact pressure of ~2 GPa). The slight increase of the friction coefficient under this load is believed to result from possible deformation of the substrate, which increases the contact area and sliding friction force. This exceptional load-bearing capacity and wear resistance must be attributed
to its good adhesion, high toughness, very low friction coefficient and reasonably high hardness. It appears that for low load applications, high hardness is critical in achieving low wear rates (refer to the coating (a) in Fig. 5), while for high load applications such as bearings, gears and cutting tools, good adhesion and high toughness play a more important role in coating life and wear performance.

4. Conclusions

Three types of chromium–carbon composite coatings were deposited by unbalanced magnetron sputtering. The mechanical and tribological properties are strongly dependent on the power applied to the substrate and the targets. For substrate bias, a pulsed DC power was found to be more effective and convenient for controlling the coating quality. The results show that:

(1) The coating deposited in H$_2$/Ar atmosphere has a typical sp$^3$/sp$^2$ bonding structure. At a H$_2$/Ar flow ratio of 0.3, the coating shows the lowest $I_D/I_G$ ratio (0.5) in Raman spectra and highest hardness, corresponding to a lowest pin-on-disc wear rate ($1 \times 10^{-8}$ mm$^3$/Nm) at wear loads less than 10 N. At higher loads (25 N and above), chipping or spalling were observed resulting in coating failure.

(2) The coating deposited in pure Ar atmosphere has a graphite-like (sp$^2$ bond) structure and high electrical conductivity. The coating has exceptional high load-bearing capacity and excellent wear resistance, which is attributed to its excellent adhesion, high toughness and low friction coefficient. Pin-on-disc wear rates against alumina were measured to be in the order of $10^{-8}$ mm$^3$/Nm for wear loads up to 95 N.

(3) The coating deposited in butane/Ar atmosphere has controllable properties with higher deposition rate, blacker colour and excellent high-load wear performance.

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References