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Prime Novelty Statement:
We report on the development of multilayer nanocomposite coatings consisting of Ti(N,C) nanocrystals embedded in amorphous C:H matrix. The carbon content in the films has been regulated to form the multilayered structure. The a-C:H content is kept between 30 to 50 at % in order to obtain the desired nanocomposite structure. Such films show great potential in high pressure applications (i.e. diesel injector nozzles) and can be deposited on steel substrates suitable for such applications without the need for a load bearing ceramic interlayer. This is the first time that high pressure contact stress tribological tests are performed to demonstrate the capabilities of such nanocomposite films.

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The submission of the manuscript has been approved by all co-authors.

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Mechanical and high pressure tribological properties of nanocrystalline Ti(N,C) and amorphous C:H nanocomposite coatings.

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ABSTRACT

This paper reports on the mechanical and high pressure tribological properties of nanocrystalline (nc-) Ti(N,C)/ amorphous (a-) C:H deposited, using low temperature (~200°C) DC reactive magnetron sputtering. The mechanical properties are affected by the nc-Ti(N,C)/a-C:H phase fraction ratio. The nanoindentation hardness (H) values were measured and found to range from 9 to 15 GPa and the reduced Young’s modulus values (E) from 80 to 150 GPa. The synthesized coatings survived up to 100 m sliding distance when tested using pin-on-disc sliding configuration and the measured friction coefficient values were around 0.25 and. A strong correlation between H/E ratio and wear performance was exhibited by the coatings.

Keywords: nanocomposite, wear, tribology, DLC

1. Introduction:

Hard, low-friction carbon-based nanocomposite coatings are widely used in highly-stressed component applications such as diesel fuel injection systems where contact pressures can reach up to 200 MPa, to avoid premature system failure [1]. For this reason such coatings are often deposited as a constituent layer of a multilayer system that contains a hard, tough load support layer (i.e. chromium nitride) and an outer low friction amorphous hydrogenated a-C:H layer [2-6]. These coatings however show limitations of their capability and failures can occur due to crack initiation [7] or loss of hardness [8]
due to adhesive and cohesive failure at high contact loads. Despite the increasing interest in nanocomposite and functionally graded low-friction carbon-based tribological coatings, based on nanocrystalline carbides in a a-C:H matrix to achieve optimal properties still remains a challenge. Furthermore, the transfer of pioneering laboratory work to larger dimensions/throughput is technologically and economically challenging [9]. In this paper we report on the mechanical properties and high contact pressure tribological testing of nanocomposite nc-Ti(N,C)/a-C:H multilayer coatings with varying amount of a-C:H phase, deposited using an industrial deposition chamber. The nanocomposite is grown on top of a Ti/Ti-N transition layer that acts as improved bonding and diffusion barrier [10]. Such nanocomposite structures can offer low friction against steel counterparts (diesel nozzles, Cr-Mo implant alloys) and could negate the need for a hard ceramic load support layer. Nanocomposites with an a-C:H content between 30 to 50 at % a were specifically targeted in order to form a nanocomposite structure containing small (5-10 nm) nanocrystallites surrounded by 1 monolayer of a-C:H, to enhance the mechanical properties [11]. A process temperature of below 250 °C was selected to avoid tempering of the heat treated 100Cr6 substrate.

2. Experimental:

nc-Ti(N,C)/a-C:H coatings were deposited using pulsed DC magnetron sputtering onto 100Cr6 steel substrates and Si wafers at ~ 200 °C. Details of the deposition method can be found in [12]. X-ray photoelectron spectroscopy was undertaken using a VG-Thermo Sigma Probe spectrometer, GAXRD on an in-house built parallel beam system and TEM
on a Philips CM 20 operating at 200 kV [12]. Hardness (H) and reduced elastic modulus ($E_r$) values were determined using a Hysitron TriboScope, equipped with a Berkovich indenter. Loads were varied between 3, 6 and 10 mN with a sequence up to 15 indentations taken at each load. H and $E_r$ were measured using the procedure proposed by Oliver and Pharr [13]. The Berkovich indenter area functions used for calculation of H and $E_r$ were derived by fitting nanoindentation data on a fused quartz sample to a standard equation [14]. Ball-on-disc dry sliding experiments were conducted at room temperature (22 °C) and a controlled humidity of 20% using a Standard Tribometer [15]. The sliding velocity was 0.056 m/s at a track radius of 7 mm. For better control of the experimental conditions, namely (a) to maintain a constant contact pressure throughout the whole duration of the experiment, and (b) to only wear the coating, very hard ruby sapphire spheres of 1.5875 mm in diameter were used. Scanning electron microscopy (SEM) of the wear scar morphology was performed.

3 Results:

Table 1 displays the stoichiometry and relative phase fraction of the deposited coatings determined by XPS. The nanostructure of the coatings has been fully evaluated in our previous paper [12], but pertinent XPS, TEM and XRD results, showing evidence of this nanostructure are also presented here in Figure 1. To summarise, it was found from XPS and XRD that all the coatings are comprised of two phases Ti(N,C) and a-C:H. Peaks corresponding to f.c.c. TiN can be seen for all coatings in Figure 1a. and the C 1s peak in Figure 1b shows peaks corresponding to the formation of both Ti(N,C) and a-C:H phases.
The a-C:H content was determined by XPS [12] and was found to increase with acetylene flow rate from 31 at % to 42 at % and 47 at %, for coatings A, B and C respectively. Figure 1c shows a representative TEM cross section image for coating A where various layers of the coating can be identified. The diffraction patterns for each of these layers are also given in Figure 1c and demonstrate the gradual reduction in nanocrystalline size towards the surface. The coating consists of a Ti (~100 nm thick) interlayer a Ti-N transition layer (~100 nm thick), a nc-Ti(N,C)/a-C:H (~2 μm thick) layer and finally a top layer with a very small crystallite size and higher carbon content nc-Ti(N,C)/a-C:H (~ 400 nm thick). TEM and XRD indicates that the average crystallite size for the top layer of coatings A, B and C to be 4 nm, 2 nm and < 2 nm respectively (XRD spectrum for coating C shows only the interlayer pattern to be resolvable, the top layer is x-ray amorphous). The crystallite size of the main Ti(N,C)/a-C:H layer is found for all coatings to be ~ 5 to 7 nm (see dark field TEM images for coating A in Figure 1d). The overall coating thickness reduces with acetylene flow rate and consequent target poisoning from 2.7 μm to 2.5 μm and 2.2 μm for coatings A, B and C respectively. Figure 2 shows the average nanoindentation hardness and reduced young modulus data for the coatings plotted for against a-C:H content. It is noted that as the a-C:H content increases there is a reduction both in H and E_r. Coatings A and B demonstrate the highest H and E_r values of the group from ~13.9 GPa and ~140 GPa, to ~9GPa and 94 GPa, respectively. For higher a-C:H contents above 45 at % there is a further decrease in the measured hardness and E_r of ~5 GPa and ~59 GPa, respectively. Figure 3 displays the friction coefficient graph for coatings A, B and C. The average friction coefficient increases with a-C:H content from 0.21 to 0.25 and 0.35 for coatings A (31 at % a-C:H), B (42 at % a-C:H)
and C (47 at % a-C:H), respectively. The maximum Hertzian contact pressure for all films is about 4.5 GPa, which is significantly higher than typical operating conditions, to evaluate the films under aggressive to extreme contact conditions. Coatings A and B with 31 and 42 at % a-C:H, respectively, survived the duration of the test, coating C (47 at % a-C:H) was perforated after 23 minutes of testing (~63 m sliding distance). Figure 4a and 4b display the wear scar cross section morphology measured by profilometry along with the wear scar overview and morphologies at increased magnifications for coatings A and B, respectively. The wear depth increases with a-C:H content from ~0.89 μm for coating A (31 at. % a-C:H) to 1.09 μm for coating B (42 at. % a-C:H) to full coating perforation for coating C (47 at % a-C:H). Angular cracks perpendicular to the direction of sliding appear at the wear scar extremities (Figure 4a and 4b). The crack opening and periodicity increases with increasing a-C:H content.

4. Discussion:

4.1. Mechanical Properties

The increased carbon contents in the top layer of the film as well as smaller and rounder Ti(N,C) crystallite geometries occurs due to progressive Ti target poisoning by the acetylene gas during film deposition [16]. Based upon the relationship given by Baker [17], the amount of a-C:H present ~31 at. % and ~42 at. % for coatings A and B, respectively, is sufficient for ~1.5 to 2 monolayer coverage (estimates made using 4 nm Ti(N,C) nanocrystallites for coating A and 2 nm for coating B). Smaller crystalline grains
can lead to an increase in grain boundary sliding, since the proportion of atoms occupying intergranular sites become significantly large thus grains can rotate freely within the amorphous matrix during deformation under loading and a relaxation in measured hardness (and reduced modulus) occurs [18]. The lower fraction of the hard nanocrystalline Ti(N,C) phase for similar a-C:H monolayer coverage also contributes to a reduction in hardness - coating B contains 42 at % a-C:H compared to 31 at % a-C:H for coating A. Coating C which has ~ 47 at % a-C:H shows the formation of a Ti(N,C) phase in XPS [12] however the coating is x-ray amorphous suggesting that the Ti(N,C) phase is highly disordered thus it's hardening effect is substantially diminished causing a significant drop in hardness.

### 4.2. Tribological properties

Coatings A (31 at % a-C:H) and coatings B (42 at. % a-C:H) survived the duration of the test with up to 50% overall coating depth penetration (Figure 4a and 4b). SEM analysis shows the formation of angular cracks perpendicular to the direction of sliding (Figure 4), similar to cracks forming in scratch tests [19]. Such cracks result from high compressive stresses building up directly under the contact region and high tensile stresses developing outside the contact zone under load, leading to elastic/plastic deformation of the nc-Ti(N,C)/a-C:H layer and the substrate [20]. As the a-C:H content increases the elastic modulus is reduced, leading to an increase in the compressive stresses and a drop in the coating resistance to counterface ploughing [21], so the friction force increases. Furthermore, on a microstructural level, the following mechanism is probably operating:
the increasing total C content of the coating leads to the crystallite size of the 'hard' Ti-based phase to progressively decrease and tend to an amorphous state. As the crystalline structure of the Ti(N,C) phase starts to break down, more C becomes incorporated into this Ti(N,C) phase and it becomes over-stoichiometric (this behaviour has also previously been observed for nc-Ti(B,C)\textsubscript{2}/a-C:H coatings [22]). The underlying support for the graphitic tribo-layer at the surface given by the ‘defective’ Ti(N,C) phase is thus reduced and the poor mechanical properties of this phase enable it to be more easily broken up and incorporated into the graphitic phase under load. Both of these effects will increase the shear force required to facilitate sp\textsuperscript{2} graphitic plane sliding in the tribo-layer and hence an increase in the friction coefficient and failure of coating C (46 at. % a-C:H). When considering the relationship of wear performance to the H/E ratio of the coatings [23], it is coatings A and B coatings with highest H/E ratio, 0.089 and 0.09 respectively, that demonstrate the best tribological performance.

4. Conclusions:

The mechanical properties such as hardness and the friction coefficient of these reactively magnetron sputtered Ti(N,C)/a-C:H coatings decrease with increasing a-C:H phase content. The hardness progressively drops from 13.9 GPa to 9 GPa and 5 GPa for 31, 42 and 46 at % a-C:H, respectively. The lowest average friction coefficient (~0.21) is measured for coating A with the lowest a-C:H content (31 at % a-C:H) and larger Ti (N,C) nanocrystalline size (~ 4 nm). Coatings A and B survive high contact pressure (> 4.5 GPa) tribological testing for 100m sliding distance against a spherical ruby
counterpart. The high tensile stress build up leads to angular cracking of the coatings during testing. A strong correlation with H/E and wear performance is noted for the coatings.

Acknowledgments:

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References


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Table 1. Relative phase fractions and stoichiometry of the coatings determined by XPS

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Figure 1. a) XRD pattern of coatings A, B and C; b) XPS C1s spectrum of coating A; c) TEM micrograph of coating A with resolvable constituent layers (insert at bottom diffraction patterns demonstrating reduction in crystalline size near coating surface); d) Cross-sectional dark field TEM image of coating A showing a very small crystallite size near the surface and a larger crystallite size in the bulk of the film Figure 2. Nanoindentation hardness and reduced modulus data plotted against a-C:H content

Figure 3. Friction coefficient graphs for coatings A, B and C during tribological testing.

Figure 4. a) Wear scar profile and morphologies. Insert top: displays development of angular cracking perpendicular to the sliding direction. b) Same for coating B
<table>
<thead>
<tr>
<th>Coatings No.</th>
<th>Stoichiometry</th>
<th>Ti(N,C) (mol.%)</th>
<th>a-C:H (at.%)</th>
<th>Ti(N,C)\textsubscript{x} phase stoichiometry</th>
<th>Ti(N,C) phase stoichiometry</th>
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<tr>
<td>A</td>
<td>TiC\textsubscript{1.34}N\textsubscript{0.51}</td>
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<td>52.7</td>
<td>47.3</td>
<td>Ti(N,C)\textsubscript{1.07}</td>
<td>Ti(N\textsubscript{0.48}C\textsubscript{0.59})</td>
</tr>
</tbody>
</table>
3. Figure(s)

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