Super-low friction behavior of nanostructured DLC composite coatings

Y. T. Pei, D. Galvan & J. Th. M. De Hosson
Department of Applied Physics, Materials Science Center and
The Netherlands Institute for Metals Research, University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract

Advanced TiC/a-C:H nanocomposite coatings have been produced via reactive deposition in a closed-field unbalanced magnetron sputtering system (Hauzer HTC-1000). This work concentrates on a detailed mechanical and tribological characterization of the TiC/a-C:H nanocomposite coatings, in particular focusing on the dynamic friction and solid lubrication effects of the coatings in terms of third-body processes between the sliding contact surfaces. The tribological behavior of the nanocomposite coatings has been scrutinized by means of ball-on-disc tribo-tests, in conjunction with detailed examinations of the mechanical properties. In-situ monitoring of the wear depth with the resolution of submicrometer clearly reveals the correlation between the dynamic friction and the formation of transfer films on the ball surface. The influence of the volume fraction and grain size of TiC nanocrystallites on the coating properties has been examined. The coefficient of friction of dry sliding against 100Cr6 steel ball and the wear rate of the coatings reach as low as 0.013 and $10^{-18}$ m³/(N m lap), respectively.

Keywords: DLC composite coatings, nanostructure, super-low friction, solid lubrication, wear resistance.

1 Introduction

The surface of a component is usually the most important engineering factor. It is often the surface of a work-piece that is subjected to wear and corrosion while it is in use. Since Leonardo da Vinci (1452-1519) studied an incredible manifold of tribological subtopics such as friction, wear, bearing materials and lubrication...
systems, surface and coatings technologies have become an important branch of modern surface sciences and engineering. Due to the complexity that wear processes combine individual physical events between sliding/rolling surfaces, however, it is still a challenge to understand the friction/wear mechanism even on a micrometer scale. Nevertheless, the economic aspects of friction and wear drive an increasing research effort in the development of coatings that might exhibit both super-low friction and wear rate for applications against sliding and rolling wear. In this paper, we report on the tribological behavior of advanced TiC/a-C:H nanocomposite coatings in which ultra-low friction is tailored with superior wear resistance, being two properties often difficult to achieve simultaneously. A physical model has been established to understand the self-lubrication effects of the thickness of the transfer film formed on the counterpart during wear and the optimal size of wear debris creating the transfer film. The influence of the volume fraction and grain size of TiC nanocrystallites on the coating properties has been examined.

2 Experimental

Hydrogenated TiC/a-C:H coatings were deposited with closed-field unbalanced magnetron sputtering in an argon/acetylene atmosphere in a Hauzer HTC-1000 coating system, which was configured of two Cr targets and two Ti targets opposite to each other. The Cr targets were used to create an intermediate layer between the TiC/a-C:H coating and the substrate material. To obtain different C/Ti contents and nanostructures in the coatings the flow rate of acetylene and substrate bias varied in the range of 80-125 sccm and 0-150 V, respectively. The substrates for all the coatings were Ø100 mm Si wafers of 0.5 mm thickness. The residual stresses ($\sigma_R$) developed in the coatings were examined according to Stoney’s equation, by monitoring the curvature change of the Si-wafers after deposition.

An MTS Nano Indenter XP was employed to measure the hardness and Young’s modulus of the coatings with a Berkovich indenter. Tribo-tests were performed on a CSM high-temperature tribometer with a ball-on-disc sliding configuration (Ø6mm 100Cr6 bearing steel ball or otherwise specified as the counterpart). The samples for tribo-tests were cut out from the center of a coated wafer and glued on a Ø30 mm M2 steel disc with wax. The wear rate of the coatings has been carefully quantified with a well-calibrated confocal microscope and the wear rate of the counterpart ball is measured according to the diameter of the wear scar.

The surface morphology and fractured cross sections of the coatings were examined using a scanning electron microscope, SEM (Philips FEG-XL30s). The investigation of the nanostructures was carried out in a high-resolution transmission electron microscope (HRTEM) (JEOL 4000 EX/II, operated at 400 kV) and an analytical TEM (JEOL 2010F-FEG, operated at 200 kV). Electron probe microanalysis (EPMA) with a Cameca SX-50 equipment was used to determine the chemical composition of the coatings.
3 Results

Two deposition parameters have been investigated in detail, namely the substrate bias and the flow rate of acetylene gas. Table 1 lists the chemical composition and the mechanical properties of the TiC/a-C:H nanocomposite coatings against the deposition parameters. The coatings are named in such a way that the numbers before the character V indicate the substrate bias in voltage, followed by the flow rate of acetylene in standard cubic centimeters per minute (sccm). An increase in substrate bias leads to a significant increase in both the hardness ($H$) and elastic modulus ($E$) of the nanocomposite coatings. However, the $H/E$ ratio stays almost constant when the substrate bias is equal to 60 V and above. On the other hand, a higher flow rate of acetylene gas i.e. a higher C-content results in markedly higher $H/E$ ratios, which is analogous to the results obtained in the nc-TiC/a-C nanocomposite coatings [1]. Although for a long time hardness has been regarded as a primary material property affecting wear resistance, the ratios of $H/E$ (elastic strain to failure) and $H^3/E^2$ (resistance to plastic deformation) are more suitable parameters for predicting wear resistance [2]. Within a linear-elastic approach, this is understandable according to the relations that the yield stress of contact is proportional to $H^3/E^2$ and the equation $G_c = \pi a \sigma_c^2 / E$, indicating that the fracture toughness of coatings defined by so-called “critical strain energy release rate” $G_c$ would be improved by both a low Young’s modulus and a high critical stress ($\sigma_c$) for fracture which implies a need for high hardness.

Table 1: Deposition parameters, chemical composition and mechanical properties of TiC/a-C:H nanocomposite coatings.

<table>
<thead>
<tr>
<th>Coating No.</th>
<th>Bias (-V)</th>
<th>C$_2$H$_2$ (sccm)</th>
<th>Composition (at.%)</th>
<th>V$_{TiC}$ (%)</th>
<th>$\sigma_R$ (MPa)</th>
<th>$H$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>$H/E$</th>
<th>$H^3/E^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0V110</td>
<td>floating</td>
<td>110</td>
<td>71.34 13.64 15.02</td>
<td>27.7</td>
<td>-649</td>
<td>5.5</td>
<td>61.3</td>
<td>0.091</td>
<td>0.044</td>
</tr>
<tr>
<td>60V110</td>
<td>60</td>
<td>110</td>
<td>80.21 16.33 3.46</td>
<td>29.5</td>
<td>-352</td>
<td>11.8</td>
<td>99.8</td>
<td>0.118</td>
<td>0.165</td>
</tr>
<tr>
<td>100V110</td>
<td>100</td>
<td>110</td>
<td>81.02 17.84 1.14</td>
<td>31.7</td>
<td>-761</td>
<td>15.6</td>
<td>136.6</td>
<td>0.114</td>
<td>0.203</td>
</tr>
<tr>
<td>150V110</td>
<td>150</td>
<td>110</td>
<td>80.30 18.51 1.19</td>
<td>33.1</td>
<td>-1595</td>
<td>19.8</td>
<td>168.3</td>
<td>0.118</td>
<td>0.274</td>
</tr>
<tr>
<td>100V80</td>
<td>100</td>
<td>80</td>
<td>66.60 31.75 1.65</td>
<td>60.1</td>
<td>-1184</td>
<td>20.0</td>
<td>229.4</td>
<td>0.087</td>
<td>0.152</td>
</tr>
<tr>
<td>100V125</td>
<td>100</td>
<td>125</td>
<td>87.19 11.85 0.96</td>
<td>19.7</td>
<td>-1154</td>
<td>15.8</td>
<td>128.5</td>
<td>0.123</td>
<td>0.239</td>
</tr>
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</table>

SEM micrographs of the fractured cross sections presented in Fig. 1 demonstrate the microstructural evolution of the coatings, that is to say, a transition from columnar to glassy microstructure with increase in substrate bias or/and the flow rate of acetylene gas. The coating 100V110 represents the transition point where the columnar boundaries are discontinuous and disappear partly. From thereon, with a further increase in substrate bias or/and carbon content, the nanocomposite coatings such as 150V110 and 100V125 are free of columns and appear fully glassy on the fractured cross sections. The columnar boundaries (CBs) are rich in carbon and detrimental as being the origin of micro-crack initiation and propagation channel under loading contact [3,4]. High-resolution transmission electron microscopy (HR-TEM) reveals that
nanocrystalline TiC particles are homogeneously embedded in and well separated by a-C:H matrix, with particle size and separation width of 4.5nm/0.3nm, 2.2nm/0.7nm and 2.2nm/1.3nm in the coating 100V80, 100V110 and 100V125, respectively [3,4].

![Figure 1](image1.png)

Figure 1: SEM micrographs showing the fractured cross-sections of TiC/a-C:H nanocomposite coatings deposited under different parameters indicated.

![Figure 2](image2.png)

Figure 2: (a) Friction vs laps graphs and (b) steady-state CoF and wear rate ($W_R$) in dimension of $\times 10^{-15}$ m³/(N m lap) of TiC/a-C:H nanocomposite coatings under the same sliding wear conditions indicated.

Ball-on-disc tribo-tests have been systematically performed on the TiC/a-C:H nanocomposite coatings with ø6 mm balls under 5N normal load. The representative graphs of friction coefficient versus running laps are shown in Fig. 2a, where three different kinds of friction behavior of the nanocomposite coatings are recognized. Coating 0V110 exhibits a nearly constant coefficient of friction (CoF) and the coating 100V80 shows rather large fluctuations in the friction coefficient curve. The mean CoF of the coatings 0V110 and 100V80 is above 0.2, i.e. much higher than that of the rest three coatings. All the three coatings show not only a low steady-state CoF (0.047-0.069), but also a quick drop of the CoF from an initially high value of about 0.2 at the beginning of
sliding until the transition point where the steady state is reached. Such a behavior is attributed to the gradual formation of a transfer film on the counterpart surface during the early stage of a tribo-test, which makes the contact in between two basically similar hydrophobic a-C:H surfaces that contribute to self-lubrication.

Figure 3: (a) Dynamic frictional behavior of coating 100V110 sliding in air of 25% relative humidity and (b) wear scar of 100Cr6 steel ball (an arrow indicating the sliding direction of the coating in contact).

To prove that the self-lubrication is induced by the formation of transfer films, the wear depth was in-situ monitored with a resolution of 0.02µm by a RVDT sensor during the tribo-tests. As marked by the arrows in Fig. 3a, segments with a negative slope were observed in the depth vs laps graph and indicated a significant growth of the transfer film on the ball surface, rather than a real reduction in the depth of the wear track on the coatings. Correspondently, substantial decreases in the CoF were detected. The maximum growth amplitude in the thickness of the transfer films was measured about 100 nm and the minimum at the level of 20 nm, which is the limit of the sensor. Once the transfer film stopped growing, the CoF could not decrease further and it started to fluctuate. Because the transfer film covered the ball surface in contact, the wear rate of the coating diminished and led to less debris. As a result, the transfer film became thinner with sliding until it fully spalls off, leading to a sudden rise in the CoF. Sliding at higher a CoF would generate more debris from the wear track, which in turn provided the necessary materials for the growth of new transfer film. Thereafter, a new cycle of the dynamic friction process is repeated cyclically. Figure 3b shows the wear scar of the 100Cr6 ball covered with transfer films and also the wear debris collected in front of and beside the wear scar. One can imagine that all the factors influencing the ejection and pickup of the debris onto the ball surface will affect the dynamic friction behavior of the coatings, such as the humidity and sliding velocity. Change in relative humidity from humid air ($H_r=75\%$) to fully dry air results in a continuous decrease in the CoF from 0.092 to 0.018, as seen in Fig.4a. In addition, the steady state of friction can be reached in a shorter sliding distance at lower humidity. In another word, transfer films can be built up much quicker at lower humidity, for
instance, the transition points are at 2250, 890 and 380 laps when $H_R = 75\%$, $50\%$ and $0\%$, respectively. It is understood that the debris in hydrophobic nature can more easily adhere onto the hydrophilic steel surface if water molecules are absent or less intensively adsorbed.

It is clear that the gradual formation of transfer films on the surface of counterpart balls changes the nature of sliding contact and leads to a significant drop in the CoF at the beginning of sliding. It is natural to expect that a coated counterpart will exhibit the characteristic low friction from the beginning of sliding. This is just the case shown in Fig. 4b where super-low friction is reached directly when the coated counterpart comes into contact with the same coating on Si-wafer. There is no need for transfer films and, actually, any debris ejected between the contacting surfaces of hard coatings will cause abrasive wear that increases the CoF during the course.

The wear rates ($W_R$) of all the coatings are summarized in Fig. 2b. According to the findings of the mechanical properties (Table 1) it is clear that the wear rate of the nanocomposite coatings significantly decreases with increasing the hardness and especially the H/E ratio. The humidity dramatically affects the wear properties of the coatings with self-lubrication, including both the friction coefficient and the wear rate. The lowest wear rate of $1.31 \times 10^{-17}$ m³/(N m lap) is achieved on the coating 100V125 in the high humidity. Interestingly, the wear rate at high humidity is only one third as low as the one measured in the ambient air. Such an unusual combination of superior wear resistance with a little expense of friction at high humidity has also been observed on the coatings 100V110 and 150V110. SEM observations on the wear tracks reveal that micro-cracks initiate at and readily propagate through the columnar boundaries in the coatings 0V110, 60V110 and 100V80 under sliding ball contact, as shown in Fig. 5a. No cracks are observed in the wear tracks on the coatings 100V110, 150V110 and 100V125 where columnar structures are restrained. As demonstrated in Fig. 5b, the surface of the wear tracks is featureless and rather smooth along the sliding direction.

Figure 4: (a) Influence of the relative humidity on the CoF of the coating 100V125 against uncoated 100Cr6 bearing steel ball; (b) super-low friction reached directly at the beginning of sliding under self-mating between coating 130V115 and coated 100Cr6 balls.
Figure 5: SEM micrographs of wear tracks: (a) micro-cracks formed along the columnar boundaries in the coating 100V80 and (b) smooth and featureless wear track on the coating 150V110 under the same wear conditions (5N load, 10cm/s sliding velocity, T=20°C, 50% relative humidity and against ø6mm 100Cr6 ball). An arrow indicates the moving direction of the counterparts.

4 Discussion

The self lubrication effects exhibited by the nanocomposite coatings, leading to a CoF as low as 0.05 in ambient air and below 0.02 in dry air under dry sliding conditions against uncoated 100Cr6 steel balls, are attributed to the tribological characteristics of the a-C:H matrix and may be affected by the volumetric fraction, size and distribution of TiC nanocrystallites contained. It is clear from the data presented in Fig. 2a that the steady-state CoF in ambient air decreases with increasing C content of the coatings until an appropriate width of the a-C:H matrix separation among the TiC nanograins is reached, for instance, in the case of coating 100V110. A further increase in the width of the a-C:H in the coating 100V125 does not contribute to further improvement on the reduction of friction, since the a-C:H matrix is already wide enough to shield the TiC nanoparticles and to dominate the interfacial shear strength between the coating surface and the transfer films formed on the surface of counterpart ball. If the a-C(:H) matrix cannot efficiently shield TiC particles in the transfer films as in the cases of coating 100V80 with a high volumetric fraction of (rather big) TiC nanocrystallites, TiC nanoparticles may cause considerable damage to the hydrophobic contact surfaces or to the transfer films formed. This may explain the large fluctuations in the friction graph of 100V80 as shown in Fig. 2a. On the other hand, the substrate bias has only a limited influence on the CoF of the nanocomposite coatings, except the coating 0V110 on which a high CoF value of about 0.3 was recorded in ambient air. It is most likely related to the high content of oxygen in the coating 0V110, which may form oxygen terminated DLC surfaces that lead to high friction or a small contact angle with water [5, 6]. In other words, the origin of the self lubricating phenomena observed on the TiC/a-C:H nanocomposite coatings lies on the amount and tribochemical property of the a-C:H matrix.
Basically, a-C:H is an amorphous network composed of carbon and hydrogen. This network consists of strongly cross-linked carbon atoms with mainly sp² (graphite-like) and sp³ (diamond-like) bonds. Hydrogen may either bond to carbon atoms to form H-terminated carbon bonds or stay unbonded in hydrogen reservoirs. In fact, hydrogen acts as a promoter or stabilizer of the sp³-bonded carbon phase [7]. It is generally speculated that the low friction of most carbon films is largely due to the fact that these materials are chemically inert and consequently they exert very little adhesive force during sliding against other materials. The major friction-controlling mechanisms have been suggested as the followings: (a) build-up of a transfer film on the surface of the counterpart, which permits easy shear within the interfacial materials and protects the counterpart against wear [8]. However, the shear strength strongly depends on the tribochemical reaction with the surrounding gases present in the contact; (b) the ability to form graphitic surface layer under most tribological conditions. The wear-induced surface graphitization of DLC films consists of two steps [9, 10]: first hydrogen release causes lattice relaxations and then shear deformation promotes a graphitic structure at the surface; (c) hydrogen passivation of the dangling carbon bonds on the surface permitting only weak interactions between the DLC film and the sliding counterpart [11, 12]. The effects of the transfer films are clearly revealed with the in-situ monitoring of the wear depth (actually the thickness of the transfer films) and the simultaneous recording of the CoF curves during the tribo-tests.

From a physics point of view friction can be regarded as a conversion of translation motion of the solids, with respect to each other, into vibrational energy [13, 14]. It is significant to recall that, for infinite systems, the phonon spectrum consists of a continuum of vibrational modes and phonon damping can be easily realized because, due to anharmonicity, energy can be easily transferred from one mode to the other. As a matter of course, this is not the case in a finite system in which all the modes are discrete and only a certain combination of modes can carry the phonon damping. In principle, it implies that the smaller the system, the smaller is the friction and, in the limit below a critical size, the system becomes frictionless. In the case of nanocomposite coatings we are facing density fluctuations, including both the density fluctuations between nano-crystalline TiC and a-C:H phases and the free volumes in the a-C:H matrix that can be described as a distribution of stress fields having different character. In fact, the phonons are scattered by anharmonicities due to the strain field of these defects and the large volumetric fraction of TiC/a-C:H interfaces. Friction is only possible if the inverse of the phonon lifetimes are larger than the spacing of the vibrational modes. The latter depends on the size and increases with decreasing size. In a harmonic approximation, the spacing is determined by the spring constant \( \alpha \) and the mass \( m \). Friction will occur if \( \tau^{-1}_{ph} \geq N^{-1} \sqrt{\alpha/m} \) where \( N \) represents the number of vibrational units involved. The spring constant of C-H and C-C bonds are about 500 N/m leading to the prediction that for \( N \) smaller than 50 unit cells, i.e. 20-30 nm, the friction becomes negligibly small. It means that generating wear debris of these dimensions in the beginning is the best.
To understand the behavior of the coefficient of friction in the framework of size effects the following analysis is made: For an elastic contact of a ø6 mm steel ball pressed against a coating of 150 GPa elastic modulus, with a load of 5 N, a circular contact area of 100 µm diameter will develop, corresponding to a maximum contact pressure \( p_0 \) of about 950 MPa. As a consequence of the applied load, shear stresses will develop beneath the surface, with a maximum of about 0.3 GPa shear stress 20 µm below the surface, i.e. far below the interface between the thin coating and the substrate. A typical steel substrate is able to withstand this shear stress level. The shear stress gradually decreases going towards the surface, and only low shear strength materials will be able to fail locally, with the development of debris that will ensure a thin transfer layer to form for the reduction of friction. This is the reason why commonly lamellar, low shear strength materials such as graphite and MoS\(_2\) are employed as solid lubricants [15]. A distinction must be made between hydrogenated (a-C:H) and H-free (a-C) amorphous carbons. Under contact their surface undergoes a phase transition with the local formation of aromatic structures (for a-C:H) or graphite (for a-C). These phases are characterized by low shear strengths, which will cause the formation of wear debris. Because of the low shear strength of graphitized a-C (order of 10-100 MPa) wear debris will be formed, the thickness of which is related to the thickness of the graphitized layer under the surface, i.e. of the order of nanometers. It leads to very low friction in agreement with the predictions. In the present case (Figs. 2-4) the material will yield when the contact pressure \( p / \sigma_y = 1 / \mu \), where \( \sigma_y \) and \( \mu \) represent the yield stress and coefficient of friction, respectively. The point of yielding is easily reached because of the low shear strength of graphitized a-C and it expected [16] to lie beneath the contact if \( \mu \leq 0.3 \), which is the case at the onset of the friction in the experiment (see Figs. 2-4).

The last point to be considered regarding CoF arising from the minimum with further increasing C content is the functionality of TiC nanocrystallites during sliding, besides the toughening effects [3]. As described above, surface graphitization of amorphous carbon is mainly induced by shear deformation that is substantially reduced under the condition of low friction as reported here. It is a logical expectation that a large number of well-distributed and exposed TiC nanocrystalline protuberances on the transfer films or on the coated counterpart may boost the surface graphitization, by exerting locally high shear stresses and scratches at nano-scale. Increasing C-content over certain threshold will reduce the density of TiC nanocrystallites and consequently the extent of surface graphitization. This may explain why the coating 100V125 with higher C-content or pure amorphous carbon films exhibit a higher CoF than the nanocomposite coatings such as 100V110 and 100V115.

5 Conclusions

The TiC/a-C:H nanocomposite coatings designed for wear resistance and low friction have been deposited with closed-field unbalanced magnetron sputtering. The undesired columnar microstructure in the coatings can be restrained by
increasing carbon content or substrate bias. A superior wear resistance of the nanocomposite coating has been achieved under the condition of super-low friction and high toughness, both of which require fine TiC nano-particles (e.g. 2 nm) and a wide matrix separation that must be comparable to the dimensions of the nano-particles. Ball-on-disc tribo-tests confirm that the nanocomposite coatings possess strong self-lubrication effects by the formation of transfer films on the contact surface of the counterpart, with a coefficient of friction as low as 0.05 in ambient air and below 0.02 in dry air against uncoated bearing steel balls. Physical arguments are proposed to explain the toughening mechanism and the super-low friction.

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References