TRIBOLOGICAL BEHAVIOUR OF ACD Ni-P/PVD NITRIDE/DLC MULTILAYERED COATINGS

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SUMMARY
Multilayered coatings with an outer DLC layer, a PVD nitride-based inter-layer and an inner ACD Ni-P layer were deposited onto plain carbon steel. The influence of each layer on the tribological behaviour of the multilayer-coated system was evaluated by both dry sliding and abrasion tests, that have been carried out by a slider-on-cylinder tribometer and a microscale abrasion tester respectively. The deposition of the DLC outer layer increases the wear resistance of the multilayers. Furthermore, the performance of plain carbon steel coated with these multilayers is comparable with that of tool steel multilayer-coated samples.

Keywords: DLC, Ni-P, PVD, coating, multilayer

1 INTRODUCTION
The multilayering approach has been suggested as a way to extend the applicability and the endurance of DLC films [1], that are increasingly used in many optical, mechanical, electronic and biomedical applications [2]. The "DLC" term is used in the present work to designate the hydrogenated form of amorphous diamond-like carbon (a:C-H). Hydrogenated DLC films are used in many applications where a low coefficient of friction and a high wear resistance are required [3,4]. The presence of high compressive residual stresses causes increasing levels of interfacial stresses that limit the thickness of a:C-H films to a maximum value of about 2 µm [5]. Therefore, the substrate must adequately support a:C-H films in order to exploit their excellent tribological properties under high loading conditions. The deposition of PVD-TiN or other nitride-based interlayers is known to increase both the load bearing capacity and the adhesion to steel substrates [1]; however, its influence on the overall tribological performance is still controversial [1,6].

In the present study, multilayered coatings with the following sequence of layers (Fig. 1) were deposited onto plain carbon steel: an outer DLC layer, a PVD nitride-based inter-layer and an inner ACD (Auto-Catalytically Deposited) Ni-P layer.

![Figure 1: Sequence of the layers in the Ni-P/PVD nitride-based/DLC multilayers.](image)

The presence of an ACD Ni-P under-layer is expected to further increase the load bearing capacity of soft substrates such as plain carbon steel [7]. The aim of the present work is to evaluate the influence of each layer on the tribological behaviour of the multilayer-coated system; for this purpose, (i) PVD nitride coated tool steel, with and without the DLC outer layer, (ii) PVD nitride coated plain carbon steel, with and without the DLC outer layer, and (iii) ACD Ni-P/PVD nitride coated plain carbon steel were chosen as coated systems for comparison.

The tribological behaviour of the multilayer coated systems under high loading conditions was evaluated by dry sliding tests, whereas microscale abrasion tests were used to assess their abrasive wear resistance.

2 EXPERIMENTAL

2.1 Materials
The first step in the production of the multilayers was the deposition of ACD Ni-P on plain carbon steel (AISI 1040, henceforward named Fe) blocks (5x5x50 mm³). ACD Ni-P layers were deposited from hypophosphite baths at 92°C (pH 4÷5.5).

The second step was the deposition of PVD nitride-based layers by Arc Evaporation (AE) in a PLATIT coating unit; the temperature of the substrate during the deposition ranged from 430 to 450°C. TiN and Ti(C,N) layers were deposited by changing the composition of the atmosphere in the deposition chamber. The tool steel used as a substrate in the reference coated systems described in the introduction is ASP30 (henceforward named HSS).

Fracture sections of coated specimens were observed by scanning electron microscopy (SEM). X-Ray Diffraction (XRD) analyses were performed with a standard Philips powder diffractometer (Cu kα radiation) in order to evaluate the structure of the PVD layers. Composite microhardness was measured by a conventional Vickers indenter with an applied load of 50 g.
The last step was the deposition of hydrogenated amorphous DLC films (a:C-H DLC) in a PACVD reactor from hydrocarbon sources; the deposition process has been fully described elsewhere [8]. The elastic modulus E and the intrinsic hardness H of a:C-H DLC films were measured by an ultra-low depth sensing nanindentor (Berkovich indenter) from the loading-unloading curves [8]. Internal stresses were calculated by measuring the curvature of thin glass plates after the deposition [9]. The surface roughness of the multilayer coated specimens was measured by surface profilometry (tip radius: 5 µm).

2.2 Sliding

Dry sliding friction and wear tests were carried out using a computer-controlled slider-on-cylinder tribometer [10]. The stationary sliders were constituted by the coated systems under investigation, in the form of prismatic blocks (5x5x50 mm³). The counter-face was an AISI M35 steel cylinder coated with the same DLC film that was deposited on top of the multilayers. The tests were carried out under 30 N applied load, with a sliding speed of 0.6 m/s, for a sliding distance of 10000 m, at room temperature (20-25 °C) and in laboratory air (about 60% relative humidity). Both friction resistance and system wear (i.e. wear of the slider plus wear of the substrate) were continuously measured, by means of a bending load cell and a LVDT respectively, and recorded as a function of sliding distance. Separated bending load cell and a LVDT respectively, and recorded as a function of sliding distance. The surface roughness of the multilayer coated specimens was measured by surface profilometry (tip radius: 5 µm). Wear scars and debris were observed by means of OM and SEM.

2.3 Microabrasion

Microscale abrasive wear tests (MSAT) were carried out by a Plint T66 apparatus, which is based on a ball-cratering geometry and it is particularly suitable for coated materials [11]. A hard steel sphere (25.4 mm diameter, 1000 Vickers hardness) is rotating against the coated specimen in the presence of an abrasive slurry (an aqueous suspension of 4-5 µm SiC particles), a contact load of 0.2 N and a relative speed of 0.05 m/s were used. Total sliding time ranged from 5 to 13 minutes in each series of tests. The wear coefficients of the substrate (kₛ) and the coating (kₖ) were calculated from the inner and the outer diameter of the wear craters, as described in [11]. The morphology of wear scars and debris were observed by OM and SEM.

3 RESULTS AND DISCUSSION-
MULTILAYERS CHARACTERISATION

3.1 Multilayers characterisation

The thickness of the sub-layers is listed in Table I. A good interfacial continuity between the different layers was pointed out by SEM observation of the cross sections. The PVD inter-layer showed a dense fibrous microstructure; DLC films appeared to be very dense, homogeneous and well bonded to the PVD layer.

In the as-deposited condition, ACD Ni-(8.5wt.%P layers have an amorphous microstructure, but the deposition conditions of the PVD inter-layer induce the crystallisation of Ni and the precipitation of Ni₃P particles, that noticeably harden the Ni-P layer. The hydrogen fraction in a:C-H DLC films, measured by gas chromatographic analysis after burning the coating [8], is about 25 at.%. The elastic modulus E and the intrinsic hardness H of a:C-H DLC films were: E=250 GPa, H=30 GPa. DLC films were found to retain residual compressive stresses of 1.3 GPa. Microhardness and roughness of sub-layers are summarised in Table II. The nodular microstructure of Ni-P layers is responsible for the increase of roughness with respect to the other layers. The overall surface roughness Rₛ of the multilayers does not change significantly after the deposition of the outer DLC film. Microhardness values listed in Table II are composite values, i.e. microhardness of the coating/substrate system, that do not give detailed information on the contribution of individual sub-layers but can be usefully related to the wear behaviour of the multilayers, in sliding tests.

<table>
<thead>
<tr>
<th>Material</th>
<th>HV₀.⁰⁵, kg mm⁻²</th>
<th>Rₛ, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>220</td>
<td>0.18</td>
</tr>
<tr>
<td>HSS</td>
<td>910</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe/Ni-P (annealed)</td>
<td>980</td>
<td>0.31</td>
</tr>
<tr>
<td>Fe/TiN</td>
<td>840</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe/Ni-P/TiN</td>
<td>1560</td>
<td>0.32</td>
</tr>
<tr>
<td>HSS/TiN</td>
<td>1730</td>
<td>0.21</td>
</tr>
<tr>
<td>Fe/Ti(C,N)</td>
<td>1000</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe/Ni-P/Ti(C,N)</td>
<td>1640</td>
<td>0.32</td>
</tr>
<tr>
<td>HSS/Ti(C,N)</td>
<td>1910</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 2: Microhardness and roughness of layers in the multilayered coatings

Noteworthy, the deposition of an ACD Ni-P under-layer enhances the hardness of the PVD-coated plain steel substrate, thus leading to microhardness values comparable with those of PVD-coated tool steels.

3.2 Sliding

The maximum depth of wear tracks measured on the coated sliders at the end of sliding tests is shown in Figure 2. The deposition of an outer DLC layer tends to improve the wear resistance of the multilayers. The wear resistance of multilayers with a PVD-TiN inter-layer is higher than that of multilayers with Ti(C,N). The wear resistance of multilayers varies with the
substrate in the following order: plain carbon steel<Ni-P coated plain carbon steel<tool steel.

The observation of the morphology of wear scars shows that the worn surfaces are finely grooved mainly due to the abrasive action of wear debris from both the counterface and the coated slider. Wear debris are partly smeared and compacted along the wear tracks and constitute a carbon-based transfer layer. The build-up of a transfer layer is clearly shown by the dark-grey patches observed on the wear tracks (Fig. 3a) and also by the system wear vs. sliding distance plots.

It's also worth noting that (i) the coefficient of friction ($f$) of both DLC-coated and uncoated samples sliding against DLC decreases after the first stages of sliding and (ii) steady-state values of $f$ range from 0.1 to 0.15 in both cases. This suggests that also the friction behaviour of both couples is controlled by a low-shear micro-film. It is well established that the formation of adherent and stable transfer layers can substantially reduce wear losses in sliding contacts. A carbon-rich transfer layer must be particularly adherent to DLC coated samples due to their great chemical affinity. For this reason, DLC coated sliders are more wear resistant than the uncoated ones. Anyway, the protective action of the transfer layer appears to be more effective in the TiN-than in the Ti(C,N)-containing multilayers, that wear out more rapidly in spite of their superior hardness. Apparently, the transfer layer is more easily removed from the surface of Ti(C,N)-containing multilayers: in fact transfer layers are not visible on the wear tracks of the Ti(C,N)-containing multilayers at the end of the tests (Fig. 3b).

The load bearing capacity of the 'substrate' under the PVD coating also plays an important role: in the case of plain carbon steel without the ACD Ni-P layer, the multilayer fails due to the well-known 'ice-on-mud' effect, i.e. the fracture of the PVD coating deposited on a soft substrate that deforms upon loading. The presence of the Ni-P underlayer leads to wear depth values comparable with those of multilayer-coated tool steel samples.

3.3 Microabrasion

Depth measurements showed that wear craters reached the substrate of the PVD inter-layer (i.e. Ni-P, Fe or HSS). The wear coefficients $k_s$ of the substrates under the PVD inter-layer decreased with increasing hardness, in the order: Fe ($1.7 \times 10^{-12}$) > Ni-P ($9.8 \times 10^{-13}$) > HSS ($8.1 \times 10^{-13}$). The standard deviation of $k_s$ is comparable with the repeatability of the MSAT method. The wear coefficients $k_c$ of the multilayers are summarised in Figure 4.

Ti(C,N)/DLC multilayers deposited on plain carbon steel without the Ni-P under-layer do not appear in Fig. 4 because the volume of the scars could not be readily determined due to the tendency of the Ti(C,N) layer to spall at the interface with steel. Residual stresses in the Ti(C,N) coating, generated by the thermal expansion coefficient mismatch between the PVD layer and plain
carbon steel, might be held responsible for interfacial spalling. The wear coefficients $k_c$ of DLC coated samples are generally lower than the corresponding samples without DLC on top. $k_c$ also decreases with increasing hardness of the PVD inter-layer. This is not surprising because the morphology of worn surfaces (Fig. 5) suggests a wear mechanism involving multiple indentation due to the abrasive particles rotating within the contact and small scale ploughing. Further studies by scanning probe microscopy (SPM) on the sides of wear craters will be carried out in order to explain the role of the DLC layer in enhancing the abrasive wear resistance of the multilayers.

Figure 5: Microabrasion tests: side of the wear crater on Fe/Ni-P/TiN/DLC (a) and Fe/Ni-P/Ti(C,N)/DLC (after 489 revolutions)

4 CONCLUSIONS

Multilayered coatings with an outer DLC layer, a PVD nitride-based inter-layer and an inner ACD Ni-P layer were deposited onto plain carbon steel. The influence of each layer on the tribological behaviour of the multilayer-coated system was evaluated by both dry sliding and microabrasion tests.

The deposition of the DLC outer layer increases the overall wear resistance of the multilayers. Furthermore, the deposition of the ACD Ni-P under-layer makes the wear resistance of PVD/DLC-coated plain carbon steel comparable with that of a tool steel coated with the same multilayer.

The selection of the PVD inter-layer plays an important role in influencing the wear behaviour of the multilayer: hard Ti(C,N) inter-layers are detrimental in high loading sliding tests but have a beneficial influence on wear resistance in abrasive wear tests.

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6 REFERENCES