The wettability characteristics of DLC coating for tribological engineering applications

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Abstract. Hard coating deposited to tool steel surface can greatly improve wear resistance and reduce sticking. Since solid-liquid interactions are present in every lubricated tribological contact, the present study is aimed to understand the physical phenomena of contact interactions between the DLC coated surface and the liquid. In this study, double-layer DLC/TiAlN coating was prepared via Physical Vapour Deposition (PVD) process. The anti-sticking properties were assessed using contact angle measurements using two liquids with distinctly different viscosity – water and oil. No significant differences found in the contact angle values for both liquid properties. The results revealed that the DLC/TiAlN coated tool steel surfaces exhibit hydrophobic behaviour with high contact angle values. With a lower surface energy of the DLC/TiAlN coating in comparison to uncoated surface, this suggests that the DLC/TiAlN coating is a good hard coating candidate since it has a lower adhesion resistance and an improved release performance.

1. Introduction
A great number of hard coatings are available to protect the tool steel surface for a long-run production, such as TiN, CrN, TiAlN [1], AlCrN [2], TiC and TiCN [3,4]. Recently, Diamond-like Carbon (DLC) coating has gained acceptance in various industries, for example, automotive, medical, and tooling components, owing to several attractive properties, including their low friction coefficient, high hardness, good wear resistance, and protection of the tool steel surface. These properties make DLC coatings suitable for many tribological applications in mechanical systems, such as valve train tappets, gears, and piston pins [5,6]. Many studies have shown that the mixture of carbon bonds of sp3, sp2, and even sp1, with the possible presence of hydrogen, in the DLC promotes significant effects on friction and wear to protect the tool steel surface from severe wear and surface damage [7–9]. Adding interlayer coating films, i.e. TiAlN [10,11], to the DLC coated tool steel can furthermore enhance degree of freedom in tailoring the coating property [12,13]. Thereby, extending the tool steel lifetime for improved productivity. In addition to wear resistance, corrosive resistance and thermal stability, anti-sticking is one of the key important properties in many tribological engineering applications, including tribology and interface nanotechnology. The anti-sticking property of coating affects the release performance of steel surface [7], whereby an improved release performance requires low surface energy. The coating’s anti-sticking property is related to the polar components of surface energy. Low polar components correspond with increased water-repellency as well as higher contact angle value. A surface with contact angle for water below 90° can be called a hydrophilic surface, while a surface with contact angle greater than 90° is hydrophobic. A higher contact angle value corresponds with improved release performance for the steel surface. In the present paper, the anti-sticking properties in relation to the hydrophobic and
hydrophilic characteristics of uncoated and double-layer a-C:H type DLC/TiAlN coated tool steels were investigated and the relationship between the surface roughness and their respective contact angle and surface energy were also discussed.

2. Materials and method

2.1. Materials and coating

The tool steel material was a powder metallurgical cold work tool steel (Vanadis 4) with high C and Cr contents that was alloyed with Mn, Mo, Si, and V. The tool steels were through-hardened, tempered to 62 HRC, and subsequently polished to a surface roughness Ra of 0.02 µm before the coating was applied. Table 1 presents the mechanical properties and the compositions of the test materials used in the experiments. The palm oil with kinematic viscosity of 95 cSt was selected to represent the oil. A double-layer a-C:H type DLC/TiAlN coating was studied, and its performance was compared with the uncoated tool steel as shown in Figure 1(a). The double-layer DLC/TiAlN coating film shown in Figure 1(b) was deposited onto the tool steel substrates (Vanadis 4, with a surface hardness of 62 HRC) via a Physical Vapour Deposition (PVD) process. The tool steel roughness after coating was the same as before: Ra = 0.02 µm. Figure 1(c) shows the a-C:H type DLC supported by two other coating films—CrN and CrCN—which acted as bonding layers that were deposited onto the TiAlN-coated die surface. Coating binders, CrN, and Cr interlayer coatings were added to the DLC coating in the form of a gradient coating structure. The mechanical properties and surface characteristics of the test coating are presented in Table 2, where the uncertainty values represent the observed variations in the investigated areas.

| Components | Composition | Mechanical Properties |
|------------|-------------|-----------------------|
| Tool steel (Vanadis 4) | 1.4% C, 0.4% Si, 0.4% Mn, 4.7% Cr, 3.5% Mo, 3.7% V | Density ρ (g/cm³) 7.56, Poisson ratio ν 0.3, Elastic modulus E (GPa) 200 |

| Coating | Thickness (µm) | Hardness (HV) | Roughness Ra (µm) |
|---------|----------------|---------------|-------------------|
| DLC/TiAlN | 4 ± 0.40 | 3,000 | 0.026 |

![Figure 1](image)

**Figure 1**: Test specimen made of tool steel Vanadis 4 – a) uncoated, b) double-layer DLC/TiAlN, and c) DLC/TiAlN coating structures.

2.2. Wetting analysis

The wetting properties of surfaces (uncoated and coated) were assessed in terms of the change in free energy and the work of adhesion that were calculated from contact angle and interfacial tension values.
The contact angle measurement was performed using camera and ImageJ with drop analysis plug-in, see Figure 2. The drop analysis plug-in calculates the contact angle of a liquid drop on a flat uncoated and coated tool steel surface using the sphere approximation \( \theta = 2\tan^{-1}\left(\frac{2h}{l}\right) \) and the ellipse approximation. The equilibrium of forces among the surface tensions at the 3-phase boundary were described by Young’s Equation below [7].

\[
\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta
\]

where, \( \gamma_{SV}, \gamma_{SL} \) and \( \gamma_{LV} \) are respectively the surface energy of the solid–vapor, solid–liquid and liquid–vapor interfaces, and \( \theta \) is the equilibrium contact angle.

The surface energy can be determined by measuring contact angles and using Fowkes method as described below [14].

\[
\gamma_s = \gamma_s^d = \gamma_1^2(1+\cos\Theta)^2(4\gamma_s^d)
\]

If the measuring liquid is a dispersion one, i.e., the one that can be characterised by the dispersion interaction only, then \( \gamma_1 - \gamma_1^d \) and this Equation 2 simplifies to the following formula:

\[
\gamma_s = 0.25\gamma_1(1+\cos\Theta)^2
\]

where, \( \theta \) is contact angle, \( \gamma_s \) is surface energy, \( \gamma_1 \) is surface tension of liquid. In this study, the surface tension \( \gamma_1\text{ oil} \) is 35 mN.m\(^{-1}\) and \( \gamma_1\text{ water} \) is 72.75 mN.m\(^{-1}\).

Atomic Force Microscopy (AFM) analysis was used to evaluate surface morphology and roughness of the coated and uncoated tool steel surfaces. The uncoated and coated samples were cleaned in acetone for 10 minutes before contact angle measurements and AFM analysis.

Figure 2: Contact angle measurement using camera and ImageJ with drop analysis plug-in (left) and schematic of liquid drop on solid surface with surface tension indicated as arrows originating at the 3-phase interface line (right).

3. Results and discussion

Contact angle of specimen surfaces was measured to estimate the characteristic of hydrophilic or hydrophobic by means of liquid drops. The contact angle measurements were carried out at an ambient temperature of 32\(\pm\)1 °C and a relative moisture of 68 \(\pm\)2%. The contact angle measurements for both test specimens using water and lubricating oil were summarized in Table 3. It can be seen in Figure 3(a) and Figure 3(b) that no significant differences when using water and lubricating oil for this study. From Figure 3(a), the contact angle of the DLC/TiAlN coated tool steel is slightly higher than the uncoated ones. From this, it is clearly shown that both of the test specimen exhibit hydrophobic surface properties since the contact angle values greater than 90°.

The surface tension measurements for both of the test specimens were calculated using Equation 2 and Equation 3. As seen in Figure 3(b), the uncoated tool steel surface exhibit a relatively high surface energy, 69.73 mJ/m\(^2\), in comparison to the DLC/TiAlN coated tool with a very low surface energy, 3.22 mJ/m\(^2\), indicating weaker interactions with lubricating medium, and thus also poorer wetting. This explains that the DLC coating cannot form strong polar interactions with counter surfaces or liquids.

The significant differences in the surface energy can be due to the coating properties such as oxidation, and even the crystal structure of the DLC itself can have significant influence on the surface energy as discovered by Y. Yang et al. [7].
Table 3: Contact angle measurements.

| Liquid medium | Surface condition | Angle (º) | Theta C (º) | Theta Left (º) | Theta Right (º) | Theta E (º) |
|---------------|-------------------|-----------|-------------|---------------|-----------------|------------|
| Water         | Uncoated          | 113.39    | 99.9        | -18           | 159.7           | 70.8       |
|               | DLC/TiAlN         | 121.57    | 170.9       | -13.1         | 165.6           | 76.3       |
| Oil           | Uncoated          | 157.17    | 170.1       | -12.3         | 162.2           | 75.0       |
|               | DLC/TiAlN         | 158.75    | 172.4       | -12.1         | 139.5           | 63.7       |

Figure 3: a) Contact angle and b) Surface energy measurements of the uncoated and DLC/TiAlN coated tool steels.

Figure 4: Surface morphology and roughness of a) the uncoated and b) DLC/TiAlN coated tool steels.

It is known that the changes in surface roughness and surface energy generated by the coating treatment could be the factor influencing the wettability characteristics. From Figure 4, the differences between the surface energy values of the samples can be related with the roughness, so the connection was investigated. Based on the AFM results, the average roughness (Ra) value for the uncoated (polished) tool steel surface was found to be ~ 5.3 nm, while the DLC/TiAlN coated surfaces had roughness values ranging from ~ 9 to 10 nm, indicating the measured three dimensional surface topographies of the DLC/TiAlN coated tool steel surface smoother than the uncoated tool steel surface. The difference in roughness supported the findings, in which smoother surface of the DLC/TiAlN coating caused low surface energy, indicating the surface energy is related to the roughness. The findings suggest that the DLC/TiAlN coated tool steel surface is a good hard coating candidate for the tool steel surface, which further improved release performance.
4. Conclusion

The wettability characteristics of uncoated and a-C:H type DLC/TiAlN coated tool steels were investigated. Physical vapour deposition (PVD) method was used to deposit the double-layer DLC/TiAlN coating on Vanadis 4 tool steel substrate. The experimental findings show that both uncoated and DLC/TiAlN coated samples have hydrophobic properties. The wetting analysis results show that the DLC/TiAlN coated tool steel has better wettability characteristics compared to the uncoated tool steel substrate. The contact angle measurements show that the surface energy values for the DLC/TiAlN coated tool steel is lower than the uncoated ones. The findings suggest the DLC/TiAlN coated tool steel has better adhesion ability compared to the uncoated tool steel. In other words, the DLC/TiAlN coated tool steel has a lower adhesion resistance compared to the uncoated tool steel. The lower surface energy (lower adhesion resistance) for the DLC/TiAlN coated tool steel was attributed mainly due to the rougher surfaces associated with the coated surfaces in comparison with the uncoated sample. The AFM analysis clearly show that the rougher the substrate surfaces, the lower the surface energy values.

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