Abstract

In this study, ~3.5 μm thick multilayer TiAlN, AlTiN, and AlCrN coatings were deposited on the H13 steel surface by Cathodic Arc Physical Vapor Deposition (CAPVD) method. The tribological performance of the coatings were evaluated by a tribometer at dry and boundary lubrication conditions. Then, coating surfaces were investigated by optical microscope, optical profilometer and atomic force microscope (AFM) to evaluate the morphological changes, wear volumes and tribofilm thickness. Also, Scanning electron microscopy (SEM/EDX) and X-ray photoelectron spectrometry (XPS) analysis were applied to coating surfaces for the tribochemical evolution of the tribofilm. Results showed that AlCrN coating performed the best tribological behavior at dry and lubricated conditions, when compared to TiAlN and AlTiN coatings.

1. Introduction

Wear and friction of sliding surfaces are important phenomena in mechanical systems [1]. Higher friction addresses higher energy loss in mechanical systems. Wear, in addition, is an indicator of system effective life or system components life due to the material damage [2]. To decrease friction and wear in moving parts of an engine, lubricating oils are widely used. These lubricants form a protective tribofilm between sliding surfaces by decomposition of the additives such as zinc dialkyldithiophosphate (ZDDP) present in their composition [3, 4]. However, tribofilm can fail to protect sliding surfaces at boundary lubrication condition. This failure causes metal-to-metal contact, resulting in higher wear rates for sliding surfaces. The cylinder liner-piston ring tribological system, cam tappets/followers, and bearings can operate at boundary lubrication condition in internal combustion engines due to inadequate lubrication. When moving parts of an engine work at boundary lubrication condition, it is essential to provide wear resistance for sliding surfaces to protect them from any material damage. One way to have wear resistant surface to prevent metal-to-metal contacts at boundary lubrication condition is surface treatment by coatings. Therefore, some moving parts of engines are coated with various surface coatings. For example, top piston rings are generally coated with chromium to get wear resistance surface. Similarly, crank bearings are coated with different composites such as aluminum alloy, and copper-lead-tin alloys. In this tribological behavior of hard TiAlN, AlTiN, and AlCrN coatings were investigated to evaluate the possibility of being a wear resistance coating for cam tappets of an engine at dry and boundary lubrication conditions. As a result, AlCrN among all the three coatings showed the best tribological performance at both conditions.

2. Materials and Methods

2.1. Coating deposition and characterization

H13 steel samples were hardened by heat treatment through quenching and tempering at 600 °C. Following this samples were mechanically polished to average surface roughness of 150 μm, and then ultrasonically cleaned for nitrating operation. 3.5 μm thick multilayer TiAlN, AlTiN and AlCrN coatings were deposited on steel substrates by Cathodic Arc Physical Vapor Deposition (CAPVD) coating method. Al67Ti33 and Al70Cr33 targets were used to deposit TiAlN, AlTiN and AlCrN coatings, respectively. Prior to deposition process, H13 tool steel samples were first heated to 450 °C, then ion etched via Cr bombardment. During the coating process, temperature of the substrate was kept at about 450 °C due to the IR and plasma heating. The chamber was evacuated to about 10⁻⁵ Pa vacuum pressure level. Nitrating process was carried under 100V bias voltage and 99.9 % Nitrogen purity at 1 Pa pressure. After the coating application, the cross-section of the samples were polished to evaluate the coating thickness under SEM. Elastic modulus and hardness of the coatings was measured by Nano indentation analysis with Agilent G200 Nano indenter.
2.2. Tribological tests and test conditions

Tribometer tests were performed with UTS ball on disk tribometer with linear reciprocating motion module. Alumina (Al2O3) ball with 6 mm diameter and 159 nm quadratic surface roughness (Rq measured by Atomic force microscopy (AFM)) was rubbed against AlTiN, TiAlN and AlCrN samples with the Rq values of 25.1, 21 and 66 nm (see Fig. 1). AlCrN coating had the highest Rq value due to higher level of coating residues (see optical image and AFM image in Fig. 1 (d)) from the coating process while the TiAIN and AlTiN coatings had similar Rq values. The normal load was 5 and 25 N, sliding speed was 0.01 and 0.1 m/s and stroke was 5 mm with 52 and 100-meter total sliding distance for dry and lubricated condition in tribometer tests, respectively. 0.5 cc ZDDP anti-wear additives containing commercial lubricating oil (approximately 1 drop) was dropped on the sample surface and samples were heated to 100 °C before starting the tests at lubricated condition. The tests were conducted under atmospheric conditions with a relative humidity of 40–50 % and at room temperature of 20–25 °C. The maximum Hertzian contact pressure was calculated by eq.(1) [5] and the lambda ratio (λ) was calculated by the Dowson and Hamrock’s point contact formula as defined in eq. (2) and (3) for linear reciprocating wear tests. The calculated maximum Hertzian contact pressure of the TiAIN, AlTiN and AlCrN coatings were 2.72, 2.57 and 2.56 GPa, respectively. The calculated minimum film thickness of the TiAIN, AlTiN and AlCrN coatings were 69.90, 70.07 and 70.09 nm, and the lambda ratios were 0.43, 0.44 and 0.41, respectively. Lambda ratios indicate that contact regimes were at boundary lubrication condition, where λ<1.

\[ P_{\text{max}} = \frac{\pi \times 6 \times L \times E' \times R_{\alpha} \times 21}{3} \]

(1)

\[ \eta_{\text{min}} = 2.65 \times 0.54 \times 0.07 \times 0.43 \times 0.03 \times 0.13 \]

(2)

\[ \lambda_{\text{min}} = \eta_{\text{min}} \times R_{\text{aq}} \times 2 + R_{\text{aq}} \times 1/2 \]

(3)

2.3. Surface analysis

The surfaces of the tested samples were investigated by optical microscopy (Nikon LV-150) and atomic force microscopy (AFM-Nanosurf Flex-5) to evaluate surface morphology variation after the tribometer tests. The tribochemical analysis was performed by scanning SEM/EDX and Thermo Scientific K-Alpha X-ray photoelectron spectrometer using an Aluminum anode (Al Ka=1468.3 eV) at an electron take-off angle of 90° (between the sample surface and the axis of the analyzer lens). The spectra were recorded using an Avantage 5.9 data system. The binding energy scale was calibrated by assigning the C1s signal at 284.5 eV. Wear depth and volume measurements were evaluated by an optical profilometer (Nanofocus).

Figure 1. Optical microscopy and AFM topography analysis of test samples, (a) Al2O3, (b) TiAIN coating, (c) AlTiN coating, (d) AlCrN coating.

3. Results and Discussion

3.1. Characterization results of coatings

The measured elastic modulus and hardness of the TiAIN, AlTiN and AlCrN coatings are shown in Table 1. Similarly, hardness values have been measured for both coatings. However, elastic modulus value of TiAIN coating was higher than AlTiN and AlCrN coatings while the others had similar elastic modulus values.

Table 1. Elastic modulus and hardness measurement results of the coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (GPa)</th>
<th>Elastic Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAIN</td>
<td>29.75</td>
<td>416.8</td>
</tr>
<tr>
<td>AlTiN</td>
<td>31.06</td>
<td>384.7</td>
</tr>
</tbody>
</table>
Figure 2 shows coating thickness and chemical composition of coating layers. Coatings consisted of four layers; as the first and third layers were AlTiN, TiAlN, AlCrN, and thickness of these layers were 1.5, 2.8, 2.1/1.1, 2.1/1.1 μm, respectively. The second and fourth layers of AlTiN, TiAlN, AlCrN coatings were CrN layers and thickness were 0.44, 0.79, 0.69/0.30, 0.58, 0.51 μm, respectively. Thickness measurement and EDX mapping results clearly showed that desired multilayer coatings were successfully deposited on the steel substrates.

Figure 2. Coating thickness measurements by SEM/EDX analysis; (a) AlTiN coating SEM measurement and EDX mapping results, (b) TiAlN coating SEM measurement and EDX mapping results, (c) AlCrN coating SEM measurement and EDX mapping results.

### 3.2. Friction and wear test results

Friction coefficient results (COF) can be seen in Figure 3. For dry sliding condition AlCrN coating showed the lowest COF value and TiAlN coating started to crack at 25 meter while AlTiN coating started to crack at 20 meter (see Figure 3 (a)). The highest COF value observed for TiAlN coating. For the lubricated condition, the average COF of TiAIN, AlTiN and AlCrN coatings were 0.11, 0.09 and 0.08, respectively. Similar COF values were observed at steady-state boundary lubrication condition for the AlTiN and AlCrN coatings. COF of TiAlIN was again higher than the other coatings. The wear rate ($wR$) of the coatings were calculated by Archer’s formula (see eq. 4). ($V$ is wear volume in mm$^3$, which was evaluated according to the optical profilometer measurement of the wear tracks, $L$ is load in Newton and $D$ is the sliding distance in meter.)

$$wR = V/LxD$$

(4)

Figure 4 shows wear scar profiles and wear rates at dry sliding and boundary lubricating condition. Wear test results showed that AlCrN coating had lowest wear rate for both sliding condition showing the best wear resistance. Wear rates of TiAlN and AlTiN were similar at dry sliding condition (see Fig.4 (b)). However, when compared to wear rates, TiAlN coating showed better wear resistance than AlTiN at boundary lubricating condition (see Fig.4 (c)). This can be explained by better anti-wear tribofilm formation on the TiAlN surface than AlTiN.

Figure 3. The friction coefficient curves of TiAIN, AlTiN and AlCrN coatings, (a) dry condition, (b), (c) and (d) lubricated condition.

Figure 4. (a) Wear scar profiles of dry sliding condition of the coatings, (b) wear rates of the coatings at dry sliding condition, (c) wear rates of the coatings at boundary lubrication condition.
3.3. Tribochemical analysis of surfaces and tribofilms

Tribochemical analysis of the surfaces by EDX and XPS showed that ZDDP decomposed under load and heat to form tribofilm. According to the EDX analysis results, detection of the P, S, Zn and O elements was the evidence of tribofilm formation on TiAlN, AlTiN and AlCrN surfaces. When looking the XPS analysis results, combining the peak of O1s and P2p (PO₃ compound for binding energy of 132.7± 0.1) were found to be zinc orthophosphate and meta phosphate anti-wear layers on the coating surface due to decomposition of ZDDP (see Fig. 5) [6]. These results are in good agreement with the Nicholls et al. work, which reported that condensation of the phosphates/phosphothionates species turned to zinc containing compounds with decomposition in the tribofilm. The binding energy of 1021.8 eV for Zn2p peak shows ZnS compound in tribofilm and this compound improved the wear resistance of tribofilm with zinc orthophosphates and metaphosphates for TiAlN and AlCrN (see Fig. 5) [7].

![Figure 5. XPS analysis results of the coating surfaces.](image)

The higher ratio of zinc orthophosphates and meta phosphates in tribofilm of TiAlN (57.2/4.57 % in atomic) and AlCrN (50.63/2.04 % in atomic) with the presence of ZnS is one of the indicators of better wear resistance, which is also consistent with the wear rates of the coatings as shown in Fig. 4 [8]. The peak at a binding energy of 1022.1 could be attributed to ZnO in tribofilm. Furthermore, Ca2p peak at a binding energy of 347.1 eV was detected in the tribofilm of all coatings that presents calcium carbonate (CaCO₃) [9]. Ca is added to ZDDP as a detergent additive, however, it reacts with ZDDP in high concentrations (≥ 2 in weight) and it provides wear reduction by forming Ca-

PO or CaCO₃ chemical compounds on the surface [10]. Due to the lowest ratio of CaCO₃ (3.6 % in atomic) wear reducer compound in tribofilm, AlTiN had weaker anti-wear tribofilm than the TiAlN and AlCrN coatings with the lower level of zinc-orthophosphate and meta-phosphate compounds. Furthermore, the reason of lower wear rate of AlCrN coating than the TiAlN coating can be explained by sulfate formation (XPS peak at a binding energy of 168.4 eV) with its high load carrying capacity in the tribofilm. Especially, sulfate formations could improve the mechanical strength of the tribofilm by reacting with phosphates compounds on AlCrN coating surface.

4. Conclusion

Tribological performance of the multilayer TiAIN, AlTiN and AlCrN coatings were evaluated by tribometer tests at dry sliding and boundary lubrication conditions. Based on the tribometer tests and microscopic, spectroscopic analysis results, the conclusions of this study can be summarized as follows:

- AlCrN coating showed the lowest COF when compared to TiAlN and AlTiN at dry sliding and boundary lubricating conditions.
- AlCrN had the best wear resistant for both test conditions.
- All coatings reacted with ZDDP anti-wear additive and formed rich protective tribofilm. Presence of ZnS, zincorthophosphate and metaphosphate compound in tribofilm provided the best wear resistance to AlCrN.

To sum up, all coatings showed good anti-wear performance at lubricating condition since abrasive or adhesive wear was not detected on the coating surfaces.

Acknowledgement

The authors would like to thank Koç University Surface Science and Technology Centre (KUYTAM) for surface analyses.

References