Effect of Surface Wear on Corrosion Protection of Steel by CrN Coatings Sealed with Atomic Layer Deposition

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1. INTRODUCTION

Thin film coating technology enables control of surface-related properties, such as corrosion resistance, while allowing underlying substrates to be chosen for strength and toughness. Of various thin film coating methods, atomic layer deposition (ALD) has recently shown great promise in corrosion protection of steel. Unfortunately, the practically limited thickness and comparatively small hardness of ALD coatings make it unsuitable for applications under heavy load, such as cutting instruments. More durable corrosion protection can be obtained by micrometer-thick hard physical vapor deposition (PVD) coatings, such as CrN. The weakness of these coatings is that they possess a large amount of defects and pinholes, through which the corrosion can attack the less noble steel, resulting in heavy localized corrosion. Pinhole sealing by ALD coatings has been reported to greatly counteract this, improving the corrosion protection. Combining the chemical stability of TiO₂ or Ta₂O₅ with the excellent sealing properties of Al₂O₃ has been shown to give enhanced corrosion protection. Although the sealing of PVD pinholes has been shown by both corrosion measurements and focused ion beam (FIB) cross-sectioning, the effect of surface wear on structure and obtained corrosion protection by hybrid PVD/ALD coatings has not been reported previously.

The hypothesis of this work was that if the excellent corrosion protection by hybrid PVD/ALD coating is due to PVD pinhole sealing of ALD coating, the surface wear of the hybrid coating should have negligible effect on the corrosion protection properties. The investigation was conducted by alternating the corrosion exposure of the coated steel (salt solution) and wear of the surface, resulting in gradual increase of surface wear until a major loss in the corrosion protection was observed by linear sweep voltammetry (LSV) measurements and optical microscopy. After the last wear step, cross-sectional SEM images obtained with focused ion beam milling showed not only the presence of the ALD coating at the CrN defects but also the opening of new pathways for the corrosion to attack the substrate.

The successful sealing of high-aspect-ratio (HAR) defects and pinholes with differing geometries is possible by ALD due to the self-saturating surface reactions that allow conformal and uniform deposition on three-dimensional morphologies. With standard ALD mode, conformal deposition on up to 200:1 aspect ratios has been reported. Combining the chemical stability of TiO₂ or Ta₂O₅ with the excellent sealing properties of Al₂O₃ has been shown to give enhanced corrosion protection. Although the sealing of PVD pinholes has been shown by both corrosion measurements and focused ion beam (FIB) cross-sectioning, the effect of surface wear on structure and obtained corrosion protection by hybrid PVD/ALD coatings has not been reported previously.

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sectioning of the sample surface by focused ion beam (FIB) milling and consecutive scanning electron microscopy (SEM) verified the existence of ALD coating in the defects of the CrN. The defects in PVD coatings can be identified as the main pathway for the corrosion to attack the steel substrate, and ALD can be used to seal these pinholes.

2. RESULTS AND DISCUSSION

Hereafter, the samples are described with a running numbering in the form of LSVX-WearY, in which X stands for the number of LSV tests done (1−5) and Y stands for the number of wear steps (0−4). See Section 4 for details.

2.1. Electrochemical Measurements. Figure 1 shows the results of LSV measurements. Figure 1a shows polarization curves before any wear (LSV1-Wear0), whereas Figure 1b shows the polarization curves at the end of the investigation for both, with wear (LSVS-Wear4) and without wear. From Figure 1a, it is seen that the CrN coating initially reduces the corrosion current density approximately with an order of magnitude compared to noncoated high-speed steel (HSS) and shifts the corrosion potential to less negative. With addition of ALD coating, corrosion current density is reduced further by almost 2 orders of magnitude due to the sealing of pinholes. Similar results have been reported previously by growing ALD nanolaminates on PVD CrN coatings.4,10 Wearing the top surface of the hybrid PVD/ALD coating reduces the corrosion protection to some extent. As seen in Figure 1b, the corrosion current density is almost an order of magnitude higher with the extensive surface wear of the sample LSV5-Wear4. The corrosion potential has also moved to −700 mV, close to the value of the PVD CrN coating itself.10 This is as expected, as the ALD nanolaminate has been completely removed from the top surface of the PVD CrN coating. Even after the complete removal, the corrosion current density of worn hybrid PVD/ALD coatings is still less than half compared to the CrN coating only, without any wear.

Figure 2 shows all LSV measurement results (Figure 2a for corrosion potential, and Figure 2b for corrosion current densities versus the number of LSV measurements done. The bottom axis shows the total number of the LSV measurements done. The total contact time to the salt solution was approximately 2.5 h for each LSV measurement. The top axis shows the amount of wear steps in samples with wear—the first three wear steps were with ball-on-disk, and the last one was by sandpaper grinding. Each data point was averaged from three measurements, and the mean of standard deviation was used as error bars.
density), with each measurement point averaged from the three LSV measurements done. For HSS, the surface is completely rusted and corrosion potential has stabilized to approximately −1000 mV already after the second LSV measurement. With the CrN coating, corrosion potential and corrosion current density approach those of noncoated HSS with increasing
amount of time in salt solution and LSV measurements done. Wearing the CrN surface has a minor effect on the electrochemical behavior, as the differences between samples with and without wear are generally smaller than the measurement variation.

After the first three wear steps, the corrosion current density for the hybrid PVD/ALD-coated HSS slightly increases, whereas the corrosion potential remains approximately the same. Only after the complete removal of the ALD nanolaminate from the PVD CrN surface, a notable difference is observed between the samples without wear as the corrosion potential has moved to a more negative value (−560 mV) and the corrosion current density has increased by an order of magnitude.

Heavy wear with material removal from the top of the PVD CrN surface can open pinholes and defects that were previously closed and thus not sealed by the ALD coating. Wear can also cause cracks that might propagate through the whole PVD coating. This would create new pathways for corrosion to attack the steel substrate, resulting in corrosion current density closer to the values obtained by the PVD CrN coating alone. Nevertheless, the initially open voids remain sealed by the ALD nanolaminate, and the corrosion current density of the worn hybrid PVD/ALD-coated HSS is still less than half of that with the PVD CrN coating only.

2.2. Surface Analysis on Wear and Corrosion. Figures 3–5 show the optical microscopy images of each sample type after each test step. Figure 3 shows that the surface of the noncoated HSS is rusted already after one LSV measurement (Figure 3a), and this rusting progresses by further LSV measurements and time in salt solution (Figure 3c,e,g,i). The wear steps carried out for the noncoated disks (Figure 3b,d,e,h) remove rust from the surface, as observed from the lighter color of the wear tracks.

The surface of the PVD CrN coating is oxidized in the LSV measurements, as can be seen in Figure 4. The final wear step by sandpaper grinding (Figure 4h) has removed all of the oxidized CrN surface. The grinding step has also removed the wear tracks from first two wear steps with shorter run distance. Some rusted steel surface is observed as dark areas on wear tracks after the second LSV measurement (Figure 4c), and the amount of these areas increases as the test progresses.

As seen in Figure 5, the hybrid PVD/ALD-coated surface appears initially unaffected by corrosion. Surface oxidation of the PVD CrN coating can be seen at wear tracks on the second LSV measurement (Figure 5c). After the third LSV measurement, a small amount of rusted steel is observed as darker area in Figure 5e. The number of these dark spots increases as the testing progresses. These rust spots are located preferentially at spots where the wear tracks converge, such as in positions shown in Figure 5g. After sandpaper grinding, only wear tracks from the longer total distance ball-on-disk test remain (Figure 5h). At this point, the rust spots are almost solely located on these deepest wear tracks (Figure 5h,i).

The wear depth of individual ball-on-disk test (25 m distance) on PVD CrN coating was 90 ± 70 nm. The large variance was easily observable in microscope images, with some areas having much greater wear than others. The wear of the surface ALD coating can be assumed rapid because it was observed to wear out at the very start of all wear steps. Thus, the wear of the PVD CrN coating and the hybrid PVD/ALD coating are the same within measurement variation. Sandpaper grinding (Wear4) removed the ALD nanolaminate from the PVD CrN surface in a few seconds. The grinding step (total time, 15 s) removed approximately 100 nm of the PVD CrN.

Figure 5. Optical microscopy images after each measurement step for the hybrid PVD/ALD-coated HSS: (a) LSV1-Wear0, (b) LSV1-Wear1, (c) LSV2-Wear1, (d) LSV2-Wear2, (e) LSV3-Wear2, (f) LSV3-Wear3, (g) LSV4-Wear3, (h) LSV4-Wear4 (sandpaper grinding), and (i) LSV5-Wear4.
The approximate depths of the rust spots observed at coated sample surfaces after LSV5-Wear4 was $22 \pm 14 \mu m$ for the PVD CrN-coated samples (Figure 4i) and $12 \pm 5 \mu m$ for the hybrid PVD CrN-coated samples (Figure 5i). Both of these values are greater than coating thickness, showing that a significant amount of base steel material has corroded and...
dissolved from these positions. A larger amount of steel dissolution with the PVD CrN coating alone coincides with the electrochemical measurement results.

Figure 6 shows photographs of noncoated (Figure 6a,d), CrN-coated (Figure 6b,e), and hybrid PVD/ALD-coated (Figure 6c,f) steel disks after all of the measurements, for both without wear and with wear (LSV5-Wear4). The noncoated HSS is completely rusted in both cases (Figure 6a,d). The PVD CrN-coated samples appear quite identical (Figure 6b,e), which is as expected by the electrochemical measurement results. On the basis of the surface images, the profilometer results, and the electrochemical analysis, most of the PVD CrN coating still remains after the wear procedure, and the protection by the PVD CrN coating alone is mostly unaffected by the surface wear. For the hybrid PVD/ALD-coated HSS without wear (Figure 6c), there are only few small rust spots. In the case of the hybrid-coated samples with wear, some surface oxidation of the CrN coating is observed after the LSV5-Wear4 (Figure 6f). Additional rust spots are observed on the wear tracks of the hybrid PVD/ALD-coated samples.

The rust spots were observed to be located preferentially at the wear tracks of the PVD CrN-coated and hybrid PVD/ALD-coated steel. Figures 7 and 8 show SEM images of coated sample surfaces after LSV4-Wear3 and LSV5-Wear4, respectively. With the CrN coating only (Figures 7a and 8a), some rust spots are seen outside the wear tracks, whereas for the hybrid PVD/ALD-coated HSS (Figures 7b and 8b), the rust spots are almost exclusively located at the wear tracks. After grinding the surface by sandpaper (LSV4-Wear4), only the deepest wear tracks remain, and higher-magnification SEM images of rust spots in these wear track positions are presented in Figure 8. These rust spots were up to 2 orders of magnitude larger than the biggest pinholes (few micrometers) observed in the CrN coating.

The energy-dispersive spectrometry (EDS) analysis gave strong Fe signals from the rust spots. A strong Cr signal without any Fe or Ti signal was observed from the wear tracks. For the hybrid PVD/ALD-coated HSS after LSV4-Wear3, an EDS Ti Kα peak at 4.5 keV for the ALD nanolaminate was observed outside the wear tracks. At the edge of the wear track, increased aluminum signal was obtained, indicating residues from the counterface alumina balls.

The area fraction (from the total contact area to salt solution) of removed ALD nanolaminate after the final ball-on-disk test (LSV3-Wear3) was approximately 66%. The final wear step (LSV4-Wear4) with sandpaper removed the ALD coating completely and 100–200 nm CrN from the top surface. Table 1 shows the total rust areas for samples with wear (LSV4-Wear3 and LSV5-Wear4) and without wear (LSV5). For the noncoated HSS, the rust area was equal to the total lacquer-

Table 1. Total Rust Area after the Two Final LSV Measurements

<table>
<thead>
<tr>
<th>sample</th>
<th>rust area after LSV4-Wear3 (mm²)</th>
<th>rust area after LSV5-Wear4 (mm²)</th>
<th>rust area after LSV5 (without wear, mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSS</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>HSS/PVD CrN</td>
<td>1.4 ± 0.3</td>
<td>6.9 ± 0.9</td>
<td>2.9 ± 0.5</td>
</tr>
<tr>
<td>HSS/PVD CrN/ALD</td>
<td>0.63 ± 0.12</td>
<td>2.9 ± 0.3</td>
<td>0.8 ± 0.2</td>
</tr>
</tbody>
</table>

“The total contact area to salt solution was approximately 170 mm². The total contact time to salt solution (0.2 M NaCl) was about 13 h after the final LSV measurement.
has caused some steel dissolution at the right-hand side of the recess.

2.4. Coefficient of Friction (CoF) for the Hybrid PVD/ALD Coating. Figure 11 shows coefficient of friction (CoF) value for ball-on-disk measurement on the PVD CrN-coated and the hybrid PVD/ALD-coated steel (LSV1-Wear1). The CoF of oxidized PVD CrN surface (see Figure 4b) is lower than that of PVD CrN protected from surface oxidation by the ALD nanolaminate (0.44 ± 0.03 vs 0.67 ± 0.04). This oxidized layer did wear away as the tribometer test progressed, and the CoF approaches the value for nonoxidized PVD CrN (0.67).

For the hybrid PVD/ALD-coated steel, low CoF (0.16 ± 0.01) of the ALD nanolaminate is observed at the start of the measurement. Mayer et al. reported a larger value of CoF (0.3) for ALD Al2O3, although they used silicon substrate and Si3N4 counterface ball, so the results are not directly comparable. Mohseni et al. obtained more similar CoF (0.15−0.22) for ALD nanolaminate, although their investigations focused on different nanolaminates (ZnO/Al2O3/ZrO2) and their tests used pin-on-disk configuration. In the research reported here, the ALD nanolaminate was worn off after 200 ± 100 wear cycles (using 10 N force; 0.2 m/s linear speed; 6 mm diameter alumina ball). After this, the CoF increased rapidly, until it stabilized to CoF value of nonoxidized PVD CrN coating. Huang et al. reported similar rapid increase in CoF, followed by stabilization to a value above 0.6 with identical loads and similar sliding speed for PVD CrN.21

In addition to the CoF value change, the typical colors caused by Al2O3/TiO2 thin films could not be seen after the wear steps even though the thin films are known to be observable by eye still in 10 nm range. The removal of the ALD nanolaminate was further confirmed with EDS analysis, which did not show the characteristic Ti Kα peak at 4.5 keV obtained from TiO2 in the nanolaminate.10 The ALD nanolaminate was also not observed on the PVD CrN surface in FIB/SEM cross-sectional images.

2.5. Wear Mechanism Schematic on Corrosion-Protecting Hybrid PVD/ALD Coatings. It was shown that removal of the ALD nanolaminate from the top surface of the CrN coating reduced the corrosion protection of the hybrid PVD/ALD coatings. Despite this, the corrosion protection was superior to that of the corresponding PVD CrN coating alone. Figure 12 shows the schematic of the effect of wear on the
After all of the wear steps and LSV measurements, the area fraction of rust to the total salt solution contact area was 4% for the PVD CrN-coated HSS and less than 2% for the hybrid PVD/ALD-coated HSS. SEM analysis showed that for the hybrid PVD/ALD-protected HSS the rust spots were located almost exclusively on areas with heavy wear from repeated wear steps.

FIB/SEM cross-sectional images showed that ALD nanolaminate is present at defects even after the wear procedure, but corrosion had progressed underneath the PVD CrN coating. Defects on steel surface can result in cracks in the PVD CrN. These cracks can expand when the surface is worn, exposing areas not covered by ALD. Surface wear-induced cracks in the PVD CrN can act as channels for the corrosion to attack through and can cause local collapse of the PVD CrN when the surface was further worn. Thus, some of the corrosion protection by hybrid PVD/ALD coating is lost, even if the sealing of the PVD CrN pinholes is perfectly successful.

4. EXPERIMENTAL METHODS

4.1. Materials. Highly alloyed high-speed steel (HSS) disks were used as substrates: the details can be found in the previous publication of the authors. In addition, (100) silicon die were employed as reference samples to confirm expected ALD thickness and density. Approximately 3 μm of commercial BALINIT CNI CrN coating (Oerlikon Balzers) was deposited by sputtering on top of the HSS disks. The surface roughness of the PVD CrN coating was approximately 85 nm root-mean-square.

Nominally 100 nm thick Al2O3/TiO2 ALD nanolaminate was deposited on these CrN-coated steel disks with Picuson R-200 Advanced system. The deposition was done as reported previously, using trimethylaluminum/H2O and TiCl4/H2O precursors for the two laminates consisting of alternating, 5 nm thick layers. Prior to the ALD process, an oxygen plasma pretreatment was used, as it has been shown to improve adhesion and obtain corrosion protection of the nanolaminate.

Noncoated steel disks, PVD CrN-coated steel disks, and hybrid PVD/ALD-coated steel disks were used in this investigation. The effect of wear on corrosion protection of these samples was evaluated by alternating test sets between electrochemical LSV measurements in salt solution (0.2 M NaCl) and the wear of the surface.

4.2. Electrochemical Measurements. The LSV measurements were conducted with a traditional three-electrode setup, as reported previously, except the test was modified as follows: Viton O-Ring limited contact area was approximately 180 mm², a 30 min waiting period was used before scanning the voltage from −1.5 to 0.0 V, and the samples remained in contact to the salt solution for approximately 2.5 h before taken out and cleaned by 5 min ultrasonication in ethanol. The 0.25 mm pit at the middle of the disk was covered by lacquer (Duran Schott, Germany) to eliminate its detrimental effect on corrosion protection, reducing the effective corrosion contact area to 170 mm². Tafel analysis for the determination of corrosion potentials and corrosion current densities from polarization curves was conducted as per guidelines described in standard ASTM G59-97. A total of five LSV measurements were conducted in this manner, for an approximate total 13 h in salt solution. A secondary sample set without any surface wear, but identical amount of LSV measurements and time in salt solution, was conducted to evaluate the effect of wear on the corrosion.
electrochemical properties measured by LSV. Three of each sample type were used in all tests, and the mean of standard deviation was used as measurement error.

4.3. Surface Wear. Between each of the five LSV measurements, the surface of the disks was worn. A high-temperature Anton Paar THT tribometer was used for the first three wear steps. The tests were carried out on ball-on-disk configuration with 6 mm diameter alumina balls (Anton Paar), 10 N load, and 0.2 m/s linear speed. These tests were conducted under controlled environmental conditions of temperature 23 °C and humidity 50%. The first two runs used 25 m total distance, and the third run used 50 m total distance. In each of these runs, three circular ball-on-disk tests were conducted for each disk, with radii of 2.5, 3.5, and 4.5 mm.

The samples were manually positioned in each wear run. A Dektak profilometer was used to estimate the depth of the wear tracks and rust spots observed after the final ball-on-disk step. Profilometer analysis of ball-on-disk wear tracks was done for the PVD CrN-coated samples, using six measurements, with standard deviation as error.

The fourth wear step was conducted by sandpaper grinding: the top surface was ground away with 1200 grit sandpaper for 15 s, a time chosen to ensure complete removal of ALD from the top, as ALD coating was observed to be removed already after a few seconds. An approximate amount of PVD CrN surface wear by sandpaper grinding was indirectly estimated on the basis of wear track depths measured by the Dektak profilometer, using optical microscopy to evaluate which wear tracks (with previously measured depths) were removed by the sandpaper grinding.

4.4. Coefficient of Friction Measurement. The main purpose of the ball-on-disk tests was to wear the surface of the coated disks. In addition, the coefficient of friction (CoF) was measured for the PVD CrN and the hybrid PVD/ALD coating to evaluate the progress of the wear and the required amount of cycles to wear the ALD away from the wear track. The CoF and time to wear for ALD nanolaminate were measured with a time period starting from 2 s after the measurement began and ending when friction was observed to increase due to a contact to the PVD coating. The CoF development of the hybrid PVD/ALD coating was compared to that of the CrN coating only. The CoF measurements were repeated three times, with different samples, and standard deviation was used as the measurement error.

4.5. Microscopy. All samples with wear steps were examined and imaged by an optical microscope after each LSV measurement and each wear step. The PVD CrN-coated and the hybrid PVD/ALD-coated steel disks were analyzed in more detail with SEM and EDS (Tescan Mir3; 13.0 kV acceleration voltage) after two final wear steps (LSV4-Wear3 and LSV5-Wear4). The presence and removal of ALD Al2O3/TiO2 nanolaminate was confirmed using EDS Ti Kα peak at 4.5 keV, as described in a previous publication.24 The amount of rust spots and their position on the sample surface was evaluated with SEM and EDS. Image-processing software ImageJ (version 1.51 k; U.S. National Institutes of Health) was used to adjust contrast and calculate area fraction of rust spots to the total effective corrosion contact area.

The hybrid PVD/ALD-coated samples were investigated by FIB/SEM after the whole test procedure (LSV5-Wear4). FIB-milled cross sections were studied by SEM at two types of position: major defects at wear track and defects observed outside the wear tracks.

The cross-sectional samples were prepared by FEI Helios NanoLab 600 FIB dual-beam system using 30 kV acceleration voltage rough milling, with 6.5 and 2.7 nA currents. Fine milling was conducted with 0.44 nA. The working distance during the operation was 4.1 mm. Rough milling was carried out at an angle of 52° from the substrate holder surface normal to avoid a curtaining effect and hence some visible diagonal artifacts manifested on some images.

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