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

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ABSTRACT: Corrosion protection of steel obtained with physical vapor deposition (PVD) coatings can be further improved by sealing the intrinsic pinholes with atomic layer deposition (ALD) coatings. In this work, the effect of surface wear on corrosion protection obtained by a hybrid PVD CrN/ ALD Al_2O_3/TiO_2 nanolaminate coating was studied. The samples were investigated by alternating surface wear steps and exposure to salt solution and consecutively the progression of



corrosion after each wear and each corrosion step was evaluated. Optical microscopy, scanning electron microscopy (SEM), and energy-dispersive spectroscopy showed that the rust spots were almost exclusively located on positions at which the wear steps had removed the top surface of the PVD CrN coating. Nevertheless, even after complete removal of the ALD nanolaminate from the top of the CrN surface by sandpaper grinding, the corrosion current density was less than half compared to the PVD CrN coating alone without surface wear. 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. A mechanism for the effect of wear on the structure and corrosion protection of hybrid PVD/ALD coatings is proposed on the basis of this investigation.

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.²⁻¹⁰ 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.¹¹⁻¹³ 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.¹⁴ Pinhole sealing by ALD coatings has been reported to greatly counteract this, improving the corrosion protection.4,7,1

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.^{15,16} With standard ALD mode, conformal deposition on up to

200:1 aspect ratios has been reported.¹⁷ Combining the chemical stability of TiO₂ or Ta₂O₅ with the excellent sealing properties of Al₂O₃ has been shown to give enhanced corrosion protection.^{3,8} Although the sealing of PVD pinholes has been shown by both corrosion measurements and focused ion beam (FIB) cross-sectioning,^{4,10} 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-

Received: October 15, 2017 Accepted: January 24, 2018 Published: February 12, 2018 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



Figure 1. Polarization curves for the electrochemical measurements (a) before wear (LSV1-Wear0) and (b) after five LSV measurements and approximately 13 h in salt solution. Results for both samples, with wear (LSV5-Wear4) and without wear, are shown.

curves before any wear (LSV1-Wear0), whereas Figure 1b shows the polarization curves at the end of the investigation for both, with wear (LSV5-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



Figure 2. (a) Corrosion potentials and (b) 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.



500 µm

Figure 3. Optical microscopy images after each measurement step for noncoated 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.



Figure 4. Optical microscopy images after each measurement step for the CrN-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.

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



500 µm

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.

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.¹⁸ 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 protection 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 \pm 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 6. Photographs of the samples at the end of measurements, after five LSV measurements, and approximately 13 h in the salt solution. Samples without wear are shown in the upper row: (a) noncoated, (b) CrN-coated, and (c) hybrid PVD/ALD-coated. The lower row shows samples after the LSV5-Wear4: (d) noncoated, (e) CrN-coated, and (f) hybrid PVD/ALD-coated. For the samples in the lower row, ultrasonication was used to remove the lacquer before taking the images.



Figure 7. SEM images of sample surfaces after LSV4-Wear3 for (a) the PVD CrN-coated steel, where a notable amount of spot corrosion is observed, preferentially on wear tracks, and (b) the hybrid PVD/ALD-coated steel, where the corrosion is only observed at positions where wear tracks converge.



Figure 8. SEM images of rust spots at the wear tracks positions (vertical direction in the image) after sandpaper grinding (LSV5-Wear4) for (a) the PVD CrN-coated steel and (b) the hybrid PVD/ALD-coated steel.

The approximate depths of the rust spots observed at coated sample surfaces after LSV5-Wear4 was 22 \pm 14 μ m for the PVD CrN-coated samples (Figure 4i) and 12 \pm 5 μ 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/ALDcoated 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/ALDcoated 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 K α peak at 4.5 keV for the ALD nanolaminate¹⁰ 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-ondisk 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 $Measurements^a$

sample	rust area after LSV4-Wear3 (mm ²)	rust area after LSV5-Wear4 (mm ²)	rust area after LSV5 (without wear, mm ²)
HSS	170	170	170
HSS/PVD CrN	1.4 ± 0.3	6.9 ± 0.9	2.9 ± 0.5
HSS/PVD CrN/ALD	0.63 ± 0.12	2.9 ± 0.3	0.8 ± 0.2

^aThe 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.

limited contact area of the salt solution (170 mm²). For the CrN-coated HSS, the area was <1% of the total area after the LSV4-Wear3 and approximately 4% after the LSV5-Wear4. With identical amount of LSV measurements and time in salt solution (LSV5), but without any wear, the rust area was <2%. The rust areas for the hybrid PVD/ALD-coated steel were less than half of these values. For the hybrid PVD/ALD samples without wear, the rust area was <0.05% after the LSV5. This negligible amount of rust at the sample surfaces is in line with investigations by Härkönen et al., where their PVD CrN/ALD nanolaminate-coated steel remained corrosion free even after 168 h in neutral salt spray test.⁴

2.3. SEM Imaging of Defect Site Cross Sections Prepared by Focused Ion Beam Milling. FIB/SEM images of the hybrid PVD/ALD-coated sample after the whole test procedure (LSV5-Wear4) are shown in Figures 9 and 10. Figure 9a shows a top-view SEM image of a major defect on a wear track with a heavy local corrosion. A black line and an arrow have been added to Figure 9a to illustrate the crosssectioned line spot and the view in Figure 9b, respectively. The cross section shows clearly characteristic, grainlike carbides in the steel and an edge of the PVD CrN coating on top of the steel. The corrosion has progressed below the PVD CrN coating. These observations are also in line with earlier research.¹⁰ Some of the PVD CrN coating appears collapsed. The ALD nanolaminate can be seen at the bottom, following the varying surface shapes conformally. It is notable that the ALD coating can be found deeper than the bottom surface level of the PVD CrN coating; it is plausible that the original defect in PVD CrN coating was caused by a major defect on the steel surface, which prevented successful PVD coating on this spot. The ALD coating would then have been deposited to cover the bottom of this defect.

The thickness of the ALD coating at the far ends of the defect cavity is larger than 100 nm. This can be attributed to possible chemical vapor deposition (CVD) reactions between the surfaces, precursors, and byproducts. This is a known issue for ALD on complex shadowed and other high-aspect-ratio (HAR) structures when precursors or byproducts do not have enough time to diffuse out from the structure before the following precursor pulse enters the space.¹⁹ Even with long purge time set in this investigation (10 s), complete prevention of the parasitic CVD seems to be challenging due to the high structural complexity of these HAR defect cavities.

Figure 10a shows a top-view SEM image of a defect site outside of wear track. Only the last wear step, sandpaper grinding, has affected this area. A black line and arrow have been added to show the field of view for the image of the prepared cross section shown in Figure 10b. The observed defect is a shallow pit with mostly intact PVD CrN coating. Some corrosion has progressed through the right-hand side of the recess. An approximately 100 nm thick layer can be observed at the right edge of the recess. No such layer could be observed at the middle of the recess or at the top surface outside the defect.

Probably, there has been some kind of particle present at this recess, which has mostly blocked the ALD deposition on the recess. The sandpaper grinding has then removed the particle and ALD at the top surface outside the recess, but ALD at the edge of the recess and inside the PVD CrN coating remains. Removal of particle by sandpaper grinding has also probably expanded the cracks observed at recess in the PVD coating, and the one corrosion step carried out after the sandpaper grinding



Figure 9. FIB/SEM analysis done on the hybrid PVD/ALD-coated steel after the LSV5-Wear4. Top view (a) of a major defect on a wear track. The black arrow denotes the location of the cross-sectional image (b) prepared by FIB milling.



Figure 10. FIB/SEM analysis done on the hybrid PVD/ALD-coated steel after the LSV5-Wear4. Top view (a) of defect (shallow pit, probably left by a particle). The black arrow indicates the location of the cross-sectional image (b) prepared by FIB milling. Some milling artifacts are shown along the diagonal direction in the steel area (final polishing *z*-depth too short).

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)



Figure 11. Coefficients of friction after LSV1-wear1 for the PVD CrNcoated and hybrid PVD/ALD-coated HSS. The CoF for the oxidized PVD CrN is lower than that for the nonoxidized PVD CrN.

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 \pm 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 $Al_2O_{3,}^{19}$ although they used silicon substrate and Si_3N_3 counterface ball, so the results are not directly comparable. Mohseni et al. obtained more similar CoF (0.15-0.22) for ALD nanolaminate,²⁰ 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 \pm 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 Al_2O_3/TiO_2 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 K α 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

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Figure 12. (a) Schematic of corrosion protection by hybrid PVD/ALD coatings. Defects shown are based on various defects observed in FIB investigations by Panjan et al.: open voids, closed pinholes, large (>1 μ m) flakelike defects, cone-shaped submicron defects.²² (b) Surface wear of the coating opens closed pinholes and can open cracks through coating and creating paths for the corrosion to attack the substrate.

structure and the corrosion protection obtained by hybrid PVD/ALD coatings. This schematic has been constructed on the basis of the LSV results and the SEM images in this work as well as some relevant previously reported research: a simplified pinhole sealing schematic proposed by Härkönen et al.,⁴ previous FIB/SEM images showing ALD nanolaminate covering the bottom of PVD CrN pinholes,^{4,10} and defect-type investigations on PVD nitride coatings by Panjan et al.^{22,23}

Figure 12a shows the structure of the hybrid PVD/ALD coatings. This structure offers corrosion protection that is mostly unaffected by surface wear. Even with surface wear removing all ALD coating and some PVD CrN from top of the structure (Figure 12b), the pinholes remain sealed by ALD, and corrosion protection largely remains. Some of the corrosion protection is, however, lost due to four factors: (i) some of the defects in PVD coatings are closed during the PVD deposition process.²² These pinholes, which are not sealed by ALD, can be opened when the surface of the PVD coating is worn. (ii) Particles on steel-PVD CrN interface can be removed by wear, thus revealing areas that are uncovered by ALD. (iii) Wear can cause crack propagation through the whole PVD coating,¹² opening up new paths to the steel substrate. (iv) Some of the ALD coverage at pinholes can be potentially lost, if ALD film adhesion is poor due to unfavorable precursor-surface reactions. Regarding the fourth factor, plasma pretreatment has been reported critical to obtain sufficient adhesion and enhanced corrosion protection on PVD CrN and steel surfaces.^{5,10}

3. CONCLUSIONS

The corrosion current density of high-speed steel was reduced by more than 2 orders of magnitude with hybrid PVD/ALD coating. Increase in corrosion current density and amount of rust in sample surface was only observed after all of the ALD nanolaminate and 100–200 nm of the top of the PVD CrN coating were removed by sandpaper grinding. Even with complete removal of the ALD nanolaminate from the top, the corrosion current density was less than half of that with the PVD CrN coating without surface wear. 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.¹⁰ In addition, (100) silicon die were employed as reference samples to confirm expected ALD thickness and density.¹⁰ Approximately 3 μ m 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 Al_2O_3/TiO_2 ALD nanolaminate was deposited on these CrN-coated steel disks with Picosun R-200 Advanced system. The deposition was done as reported previously,¹⁰ 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.¹⁰

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,¹⁰ 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,¹⁰ 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 G59-97.²⁴ 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

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 hightemperature 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 progression 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 Mira3; 13.0 kV acceleration voltage) after two final wear steps (LSV4-Wear3 and LSV5-Wear4). The presence and removal of ALD Al_2O_3 /TiO₂ nanolaminate was confirmed using EDS Ti K α peak at 4.5 keV, as described in a previous publication.¹⁰ 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). FIBmilled 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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Notes

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