Friction transitions and connections to third bodies for a Cd coating on steel substrate

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Abstract: Cd coating is used in aerospace industries from last five decades due to its sacrificial protection and lubrication properties. Although Cd coating is primarily used due to its sacrificial corrosion protection when applied on steel substrate, the added benefit of modifying the tribological behavior by acting as a lubricious layer gives it a leading-edge than other coatings. Often the measurement of friction coefficient (CoF) is reported as a value generated after full sliding cycle. This measurement of average CoF generally limits the study of local variation in CoF occurring within one sliding cycle, which can be significantly different with change in spatial position due to change in third body morphology. In this study, a linearly reciprocating sliding test is used to measure the CoF at a sampling rate of 800 Hz along the track length to generate triboscopic image with steel countersphere. The instantaneous CoF obtained with triboscopy is correlated with the wear track morphology using scanning electron microscope (SEM) and optical profilometer for variation in contact conditions. Tribological test performed in dry atmosphere shows an average CoF of 0.4 till the end of the test whereas with increase in relative humidity to 60%, the average CoF changes from 0.4 to 0.8 at the end of the test due to change in contact conditions. Soft Cd coating on low carbon steel substrate is used to study these variations in third body morphology.

Keywords: tribology; Cd coating; triboscopy; third body; aerospace coating; humidity

1 Introduction

Metallic coatings are commonly applied to a substrate material to prevent corrosion, either as a barrier or sacrificial layer. Sometimes, if it is a softer metal, the coating can act as a solid lubricant [1] and can be used in tribological applications. Cadmium (Cd) has been used extensively for its sacrificial corrosion protection of steel [1, 2] and for its solid lubricating properties. In terms of the tribology of Cd coatings, most researchers use standard tribology testings [3, 4], such as pin-on-disc, and report average friction versus cycle and overall wear or wear rate. Testing of this sort provides an overall description of the tribological behavior but makes it difficult to examine the mechanisms behind time and spatial dependent

variability of the friction or wear.

The presence of a metallic coating can alter the wear and friction coefficient (CoF) substrate material by modifying third body formation and its recirculation [5] at the contact interface. Furthermore, application of some soft metallic coating can act as solid lubricant [1], which lowers the CoF [3, 6, 7]. These third bodies formed with metallic coatings [8–11] are dependent on the chemo-mechanical properties of the coating and the substrate. Sacrificial Cd coating applied on aerospace materials is soft and acts as a lubricant [12], forming third bodies [3] at the contact region making it beneficial for its specific use. Though there have been recent work on metallic sliding [8–11, 13–16], the dynamic nature of the third bodies formed at the interface is difficult to understand and correlate with

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the change in CoF occurring within one cycle of the test. Available literature for *in situ* tribometry method [17] used to study the evolution of third body morphology is mostly limited to transfer film and not frequently used to correlate the change in CoF when transfer film is not present. In addition to *in situ* method, Korres and Dienwiebel [18] integrated additional surface topography measurement termed as ‘on-line’ tribometry to observe the surface morphology modifications contributing to friction changes. Although this method can be utilized to study the effect of wear track morphology on the CoF, it is only limited to correlation with average values and is difficult to correlate with spatial change in CoF observed within one cycle. Belin et al. [19–21] introduced a different method of measuring spatial CoF within one cycle by ‘triboscopy’ method, but is mostly coupled with electrical contact resistance method to correlate with the coating detrition, limited to non-metallic coating evaluation.

Apart from method of friction coefficient measurement, Mercer and Hutchings [22] and Klaffke [23] reported decrease in average CoF and wear rate of uncoated steel substrate with increase in relative humidity due to change in third body morphology. Apart from uncoated steel substrate, studies done by Cuong et al. [24], Buckley [25], Bowden and Tabor [26], Lancaster [27], and Elder and Eiss [28] also observed modification in tribological behavior with change in environmental conditions for coated materials. Though much work at varying relative humidity is done for steel and various types of coatings, the effect of ambient atmosphere on the tribological properties of Cd coated steel is limited to Ar atmosphere and air [6]. *In situ* studies done by Sriraman et al. [3] on Cd coated steel observed transfer film formation with frequent recirculation of Cd at the contact region. Studies done by Behera et al. [4] integrating *in situ* and triboscopy method for Cd coating observed similar temporal features occurring due to transfer film formation and subsequent change in CoF with change in transfer film morphology. Spectral analysis performed on similar features identified from the triboscopic imagery indicated change in third body morphology with progress of the test with some similarities between sapphire and steel countersphere. Jahanmir et al. [7] studied the change in atmospheric conditions from

air to argon with relation to wear rate, which decreased by three orders with 0.1 μm Cd coated steel.

In situ tribometry method helps in understanding the third body behavior especially transfer film morphology and correlating it with CoF. On-line tribometry also helps in understanding the morphology of the wear track but is limited to average CoF data. Triboscopy method introduced by Belin et al. [19, 20, 29] measures the CoF at high sampling rate and can be correlated with the spatial CoF changes occurring within one cycle. Previous work done with triboscopy method [19–21] is limited to temporal and spatial change of CoF for non-metallic coating, coupled with electrical contact resistance method to evaluate the coating failure. Combining triboscopy method with *ex situ* analysis can help in understanding the local spatial evolution of CoF at the contact interface within one cycle. The current work focuses on studying the triboscopic maps generated for metallic coatings at varying relative humidity and correlating them with third bodies. The tribological test was performed using a linearly reciprocating ball on flat surface tribometer with steel countersphere to correlate the instantaneous CoF changes with wear track features. Scanning electron microscope (SEM) and surface profilometry were performed to investigate the spatial distribution of instantaneous CoF due to wear track morphology change and correlating these changes with triboscopy method.

2 Experimental methodology

2.1 Plating conditions

The Cd plating on steel substrate is done in an industrial facility by immersing the steel plates in an alkaline cyanide based bath solution with CdO (20–30 g/L), NaCN (90–135 g/L), Na_2CO_3 (0–60 g/L), and NaOH (11–30 g/L). The substrate is grit-blasted and acid pickled before immersion, current density of 118–120 mA/cm^2 is applied during plating to generate a coating thickness of 15 μm in 5 min. After plating, the Cd coating is immersed in trivalent chromate conversion solution to generate a passivation layer. After the plating process, the 1018 Cd coated steel panel was baked at 200 $^\circ\text{C}$ for 24 h followed by hand shearing of plates to 50 mm $\times$ 50 mm coupons for tribological test.

2.2 Characterization

Investigation of the wear track and transfer film is done by SEM (FEI Inspect F-50) equipped with field emission gun and energy dispersive spectrometer (EDS). X-ray diffraction (XRD) of low hydrogen embrittling (LHE) Cd coating is done by Bruker discover D8 diffractometer with 2D HISTAR area detector, with a Co K α radiation (1.79 Å) at 35 kV and 45 mA and indexed using ICDD JCPDS Standards. Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27 IR spectrometer, United States) is used to study the chemical composition of wear track. White light interferometer (Wyko NT 8000, USA) is used to study the wear track morphology. The post processing of the data from the white light interferometer is done using Gwyddion v2.33.

2.3 Tribological test parameters

A linear reciprocating ball on flat tribometer [30] with a 440C steel countersphere of 3.175 mm radius was used. The average surface roughness of the steel countersphere before start of test was 0.135 μm . Dead weights were applied on the loading arm to set constant normal downforce. Track length of 20 mm and sliding speed of 14 mm/s for 2,000 cycles corresponding to a total sliding distance of 80 m is used for tribology tests. The parameters correspond to an initial maximum Hertzian contact stress of 390 MPa when a normal load is 1.314 N. Triboscopic images are generated by recording the CoF at a sampling rate of 800 Hz using a lateral piezo sensor. The spatial resolution of triboscopic image is 20 μm , which is smaller than the theoretical contact radius (33.1 μm) according to

Hertzian [31] two body contact theory. Instantaneous CoF (color coded) is plotted with track position in the Y-axis and cycle number in the X-axis to generate “Triboscopic image”. Transfer film and cross-section of LHE Cd coating is investigated with FEI F-50 field emission gun SEM equipped with an EDS detector.

3 Results

3.1 Coating characterization

The surface morphology of coating after electrodeposition (Fig. 1(a)) has a porous and layered structure due to agglomeration of fine spherical Cd globules. This type of spherical morphology for Cd is typical for electrodeposition processes, reported by Plieth [32]. Cross-section of the coating shown in Fig. 1(b) has non-uniform thickness and continuous with intermittent through thickness cracks exposing the steel substrate. High current density during the electrodeposition process is intentional to increase the through thickness cracks, which is beneficial for hydrogen removal during baking. The average thickness of coating is $11 \pm 2 \mu\text{m}$.

XRD characterization of the coating corresponds to Cd hexagonal close-packed (HCP) peaks as shown in Fig. 2. The absence of steel substrate peaks indicates masking of the substrate by Cd coating.

3.2 Tribology test and triboscopy

3.2.1 Average friction data at RH60

The evolution of CoF with increase in sliding distance for LHE Cd coating at 60% RH has four distinct

Fig. 1 SEM characterization of LHE Cd coating: (a) surface morphology and (b) cross-section.

Fig. 2 XRD phase characterization of LHE Cd coating.

regimes. The test begins with a CoF of 0.53 ± 0.04 up to 250 cycles (Regime I), followed by a period of lower CoF of 0.40 ± 0.06 (Regime II). The transition from Regime I to Regime II is very abrupt, occurring over only 1–5 cycles. Regime II is followed by a period of gradually increasing CoF (Transition Regime), eventually stabilizing at a CoF of 0.79 ± 0.03 (Regime III) starting from 1,400 cycle till the end of the test. Wear track and transfer film at each regime is investigated using SEM and EDS to understand the morphology and chemistry of the contact conditions in the four regimes.

Near the end of Regime I, the wear track at 200 cycles has smeared layers of Cd coating due to adhesive wear (Fig. 4(a)). Due to the soft and lubricating nature of Cd metal [33], plastic deformation of bulk Cd layer occurs during the initial cycles of sliding test. A Cd

Fig. 3 Average CoF vs. cycle # at 390 MPa contact stress and RH 60 indicating four regimes in tribological test.

transfer film with smearing marks is also observed on the countersphere (Fig. 4(b)). EDS analysis at two spots on the wear track (Fig. 4(c)) confirms presence of Cd, especially in Spot 1. In Spot 2, which appears as darker spots in the image (Fig. 4(a)) is identified as mixture of Cd and Fe peaks (substrate). Generally, the contrast in secondary electron (SE) image on the wear track depicts Fe substrate as dark patches and Cd coating as lighter patches. Surface profilometry obtained at the same position from the wear track shows presence of Cd at elevated regions, with darker regions (Fe substrate) in Fig. 4(a) at lower elevation than Cd.

Figure 5(a) is an SE image of a larger section of the wear track, showing minor evidence of adhesive wear. Surface profilometry captured in the same region overlapped with spatial variation of CoF (Fig. 5(b)) shows early stages of sliding. Small variations in topography and Cd content does not have major influence on the CoF, CoF is relatively stable across the track at a value of 0.44 ± 0.08 .

In Regime II at 500 cycles, the morphology of wear track (Fig. 6(a)) has significantly changed in appearance from Regime I (Fig. 4(a)). The wear track now has a more distinct contrast between dark and bright patches with wear debris scattered around the dark patches. Morphology of the transfer film (Fig. 6(b)) is different than that of 200 cycles (Fig. 5(b)). Transfer film formed during the initial cycle has been mostly removed from the countersphere with few wear debris particles adhering to the sides of the contact region. From EDS analysis on the wear track (Fig. 6(c)), dark patches on the wear track have a mixture of Cd and Fe peaks, whereas bright patch is predominantly Cd phase. The wear debris are also predominantly Cd. Surface profilometry (Fig. 6(d)) showed slight change in surface morphology from Regime I (Fig. 4(a)), with the most obvious difference being the wear debris. However, the distinct Fe peak for Spot 3 in Fig. 6(c) clearly indicates that the peak regions of substrate are mostly exposed substrate with some smeared or residual Cd remaining. Thus, in Regime II, contact conditions have become mixed, with pockets of Cd and thin layers of Cd on exposed steel substrate. This leads to a smaller contact size due to the higher elastic properties of steel, and the residual Cd provides lower shear strength, both conditions that would tend to decrease the CoF [34].

Fig. 4 (a) Wear track morphology indicating smeared Cd layer, (b) adhesive wear features on countersphere, (c) EDS analysis of wear track indicating presence of Cd and Fe substrate, and (d) three-dimensional (3D) profile of wear track at 200 cycles.

Fig. 5 Instantaneous CoF with surface profilometry in Regime I at 200 cycles.

For Regime II, SE image for a larger section of the wear track is shown in Fig. 7(a) and profilometry for the same region in Fig. 7(b). Similar to Fig. 6(a), the SE image reveals larger regions of dark contrast, corresponding to exposure of the Fe substrate over

a larger portion of the wear track. The surface profilometry shows most of the regions corresponding to a dark contrast in Fig. 7(a) are higher in height (Cd layer with Fe substrate peak shown in Fig. 6(c)). For one region on the wear track, roughly from 9.8 to 10.2 mm,

Fig. 6 (a) Wear track morphology with wear debris scattered on the wear track, (b) countersphere SEM image indicating removal of transfer film and attachment of wear debris, (c) EDS analysis of wear track showing presence of Cd and Fe substrate at different positions, and (d) 3D surface profilometry of wear track showing higher relative elevation of wear debris particles at 500 cycles.

Fig. 7 Instantaneous CoF with surface profilometry indicating lower average CoF at the position where a mix of Cd and steel substrate are present.

a lower instantaneous CoF is observed. This corresponds to the relatively large dark patch seen in the same position in Fig. 7(a). This is consistent with the mechanisms mentioned in the previous paragraph for lower friction in Regime II. The other variations in the instantaneous CoF in Fig. 7(b) are not easily tied to the features on the wear track (Fig. 7(a)). This is due to the resolution of the spatial friction technique and the fact that not all friction changes are expected to be directly correlated with wear track features [4]. Third body flows such as detachment of transfer film or adhesion of coating material to the counterface may also modify the CoF, complicating direct correlations, except for some special cases, like the one noted above.

At 1,000 cycles, which is shortly after the start of the Transition Regime (Fig. 3), the wear track and transfer film have again changed in appearance and morphology (Figs. 8(a) and 8(b)). Firstly, the wear debris is not found in the Transition Regime, and while some wear debris is ejected from the contact, some of the wear debris may also be compacted as a tribofilm on the worn surface. From EDS analysis of features in Fig. 8(a), relatively bright patches (Spot 1 and 2) show predominantly Cd peaks while darker features

show predominantly Fe peaks with less evidence of Cd (lower Cd to Fe peak ratio) than found in Regime II (Fig. 6(c)). The countersurface (Fig. 8(b)) shows formation of a compact transfer film with different morphologies than Regime I. The transfer film also has a scar mark at the middle, indicating contact of transfer film with a harder material, likely the Fe substrate. Profilometry of the wear track (Fig. 8(c)) shows no evidence of wear debris as seen in Fig. 6(d) for Regime II.

Figures 9(a) and 9(b) show the wear track morphology and surface profilometry over a larger area. In this instance, different from Regime II, most of the dark features in Fig. 9(a), which are Fe substrates, are correlated to higher features in Fig. 9(b). Thus, progression to higher CoF in the Transition Regime is predominantly due to removal of Cd, leaving the Fe substrate exposed (e.g., Spot 3 of Fig. 8(c)). This leads to hard-on-hard contact without any lubricious Cd layer in between, which is associated with higher friction. In Fig. 9(b), the position with lower CoF of ~ 0.2 is correlated to a section of the track that has predominantly bright features in Fig. 9(a). This is likely a region that has higher coverage of residual Cd

Fig. 8 (a) Wear track morphology with predominant steel substrate, (b) countersurface SEM image with scar mark, (c) EDS analysis of wear track, and (d) 3D surface profile of wear track showing presence of Fe at elevated regions at 1,000 cycles.

Fig. 9 Instantaneous CoF with surface profilometry indicating lower average CoF at the position where steel substrate is absent. (a) SE image of wear track and (b) surface profilometry of the same segment with overlapped CoF.

pockets with absence of Fe substrate. Otherwise, the spatial friction shows relatively higher CoF ($\sim 0.5\text{--}0.8$) than the previous two regimes.

At 1,500 cycles, which is the onset of Regime III in Fig. 3, the wear track (Fig. 10(a)), observed by SEM,

has mostly dark patches with small pockets of bright appearance. No evidence of wear debris is observed. The countersphere (Fig. 10(b)) has a circular wear scar (diameter of $550 \pm 40 \mu\text{m}$) at the centre of the steel ball with wear debris sticking at the periphery. From EDS

Fig. 10 (a) Wear track morphology with dominant Fe substrate, (b) countersphere imaging showing wear scar at the contact region, (c) EDS spot analysis of wear track, and (d) 3D surface profile at 1,500 cycles.

analysis on the wear track (Fig. 10(c)), bright features have a mixture of Cd and Fe, whereas the dark features have dominant Fe peak. Increased coverage of dark features signifies the change of contact to mostly steel-on-steel with Cd only present in the lowest features of the rough substrate. Higher shear strength of steel substrate (due to depletion of Cd from the surface) with increased area of contact (circular scar on the steel countersphere) increases the CoF [35]. A profilometry image of the wear track (Fig. 10(d)) indicates presence of steel substrate at relatively higher height (dark patches) with no wear debris present on the wear track.

The SE image and profilometry scan for a larger region of the wear track are shown in Fig. 11. The wear track has mostly dark features (Fig. 11(a)), indicating mostly steel substrate. Overall, the wear track is more homogeneous in height and the spatial friction (Fig. 11(b)) is more stable, albeit at much higher friction than any of the previous regimes.

Using the information obtained above from specific observations of the wear tracks and counterspheres conditions during the different regimes, the evolution of the contact conditions throughout the wear process becomes apparent. Some connections between these

changing contact conditions and the CoF can be made by inspecting the triboscopic image or spatial friction map for a test at 60% RH (Fig. 12). Regimes I, II, III, and Transition Regime, same as in Fig. 3, are indicated on the triboscopic image in Fig. 12. In Regime I, the transfer film is formed by adhesive transfer of Cd to the countersphere. However, for metallic wear, these early stages of wear are dynamic and periodical, transfer film material is lost or replenished [3, 4, 9, 13]. These lead to discrete events of increased friction lasting a few cycles with no significant spatial features. That is, the friction is increased all along the wear track as the cause of the frictional rise is associated with third body flows occurring with the transfer film attached to the ball, which traverses the entire track [4]. As described above, the low average CoF (Regime II) is primarily due to favorable contact conditions of steel-on-steel with thin layers of Cd smear at the interface. However, looking at the spatial friction in Regime II (Fig. 12), there is a mixture of both temporal and spatial features. The temporal features found in Regime I are more frequent, as there are still changes occurring to the transfer film, mostly by removal (Fig. 4(b)). The spatial features are due to the variation in surface roughness of the substrate. As can be seen

Fig. 11 Instantaneous CoF with surface profilometry indicating higher average CoF throughout the wear track.

Fig. 12 Triboscopic image superimposed with average CoF at RH60.

in the early part of Regime II, the CoF across the track is mostly in the range of 0.35 with discrete positions having higher CoF in the range of 0.5–0.6. Other than the temporal event around 450–500 cycles, most of Regime II is about ‘spreading’ of the higher friction regions. This spreading that occurs, most evident in cycles 700–900, is due to Cd pockets being depleted and gradual loss of the lubricating condition of Cd smeared onto steel asperities. Eventually this loss of Cd becomes significant enough that the contact conditions across the wear track are mostly steel-on-steel, which leads to the Transition Regime and eventually Regime III. Within the Transition Regime, there is some renewed formation of transfer film (Fig. 8(b)) which can explain the more temporal type features occurring at ~950–1,100 cycles with a friction rise and then drop. Eventually at cycle 1,100, features in the tribomage become more spatial in nature, which is consistent with the lack of transfer film in Regime III (Fig. 10(b)). For most of the later stages of Transition Regime and Regime III, the contact is steel-on-steel with only very thin layers of Cd. When discrete drops in friction occur (e.g., cycle 1,880, 1,910), it is likely due to adhesive transfer of Cd from the remaining pockets in the lowest valleys of the substrate roughness.

At the end of the test (2,000 cycles), the change in instantaneous spatial friction identified from the triboscopic image is roughly correlated with wear track morphology, investigated by SEM and profilometry at different positions. Two different regions (Fig. 13) are marked after end of test to investigate the difference in instantaneous CoF values. These two regions were selected as over the length scale defined by the contact size (~550 μm), an average of the instantaneous friction in these two regions were found to be different

using a Student’s t-test (p value is the probability that the results from data occurred by chance. It is less than 0.001. In this case, it shows the mutual exclusiveness of the two regions). Other changes in friction across the track might be associated with topographic features but the length scale of the morphology of the wear track is finer than the contact size, leading to difficulty in making concrete connection between every frictional change and a wear track feature [4]. With this limitation in mind, there are distinct differences observed between the two wear track region associated with the two points of higher and lower friction in Fig. 13(a). Similar to results above, the combination of SEM (showing dark features as Fe substrate and bright features as Cd pockets) with optical profilometry can be used to understand when lubrication by Cd is possible. In Fig. 13(b), the height difference between the high and low points of the surface profile is large (~8–10 μm), which means the counterface is mostly in contact with tall steel asperities with minimal opportunity to encounter Cd remaining in the pockets. This leads to a higher friction, of steel-on-steel contact with very minimal opportunity of Cd lubrication. Comparing to Fig. 13(b), which is the region where lower CoF is observed, the wear track morphology is less rough, with only a few microns between high and low points. This provides an opportunity to have Cd in contact with the counterface, which would lower the CoF, consistent with the spatial friction measurements in Fig. 13(c).

3.2.2 Average friction and spatial friction at RH30

Often tribological behavior of materials changes with variation in relative humidity. To better understand the modification of contact condition with change in relative humidity, spatial evolution of CoF at lower

Fig. 13 (a) CoF with track position at the end of the test (2,000 cycles) showing: (b) elevated Fe substrate and (c) scattered and less elevated Fe substrate.

humidity is also investigated. The trend of CoF with sliding cycles and the features in the triboimage (Fig. 14) at RH30 are qualitatively similar to RH60. For this reason, characterization of wear track conditions is only presented for the end of the test. From the triboscopic image and average CoF, the contact conditions are within the “Transition Regime” at the

end of the test (Fig. 14) and does not enter to Regime III. Many of the same trends are observed, with discrete temporal events in Regime I that are associated with adhesive wear of Cd and formation of transfer films. In Regime II, the decrease in relative humidity to RH30 increases the occurrence of temporal features in the triboscopic image compared to RH60 (Fig. 12). This may be due to various types of third body flows, since in a previous work with similar test conditions, frequent wear debris attachment and detachment events were observed [4]. Overall, the frequent temporal events, which are correlated mostly with recirculation flows [4, 20], delayed the onset of steel-on-steel contact. After 2,000 sliding cycles at RH30, the contact has only reached the Transition Regime.

At the end of the test at RH30, the triboscopic image (Fig. 14) shows that the spatial distribution of the CoF has become mostly homogeneous compared to the significant fluctuations observed for most of this regime. Figure 15 shows the instantaneous CoF vs. track position for the final cycle of the test. Two regions are compared, one with slightly higher friction than the other, enough to pass a Student’s t-test. The percentage overlap between the mean of the selected two regions is approx. 15 at RH30. The high instantaneous CoF region (Fig. 15(a)) is associated with scattered wear debris at the contact interface with prominent contact to the steel substrate (Fig. 15(b)). The lower friction region (Fig. 15(c)) does not have significantly different features compared to that with higher friction. Overall, the contact conditions in this Transition Regime are similar to RH60, with mixed contact conditions of steel-on-steel with Cd pockets intermittently interacting with the counterface.

Fig. 14 Triboscopic image overlapped with average CoF at RH30.

Fig. 15 (a) CoF with track position at end of test (2,000 cycles) showing: (b) elevated Fe substrate and (c) Cd coating present at the contact interface.

3.2.3 Average friction and spatial friction at RH0

The decrease in relative humidity to 0% or dry air (RH0) leads further delay in the onset of steel-on-steel contact (Fig. 16). Discrete and reoccurring temporal features associated with transfer film activity, typical of Regime I, lasted for 148 cycles. The higher overall

friction and rapid occurrence of temporal variations in friction should be associated with greater adhesive wear, which is expected for dry metallic contacts [4]. This would explain the faster progression to Regime II. However, compared to RH60 and RH30, the test at RH0 mostly resulted in Regime II lasting till the end of the test (2,000 cycles).

The change in instantaneous CoF with respect to track position at the end of the test is investigated as shown in Fig. 17(a). The fluctuation in instantaneous CoF (overlap between the mean of Region 1 and Region 2 is approx. 90%) within one cycle is less as compared to RH60 and RH30. Student's t-test confirmed the regions to be mutually exclusive. Figures 16(b) and 16(c) show the wear track morphology of the coating (with average CoF of 0.5) in Regime II. The wear track morphology observed by SEM indicates presence of steel substrate, but the contact interface has scattered wear debris and patches of Cd. Wear debris scattered on the wear track till the end of the test delays the onset of steel-on-steel contact. No significant differences were observed in the two positions studied.

3.3 Wear track analysis

Table 1 shows the no. of cycles required for onset of different regimes after three tests at varying relative humidity. With decrease in relative humidity, the on-set to Regime II is quicker. However, the onset to Regime III is faster at higher humidity. In fact, at RH0 and RH30, the on-set of steel-on-steel contact (Regime III) is absent and in one test at RH0 (shown in Figs. 16 and 17), there is no evidence of the Transition Regime even after 2,000 cycles.

Fig. 16 Triboscopic image overlapped with average CoF indicating frequent occurrence of transfer film as compared to RH60 and RH30.

Fig. 17 (a) CoF with track position at end of test (2,000 cycles) showing (b) and (c) wear debris scattered on the surface with steel and Cd.

Table 1 No. of cycles required for onset of different regimes at varying relative humidity. Values are given for each individual test because the progression to the different regimes is not highly repeatable.

Relative humidity (%)	Cycles to Regime II	Cycles to Transition Regime	Cycles to Regime III
0	148, 175, 264	1,878, 1,754, —	—
30	216, 229, 272	1,554, 1,436, 1,283	—
60	267, 286, 221	896, 863, 901	1,570, 1,401, 1,338

The FTIR spectra of wear track after 1,000 cycles of sliding test is shown in Fig. 18. Based on the results presented in Table 1, this would correspond to Regime III conditions for RH60 and Regime II conditions for RH30 and RH0. FTIR spectra peaks show characteristic peaks for oxide and hydroxide formed on the wear track. Characteristic peak for $\text{Cd}(\text{OH})_2$ [36] is at $1,628\text{ cm}^{-1}$ (overlaps with Fe_3O_4) and at $3,554\text{ cm}^{-1}$ (overlaps with Fe_3O_4). With increase in relative humidity in the atmosphere, the relative percentage (intensity) of cadmium hydroxide and iron oxide formed on the wear track increases. The peak at $2,929\text{ cm}^{-1}$ corresponds to iron oxide [37, 38]. The broad peak identified at $3,400$ and $1,635\text{ cm}^{-1}$, respectively, was due to ferrihydrite peak from the substrate steel [39]. The presence of the oxides and hydroxides can play a role in third body flows by modifying the

Fig. 18 FTIR spectra of wear track.

mechanical properties and/or the cohesiveness of the third bodies. In the case of RH0, where debris persists on the wear track for longer times, the particles can separate the contact between the counterface and Cd coating/substrate, delaying the onset of steel-on-steel contact. The lower amount of hydroxide formation at RH0 and intermittent sharp changes in CoF indicates frequent recirculation of wear debris at the contact interface. With increase in relative humidity, the amount of hydroxide formation increases. This leads to a change in contact conditions, decreasing the cycles required for the onset of steel-on-steel contact with increase in relative humidity. As compared to Cd coating forming hydroxide peaks, steel substrate hydroxide formation is similar irrespective of the change in relative humidity. This leads to the inference that cadmium hydroxide, not the steel substrate hydroxide, plays primary role in the tribological differences with change in humidity.

4 Discussion

Due to low hardness of Cd coating, initial run-in period is associated with extensive plastic deformation and adhesive wear leading to high CoF. The bulk layer of Cd is removed within 150–300 cycles irrespective of the relative humidity. The presence of a thin layer of Cd at the contact interface between counterface and steel substrate promotes reduction in CoF. Similar observation was reported by Jahanmir et al. [7], where the presence of 0.1 μm thick Cd coating reduces CoF and wear as compared to uncoated steel. This can be correlated with the current study, where the bulk layer of Cd is gradually removed until a steady thickness layer is formed to increase the wear resistance when a soft coating is applied on hard substrate [6].

The difference in average CoF with progress of the test is due to the modification in third body morphology at the contact interface. Tribological behaviour evaluated for Cd coating at RH60 has four distinct regions of average CoF as shown in Fig. 19. Regime I is associated with high CoF due to formation of the transfer film by adhesive wear, increasing the area of contact and friction force, which is also observed as temporal features in triboscopic image [4]. When the bulk layer of Cd is removed, the average

Fig. 19 Schematic representation of change in average CoF with change in relative humidity.

CoF decreases due to mixed mode (Regime II). In Regime II, presence of wear debris and Cd coating act as a lubricant and decrease the average CoF. The subsequent removal of the thin Cd layer observed in Regime II is gradual, signifying the stability of Cd layer. The transition from Regime II to Regime III is slow, where the Cd at the contact interface is progressively removed with increase in sliding cycles. As the islands of Cd is depleted, the average CoF increases, and is termed as Transition Regime. Regime III is associated with the depletion of the Cd pockets leading to increased lateral force due to increase in shear strength by steel-on-steel contact. Similar features were also observed by Sriraman et al. [3], where they observed initial smoothing of the wear track due to adhesive wear, followed by the appearance of the substrate steel during later cycles. The decrease in relative humidity modifies the contact conditions, leading to decrease in the number of steady state friction regimes as shown in Fig. 19.

Spatial features observed from the triboscopic images at the end of the tests helped in better understanding of instantaneous CoF. At RH60, the change in instantaneous CoF at Regime III is associated with the presence and absence of Cd coating at the contact interface. The increase in instantaneous CoF is associated with depletion of Cd at the contact interface and protuberance of steel substrate; whereas the regions with dominant Cd islands decrease this instantaneous CoF due to lubricating properties. At

the end of RH30, the average CoF is in the Transition Regime where the low instantaneous CoF is associated with presence of Cd layer at an elevated point on the wear track, whereas the presence of the steel substrate increases the average CoF. At the end of RH0, the average CoF is at Regime II, where the wear debris is scattered throughout the contact interface and the steel countersphere has a mixed mode contact of Cd and steel. This leads to a more uniform instantaneous CoF as compared to that at RH30 and RH60. Similar triboscopic studies were done by Wahl et al. [29] for MoS₂ coatings, where the degradation of the coating is correlated with change in CoF. The study illustrated that with progressive removal of MoS₂ coating at some locations on the wear track, the local CoF increased. Belin et al. [19, 21] also performed similar studies on polymer coated surface by micropatterning to observe time-dependant local phenomena of wear. Similar results to the current study were observed when a combination of electrical contact resistance and triboscopy is used, and spatial distribution of CoF within one cycle can be observed from the triboscopic image.

Humidity changes have a significant effect on the tribological behavior of Cd coatings on steel substrate. From the wear track analysis by FTIR, it was found that presence of oxides and hydroxides groups formed during the tribological test can modify the tribological properties. The change in chemical composition can significantly vary the CoF evolution. With increase in relative humidity, the amount of cadmium hydroxide phase increases considerably, leading to modification of the contact conditions. Tribological studies done by various authors [24, 27, 40] on the effect of relative humidity shows similar results, where a change in CoF was observed with modification of moisture content of the environment during the sliding wear test.

5 Conclusions

The tribological behavior of Cd coating at varying relative humidity was studied using traditional pin-on-disk tests with post-characterization, and also with spatially resolved friction measurements (i.e., triboscopy). The major effects of changes in relative humidity were the differences in average CoF and the evolution of the average friction with time. Four

‘Regimes’ of friction behavior were identified for the tests at RH60. While the regimes were also observed for lower relative humidity tests, their onset was slower and were not always observed depending on test duration. Based on post-test characterization, the frictional differences for the four Regimes were linked to changing contact conditions. High CoF at Regime I was associated formation of transfer film by adhesion. Low average CoF at Regime II was associated with a mixed mode contact between the steel countersphere and thin Cd layer on steel substrate. The gradual depletion of Cd coating at the contact interface leads to initiation of the Transition Regime and subsequent change to a high CoF (Regime III) associated with contact of steel countersphere with steel substrate. The primary effect of increasing humidity was an acceleration of the removal of the soft Cd coating, leading to steel-on-steel contact earlier in the test.

Using triboscopy, instantaneous and spatial differences in CoF were correlated to variations in wear track morphology. Generally speaking, many events where spatial CoF was different could be attributed to the availability of Cd at the contact interface, whether it be remaining coating, pockets of Cd in valleys of roughness or redeposited Cd through third body flows. This presence of Cd decreased the local CoF.

FTIR analysis of the wear track showed that there are chemical differences in third bodies as a function of humidity. At higher relative humidity, Cd hydroxide formation was linked to the more rapid progression through different regimes. Hydroxide formation could modify the near surface mechanical properties, the adhesion, and cohesion of third bodies to the counterface and themselves, respectively. Lower amount of Cd hydroxide at RH0 resulted in extended time spent in Regime II, where oxide particles persisted in the wear track rather than complete exposure of the steel substrate observed for the higher RH tests.

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References

- [1] Štěpina V, Veselý V. *Lubricants and Special Fluids*. New York (USA): Elsevier, 1992.
- [2] Sriraman K R, Brahimi S, Szpunar J A, Osborne J H, Yue S. Characterization of corrosion resistance of electrodeposited Zn–Ni Zn and Cd coatings. *Electrochim Acta* **105**: 314–323 (2013)
- [3] Sriraman K R, Strauss H W, Brahimi S, Chromik R R, Szpunar J A, Osborne J H, Yue S. Tribological behavior of electrodeposited Zn, Zn–Ni, Cd and Cd–Ti coatings on low carbon steel substrates. *Tribol Int* **56**: 107–120 (2012)
- [4] Behera P, Sriraman K R, Chromik R R, Yue S. Combining in situ tribometry and triboscopy to understand third body behavior of a Cd coating. *Surf Topogr Metrol Prop* **5**(1): 014001 (2017)
- [5] Berthier Y. Maurice Godet's third body. *Tribol Ser* **31**: 21–30 (1996)
- [6] Jahanmir S, Abrahamson II E P, Suh N P. Sliding wear resistance of metallic coated surfaces. *Wear* **40**(1): 75–84 (1976)
- [7] Jahanmir S, Suh N P, Abrahamson II E P. The delamination theory of wear and the wear of a composite surface. *Wear* **32**(1): 33–49 (1975)
- [8] Lee L, Régis É, Descartes S, Chromik R R. Fretting wear behavior of Zn–Ni alloy coatings. *Wear* **330–331**: 112–121 (2015)
- [9] Shockley J M, Descartes S, Irissou E, Legoux J G, Chromik R R. Third body behavior during dry sliding of cold-sprayed Al–Al₂O₃ composites: In situ tribometry and microanalysis. *Tribol Lett* **54**(2): 191–206 (2014)
- [10] Zhang Y Y, Shockley J M, Vo P, Chromik R R. Tribological behavior of a cold-sprayed Cu–MoS₂ composite coating during dry sliding wear. *Tribol Lett* **62**(1): 9 (2016)
- [11] Stoyanov P, Chromik R R, Goldbaum D, Lince J R, Zhang X L. Microtribological performance of Au–MoS₂ and Ti–MoS₂ coatings with varying contact pressure. *Tribol Lett* **40**(1): 199–211 (2010)
- [12] Heath A N, Horwedel L C. Solid lubricant film resistant to corrosion. U.S. Patent 3051586A, Aug. 1962.
- [13] Shockley J M, Strauss H W, Chromik R R, Brodusch N, Gauvin R, Irissou E, Legoux J G. In situ tribometry of cold-sprayed Al–Al₂O₃ composite coatings. *Surf Coat Technol* **215**: 350–356 (2013)
- [14] Sriraman K R, Manimunda P, Chromik R R, Yue S. Effect of crystallographic orientation on the tribological behavior of electrodeposited Zn coatings. *RSC Adv* **6**(21): 17360–17372 (2016)
- [15] Zhang Y Y, Brodusch N, Shockley J M, Gauvin R, Chromik R R. Sliding-induced microstructure of cold-sprayed copper coating observed by electron channeling contrast imaging. *Microsc Microanal* **20**(S3): 2104–2105 (2014)
- [16] Stoyanov P, Chromik R R, Gupta S, Lince J R. Micro-scale sliding contacts on Au and Au–MoS₂ coatings. *Surf Coat Technol* **205**(5): 1449–1454 (2010)
- [17] Chromik R R, Strauss H W, Scharf T W. Materials phenomena revealed by *in situ* tribometry. *JOM* **64**(1): 35–43 (2012)
- [18] Korres S, Dienwiebel M. Design and construction of a novel tribometer with online topography and wear measurement. *Rev Sci Instrum* **81**(6): 063904 (2010)
- [19] Belin M. Triboscopy: A new quantitative tool for micro-tribology. *Wear* **168**(1–2): 7–12 (1993)
- [20] Belin M, Lopez J, Martin J M. Triboscopy, a quantitative tool for the study of the wear of a coated material. *Surf Coat Technol* **70**(1): 27–31 (1994)
- [21] Belin M, Martin J M. Triboscopy, a new approach to surface degradations of thin films. *Wear* **156**(1): 151–160 (1992)
- [22] Mercer A P, Hutchings I M. The influence of atmospheric humidity on the abrasive wear of metals. *Wear* **103**(3): 205–215 (1985)
- [23] Klaffke D. On the repeatability of friction and wear results and on the influence of humidity in oscillating sliding tests

- of steel-steel pairings. *Wear* **189**(1–2): 117–121 (1995)
- [24] Cuong P D, Ahn H S, Yoon E S, Shin K H. Effects of relative humidity on tribological properties of boron carbide coating against steel. *Surf Coat Technol* **201**(7): 4230–4235 (2006)
- [25] Buckley D H. *Surface Effects in Adhesion, Friction, Wear, and Lubrication*. New York (USA): Elsevier, 1981.
- [26] Bowden F P, Tabor D. *The Friction and Lubrication of Solids*. Oxford (UK): Clarendon Press, 2001.
- [27] Lancaster J K. A review of the influence of environmental humidity and water on friction, lubrication and wear. *Tribol Int* **23**(6): 371–389 (1990)
- [28] Elder Jr J A, Eiss Jr N S. A study of the effect of normal stiffness on kinetic friction forces between two bodies in sliding contact. *ASLE Trans* **12**(4): 234–241 (1969)
- [29] Wahl K J, Belin M, Singer I L. A triboscopic investigation of the wear and friction of MoS₂ in a reciprocating sliding contact. *Wear* **214**(2): 212–220 (1998)
- [30] Strauss H W, Chromik R R, Hassani S, Klemberg-Sapieha J E. *In situ* tribology of nanocomposite Ti-Si-C-H coatings prepared by PE-CVD. *Wear* **272**(1): 133–148 (2011)
- [31] Johnson K L. *Contact Mechanics*. Cambridge (UK): Cambridge University Press, 1987.
- [32] Plieth W. Nucleation and growth of metals. In *Electrochemistry for Materials Science*. Plieth W, Ed. Amsterdam: Elsevier, 2008: 195–229.
- [33] Tabor D. *The Hardness of Metals*. Oxford (UK): OUP Oxford, 2000.
- [34] Singer I L. Solid lubrication processes. In *Fundamentals of Friction: Macroscopic and Microscopic Processes*. Singer I L, Pollock H M, Eds. Dordrecht (Netherlands): Springer, 1992: 237–261.
- [35] Blau P J. *Friction Science and Technology: From Concepts to Applications*. 2nd edn. London (UK): CRC Press, 2008.
- [36] Mazaheritehrani M, Asghari J, Lotfi Orimi R, Pahlavan S. Microwave-assisted synthesis of nano-sized cadmium oxide as a new and highly efficient catalyst for solvent free acylation of amines and alcohols. *Asian J Chem* **22**(4): 2554–2564 (2010)
- [37] Gu B H, Schmitt J, Chen Z H, Liang L Y, McCarthy J F. Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environ Sci Technol* **28**(1): 38–46 (1994)
- [38] Hwang S W, Umar A, Dar G N, Kim S H, Badran R I. Synthesis and characterization of iron oxide nanoparticles for phenyl hydrazine sensor applications. *Sens Lett* **12**(1): 97–101 (2014)
- [39] Russell J D. Infrared spectroscopy of ferrihydrite: Evidence for the presence of structural hydroxyl groups. *Clay Miner* **14**(2): 109–114 (1979)
- [40] Lee L, Behera P, Sriraman K R, Chromik R R. Effects of humidity on the sliding wear properties of Zn–Ni alloy coatings. *RSC Adv* **7**(37): 22662–22671 (2017)

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