New Methods to Examine Formation and Properties of Interfacial Films in Sliding Contacts

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Motivation

• To understand and control lubrication, friction, and wear processes, we need to know what is happening \textit{in the contact} (chemistry, dynamics, mechanics....)

Approach

– develop tools, techniques to explore the buried interface
## Approaches to studying buried interfaces

**Ex Situ Analyses**
- Optical Interferometry
- EDS
- AES
- XPS
- Raman

**In Situ Triboscopy**

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**“In Situ” Surface Analyses**
- UHV: $H_2S$, $O_2$, $SO_2$
- AES
- XPS

**In Situ Raman Tribometry**
- Optical Microscope
- Raman Spectrometer

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1. *In Situ* Raman Tribometry

Goal: Identify Third Bodies in Sliding Interface and Relate them to Friction and Wear Evolution

2. Scanning Nanomechanics
Third-body Effects in Sliding Contacts

Tribochemical build-up of third-body material
Sliding between layers of third-body material: Velocity Accommodation
Breakdown of transfer films: ejection of debris

Test Type: Reciprocal Sliding  Load: 24 N
Counterface: Glass Hemisphere (R = 6.25 mm)  Track Length: 6 mm / 4 mm
Sliding Speed: 1 mm/s  Relative Humidity: 0% to 60%
Temperature: ≈ 24°C
Raman Tribometer System

Video and VCR

Focus and Positioning

Microscope and CCD Camera

Micro-Raman System

Reciprocating Stage
Examples: 5 Simple Questions

1. Can we correlate *chemistry* in the contact to friction?
2. What is the *thickness* of the interfacial films?
3. Where does sliding take place (*what interface*)?
4. Can we correlate *dynamics* in the contact to friction events?
5. What are the *mechanical properties* of the interfacial films?
Pb-Mo-S Coating Characteristics

Deposition Technique: Ion Beam Deposition (IBD)

Substrate: 35 nm TiN/M50 Steel  Film Thickness: 320 nm

Film Structure: Amorphous (XRD, TEM, Raman)

Film Composition: 12% - 15% Pb

Wahl et al., *Wear* (1999)
Chemistry of Third Body

Raman Reference Spectra:

- Crystalline MoS$_2$ through glass
- Glass hemisphere
- Crystalline MoS$_2$
- As-deposited Pb-Mo-S Coating

Wave Number [cm$^{-1}$]

Cycle 0

To video or Raman microscope objective

Hemisphere

Coating

50 µm
Results Pb-Mo-S: Low Humidity Testing

Transfer Film Development

Cycle 80
Cycle 500
Cycle 870

Average Friction Coefficient

Cycles

Transfer Film Development
Tribochemical formation of third-body material

In situ Raman shows formation of MoS$_2$ during low-humidity sliding

Confirms ex situ Raman and HRTEM showing formation of crystalline MoS$_2$ during low-humidity sliding:

Wahl, Dunn, Singer
Wear 230 (1999) 175-183
5 Simple Questions:

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**In situ** measurement of transfer film thickness using Raman spectroscopy

- DLC coating exhibits a different Raman spectrum than its respective transfer films
- Consistent with shifts observed by *ex situ* Raman spectroscopy

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Profilometry and Raman Across Transfer Films

Raman G-peak Intensity (a.u.)

Position (µm)

Transfer Film Thickness (µm)

Raman Shift (cm⁻¹)

Intensity (a.u.)
Model: *Ex Situ* Raman Intensity vs. Transfer Film Thickness

Applying Beer’s Law:

\[
I_f(\nu_f) = \int_0^t I_f(z, \nu_f) \, dz = I_\infty f(\nu_f)(1-e^{-2t/\lambda_f})
\]

\[
I_S(\nu_S) = \int_{R}^{\infty} I_S(z, \nu_S) \, dz = I_\infty S(\nu_S)(e^{-2t/\lambda_f})
\]

\(\lambda = \) optical mean free path (assume \(\lambda \neq \lambda (\nu)\))

\(I_\infty f, I_\infty S = \) Raman intensity for thick layers

\(\lambda << t_\infty, R\)

\(\nu_f, \nu_S = \) frequency (usually at a peak value)

assume normal incidence (\(\alpha = 90^\circ\))
Raman Mean Free Paths for Transfer Films

<table>
<thead>
<tr>
<th>Profiles</th>
<th>$\lambda_f$ (nm)</th>
<th>±</th>
<th>$\lambda_f$ (nm)</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry Air</td>
<td></td>
<td>Ambient Air</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>490 22</td>
<td></td>
<td>536 32</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>476 18</td>
<td></td>
<td>496 24</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>--</td>
<td></td>
<td>510 26</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>502 24</td>
<td></td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Mean±S.D.</td>
<td>489 13</td>
<td></td>
<td>514 20</td>
<td></td>
</tr>
<tr>
<td>Coating</td>
<td>245±26 nm</td>
<td></td>
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</tbody>
</table>

The thickness of the transfer film can be calculated from $I(\nu)$ once $I_\infty f$, $I_\infty C$ and $\lambda_f$ are known.
In situ measurement of transfer film thickness

How thick is the transfer film?

$I(\nu) = I_\infty^f(\nu)(1-e^{-2t/\lambda f}) + I_\infty^c(\nu)(e^{-2t/\lambda f})$

Convert intensities to thickness:

$t(\nu) = \left(\frac{\lambda f}{2}\right) \ln \left[ \frac{I_\infty^C(\nu) - I_\infty^f(\nu)}{I_m^f(\nu) - I_\infty^f(\nu)} \right]$
Use Newton’s Rings to monitor third body thickness

- Fast building of thick third body transfer film of Ti-Mo-S coatings in ambient condition

Gun Lee
5 Simple Questions:

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Rheological Models for Velocity Accommodation in Thin Films

Applied Load

Intrafilm Flow

Thin Film

Interfacial Sliding

Sliding Velocity

Interfacial Sliding with Third Body

Godet, Wear, 100 (1984), 437-452

Berthier, Godet, Brendle, Trib. Trans. 32 (1989), 4, 490-496
DLC vs. Sapphire Friction Behavior: Run-in

Transfer Film Formation

Cycle 0

Cycle 8 $\mu=0.065$

Dry (3%RH) Air
Low (0.7 GPa) Stress

Contact region

Wear Track

Sliding

50 $\mu$m
Steady-State Friction

- Cycle 1300 $\mu=0.035$
- Cycle 1605 $\mu=0.036$

- Ambient (45%RH) Air
- High (1.1 GPa) Stress

“Thick” transfer film

Center of transfer film thins

100 $\mu$m
Friction Spiking - Ambient Air

3 examples of transfer film depletion and recovery

Ambient Air
High Stress
(Continued)

Cycle 1674
\( \mu = 0.046 \)

Cycle 1730
\( \mu = 0.038 \)

Cycle 1798
\( \mu = 0.044 \)

Cycle 1925
\( \mu = 0.039 \)

Cycle 1938
\( \mu = 0.071 \)

Cycle 2000
\( \mu = 0.047 \)

[Graph showing friction variation over cycles with images of samples at different cycles]
3rd body thickness and friction - *in situ results*

Steady-state friction
- controlled by interfacial sliding
- lost when transfer film thins and first body counterface makes contact w/coating surface

High friction sliding
- Combination of interfacial sliding & shearing, detachment, and/or recirculation of the third bodies

Scharf and Singer (Trib. Letts., 2003)

![Graph showing friction versus sliding cycles for DLC vs sapphire](image)
Third body dynamics and friction

In Pb-Mo-S coating, we see no motion
In transfer film for low humidity sliding

Dvorak, Wahl, Singer
Third Body Motion During Humidity Transition

Typical Contact Area

- Compacted Debris
- Moving Material
- Stationary Material

200 microns
Observed Velocity Accommodation Modes

Interfacial Sliding with Third Body

Shear / Extrusion of Third Body Material
Third Body Motion During Humidity Transition

From video, we can measure the shear/extrusion velocities of third bodies.
Viscoplastic behavior of Pb-Mo-S thirdbody transfer film

Shear stress = \( \frac{\text{lateral force}}{\text{contact area}} \)

\[ \tau = \frac{F_L}{\pi a^2} \]

Strain rate = \( \frac{\text{extrusion velocity}}{\text{film thickness}} \)

\[ \dot{\gamma} = \frac{v_x}{\Delta z} \]

- Area of contact is measured using \textit{in situ} image data
- Film thickness is measured from \textit{in situ} interferometry (Newton’s rings)
- Shear/extrusion velocities are measured using video playback
Viscoplastic Response of Transfer Film

\[ \tau = \tau_0 + k(\dot{\gamma}) \]

\( \tau_0 \sim 20 \text{ MPa} \)
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Scanning Nanomechanics


Nanomechanics of Worn Surfaces (tracks, balls)

Indentations on the wear track and transfer material

Load-displacement curves

Gun Lee
Indentation procedures for transfer film

100 µm

*In situ* image

Indentation map/plan

35 µm

(II)

(IV)

(I)

(III)

(V)

20 µm

Scanned image

Indentation

Measuring film thickness
Transfer film thickness

(I) = 380 nm
(II) = 250 nm
(III) = 400 nm
(IV) = 500 nm
(V) = 150 nm

(h/t = ~ 0.1)
Summary

*In Situ* Raman tribometry can explore friction changes and quantitatively monitor transfer film health and thickness in solid lubricants:

- Low friction (at low humidity) determined by interfacial shear strength
  - Velocity accommodation through *interfacial sliding*
  - Low friction correlated with stable third body and chemistry

Friction transitions (spikes)
  - Correlated to loss of transfer film
  - *In situ* measurement of transfer film thickness enables prediction of high friction events, failure
Conclusions – cont.

High friction (at high humidity) determined by increasing interfacial shear strength

- Velocity accommodation through both interfacial sliding and shear/extrusion of transfer film
- Dynamics are complex but modelable (know shear strength, thickness, strain rate)

In progress: Mechanics of transformed interfaces
"Tribo" Materials Research Paradigm

- Processing
- Characterization
- Performance
- Tribotesting

Thin film analysis
Characterization
modeling

In contact synthesis

Optical Microscope
Raman Spectrometer

$f(x,t)$