Tribology in Full View, From Atomic Transfer Layers to Hip Replacements

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“…the greatest source of new energy is the energy we waste today.”

Samuel Bodman, U.S. Secretary of Energy, 2008
Friction ~5% of GDP

40-50% of power in a new auto engine

http://www.fueleconomy.gov
Tribology: The study of friction. From Greek “tribein” to rub

Empirically, we do better in reducing friction than the Egyptians, but we certainly do not understand everything.

Friction is from plastic/elastic sliding of asperities

Experimental Approach
Simple Examples

Sliding of a W tip on Au: Ploughing

Liquid-like\textsuperscript{1} deformation of Au (surface diffusion dominated)

\textsuperscript{1}D.W. Pashley, M.H. Jacobs, M.J. Stowell, T.J. Law, Phil Mag \textbf{10}, 127 (1964);
Tribological Recrystallization

Y. Liao et al, Phil Mag Letts 90 (2010) 219
Localized tribochemical etching by water
$C + H_2O \rightarrow CO + H_2$ (water-gas shift)

Sliding on NFC in H₂

Minimal wear, hydrogen passivation
Consistent with “classic” tribochemical opinion

Arthritis and Hip Replacement

Cause of Disability (U.S. 2005)

- 8.5 M (19%) Arthritis or rheumatism
- 7.5 M (17%) Back or spine problems
- 6.0 M (14%) Mental or emotional problem
- 5.0 M (12%) Deafness or hearing problem
- 4.5 M (11%) Blindness or vision problem
- 3.5 M (9%) Cancer
- 3.0 M (7%) Heart trouble
- 2.5 M (6%) Lung or respiratory
- 2.0 M (5%) Diabetes
- 1.5 M (4%) Stiffness
- 1.0 M (3%) Stroke
- 0.5 M (1%) others
Hip Joint

acetabulum cup

femoral head

femoral stem

www.zimmer.com
Wear-Mediated Osteolysis

Disrupted balance between osteoclasts/PMNs and osteoblasts: osteoclasts ↑, osteoblasts ↓

Archibeck, MJ; Jacobs, JJ; Roebuck, KA; Glant, TT. *Journal of Bone & Joint Surg*, 2000

http://academic.brooklyn.cuny.edu/biology/bio4fv/page/aviruses/cellular-immune.html
Some Issues

Grain Boundary Corrosion
P. Panigrahi et al; Hoffman et al

In-situ Wear
Liao & Marks, submitted

Graphitic Tribolayer
Liao et al., Science 334, 1687 (2011)

Transfer Layer
Castillo et al, submitted
Carbonaceous layers formed by tribochemical reactions were observed on most of the MoM retrievals (80% of 42 retrievals, Wimmer et al., Wear, 255, 1007, 2003)
Key Observation

- This tribolayer correlates with lower wear, corrosion etc
- Implication: this is the triboactive region where sliding takes place
- The layer has been *assumed* to be denatured protein (due to referee) – *without proof*
Experimental Method

- Follow the Science, not the electron
- Biological TEM
  - Low-dose (~50 e/Å² or less) EELS
  - Control samples (BCS/Albumin)
  - Measure effect of sample preparation & electron dose on controls
- Cross-check with Raman
- Controls, controls, controls
- Not just one measurement
Tribofilm collection

Tribofilm on #17 retrieval was collected using a nanoprobe in FIB. Care was taken to minimize the exposure to ion/electron beam.
Minimize radiation damage

Dried Bovine Calf Serum

EELS spectrum of the serum dried on copper grid
Graphitic carbon (~82% sp²)

Sample from pole of retrieval, removed due to loosening of the acetabular component (not excessive wear)
Graphitization of carbons due to sliding


HREM: Graphitic carbon

“Classic” basal-plane fringes from graphitic material
Raman Results

D band (disordered, sp$^3$) at 1388 cm$^{-1}$

G band (graphitic, sp$^2$) at 1567 cm$^{-1}$
(Stage 2 graphitic carbon)

Similar results

• Different Locations (pole/side of head/cup)
• Different Retrievals
• Simulator Tests
• Blood is different
Raman Mapping

Amount of carbon varies in the tribofilm (presumably due to the thickness)
Raman spectra of carbon

Nano graphite

Typical Raman spectra of carbon films
Chu and Li, Mater. Chem. Phys, 2006

Amorphization trajectory showing variation of the G position and I(D)/I(G) ratio.
Ferrari and Robertson, Phys Rev B, 2000
Simulator Experiments

Raman results show that tribological film is generated when $16N < F < 56N$, consistent with optical/SEM observations.
What it is not

- Graphite (short-range ordered sp²/sp³)
- It is not temperature (too low)
- It is not adventitious carbon (too thin)
- It is not beam damage (control experiments)
- It is not an artifact of sample preparation (control experiments)
- It is not simply mechanical
- Athermal effects (x-rays from sellotape), probably not
What do we know?

- It is linked to Mo (not Cr or Co)
- Film is yellow/brown, similar to degraded PTFE, hydraulic oil varnish…..
- There is an electrochemical link
- It requires both sliding and pressure to form
  - Not too much, not too little (like vodka)
- No evidence of CrO$_x$ co-existing with layer (i.e. conditions at metal are reducing)
- Albumin is $C_{3076}H_{4833}N_{821}O_{919}S_{42}$, and eliminating water, ammonia (and hydrogen sulfide) gives $C_{3076}H_{448}$ – close to NFC/DLC
Much to be done to understand tribology at the nanoscale (fun)

- Long-range elastic/plastic processes can occur
- Local tribochemical processes
- Local wear processes (ultra-low wear) at the monolayer even in hard materials
- Unexpected processes
- Formation of transfer layers which only need to be single layers
Questions?

**Input**

Basic materials parameters from experiment and/or theory, e.g. $\sigma_p$

**Output**

Scale independent models without free parameters

$$E_{eff} = E_0 + kT (\exp(-E_0 / kT) - 1)$$