SAND2014-3362C

Nanostructured Materials for Solid Lubrication

Plenary Talk

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U.S. DEPARTMENT OF ENERGY

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- Bonnie McKenzie (SEM)

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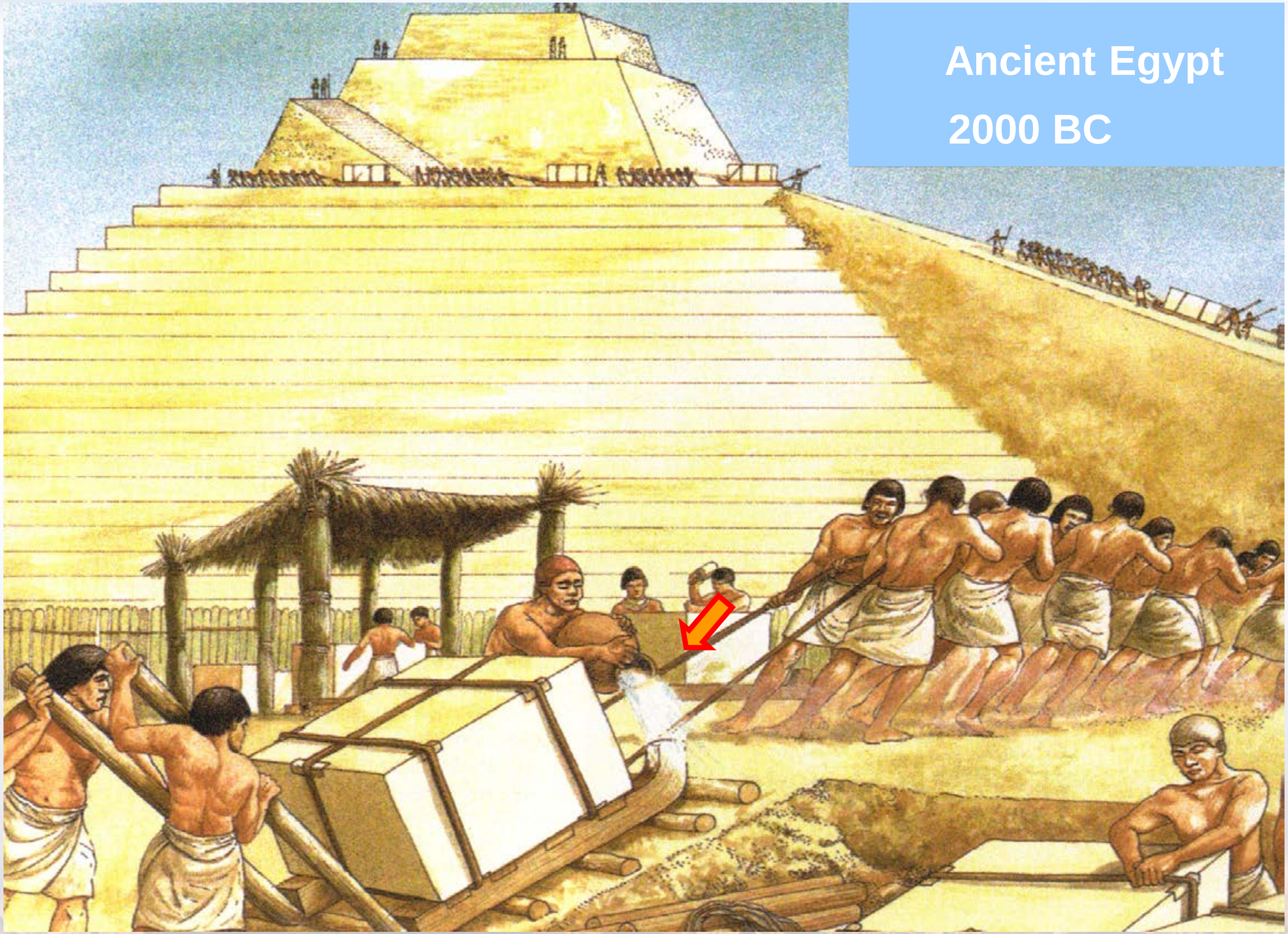
- Jeff Zabinski (ARL)
- Jon-Erik Mogonye(UNT/Sandia)
- Greg Sawyer (U of Florida)
- Brandon Krick (Lehigh U)
- Rob Carpick (U Penn)
- Chandra Venkatraman (Entegris)
- Cindy Broadbeck (SulzerMetco)

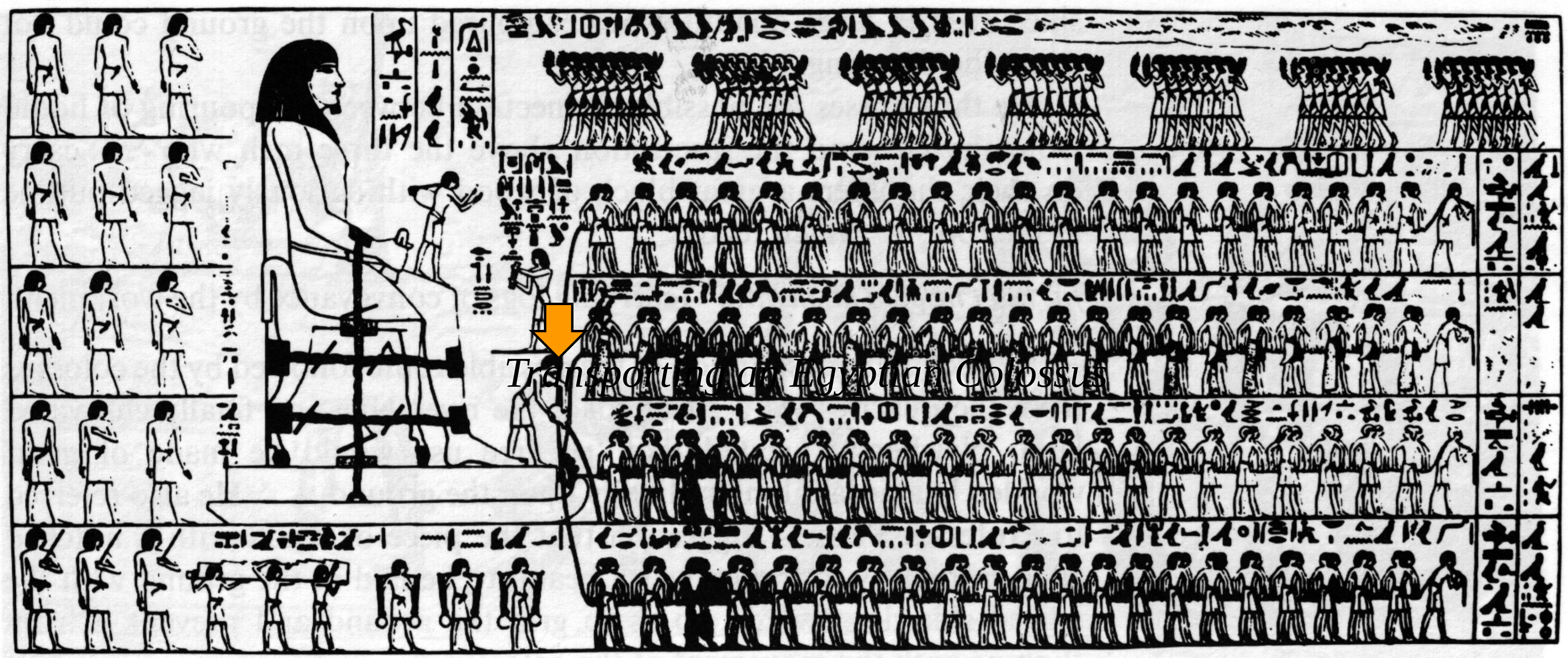
Lubrication in Pyramid Building



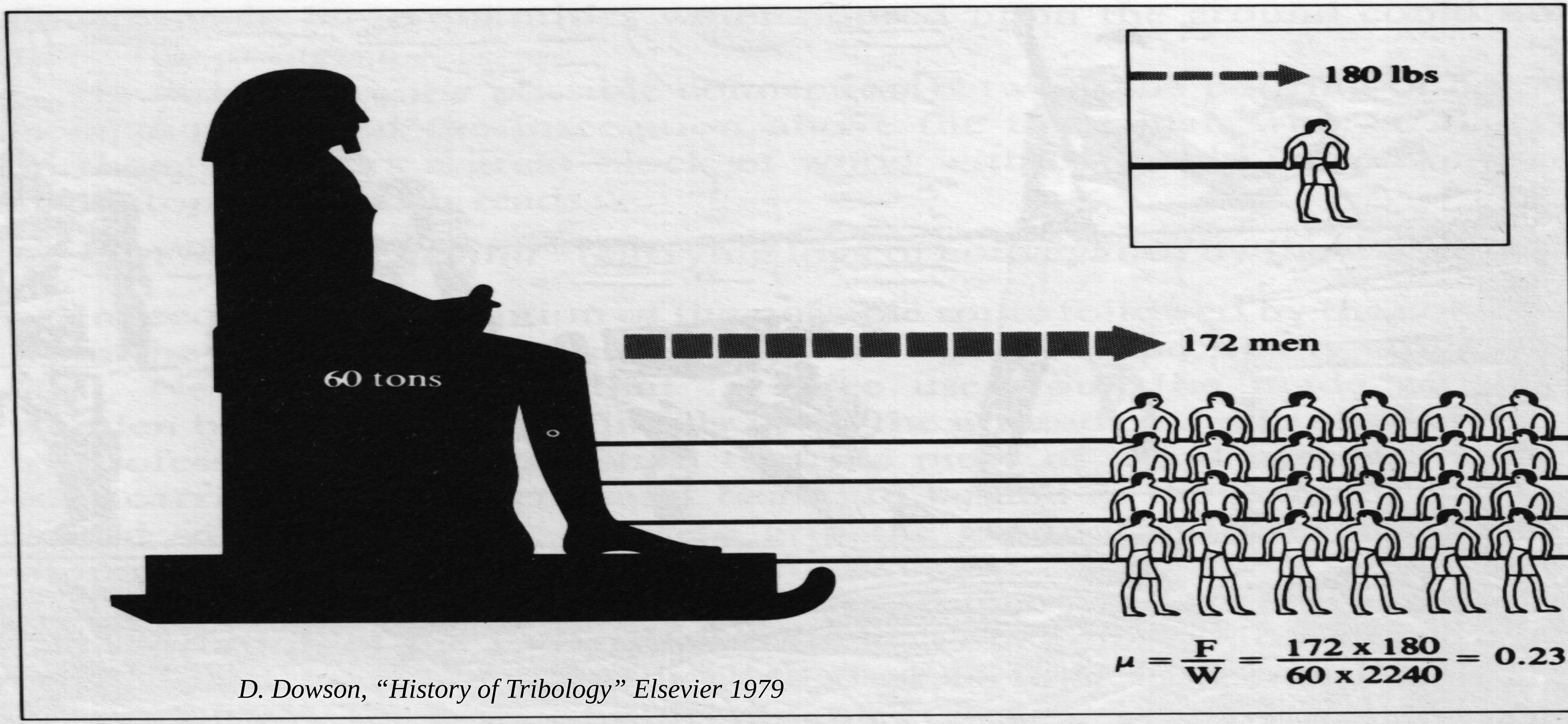
Ancient Egypt

2000 BC

Transporting an Egyptian Colossus (Lubrication)



Painting from a Grotto at El-Bersheh
Source: Duncan Dowson, History of Tribology , Elsevier, 1979



D. Dowson, "History of Tribology" Elsevier 1979

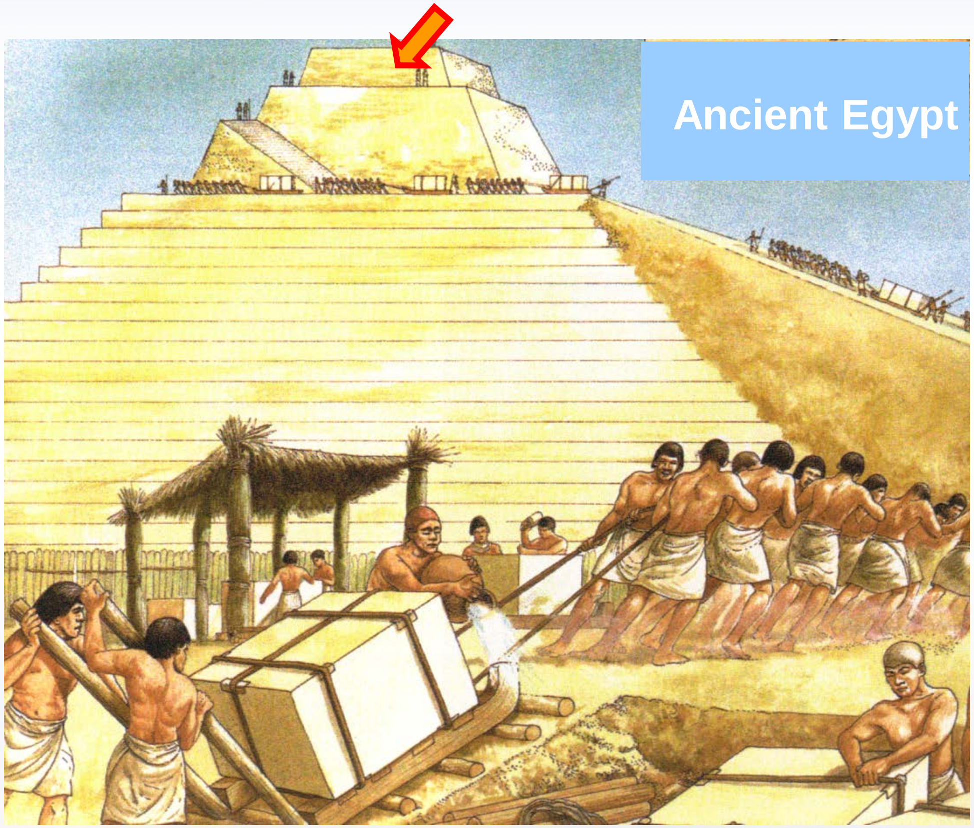
Bowden and Tabor, "Friction and Lubrication of Solids-Part I" Oxford 1950

- **The coefficient of friction, μ, for hard wood sliding on wet/moist wood is 0.2**
- **The coefficient of friction of wood-on-wood in dry condition is 0.45-0.50**

In ancient Egypt, about 100, 000 men were employed each year to transport massive objects.

Without a lubricant, 200, 000 for a state in 2000 BC can be large expense even if the monarchs fed them only one meal and paid no wages!!!

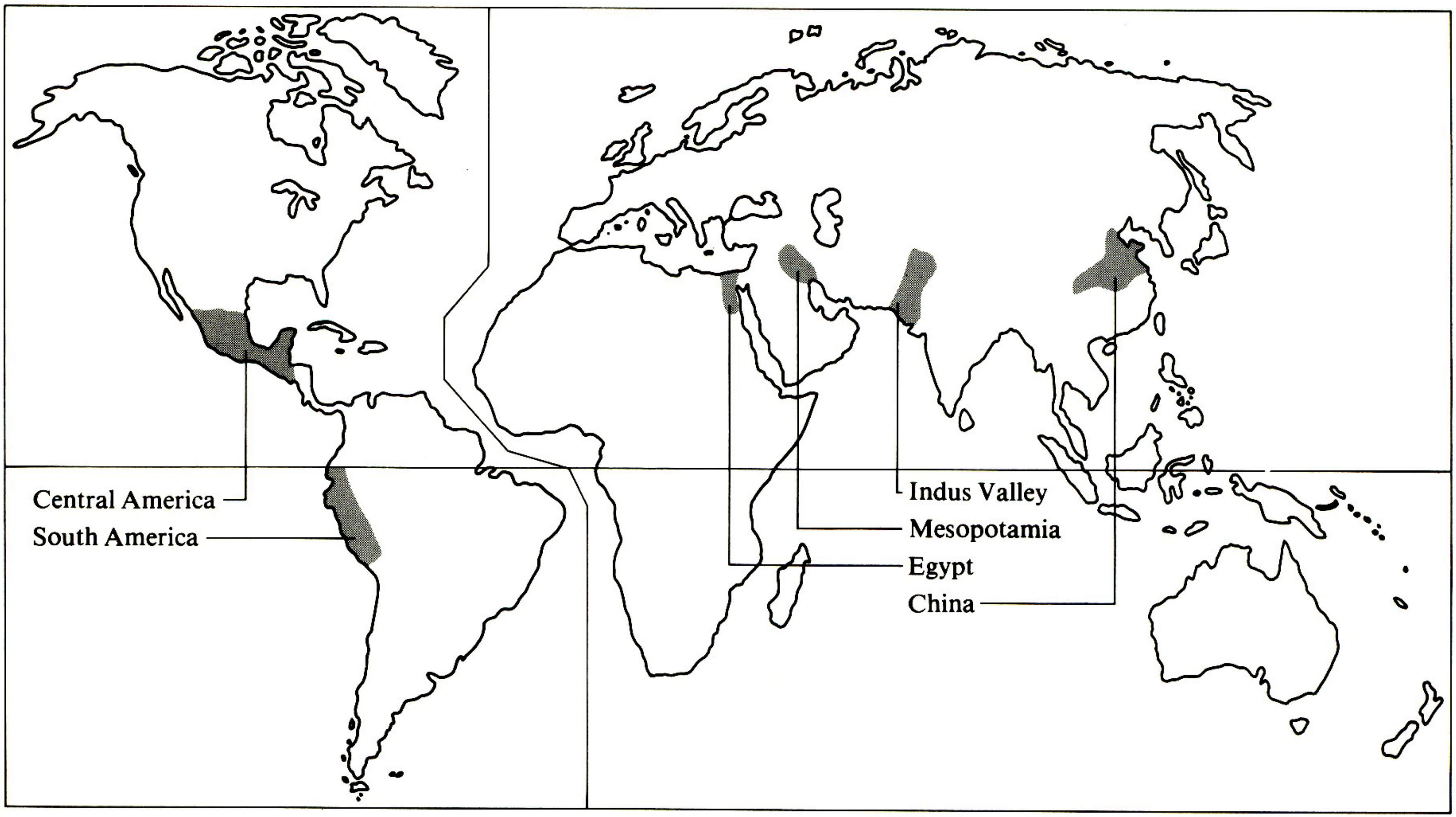
Limited space as the apex is reached



Tribology

Cost and Energy Savings ⟺ Performance and Reliability

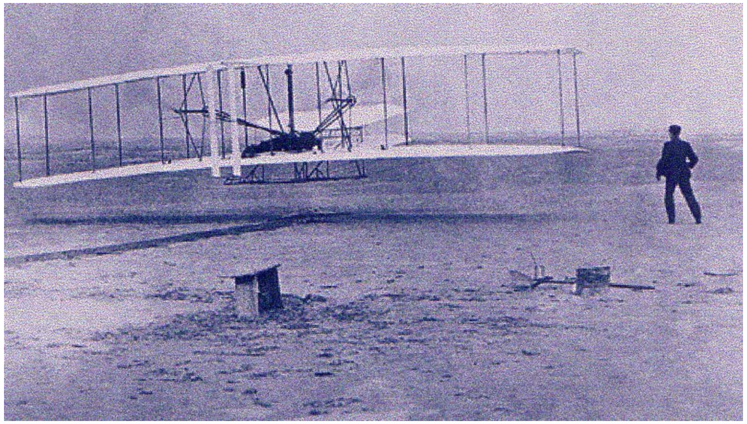
Early Civilizations Across the World



Archeological Studies confirm tribological innovations during early civilizations

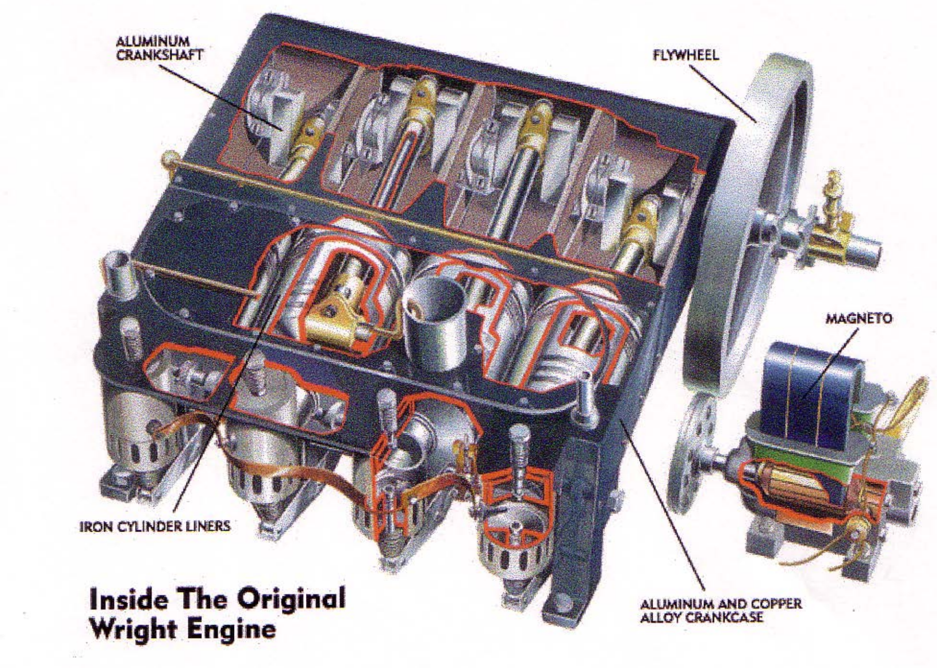
The Saga of Wright Brothers' Engine

1903



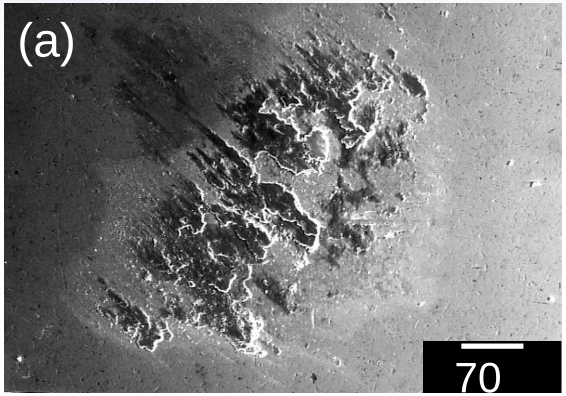
Mr. Charles Taylor (Mechanic)
Considered replacing CI with Al-Cu

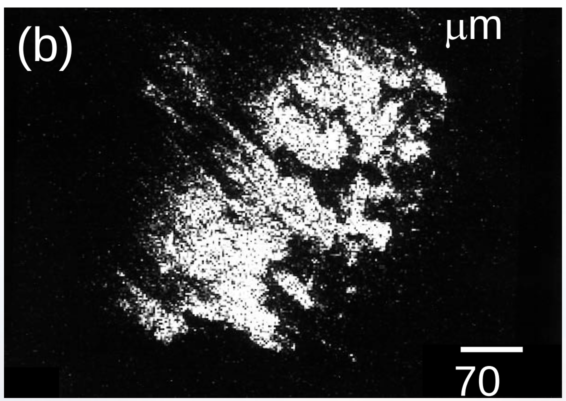
- The Brothers needed an Engine with 8 HP weighing <180 lbs



- 16 HP-12HP 178 lbs
- The Brothers used the extra weight allowance to strengthen the wings and frame
- But Al has a tendency for seizure and galling in the absence of complete fluid film lubrication

Mr. Taylor had the foresight to avoid Al in sliding contacts





Smearing of Al on a steel ball during a ball-on-disk wear test. SEM showing adhesive transfer of Al on steel ball (a) with corresponding X-ray map (b).

S. V. Prasad and K. R. Mecklenburg, Lubrication Engineering, 50 (1994) 511-518.

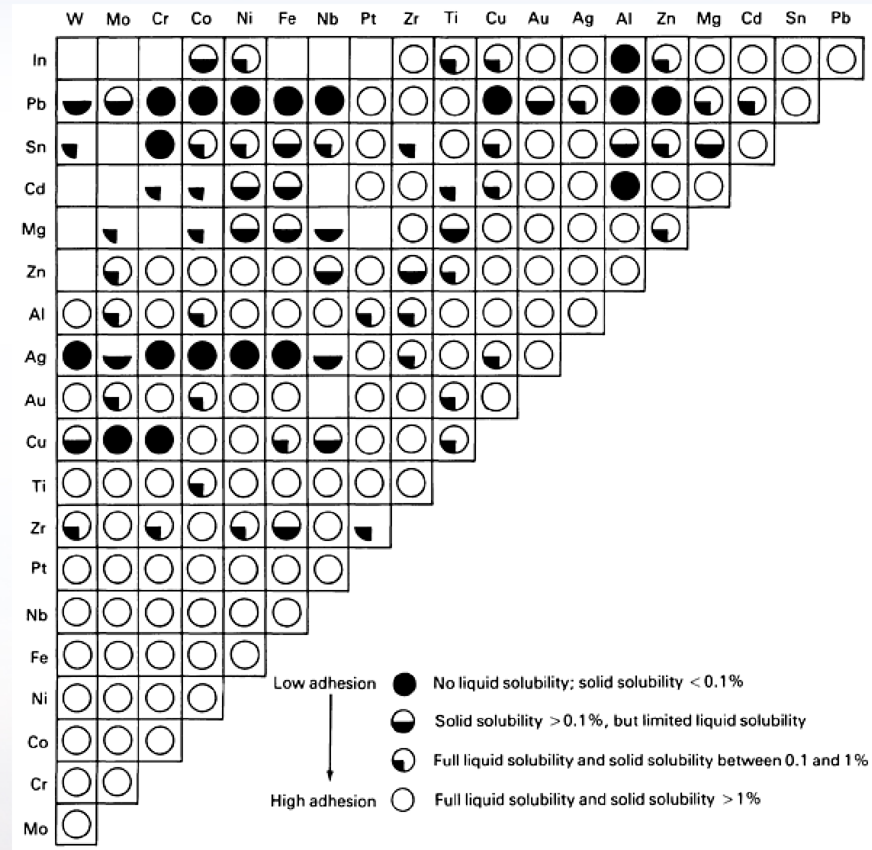
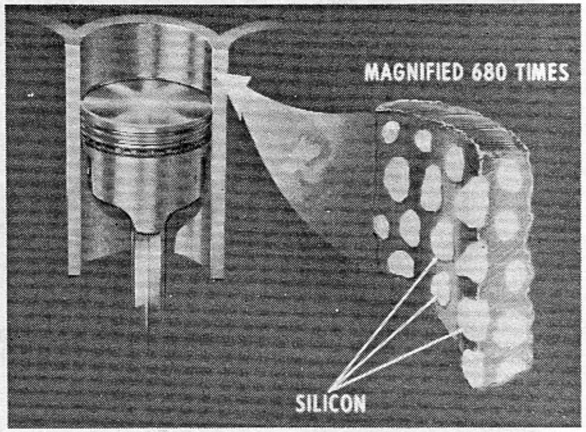


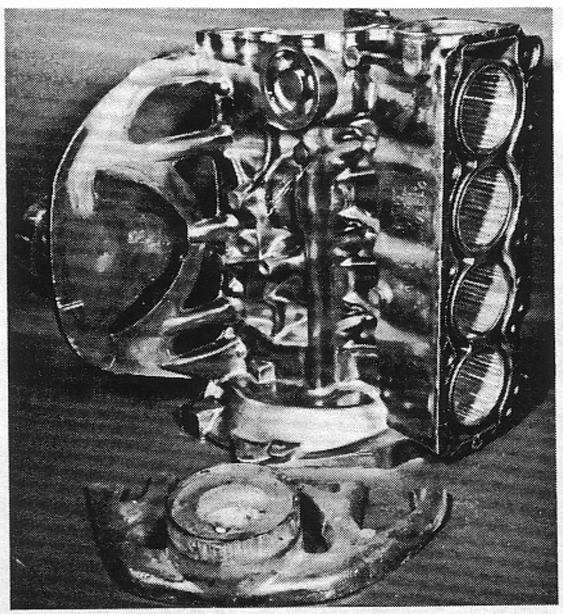
Chart indicates the degree of expected adhesion (and thus friction and wear) between the various metal combinations derived from binary equilibrium diagrams.

E. Rabinowicz (1971) ASLE Trans 14:198

The (Short) Legacy of the Vega Engine



Silicon surface cylinder bores



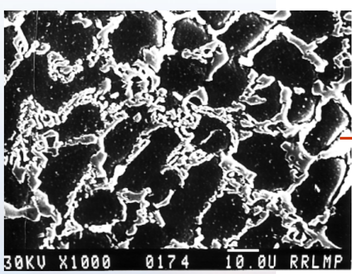
Vega engine block as removed from die

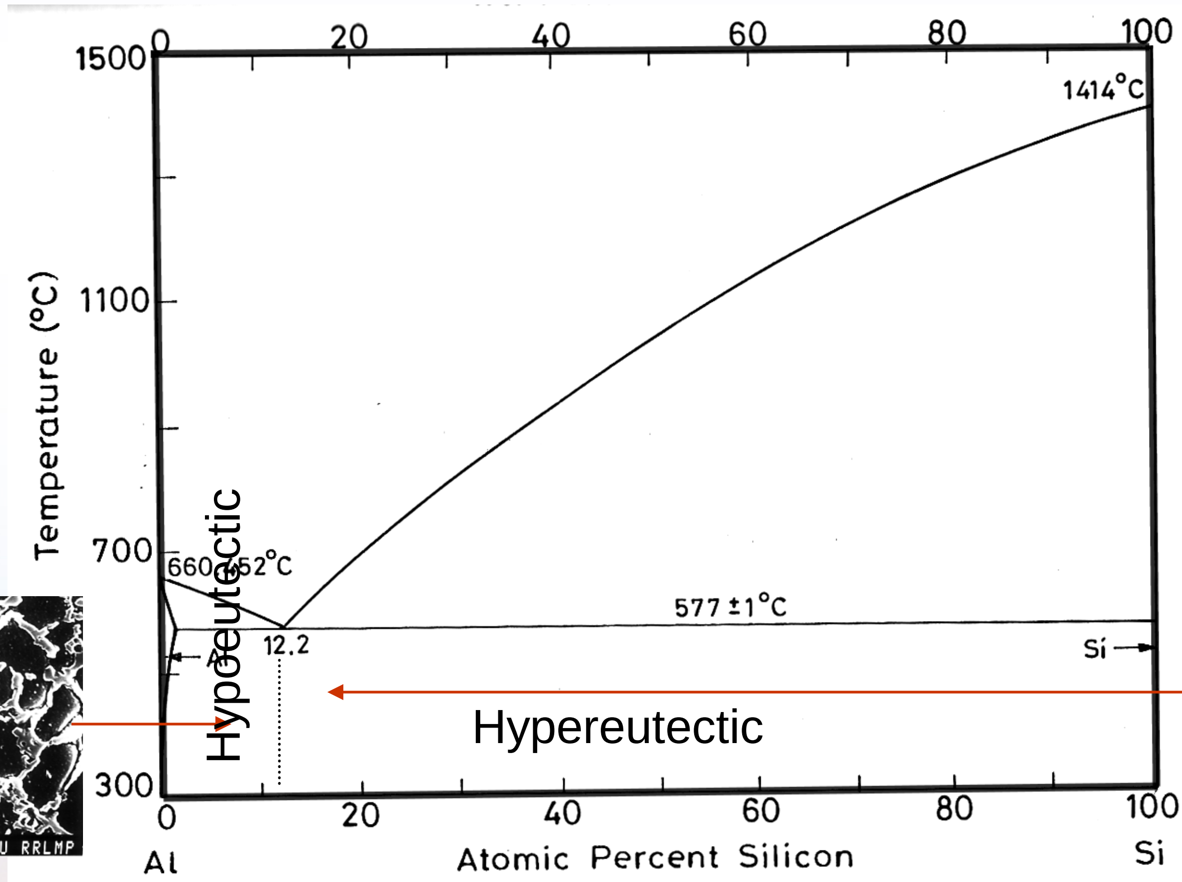
BASIC SPECIFICATIONS
VEGA 2300–140 cu in. Overhead Cam 4-cyl Engine

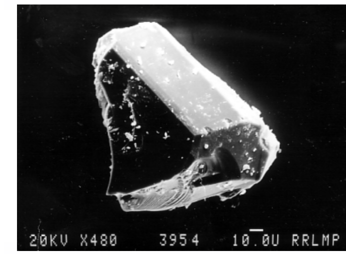
GENERAL	
Type	In-Line OHC 4-cyl (L-4)
Gross horsepower	
Standard engine	90 at 4600-4800
Optional engine	110 at 4800
Gross torque	
Standard engine	136 at 2400
Optional engine	138 at 3200
Compression ratio	8.00:1
Bore and stroke	3.501 × 3.625
Firing order	1-3-4-2
Engine installation angle	3 deg 50 min
Fuel	Regular leaded and nonleaded 91 Octane
Carburetor	
Standard engine	One-barrel, Monojet
Optional engine	Two-barrel, downdraft
CYLINDER BLOCK	
Material	Die-cast high-silicon aluminum alloy
Bore spacing (C/L to C/L)	4.00
Number of bulkheads	Five

The Vega 2300 Engine, SAE 710147

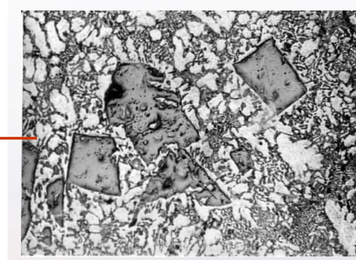
Both the eutectic and the primary Si have undesirable morphology







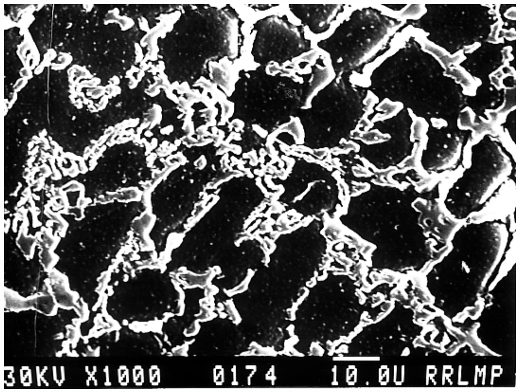
Silicon Debris From Wear Test

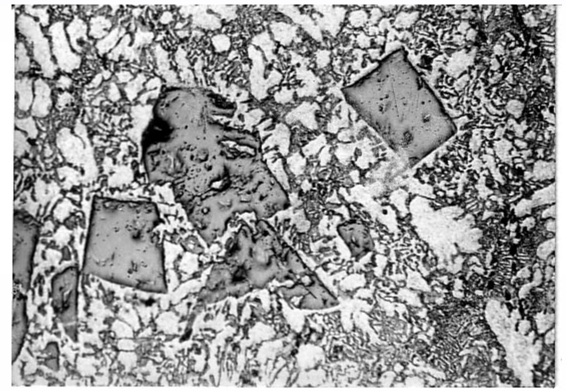


Microstructural Modification of Al-Si Alloys for improved wear resistance

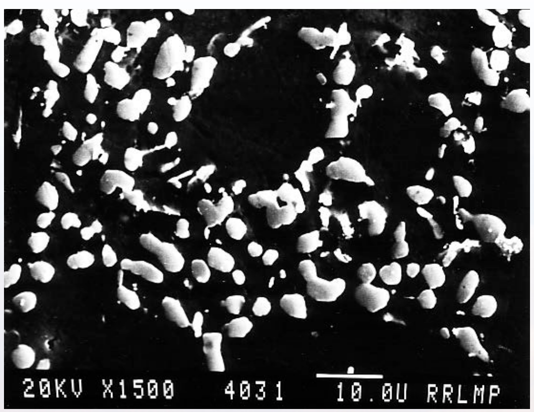
Hypoeutectic | Hypereutectic

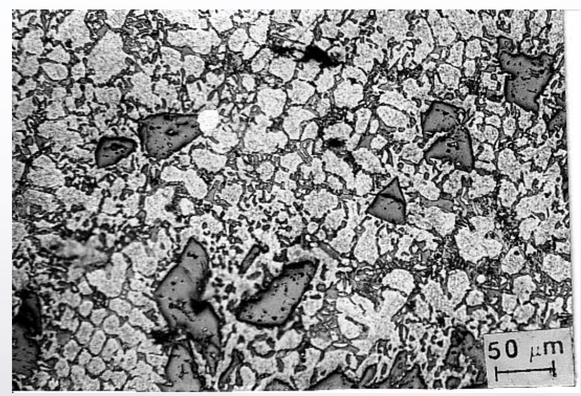
As-Cast





Modified
Refined

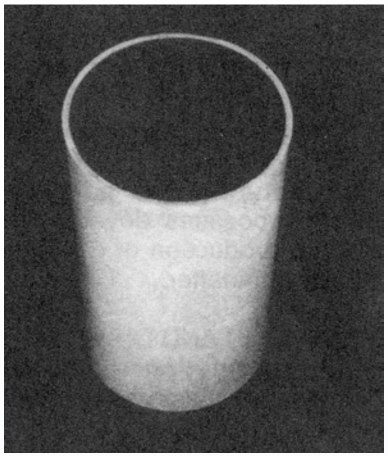




However, thermal mismanagement (arising from poor thermal conductivity of Si) was an issue that wasn't factored during the initial engine development, which essentially killed the engine.

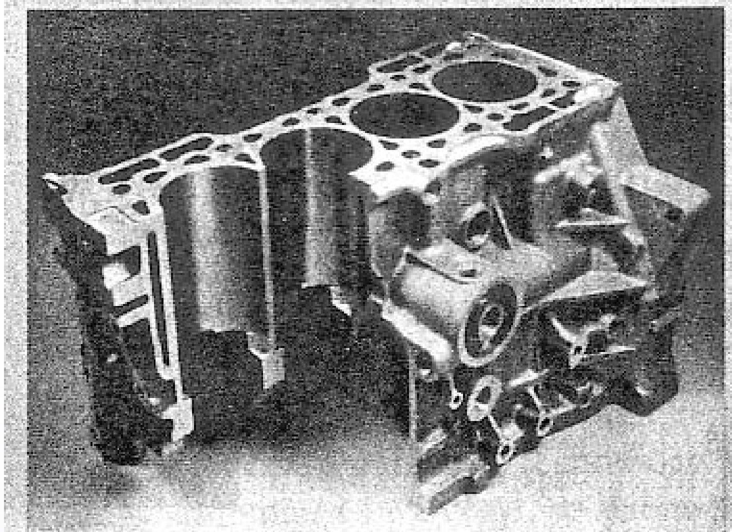
S. V. Prasad and R. Asthana, Tribology Letters, 17 (2004) 445-453.

Integrally Cast MMC Cylinder: Honda Corporation (1980's)



Preform

A porous hybrid material made out of Short alumina and Carbon fibers



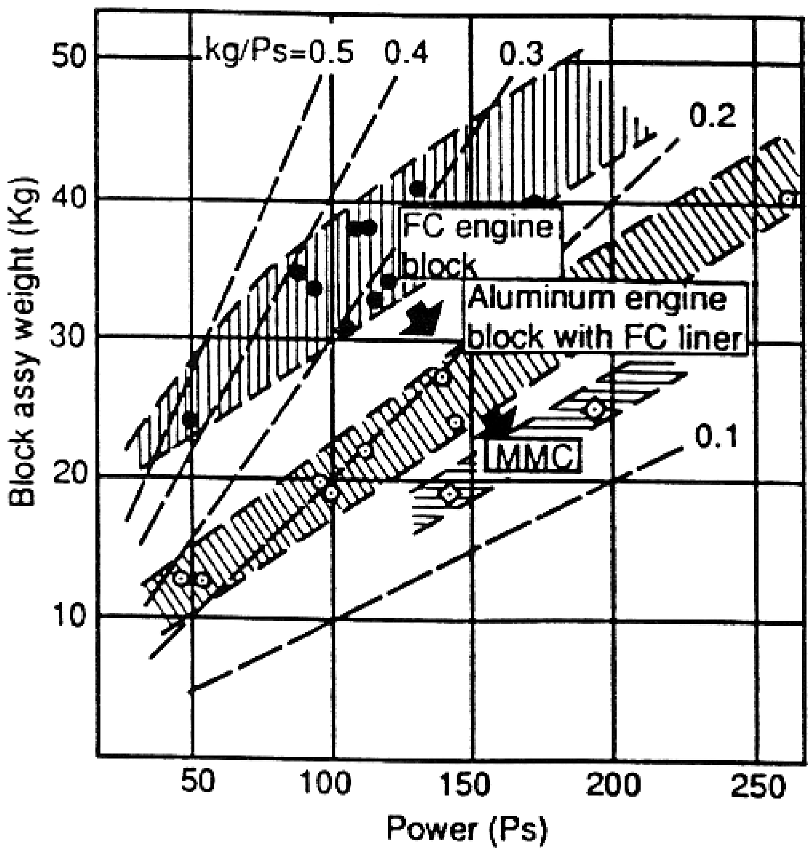
The integrally cast metal-matrix composite cylinder walls of the engine save weight and space, while improving its durability and ability to dissipate heat.

- **Ceramic "preform" production**
- **Pressure casting process**
- **Honing**

- Hybrid preforms: Carbon for thermal conduction, Aluminosilicate for strength
- Honing to minimize direct contact between Al and the piston ring

First introduced in Honda Prelude

Relationship between Power and Engine Block Weight



The new engine block features higher performance, further compactness and weight reduction compared to cast-iron engine blocks and those made out of Al alloy with cast-iron liners

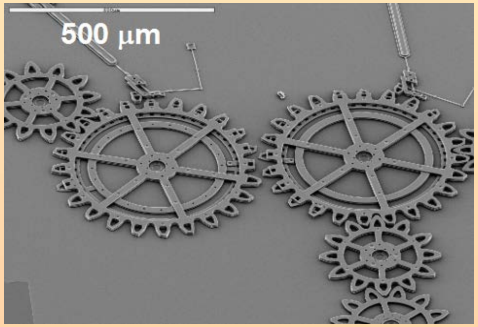
M. Ebisawa et. al, "The Production Process for MMC Engine Block", *SAE 910835*

Outline

- Examples from Ancient and Modern History

- Solid Lubricants
    - Environmental Effects
    - Synthesis of Nanocomposites (MoS_2-Au, DLC-SiO_2)
    - Subsurface Deformation (FIB-EBSD-TEM)
    - Load Bearing and Barrier Layers

Harsh Environments



Energy and Communications

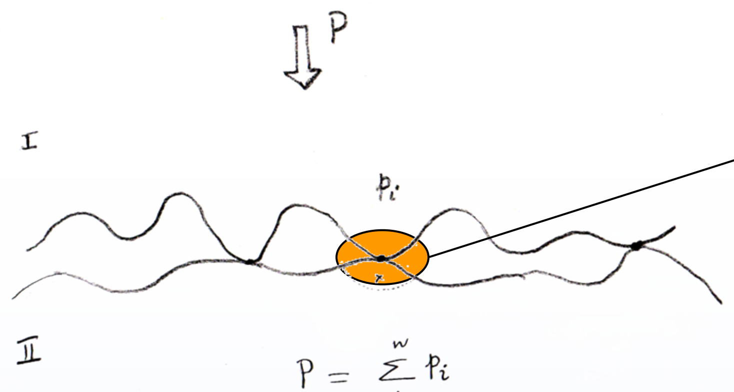
Solid Lubricants

- *The major of lubrication needs still met by fluids and greases*
- *When the operating conditions are beyond the liquid realm (e.g., high temperature or vacuum), or situations where liquids cannot be introduced, attention turns to solids*

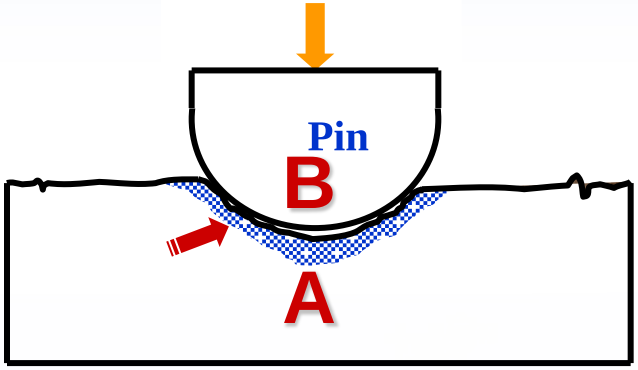
1. Carbon-based materials (graphite, DLCs, nanocrystalline diamond)
2. Transition metal dichalcogenides (MoS_2, WS_2)
3. Polymers (e.g., PTFE)
4. Soft Metals (Ag, Sn, Pb, In , Au)

Frictional Contact Typically Results in Plastic Deformation Below Wear Surfaces

Engineering surfaces are not flat



Contact will be at asperity level



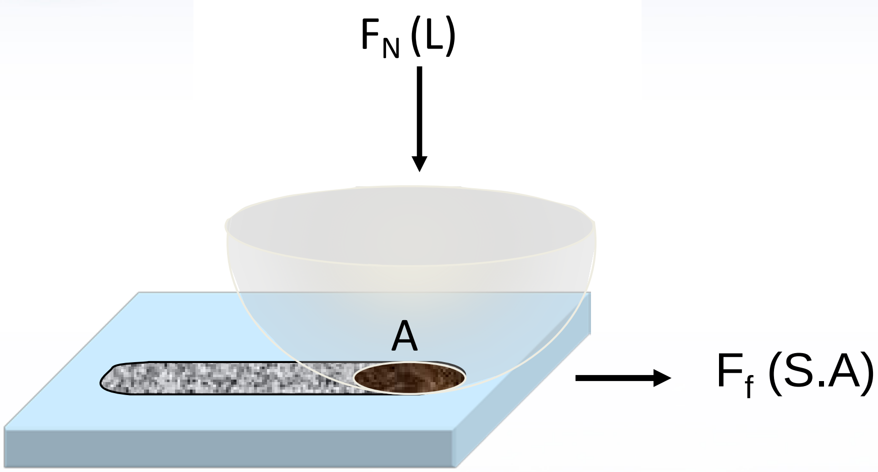
- Sliding contact results:
  - Plastic deformation
  - Diffusion

Barrier layers may be necessary to prevent the plastic deformation and diffusion (substrate species into coating)

J. F. Archard, J. Appl. Phys. ***24*** *(1953) 981*
R. Holm, Electrical Contacts (Springer, 1946)

Rigney, D.A., Hirth, J.P. Wear ***53*** *(1979) 345*

Many Solid Lubricant Coatings Exhibit Load Dependence on Friction



Elastic Contact (Sphere-on-Flat)

$$P = F_N / A$$

$$F_f = S\,A$$

$$S = S_o + \alpha\, P$$

$$\mu = S_o \pi \left(3R/4E\right)^{2/3} L^{-1/3} + \alpha$$

$$\mu = F_f/F_N = S.A/P.A$$

- S_o is the interfacial shear strength (a ‘velocity accommodation parameter’), a property of the interface.
- α is a fit constant (the pressure-dependence of ‘S’)

Friction is NOT independent of Load

F. P. Bowden and D. Tabor, “The Friction and Lubrication of Solids”, Oxford Science Publications, 1986

I.L. Singer, et al. *Applied Physics Letters* 57, 995 (1990).

B.J. Briscoe and D.C.B. Evans, *Proc. R. Soc. Lond. A* 380, 398 (1982).

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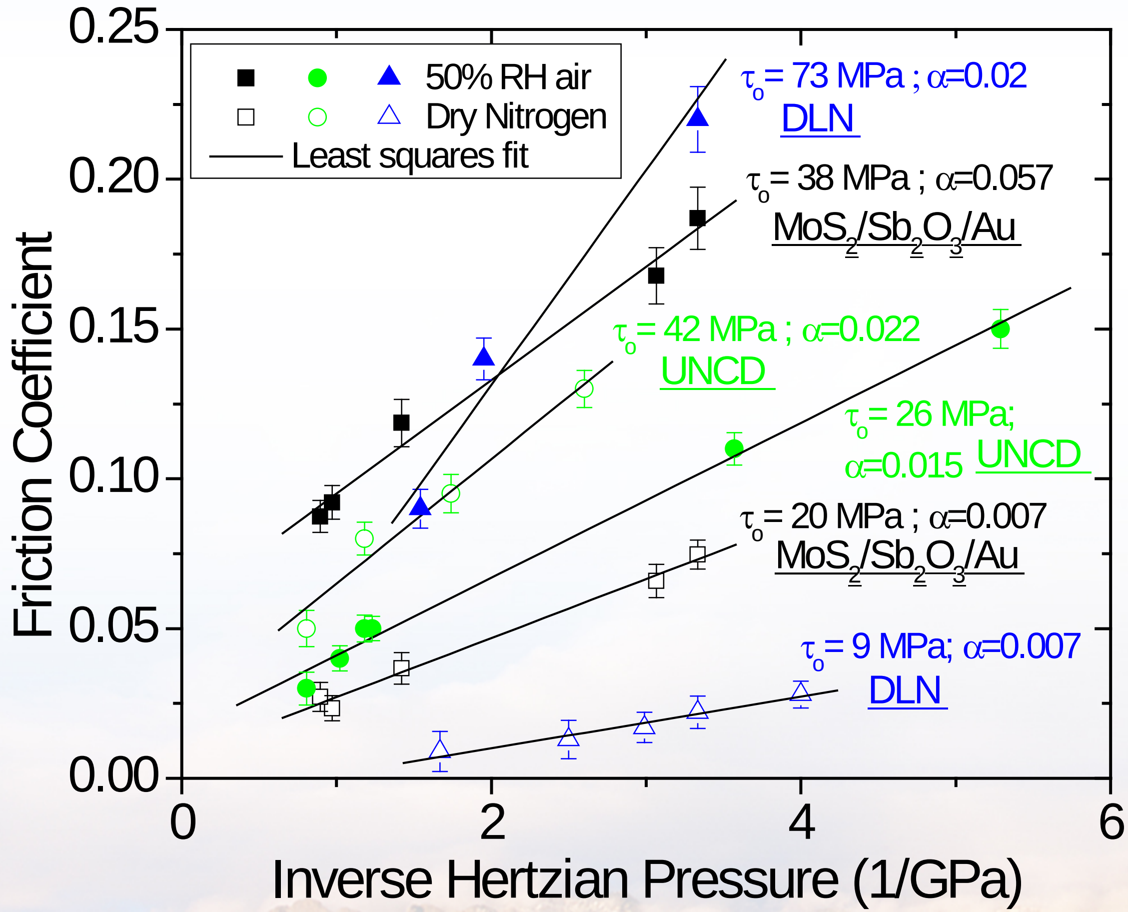
Inverse Hertzian Behavior— Non-Amontonian



T. W. Scharf and S. V. Prasad, Solid Lubricants: A Review, J. Maters. Science (2013) 48:511-531

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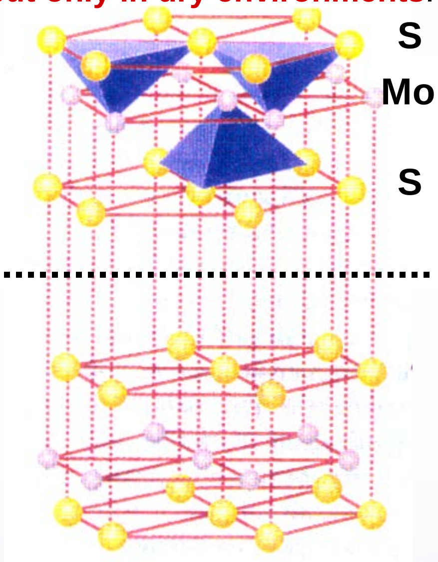
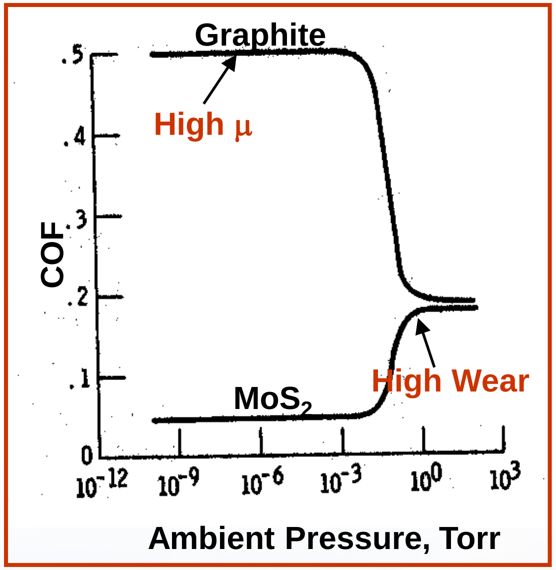
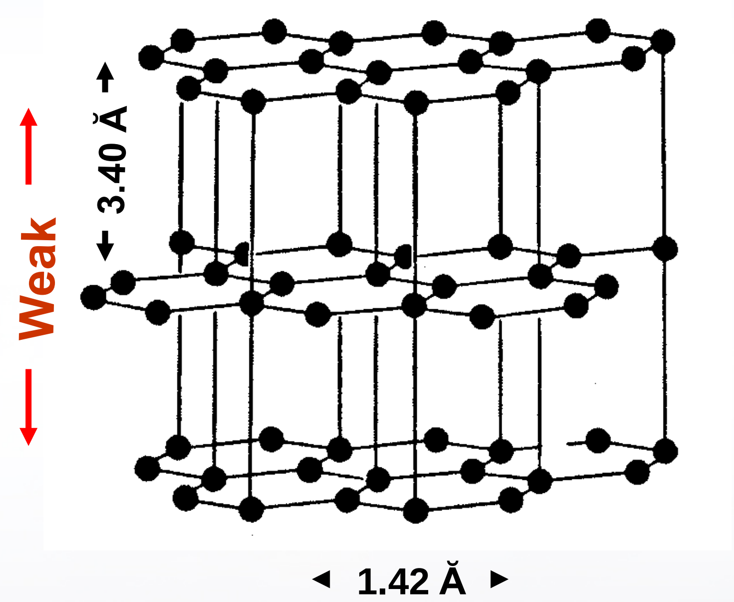
Classic Examples of Environmental Effects on Transfer Films & Friction

MoS_2: Extremely low COF (0.01-0.05) and long wear life, **but only in dry environments**.

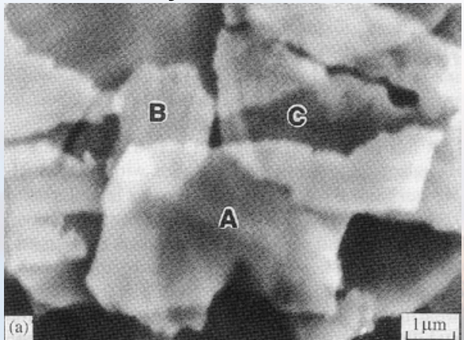


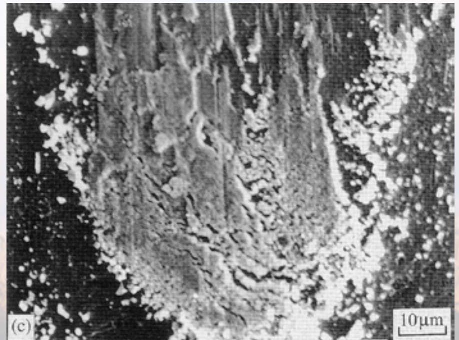




<u>Mo/W Disulfide</u>

They form thin transfer films on the counterface



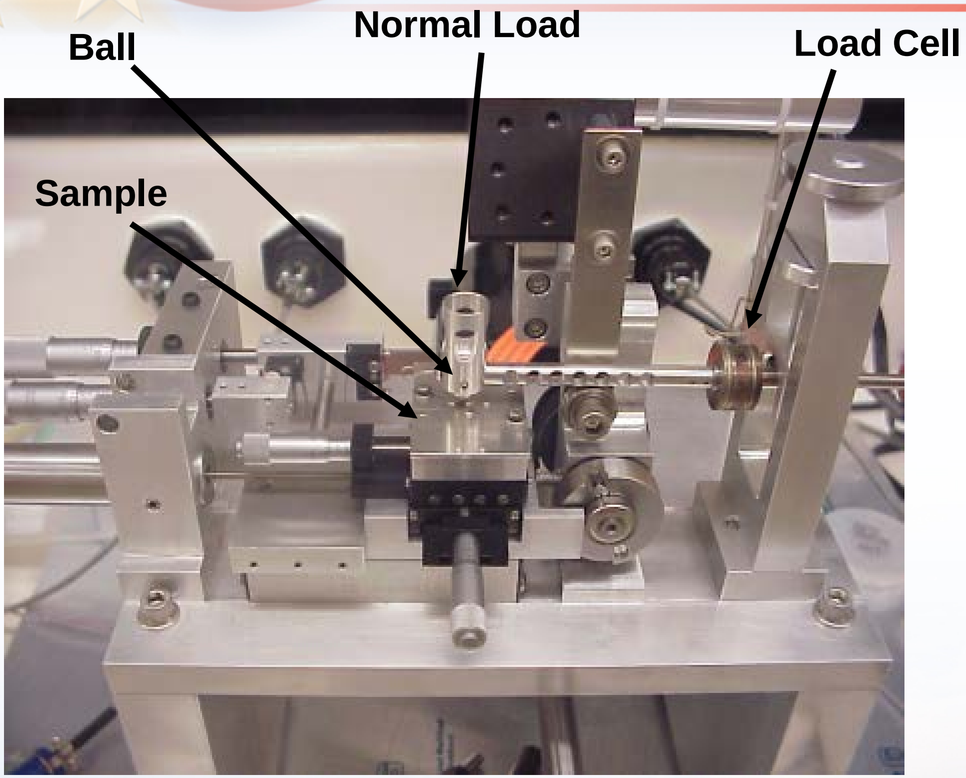


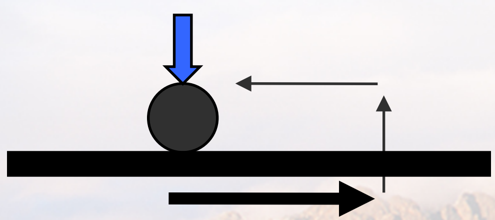
<u>Graphite</u>

- Graphite needs moisture or adsorbed gases in the environment (>100 ppm) (they either act as intercalants, or passivate the dangling covalent bonds) to lubricate.
- In vacuum, graphite exhibits high friction and wear—a phenomenon known as "dusting", first observed in the late 1930's on graphite brushes in aircrafts that exhibited accelerated wear at high altitudes.

S. V. Prasad and J. S. Zabinski, J. Mater. Sci. Lett. 12 (1993) 1413-1415

Friction and Wear Measurements





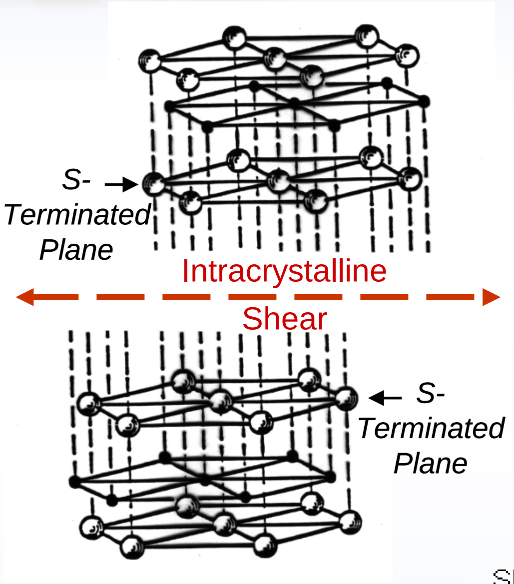
Linear Wear Tester
(Ball-on-Flat configuration)

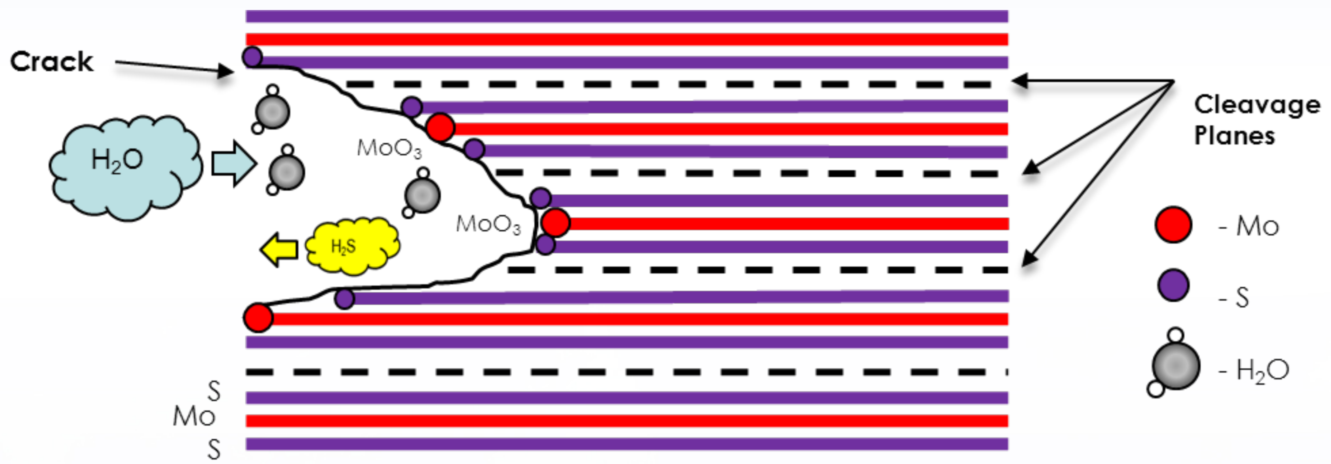
•Contact Pressures: 0.44 GPa to 1.7 GPa
•Environment: Dry Nitrogen; Air (50% RH)

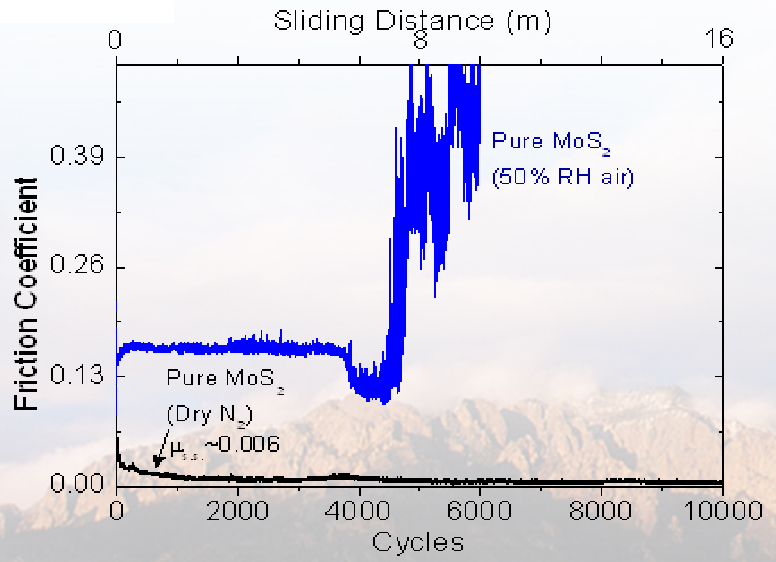
Oxygen Analyzer
Dew Point Measurement

Environmental Control

Effect of humidity and water vapor on the friction behavior of MoS_2

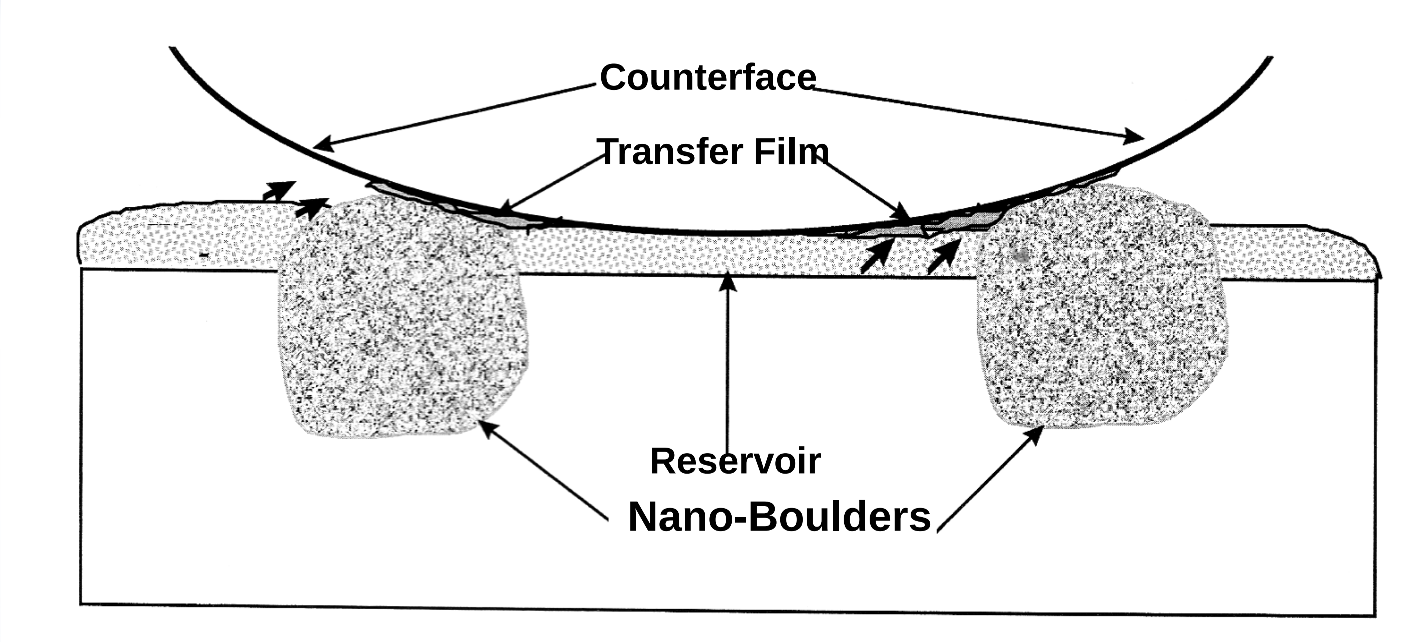


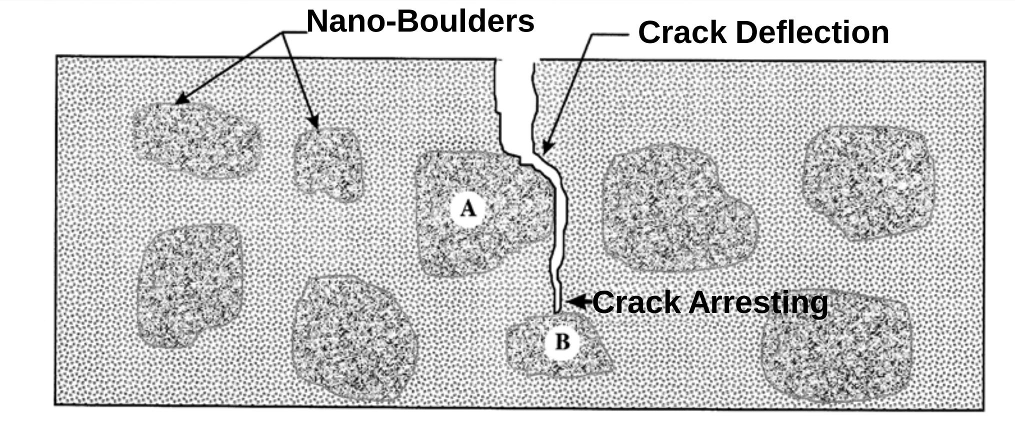




Reactions with water
Tribo-oxidation (MoO_3 formation)
Increase in the COF
Reduced Wear Life

Novel Concepts for Materials Synthesis



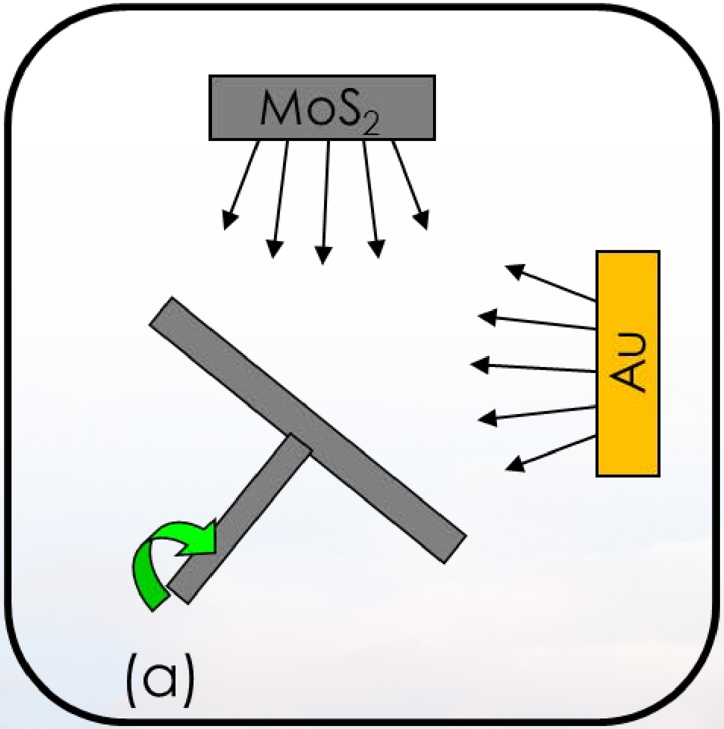


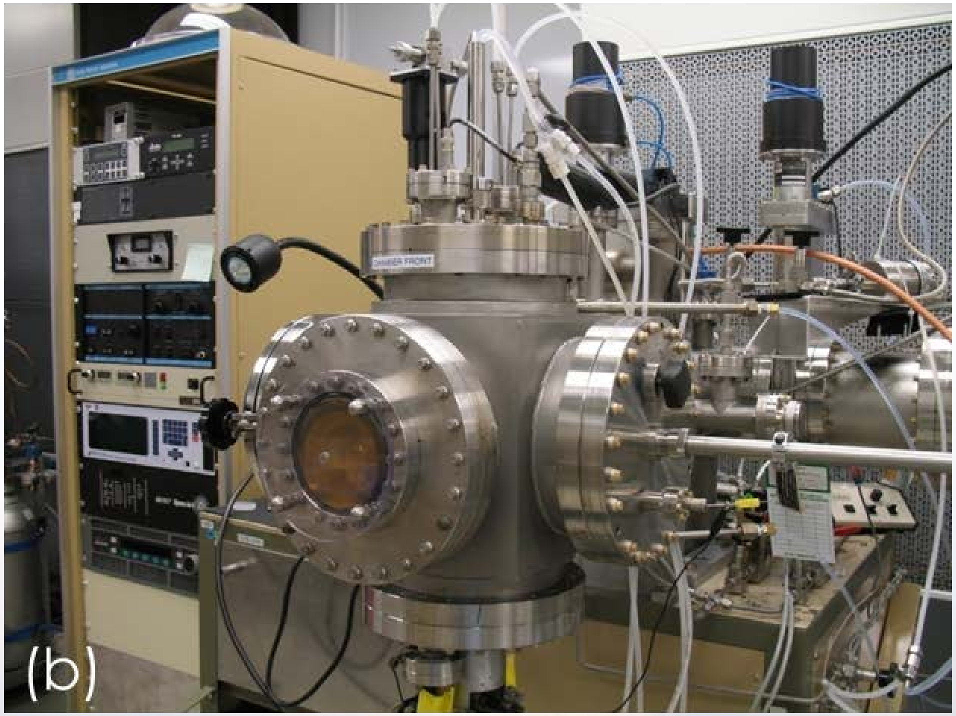
S. V. Prasad, N. T. McDevitt and J. S. Zabinski, Wear 230 (1999) 24-34

PVD-Co-Deposition for the Synthesis of MoS_2-Au Nanocomposites

Sputter targets located at 90 ° to each other and ~45° to the substrate stage

Experimental sputter co-deposition system used in this study

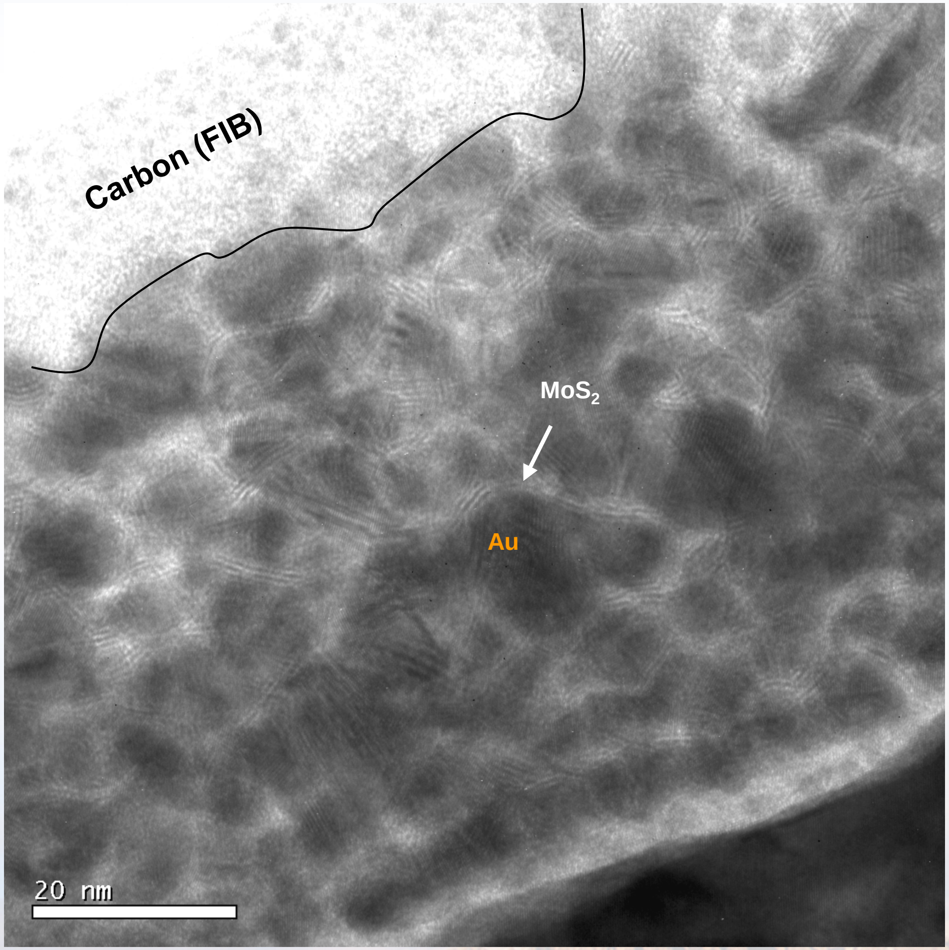


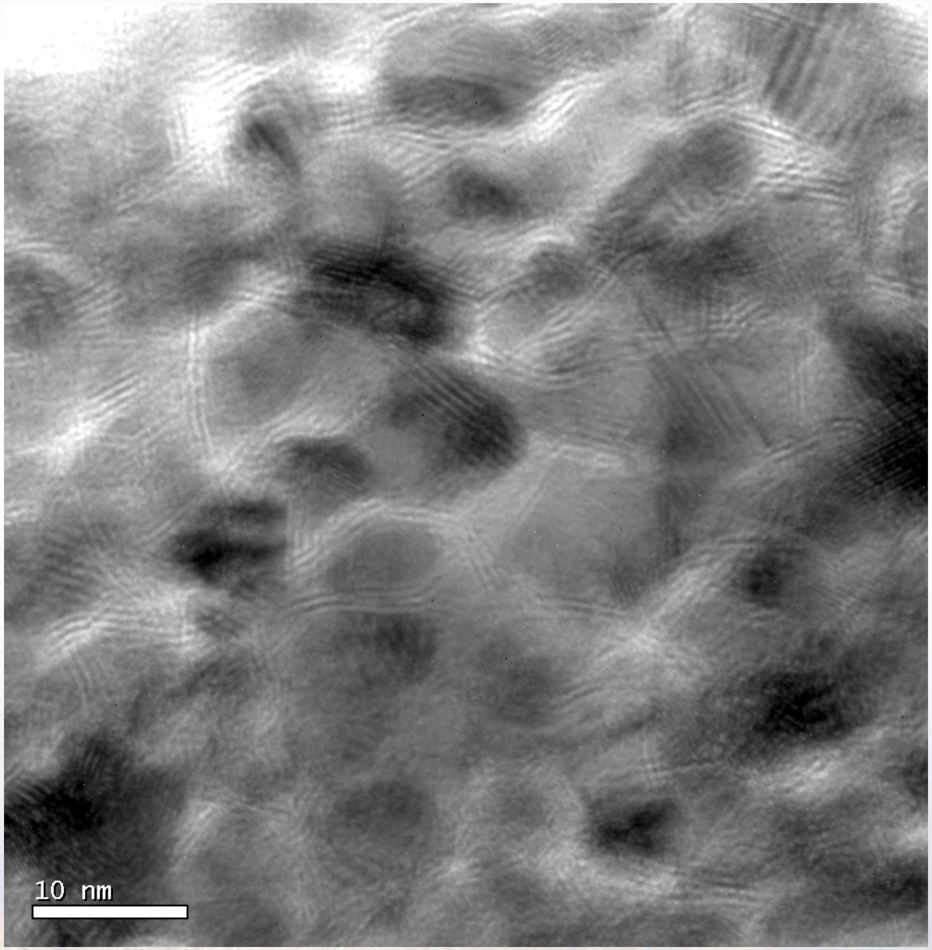


Independent rate control with stage rotation for uniformity

Independent QCM for rate monitor and control
Hot stage
DC Bias

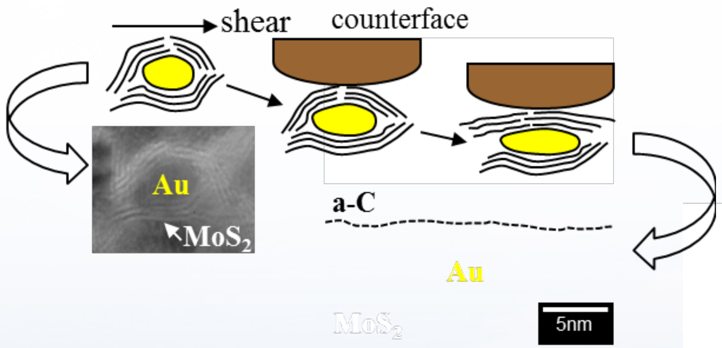
XTEM of MoS_2-Au nanocomposite grown at 200°C

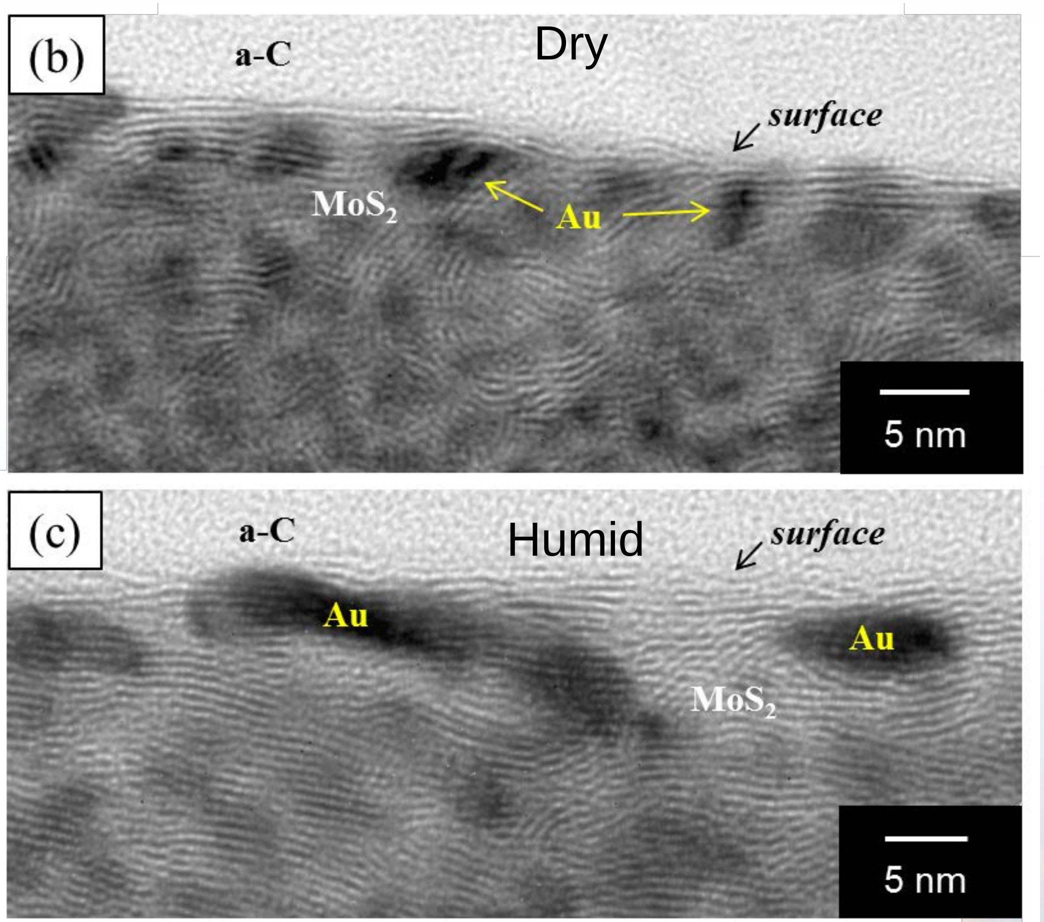




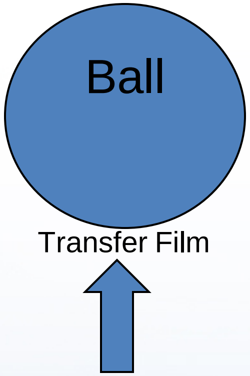
Nanocrystalline Au (~10 nm) core with MoS_2 basal planes encircling

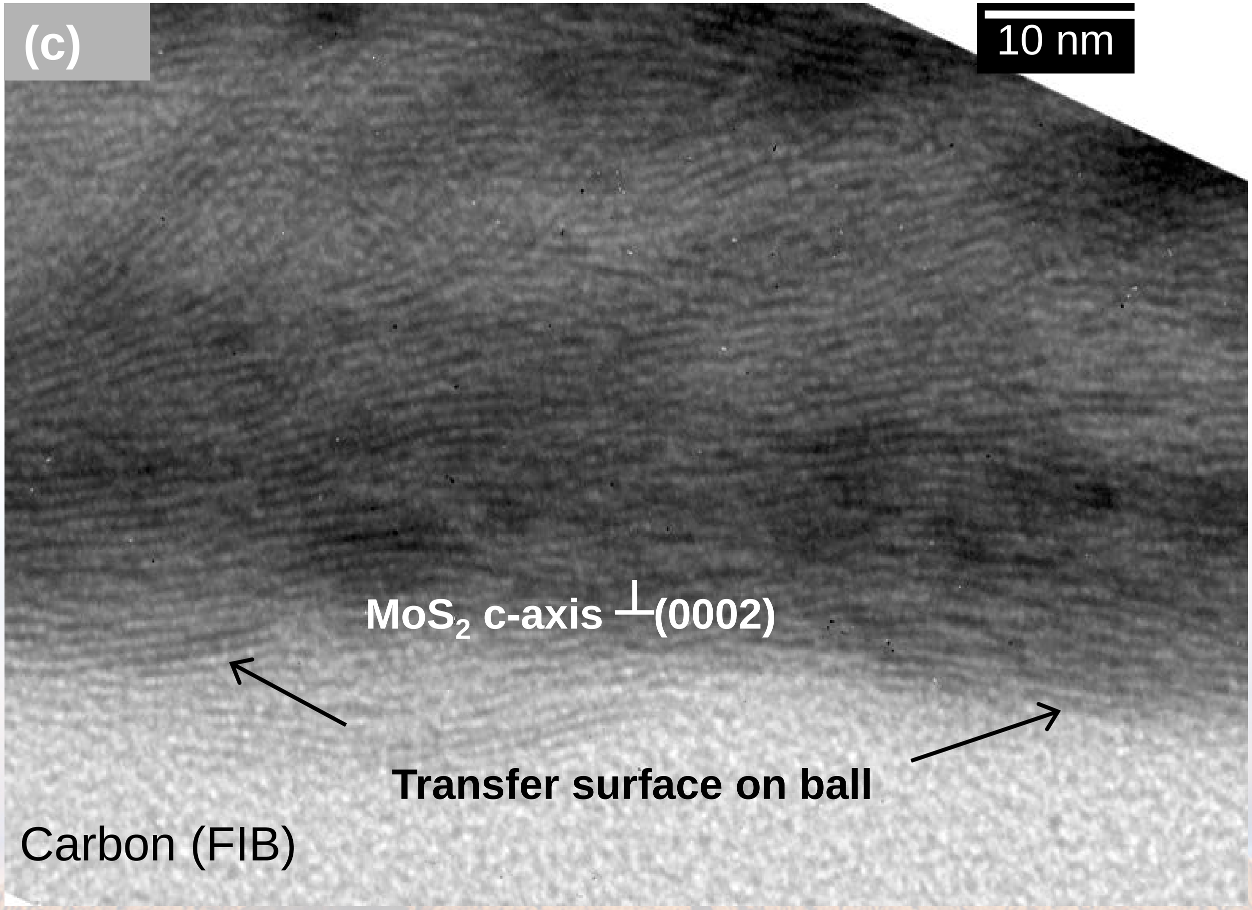
Shear-induced exfoliation of MoS_2 (0002) with basal planes parallel to the sliding direction





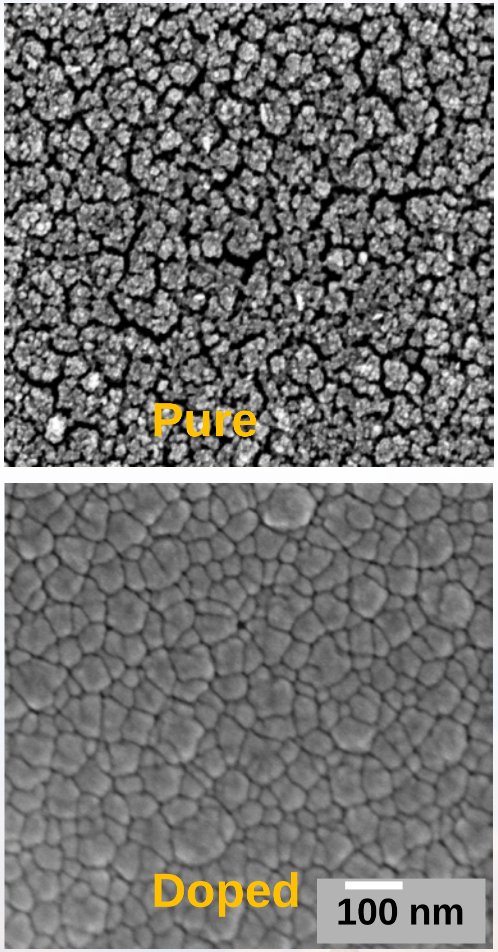
Cross-section of a Transfer Film
Air (50% RH)

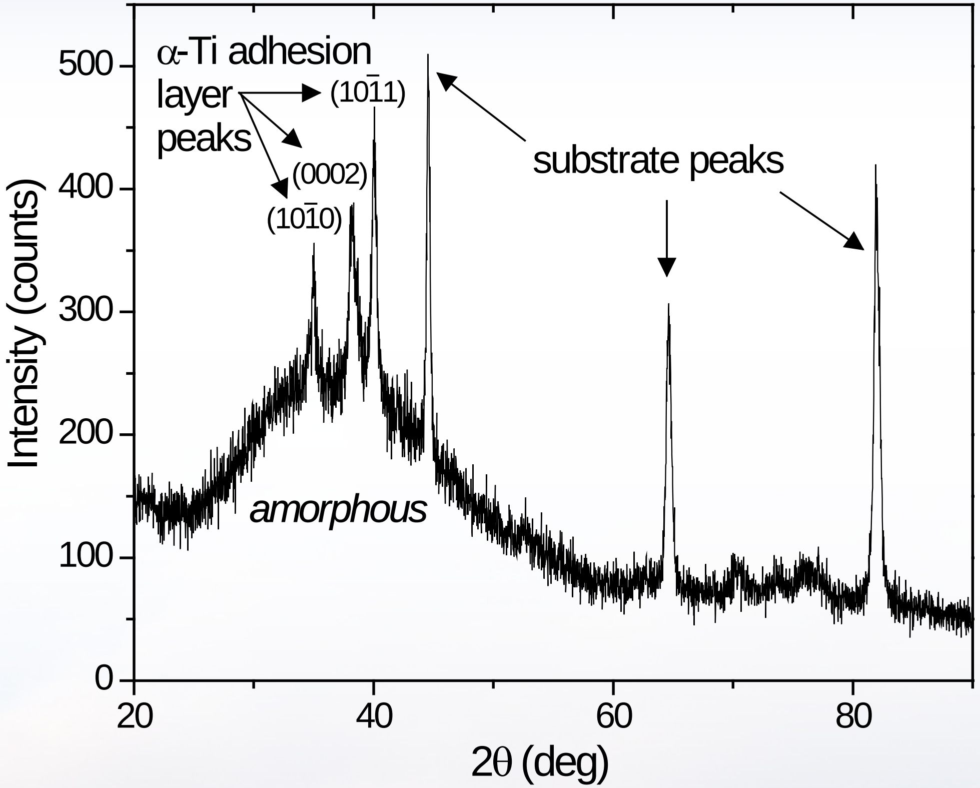




HRTEM

Doped MoS_2 (Sb_2O_3 and Au) from Tribologix

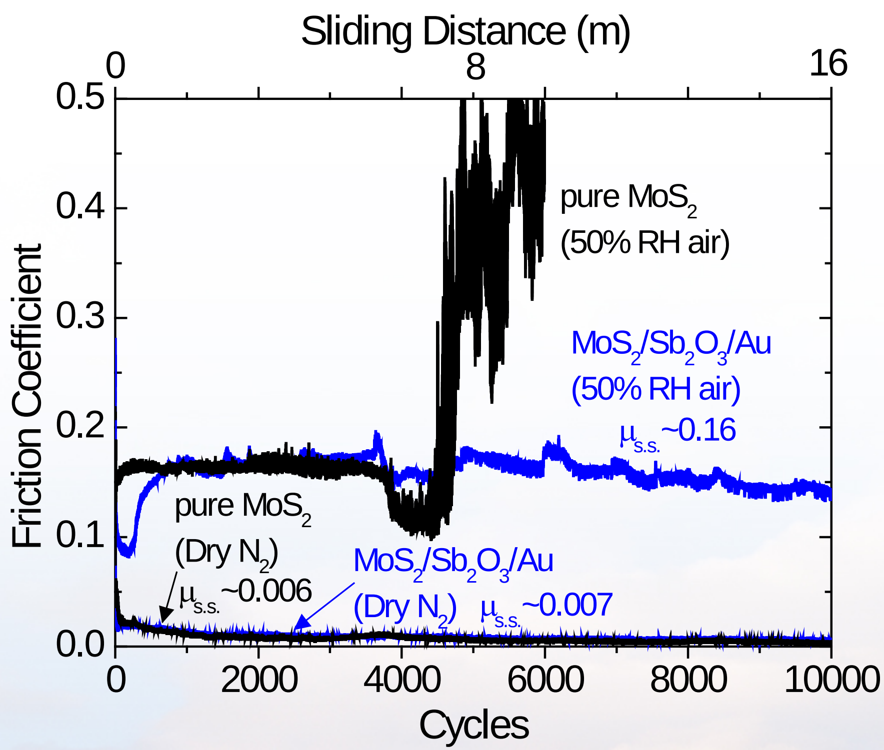


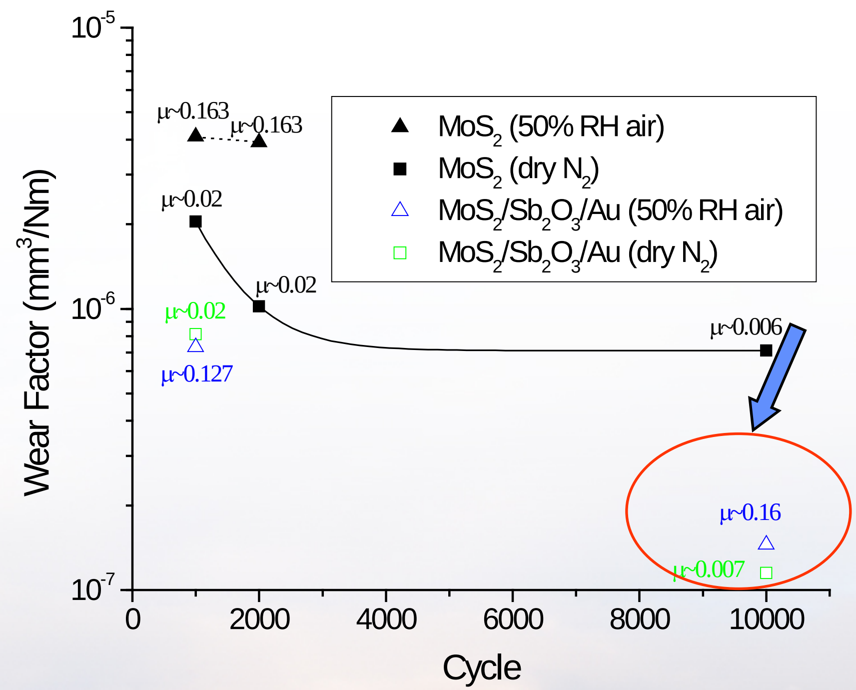


- Note the absence of peaks characteristic of any of the three constituent phases
- Instead there is a broad indicating the presence of an amorphous phase
- Doped films are much denser

Friction and Wear of Doped and Undoped MoS_2

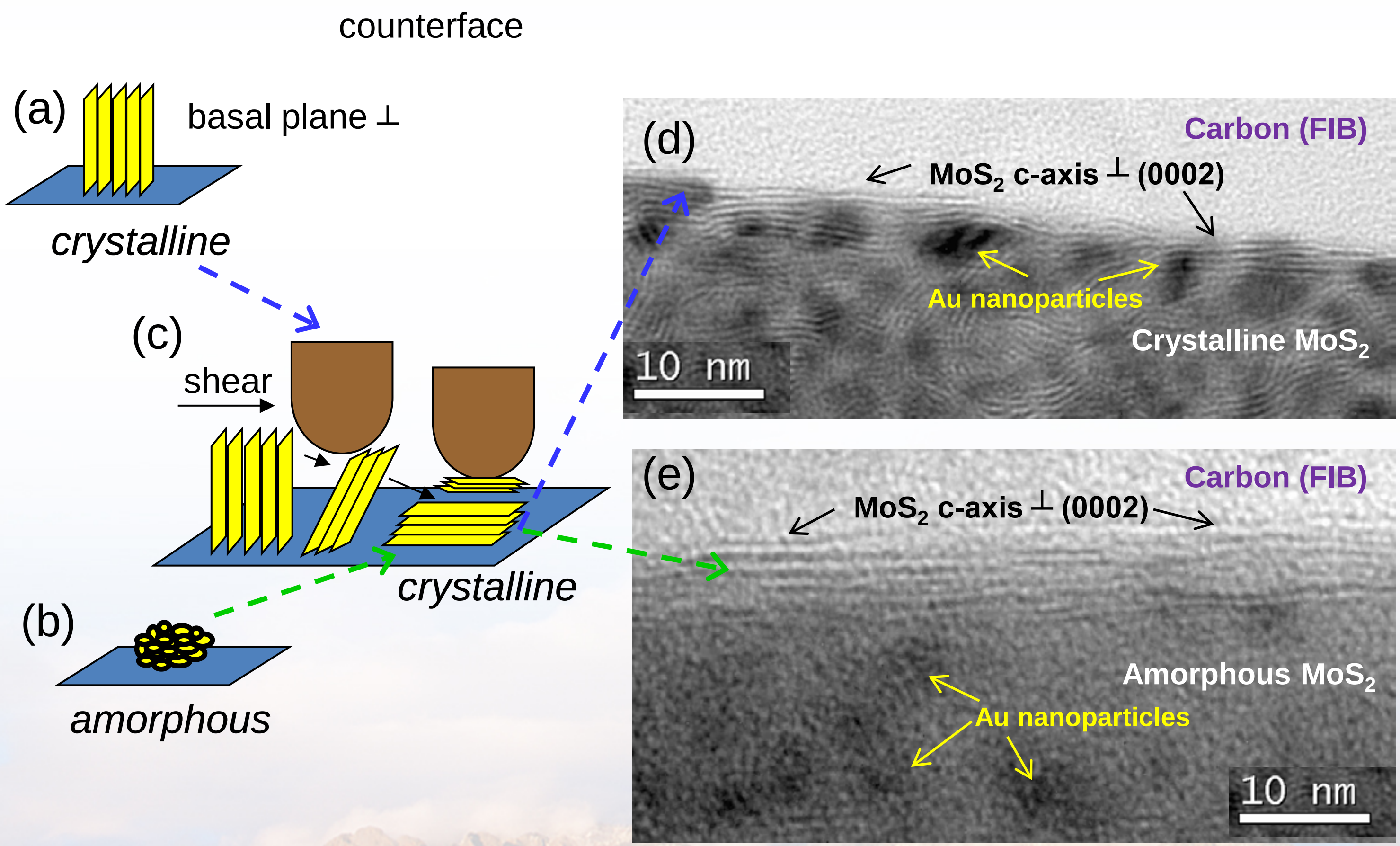
Whether the MoS_2 is in nanocrystalline form or amorphous, friction induces crystallization with basal planes aligning parallel to the surface





T. W. Scharf, P. G. Kotula and S. V. Prasad, Acta Materialia 58 (2010) 4100-4109

Friction-induced crystallization and reorientation of basal planes



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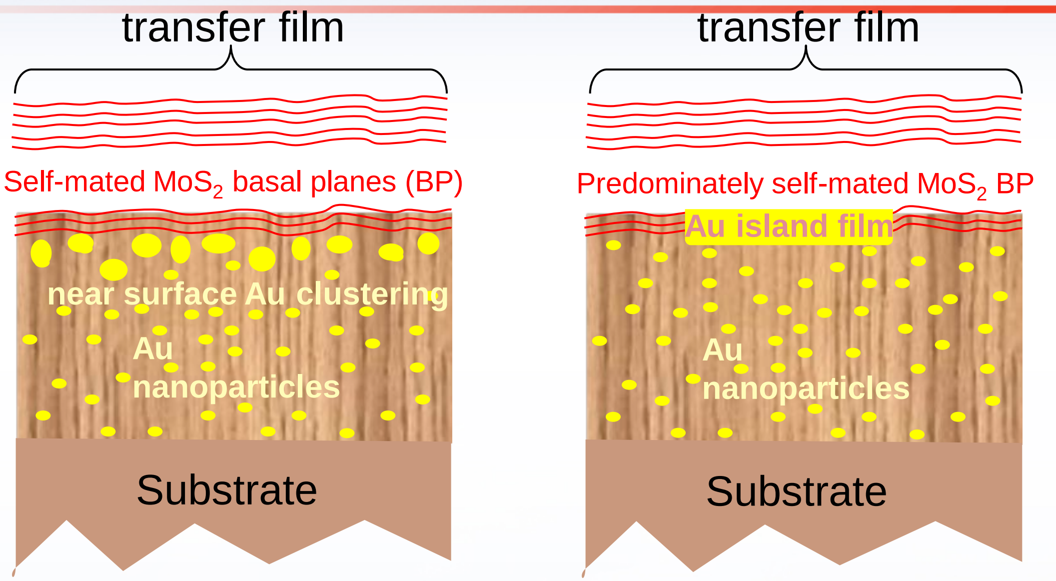
Mechanisms of Friction



Worn (dry nitrogen)　　Worn (air with 50%RH)

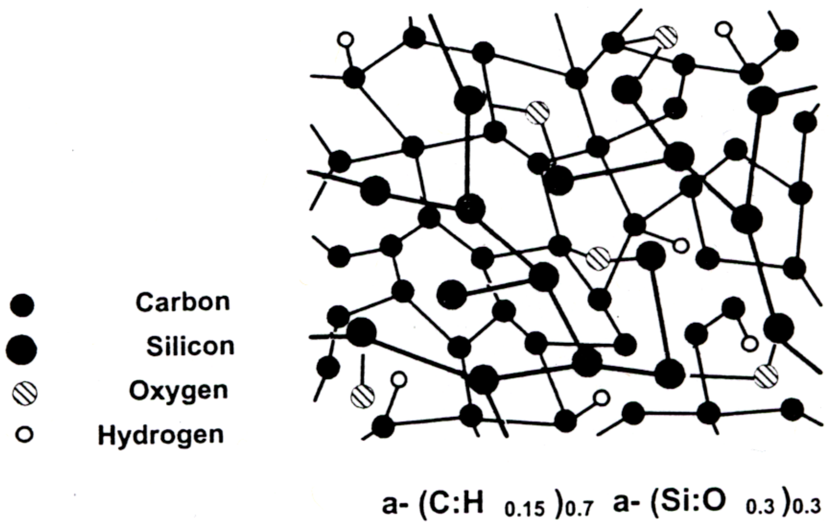
- Whether the MoS_2 is in nanocrystalline form or amorphous, friction induces crystallization with basal planes aligning parallel to the surface
- COF in air is higher but the wear rate is almost identical, indicating the environmental robustness of wear for the nanocomposite (MoS2/Sb2O3/Au) coating
- Sb_2O_3 makes the coating brittle

- Diamond-Like Carbon
- Subsurface Deformation
- Load Bearing and Barrier Layers

Diamond-Like Carbon Nanocomposites

Plasma Enhanced CVD

Ployphenylmethylsiloxane precursor



Schematic of DLN atomic structure.

Interpenetrating random networks
DLC (a-C:H) and glass like a-Si:O

- Conformal coatings could provide coverage of sidewalls
- Substrate temperatures do not typically exceed 150 to 200 ºC

Hardness: 9-17 GPa
Modulus: 90-140 GPa

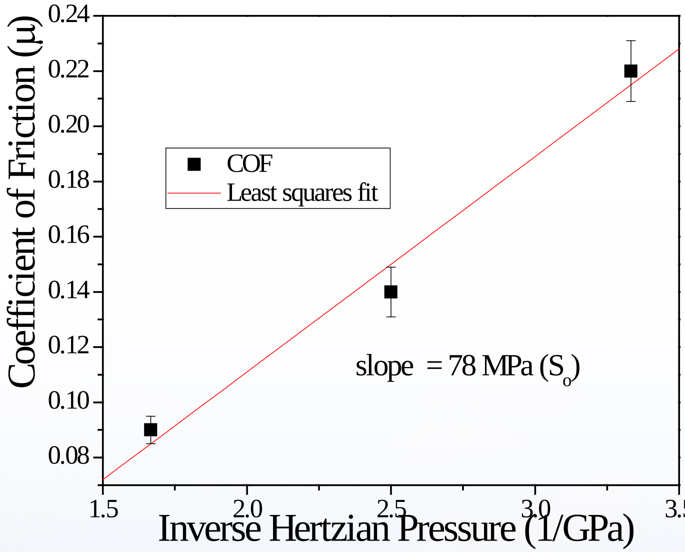
V. F. Dorfman, *Thin Solid Films*, 212 (1992) 267-273

D. J. Kester, C. L. Brodbeck, I. L. Singer and A. Kyriakopoulos, *Surface and Coatings Tech*. 113 (1999) 268-273.

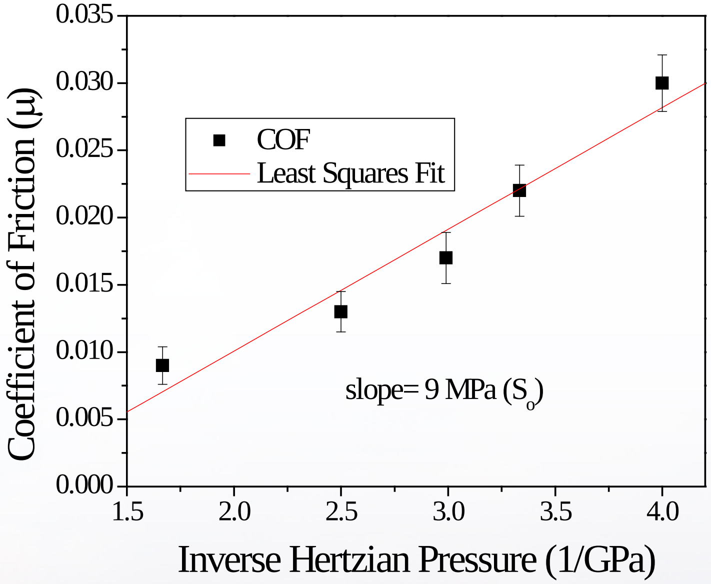
C. Venkatraman, C. Brodbeck and R. Lei, *Surface and Coatings Tech*. 115 (1999) 215-221.

The Friction Behavior is non-Amontonian

Air (50% RH)



Dry Nitrogen



- Load Dependence
- Environmental Effects
- (Note the difference in the slopes)

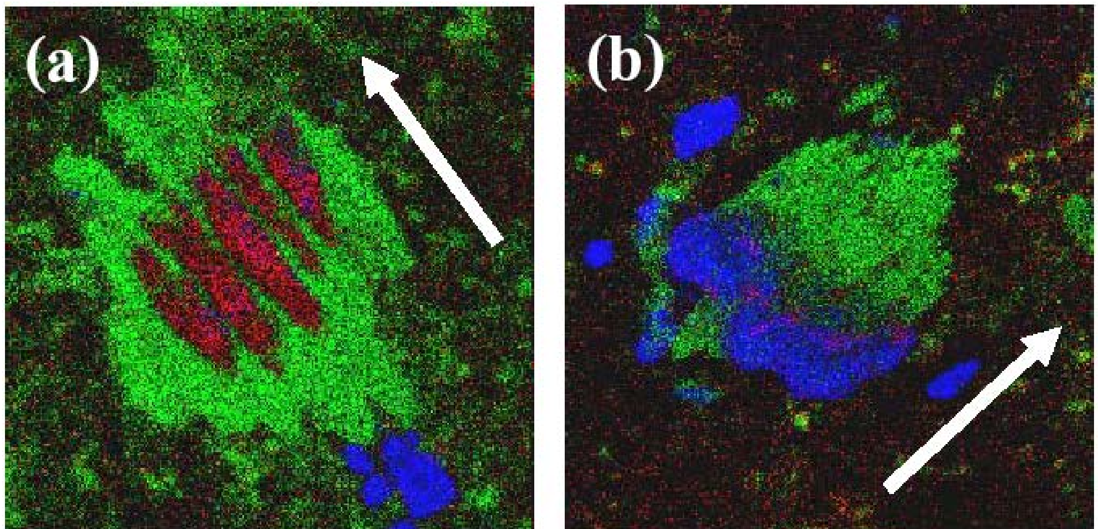
T. W. Scharf, J. A. Ohlausen, D. R. Tallant, S. V. Prasad, J. Appl. Phys. 101 (2007)

Sandia National Laboratories

ToF-SIMS of Transfer Films illustrating the Chameleon Nature

Humid Air (μ~.2) | Dry Nitrogen (μ~.02)

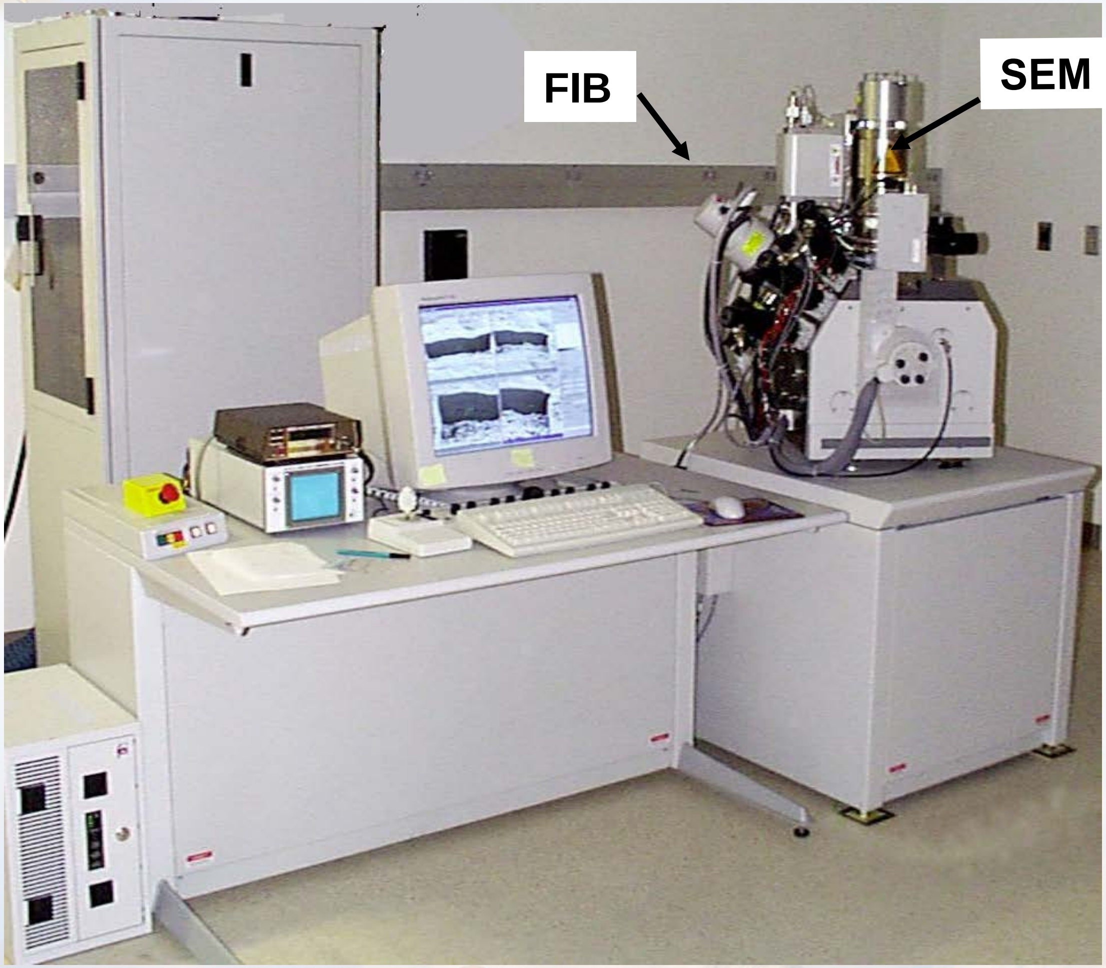
ToF-SIMS



Red: SiO_2 ($O + Si + SiO_2 + SiO_3$)
Green: Long Range Carbon (C_1 to C_4 fragments)
Blue: Hydrogenated Carbon ($CH + CH_2 + C_2H$)

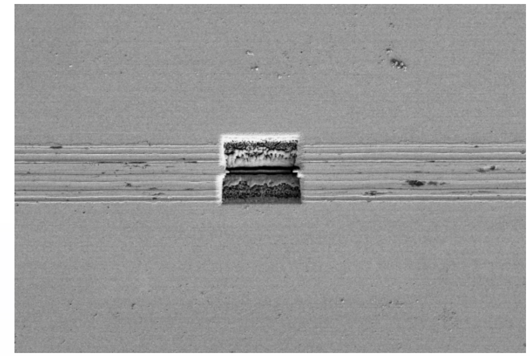
78 MPa | 9 MPa

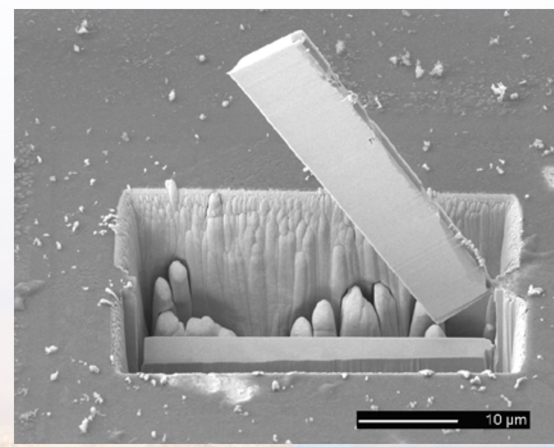
FIB-EBSD-TEM were used for analyzing the friction-induced damage below the wear surfaces



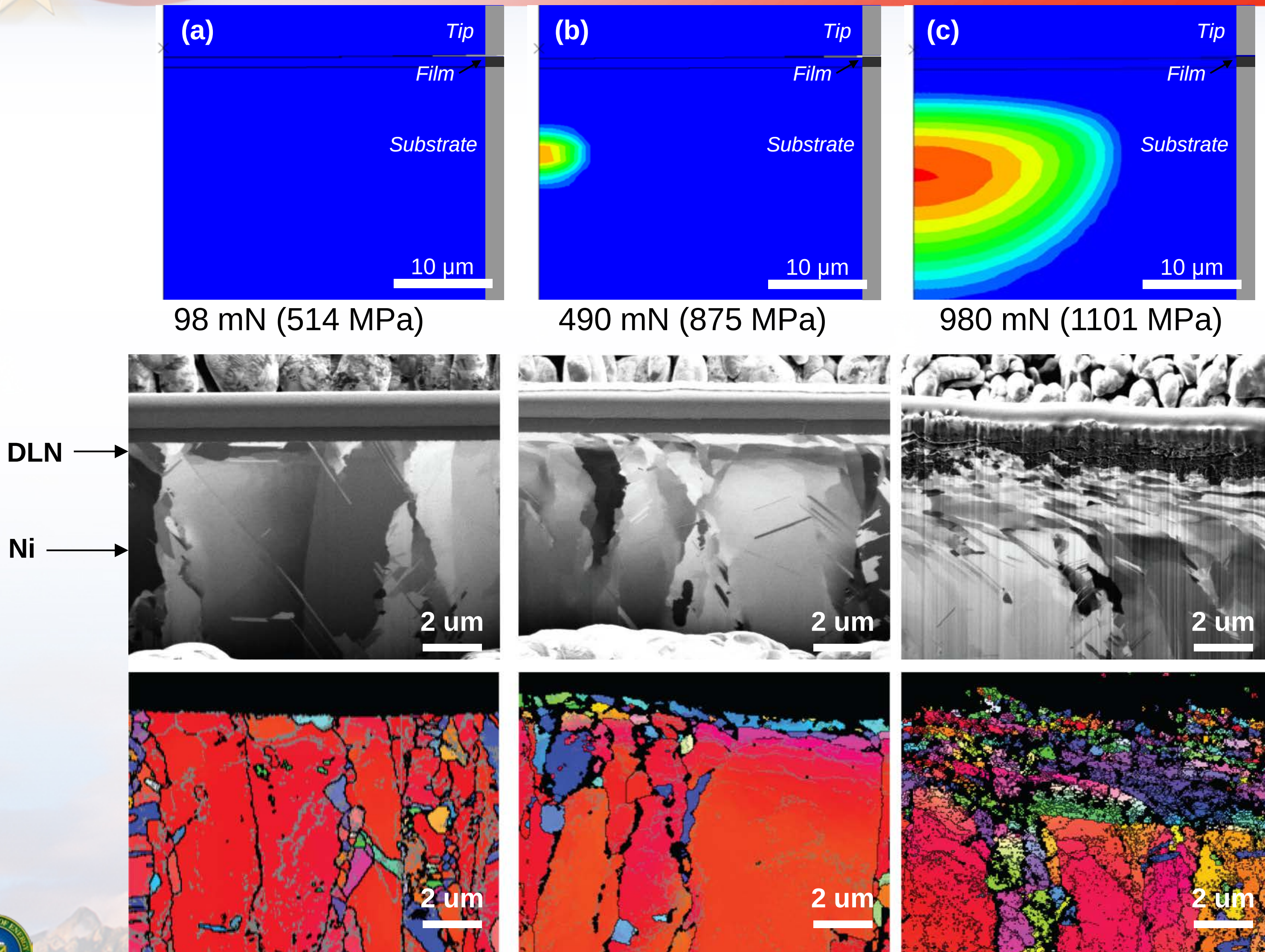
Dual-beam system: Both a FIB column and a SEM column are present on one sample chamber.

Sliding Direction



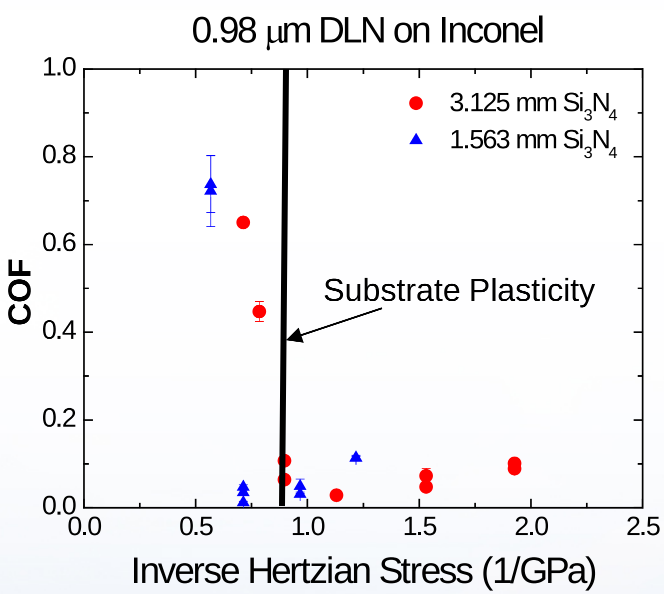


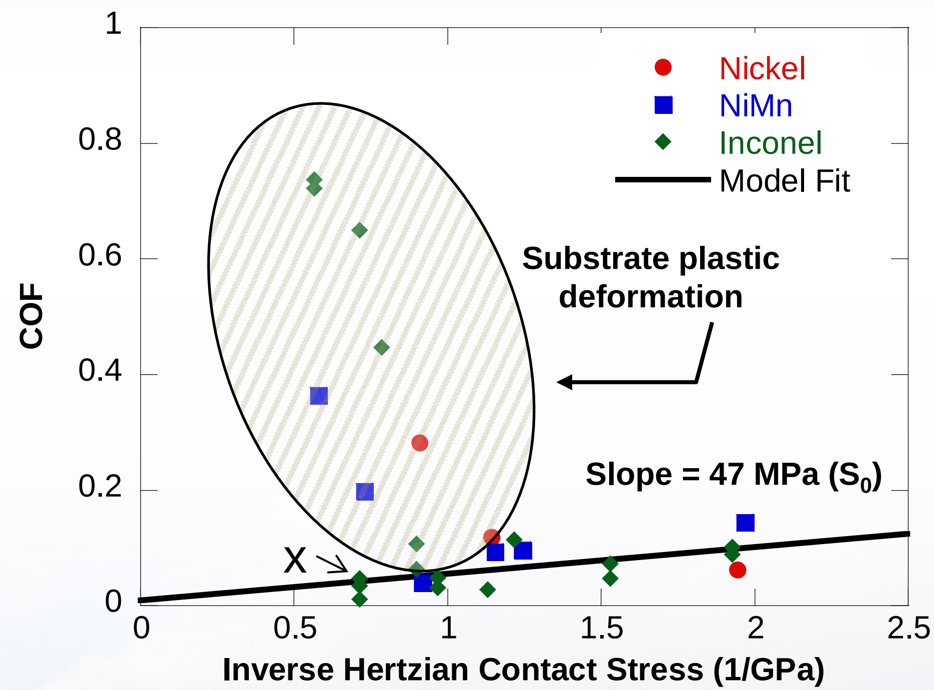
Friction Induced Plastic Deformation in the Substrate



S.V. Prasad, J.R. Michael T. R. Christenson, Scripta Materialia, 48 (2003) 48

Deviations from Predicted Behavior





FEM predictions of substrate plastic deformation are in general agreement with observed deviations in Hertzian contact model

Multi-Layer Architectures may be necessary to mitigate substrate plastic deformation

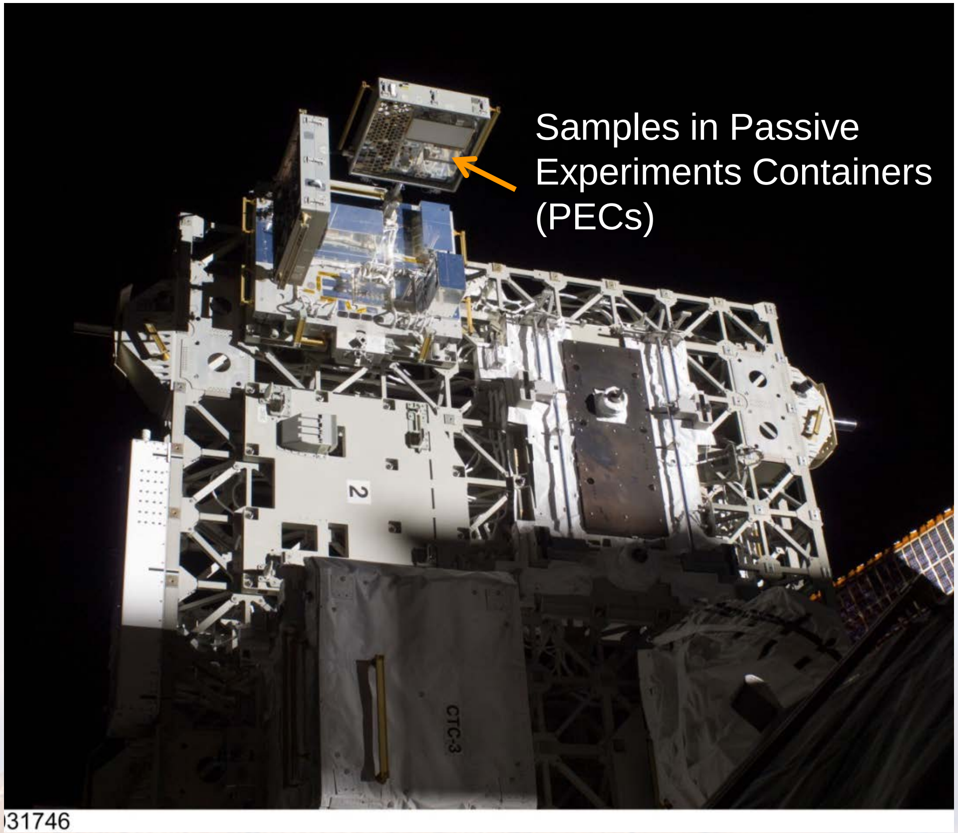
J.M. Jungk, J.R. Michael and S.V. Prasad, Acta Materialia, (2008) 56: 1956-1966.

Space

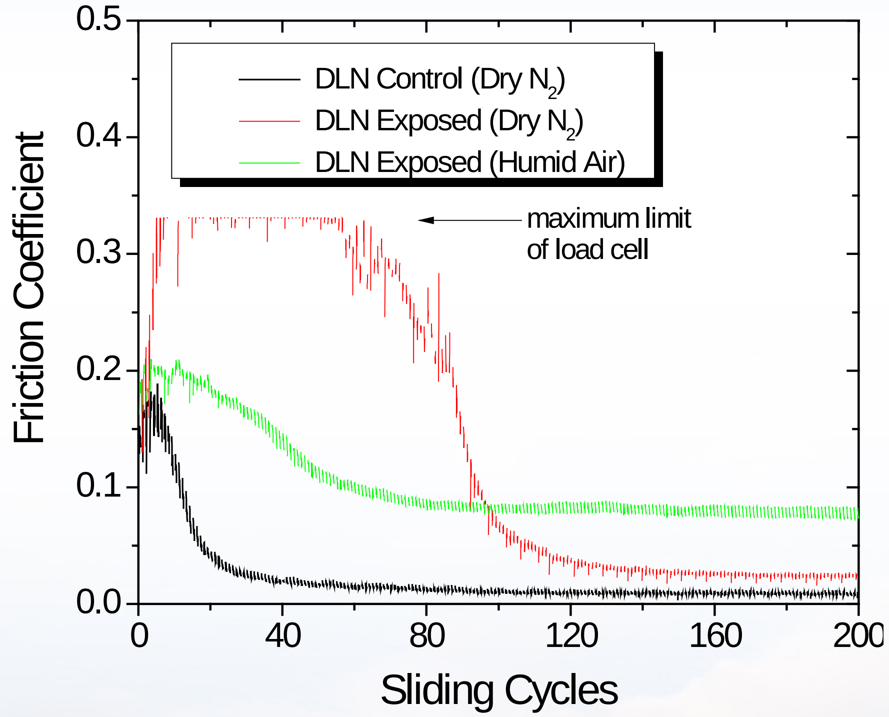
Materials on the International Space Station Experiment (MISSE-7)

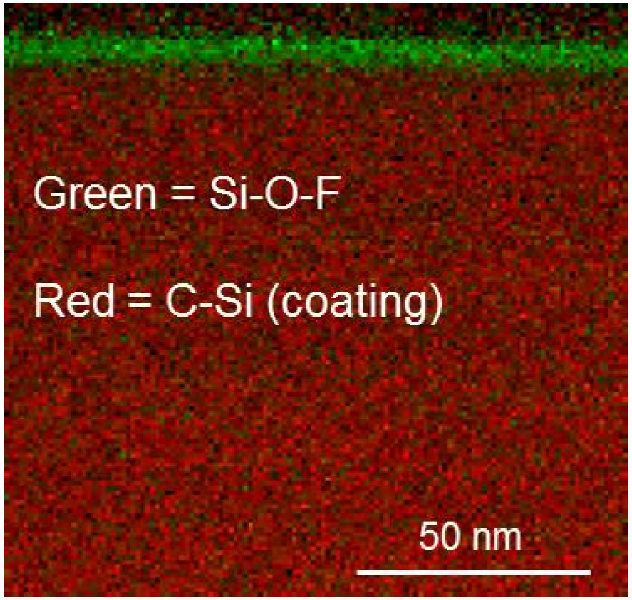
STS-129 (November 16, 2009): To ISS
STS-133 (March 1, 2011): Recovery

1. DLN
2. MoS_2-Sb_2O_3-Au



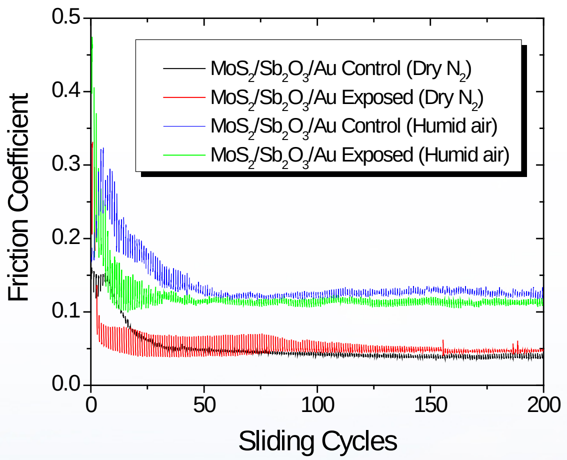
The Effects of LEO environments: DLN

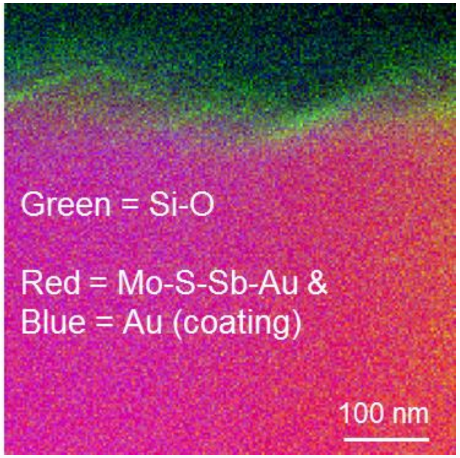




- Surface Contamination
- Increase in the Run-in Period

The Effects of LEO environments: MoS_2-Sb_2O3-Au





- Surface Contamination
- But the increase in the Run-in Period is significantly less

M.T. Dugger, T.W. Scharf and S.V. Prasad, "The Effects of Low Earth Orbit on Thin Film Solid Lubricants" Advanced Materials and Processes, May 2014

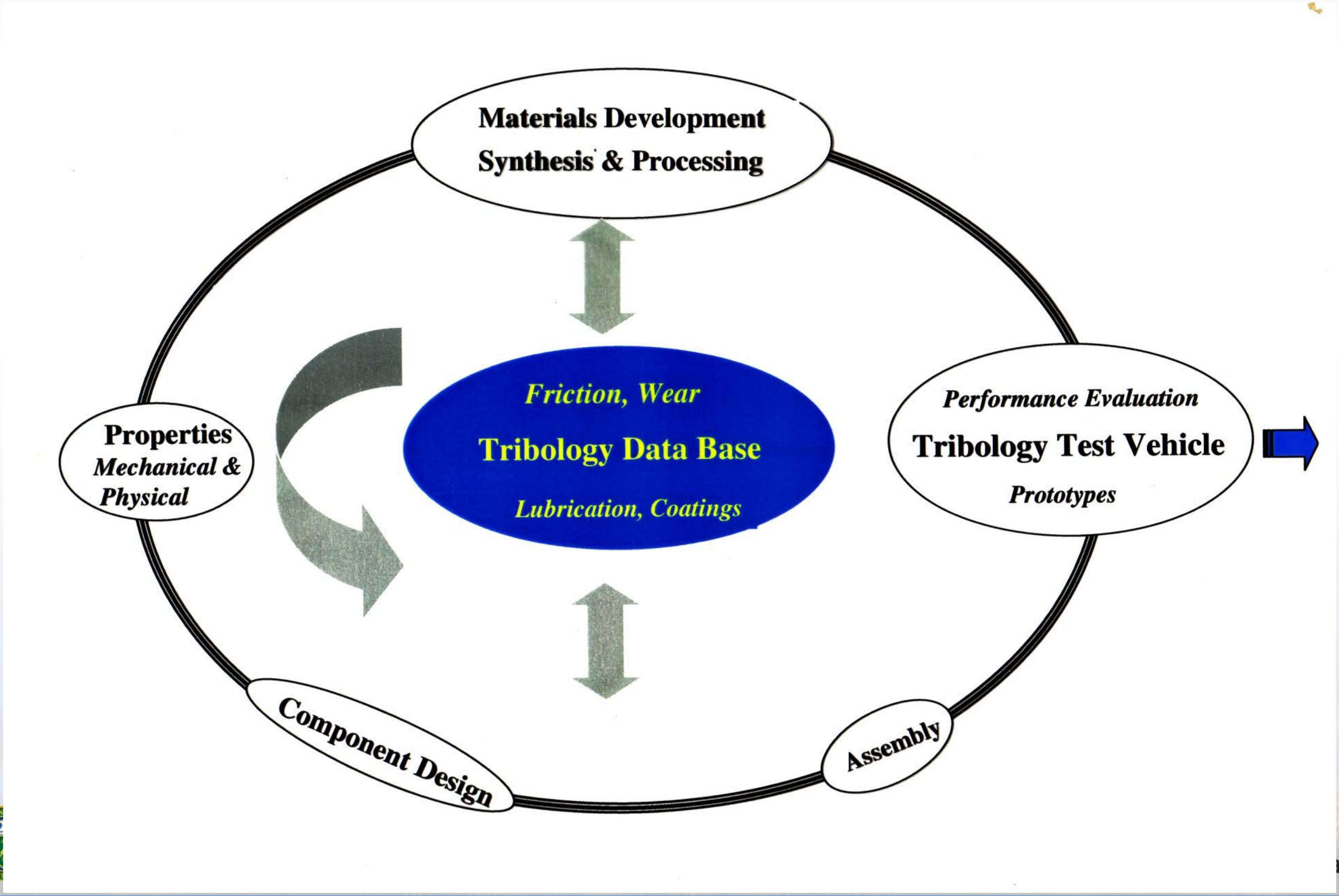
Concluding Remarks

- **Solid lubricant coatings are needed, specifically when the operating conditions are beyond the liquid realm or in situations where liquids cannot be introduced.**

- **No single phase material can give low friction and wear in all environments and under all operating conditions**
  - Many Solid Lubricant Coatings Exhibit Load Dependence on Friction
  - Environment plays a very significant role in determining the tribological behavior
  - Introduce multilayer coatings if subsurface plastic deformation cannot be avoided

- **Materials designed for friction and wear mitigation, commonly referred to as tribological materials, must also meet mechanical and physical property requirements. From a practical design perspective, it becomes almost impossible to balance these diverse requirements and mitigate friction from bulk materials that are used to build tribological components.**
- **Avoid using metallurgically compatible metals/alloys in sliding contacts**
- **Use systems approach for the design of tribological contacts**

Systems approach is an integral part of Tribology



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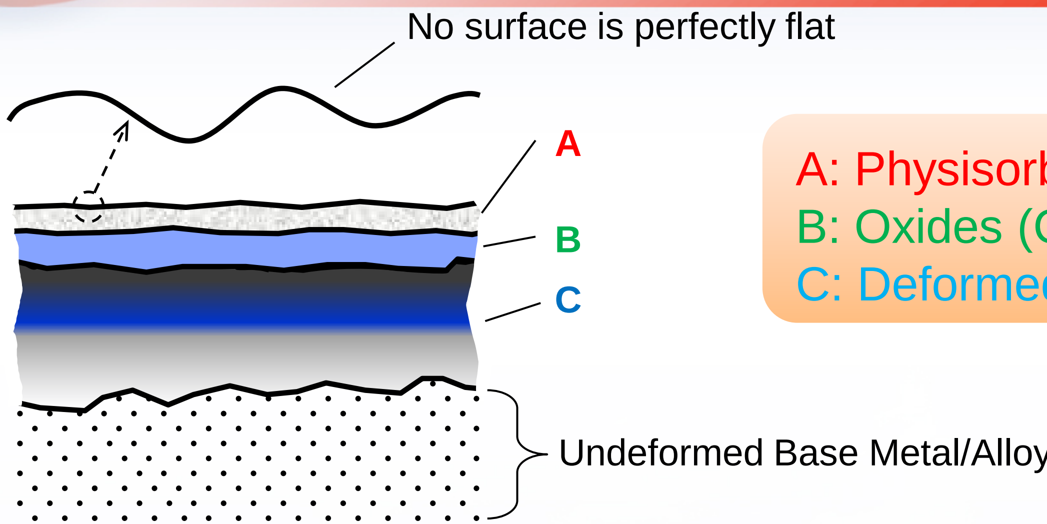
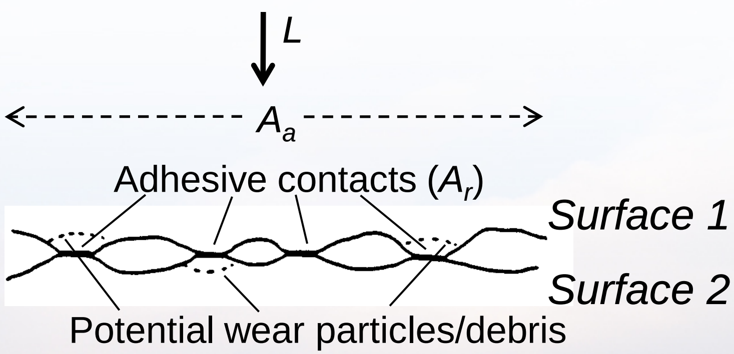
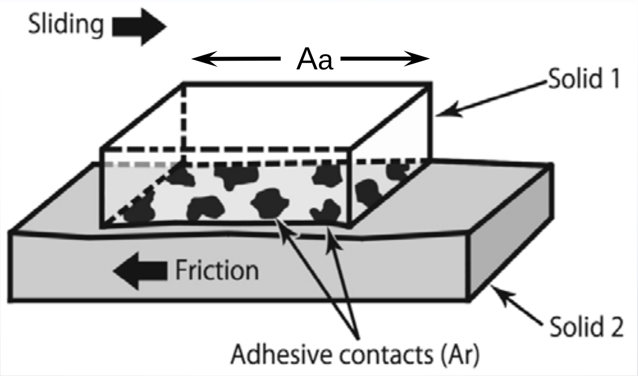
Backup Slides

Nature of Metallic Surfaces



A: Physisorbed/Chemisorbed
B: Oxides (Chemically Reacted)
C: Deformed layers





The real area of contact is a small fraction of the apparent area of contact.

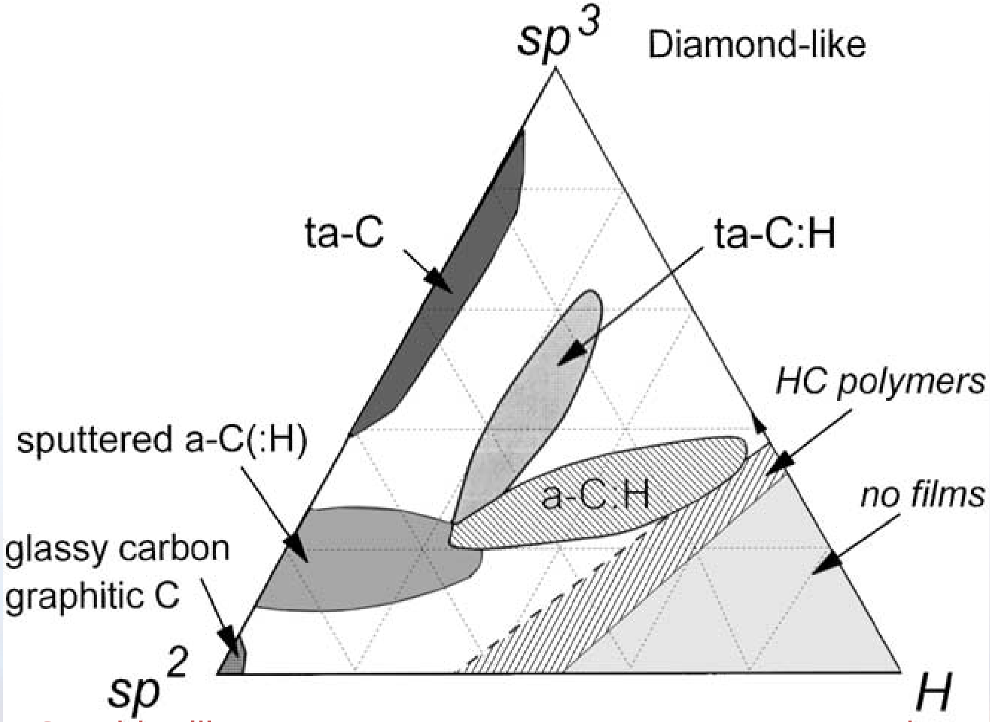
- *Surface topography and cleanliness are critical to performance and reliability of the coated component*

T.W. Scharf , S.V. Prasad, Journal of Material Science (2013) 48:511-531

Ternary phase diagram of bonding in amorphous carbon-hydrogen materials

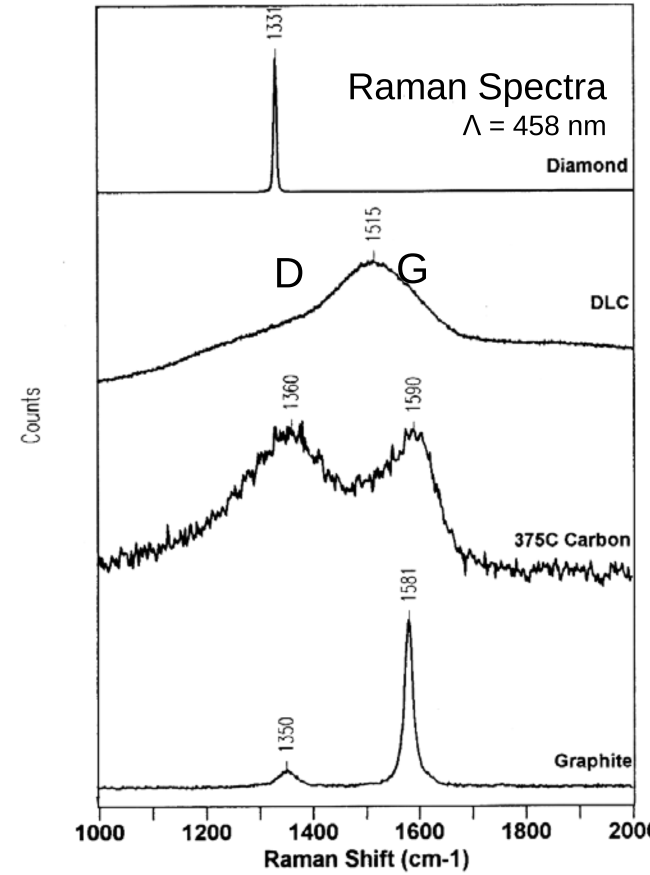
- Diamond-like Carbon has mixed sp^2/sp^3 bonding with majority being metastable sp^3, unless it is stabilized with C-H bonds.
- DLC cab be amorphous (a-C) or hydrogenated amorphous carbon (a-C:H) (typically 10-50 atomic % H).

Diamond-like



Graphite-like

Hydrogen

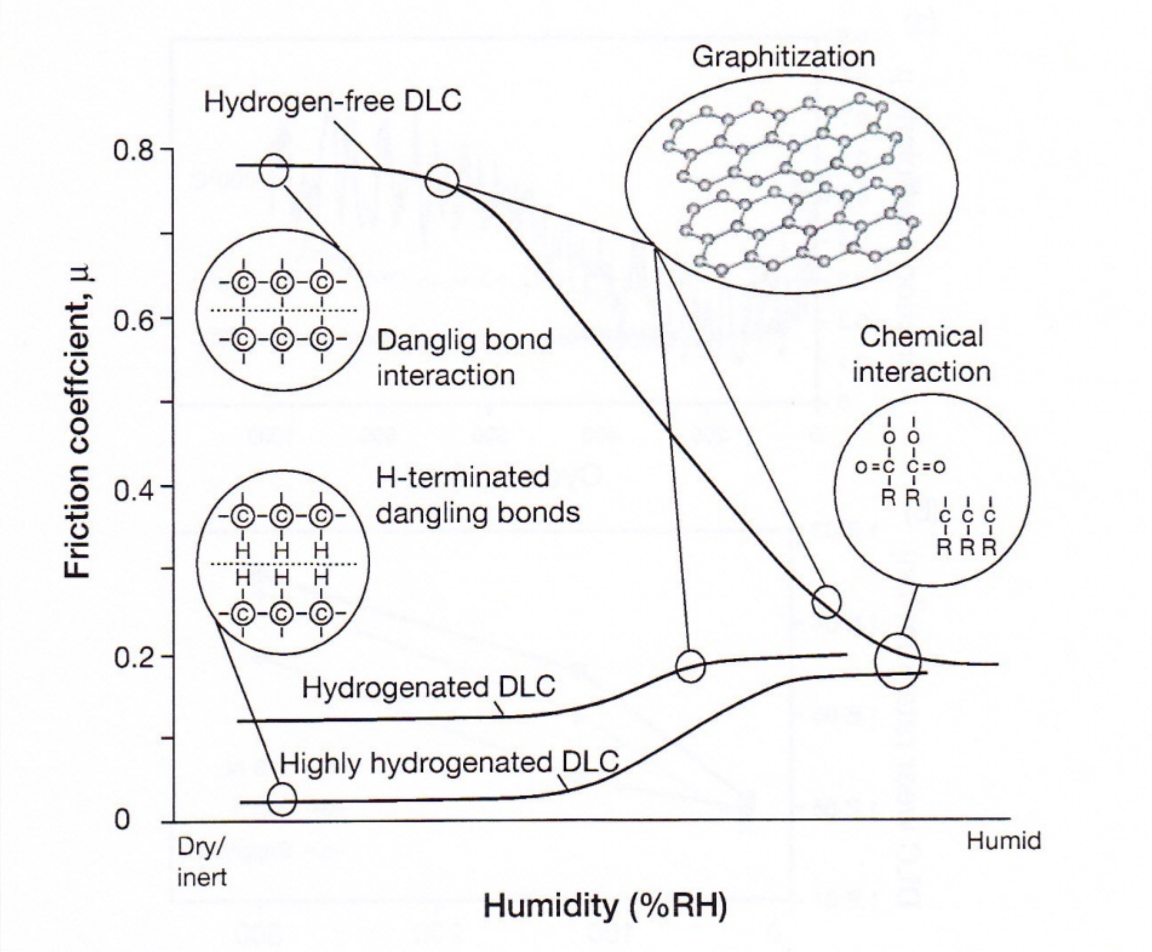


From J. Robertson (2002) Mater Sci Eng R 37: 129.

D. R. Tallant et. al, *Diamond and Related Materials* 4 (1995) 191-199

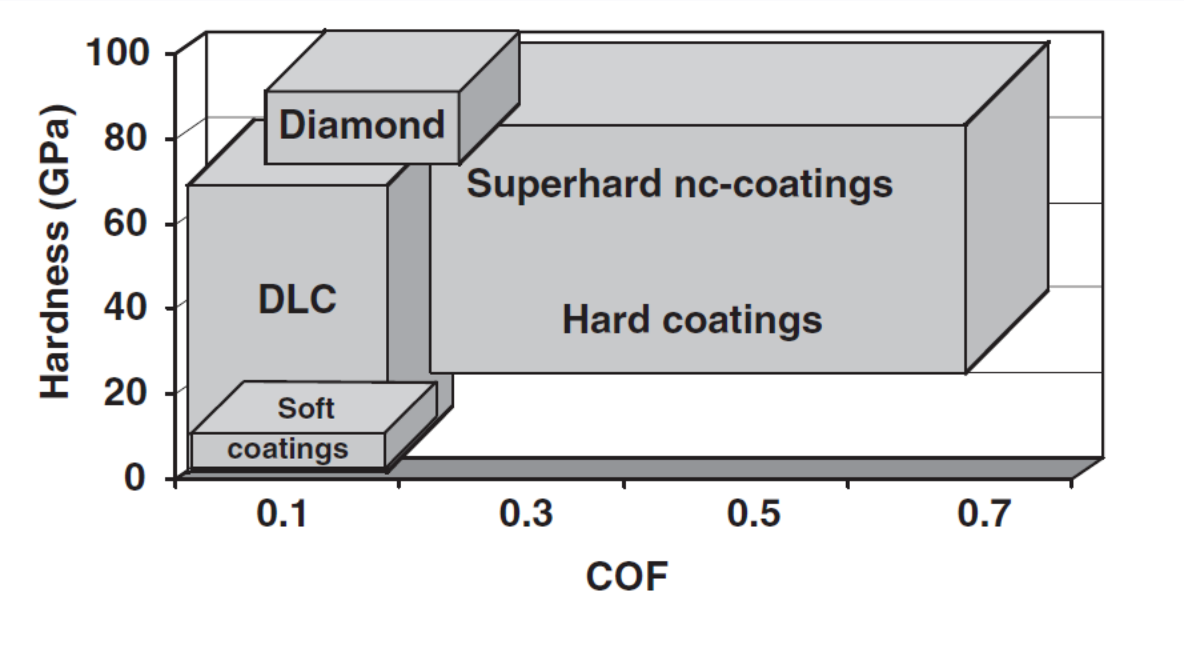
Synthesizing an Environmentally Robust DLC is Still a Challenge!

- Hydrogenated DLCs give low friction in dry environments.
- Hydrogen free DLCs require moisture to terminate dangling bonds.



H. Ronkainen and K. Holmberg, "Environmental and Thermal Effects on the Tribological performance of Coatings", In: C. Donnet and A. Erdemir (eds.), *Tribology of Diamond-Like Carbon Films: Fundamentals and Applications*. Springer 2008

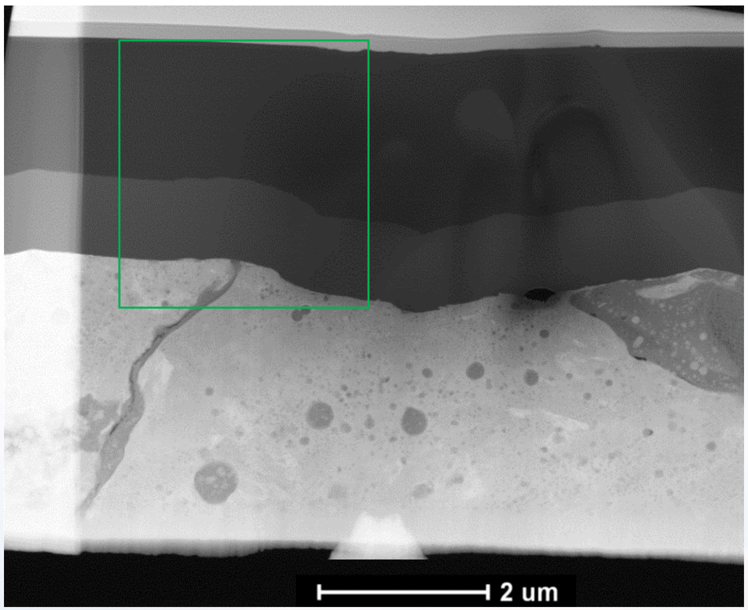
DLC can provide both high hardness and low friction

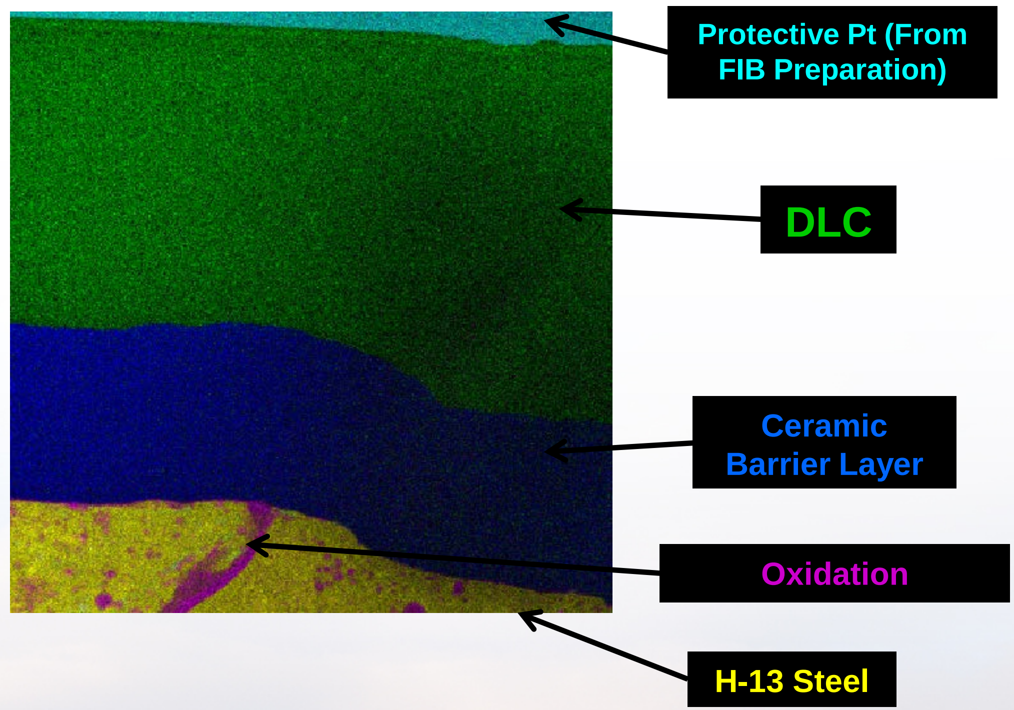


- DLCs exhibit the unusual combination of high hardness and elastic modulus in conjunction with low friction.
- This appears like an exception to the Bowden and Tabor Model which requires a low hardness for shear accommodation to achieve low friction.

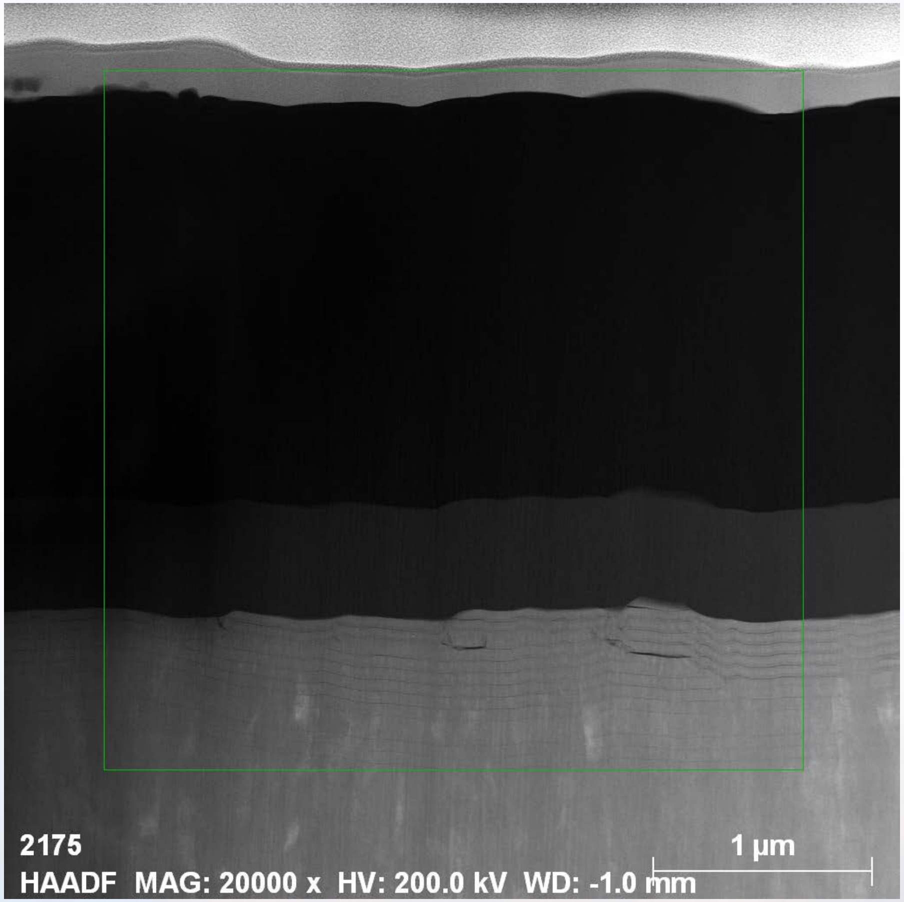
C. Donnet and A. Erdemir "Diamond-like Carbon Films: A Historical Overview," from C. Donnet and A. Erdemir (eds.), *Tribology of Diamond-Like Carbon Films: Fundamentals and Applications*. Springer 2008

Ceramic Barrier Layers may be needed for high temperature applications

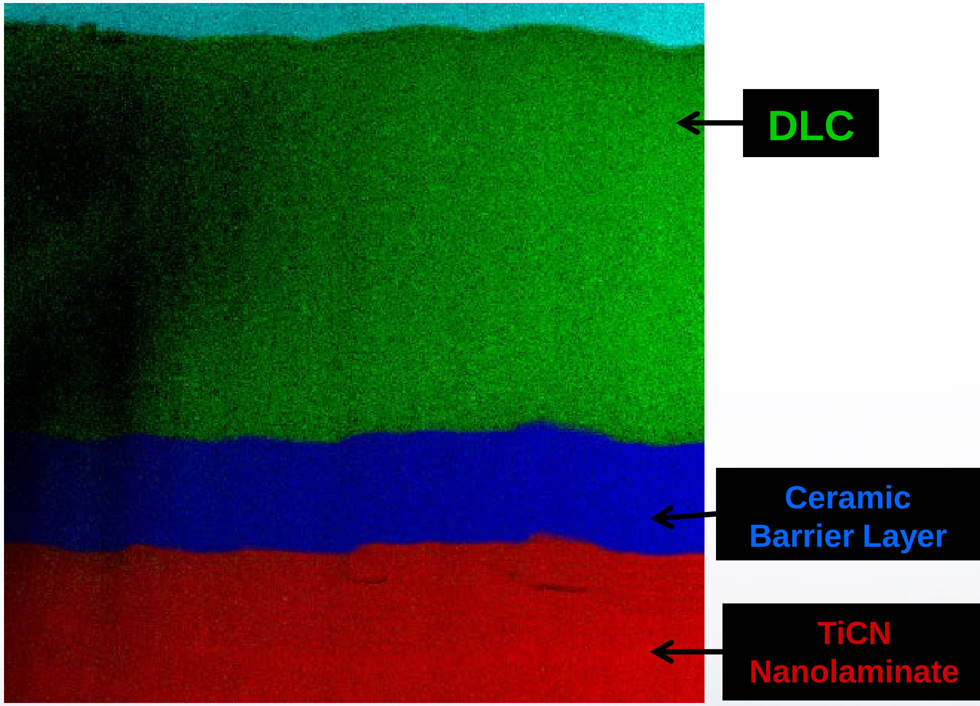




Multilayer Coatings: Adhesion, Load Bearing, Diffusion Barrier



Micro-cracks between nanolaminate layers



Robust Barrier

Tribo-Oxidation seen from the TEM of H-13 tested at 300C