

# Nanostructured Materials for Tribology

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***Oak Ridge National Laboratory, September 25<sup>th</sup>, 2105***

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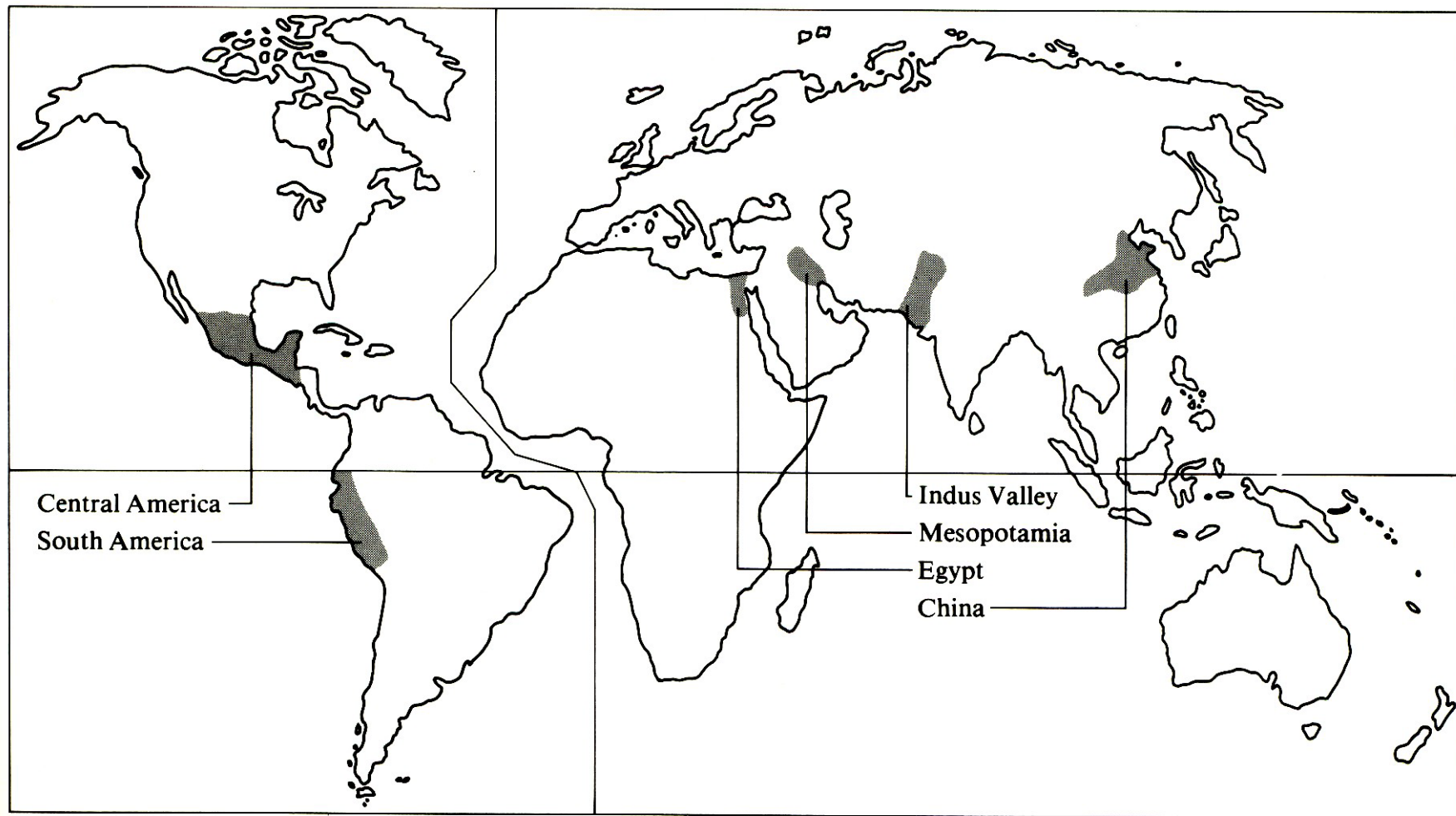
# Outline

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- **Historical background**
- **Metal-Matrix Composites (MMCs) for Automotive Applications**
- **Solid Lubricants and Coatings**
- **Electrical Contact Materials**



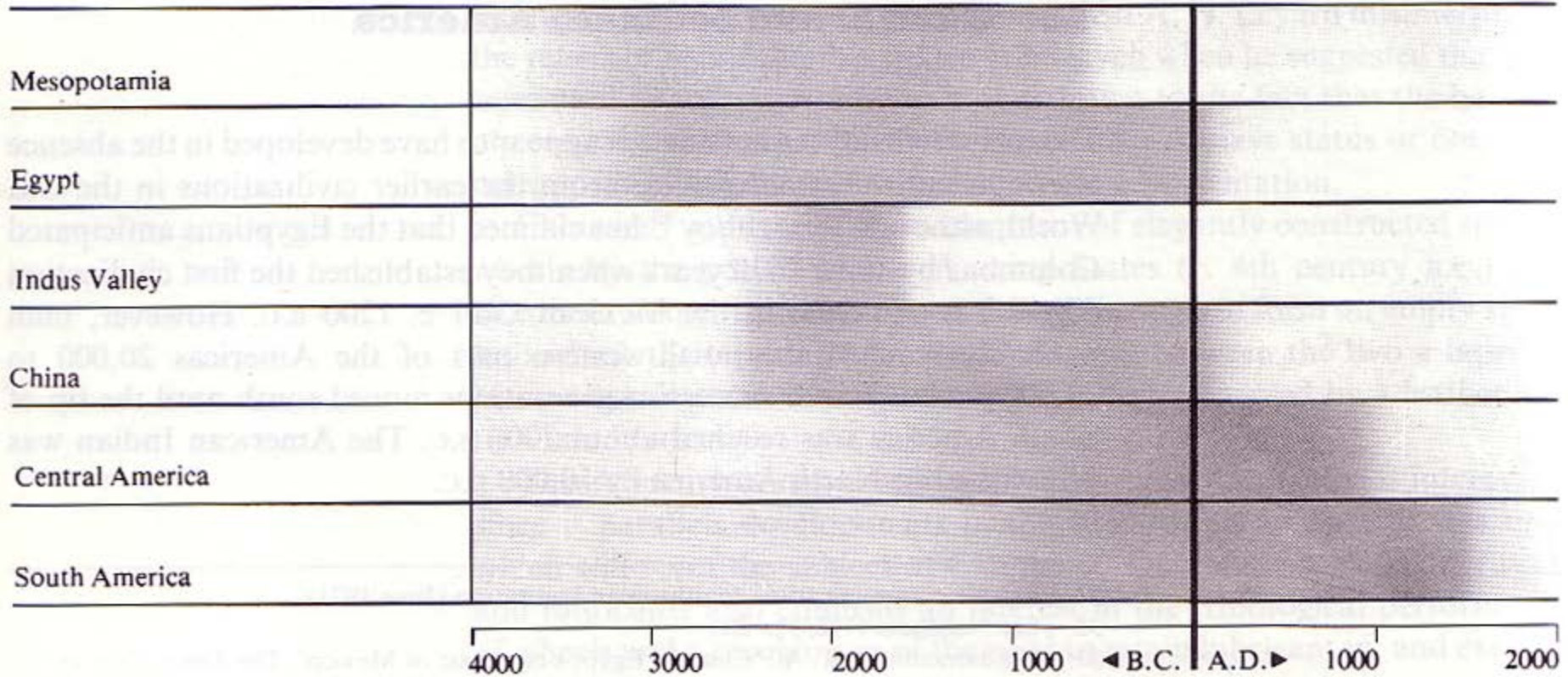
# Tribological innovations during early civilizations



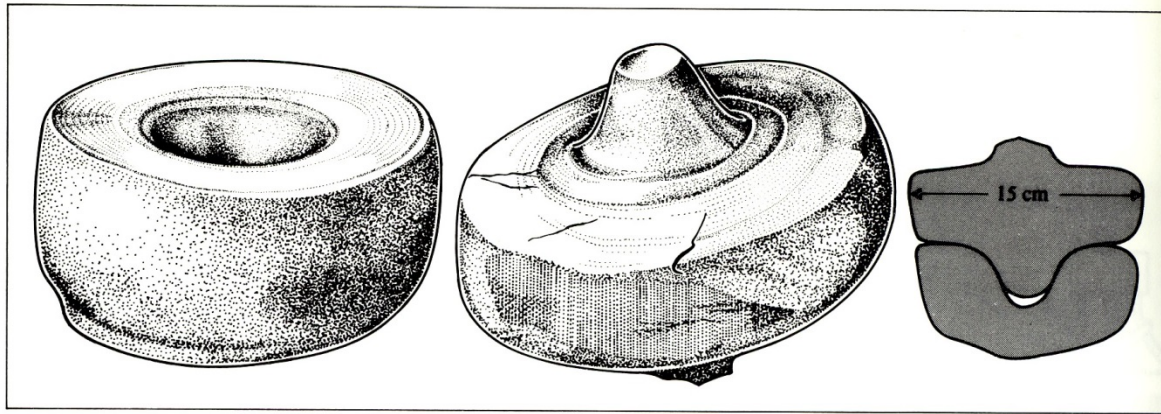
## Early Civilizations Across the World from Archeological Studies



# Approximate dates of the early civilizations



# Tribological inferences from carvings



## Potter's Wheel

|                   |           |
|-------------------|-----------|
| Sumer             | 3250 B.C. |
| Syria & Palestine | 3000 B.C. |
| Egypt             | 2750      |
| England           | 50 B.C.   |
| Americas          | 1550 A.D. |



Egyptians using a bow-drill



Sledge and wheeled vehicle (3000 B.C.)



Man on skis: Stone painting from Northern Norway



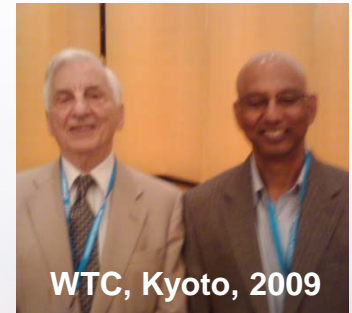
# Birth of the Phrase “Tribology”



Sir Peter Jost, CBE

Methods by which financial savings could be made through improved tribological practice in UK industry. The percentages represent proportions of the total annual saving, which was estimated at £515 million (at 1965 prices) (from UK Department of Education and Science, Lubrication (Tribology): Education and Research, HMSO, 1966)

|  |     |
|--|-----|
| Reduction in energy consumption from lower friction                      | 5%  |
| Reduction in manpower  | 2%  |
| Savings in lubricant costs   | 2%  |
| Savings in maintenance and replacement costs                             | 45% |
| Savings in losses resulting from breakdowns                              | 22% |
| Savings in investment through greater availability and higher efficiency | 4%  |
| Savings in investment through increased life of plant                    | 20% |



WTC, Kyoto, 2009

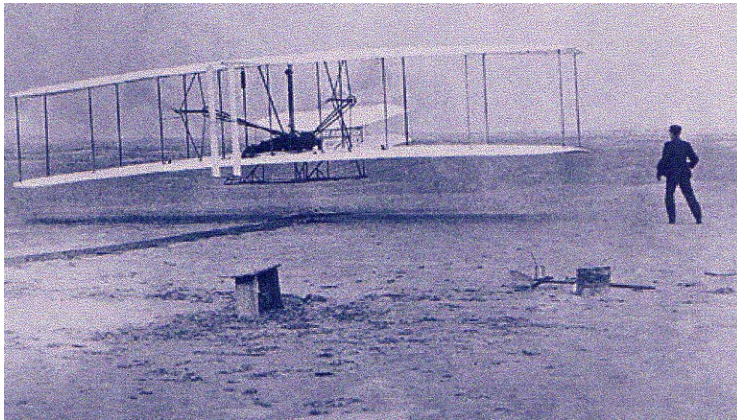
British Government Report published on **9 March 1966**

After much consideration, the concept was defined as being “the science of interacting surfaces in relative motion and associated practices” (later amended to associated subjects and practices), and after consultation with the *Editor of the Oxford Dictionary*, given the name “Tribology”, based on the Greek “Tribos” (rubbing)



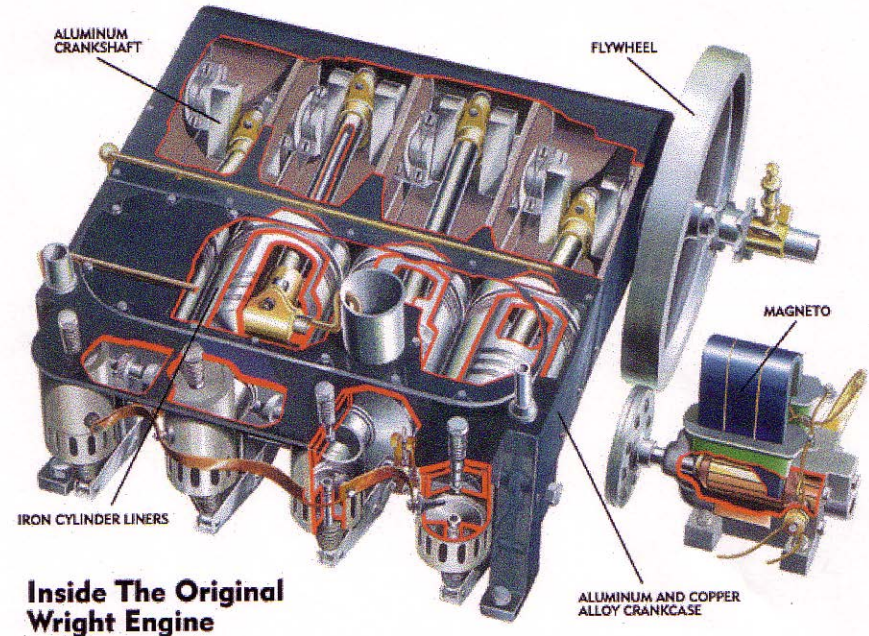
# The Saga of Wright Brothers' Engine

1903



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

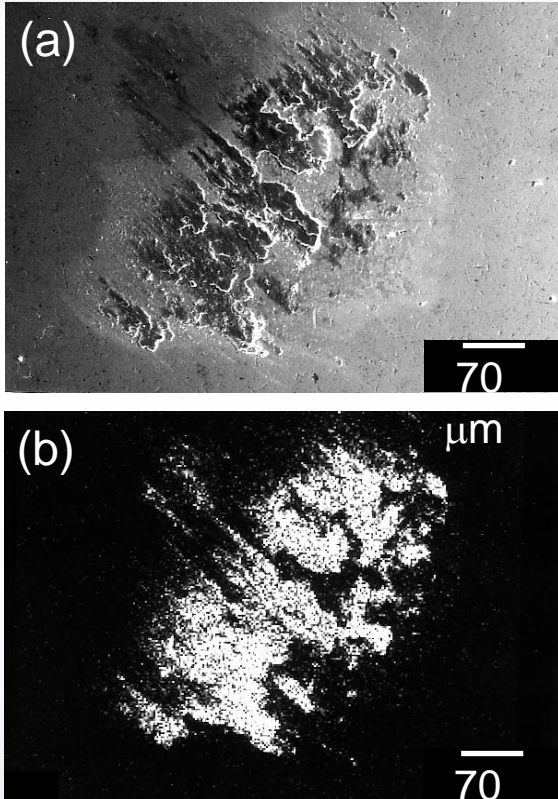
- The Brothers needed an Engine with 8 HP weighing <180 lbs



- 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.

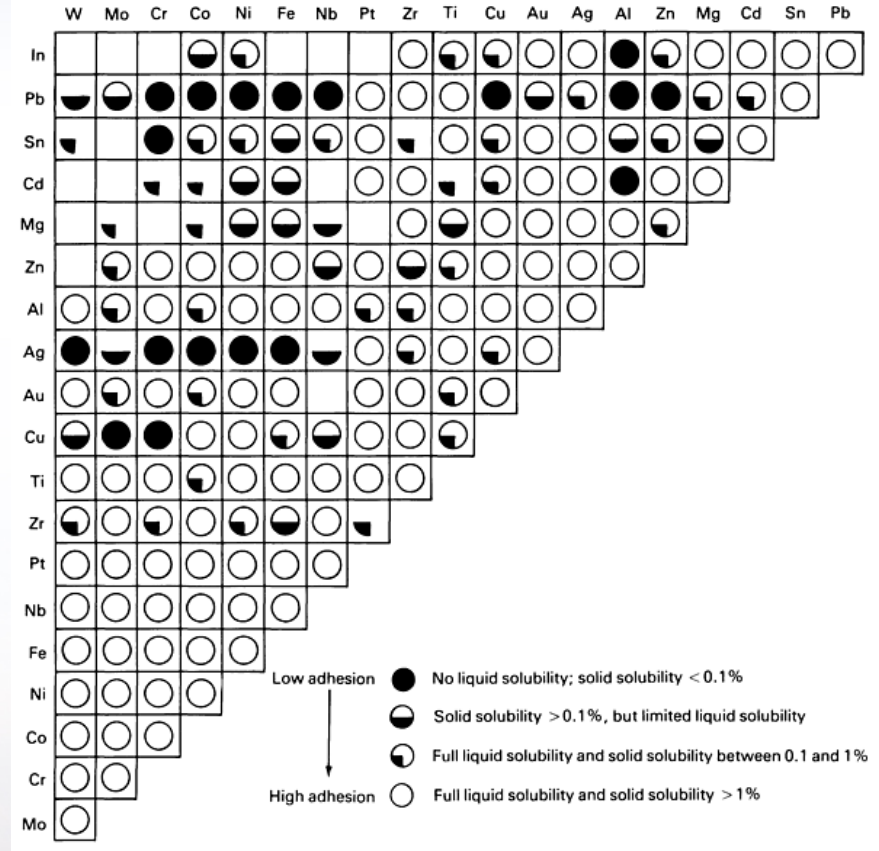
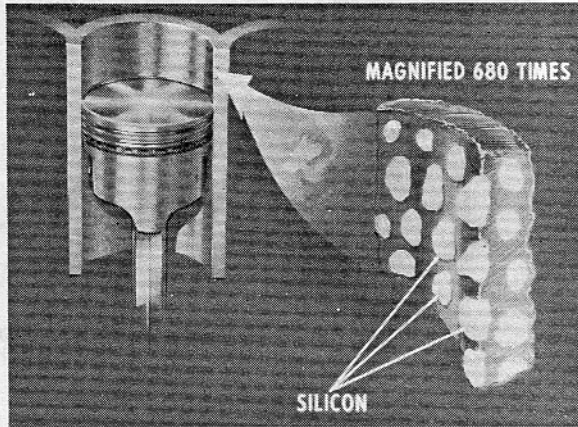


Chart indicates the degree of expected adhesion (and thus friction and wear) between the various metal combinations derived from binary equilibrium diagrams.

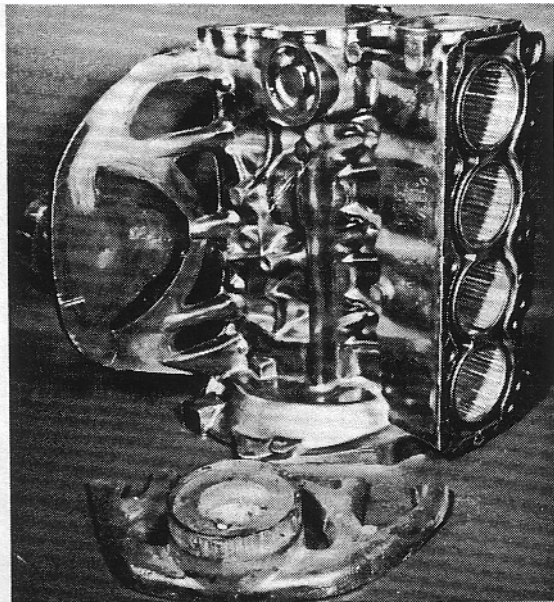
E. Rabinowicz (1971) ASLE Trans 14:198



# 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<br>91 Octane |
| Carburetor                |   |
| Standard engine           | One-barrel, Monojet                       |
| Optional engine           | Two-barrel, downdraft                     |

### CYLINDER BLOCK

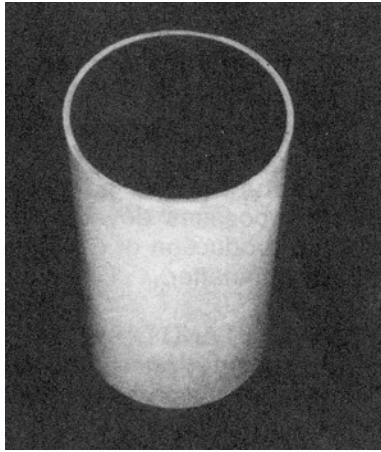
|                           |   |
|---------------------------|---|
| Material                  | Die-cast high-silicon<br>aluminum alloy |
| Bore spacing (C/L to C/L) | 4.00                                    |
| Number of bulkheads       | Five                                    |

The Vega 2300 Engine, SAE 710147



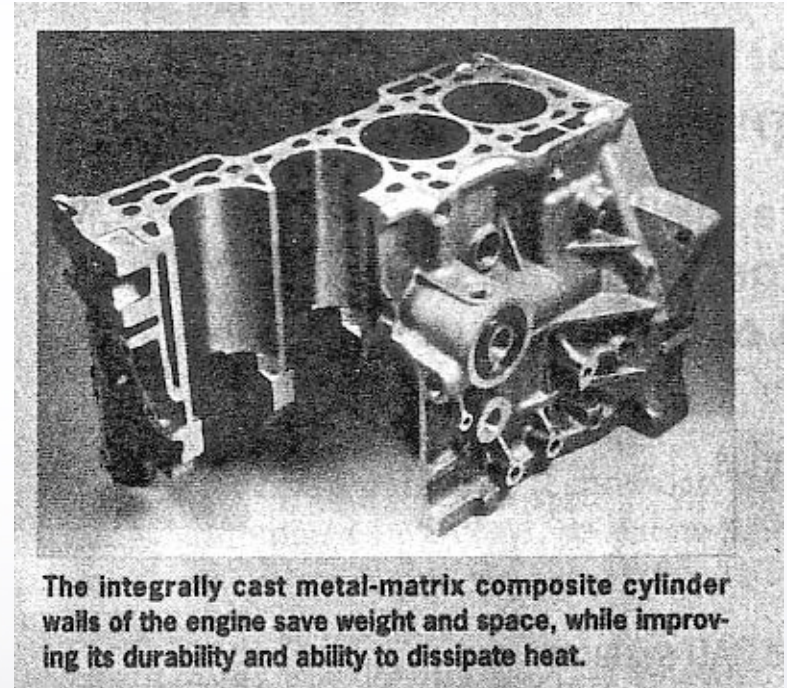
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# Integrally Cast MMC Cylinder: Honda Corporation (1980's)



**Preform**

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

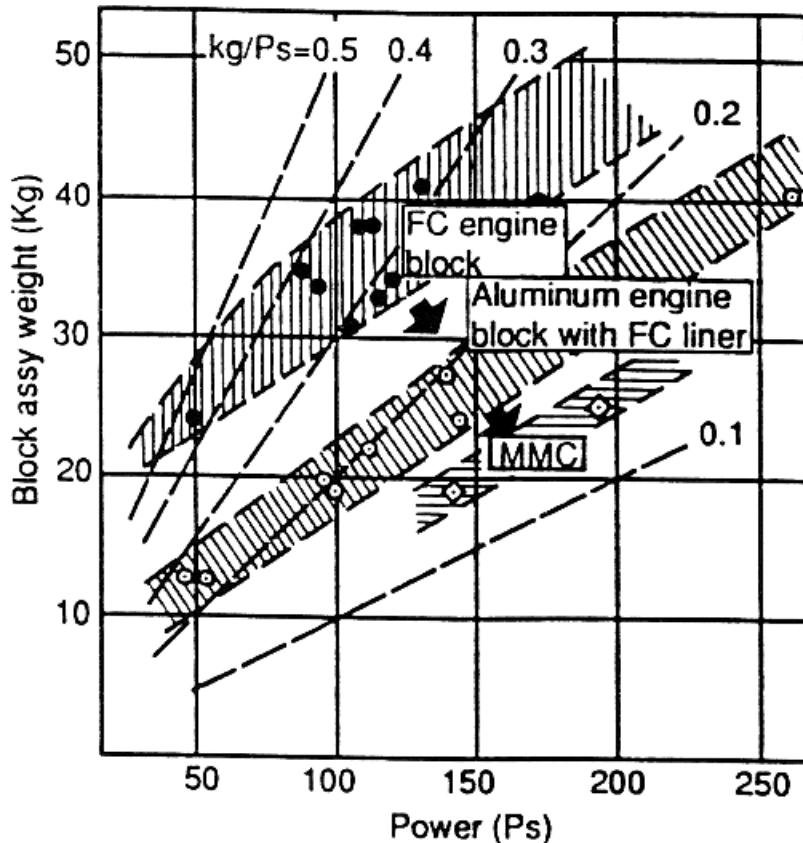


- **Ceramic “preform” production**
- **Pressure casting process**
- **Honing**
- Hybrid preforms: Carbon for thermal conduction, Aluminosilicate for strength
- Honing to minimize direct contact between Al and the piston ring

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



\*Additive Manufacturing\*



Sandia National Laboratories

# From Wright Brothers to the 21<sup>st</sup> Century

## ■ Satellites

- Communications
- Reconnaissance

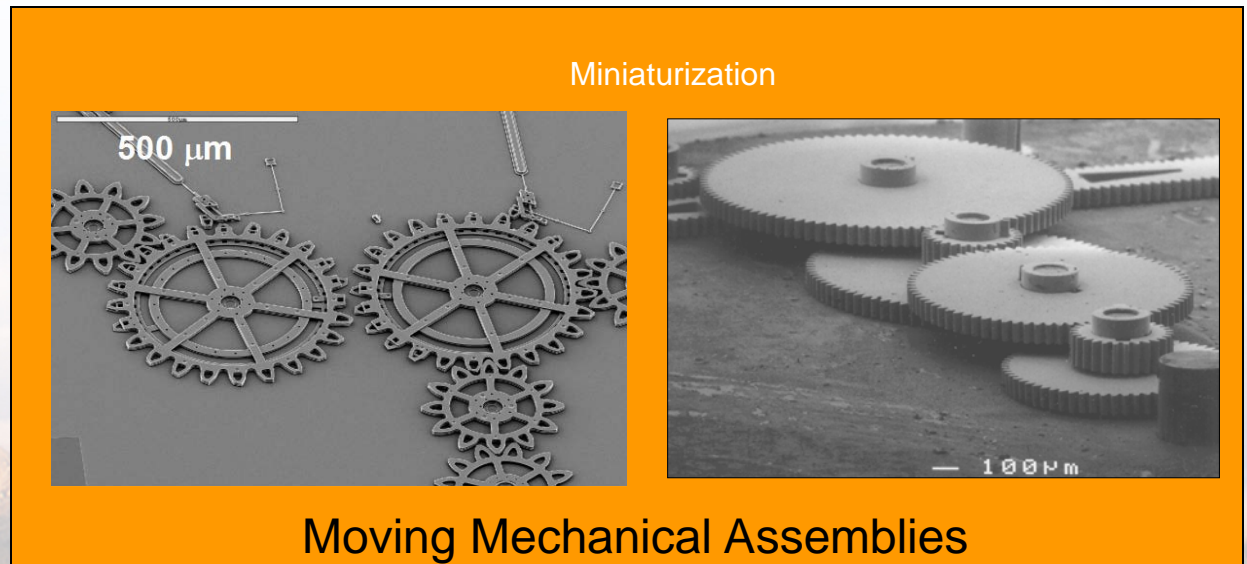
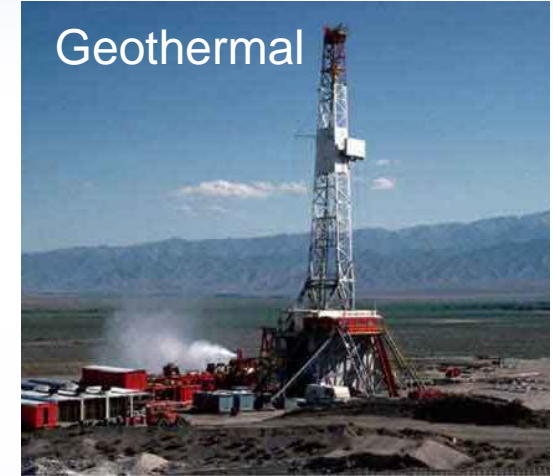
## ■ Energy and Climate

- Geothermal Drilling



## ■ Electromechanical Switches for NW

- Reliability
- Safety



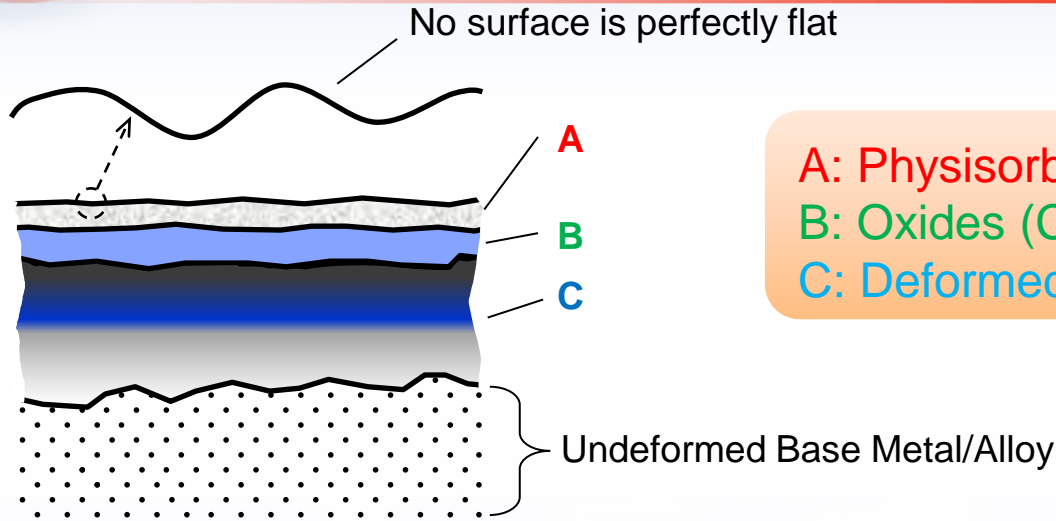


# Solid Lubricants and Coatings

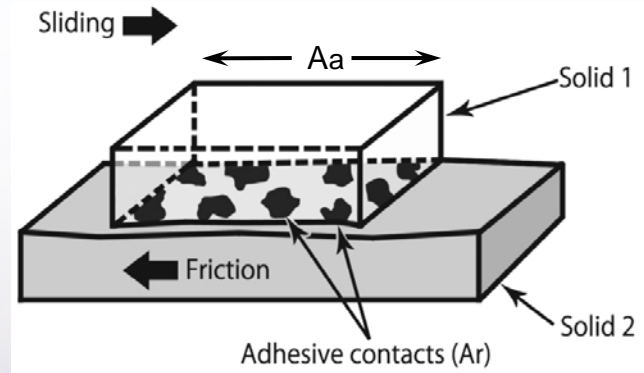
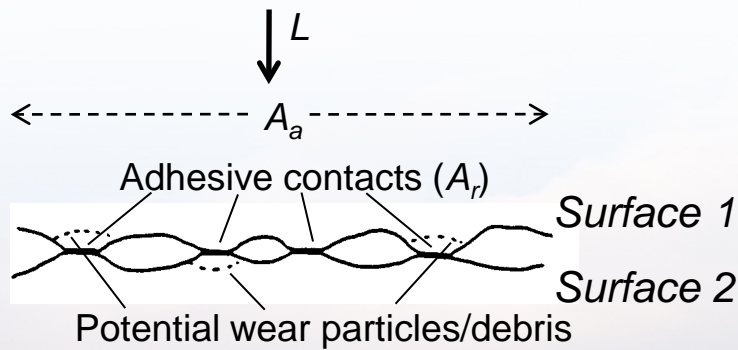
- *The major of lubrication needs still met by fluids and greases*
  - *When the operating conditions are beyond the liquid realm (e.g., high temperature or vacuum), or situations where liquids cannot be introduced, attention turns to solids*
1. Carbon-based materials (graphite, DLCs, nanocrystalline diamond)
  2. Transition metal dichalcogenides ( $\text{MoS}_2$ ,  $\text{WS}_2$ )
  3. Polymers (e.g., PTFE)
  4. Soft Metals (Ag, Sn, Pb, In , Au)



# 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.*

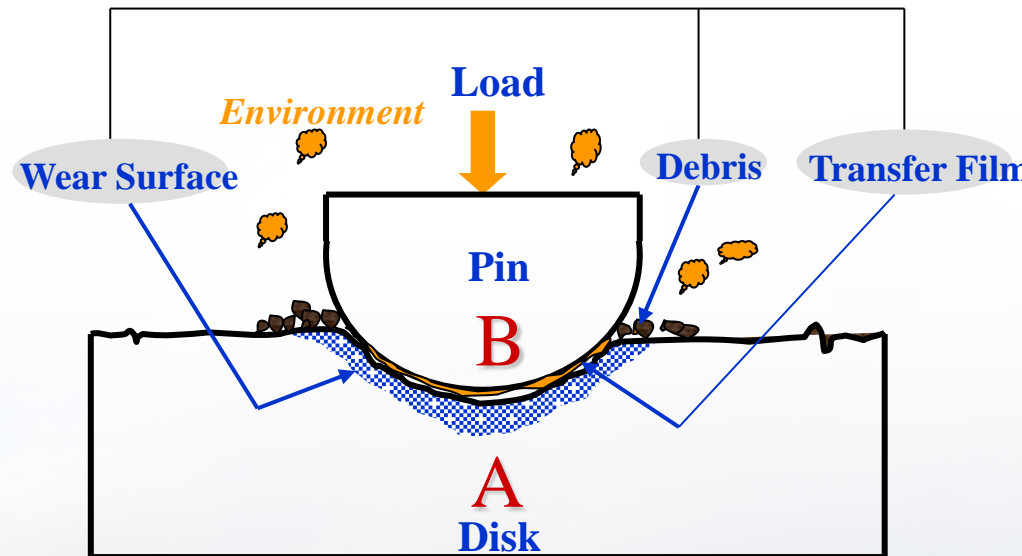
- *Surface topography and cleanliness are critical to performance and reliability of the coated component*



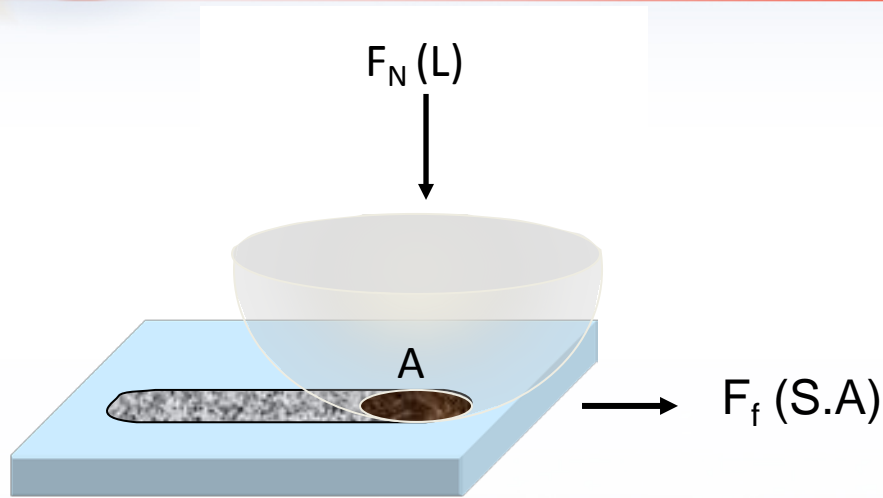
# We must recognize the limitations of the laws of friction

Tribology (friction and wear) is a systems property

- Engineering surfaces are not atomically flat
- Sliding contact results:
  - Plastic deformation
  - Diffusion (Diffusion Barriers)
  - Tribochemistry and Environmental Reactions



# Many Solid Lubricant Coatings Exhibit Load Dependence on Friction



$$P = F_N / A$$

$$F_f = S A$$

$$S = S_0 + \alpha P$$

Elastic Contact (Sphere-on-Flat)

$$\mu = S_0 \pi \left( \frac{3R}{4E} \right)^{2/3} L^{-1/3} + \alpha$$

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

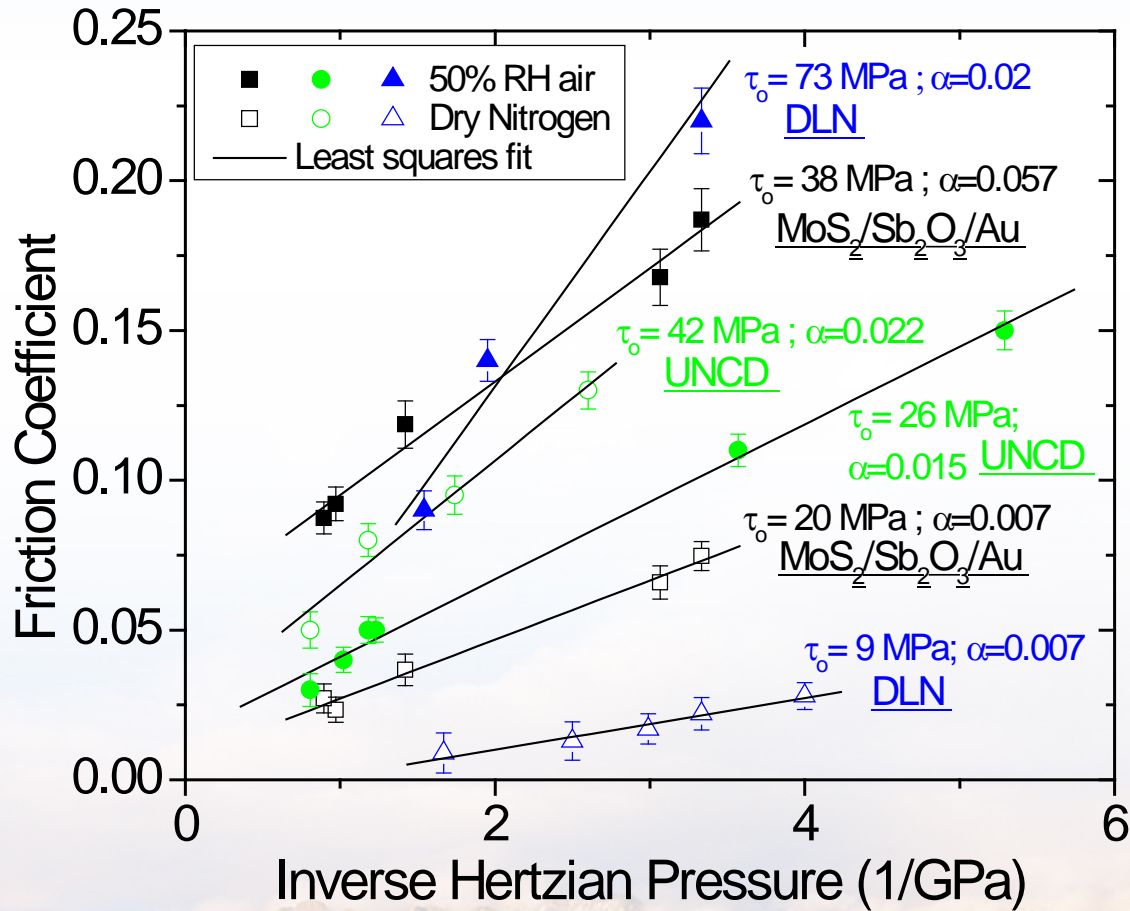
- $S_0$  is the interfacial shear strength (a 'velocity accommodation parameter'), a property of the interface.
- $\alpha$  is a fit constant (the pressure-dependence of 'S')

**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).



# Inverse Hertzian Behavior— Non-Amontonian

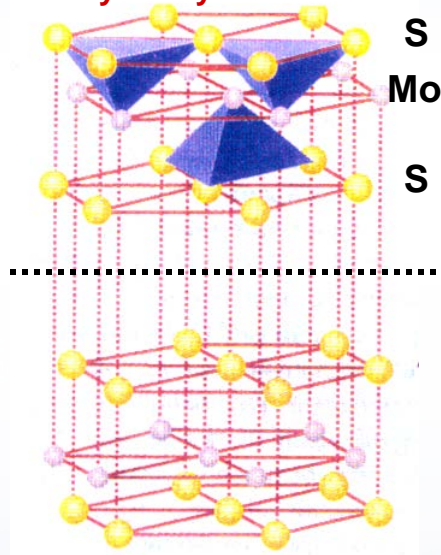


T. W. Scharf and S. V. Prasad, *Solid Lubricants: A Review*, *J. Mater. Science* (2013) 48:511-531



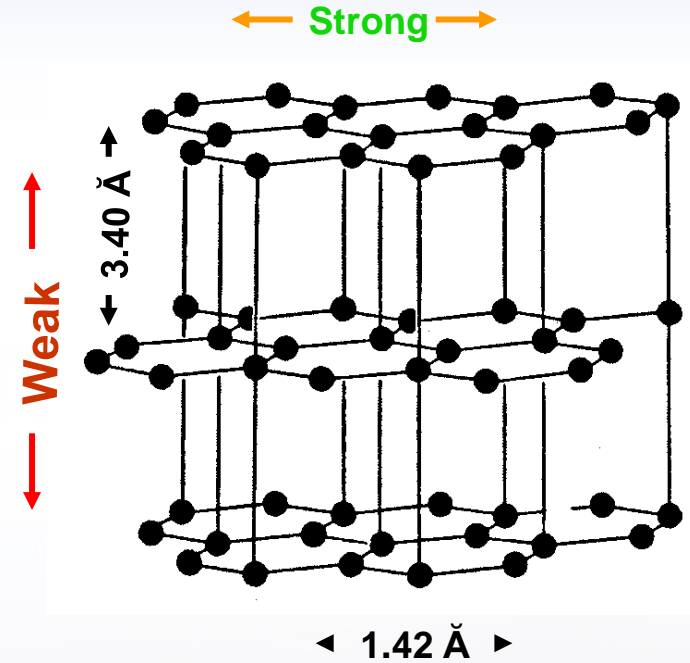
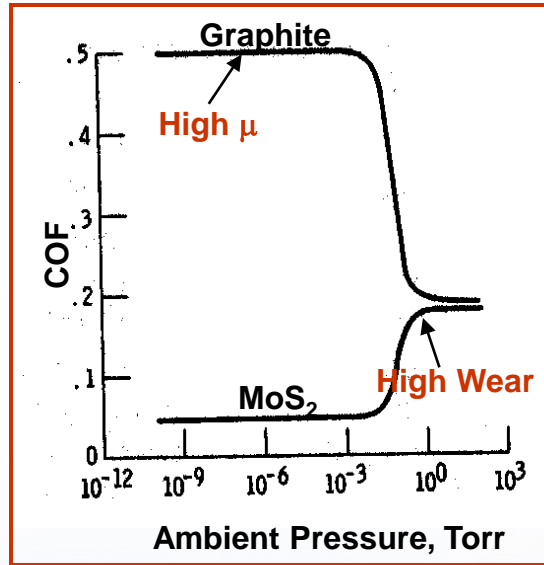
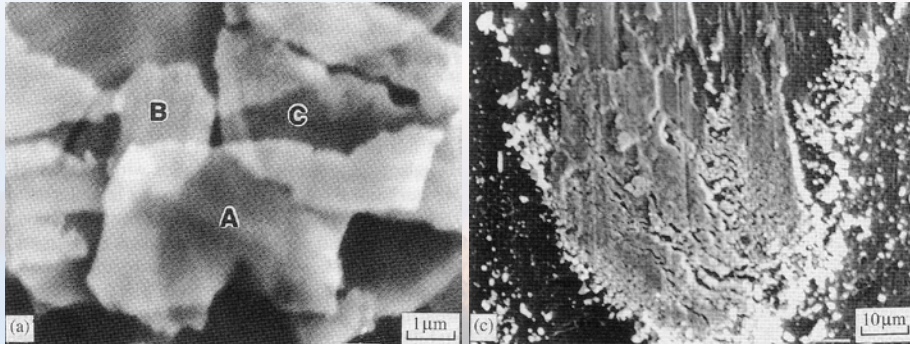
# Environmental Effects

MoS<sub>2</sub>: Extremely low COF (0.01-0.05) and long wear life, **but only in dry environments.**



## Mo/W Disulfide

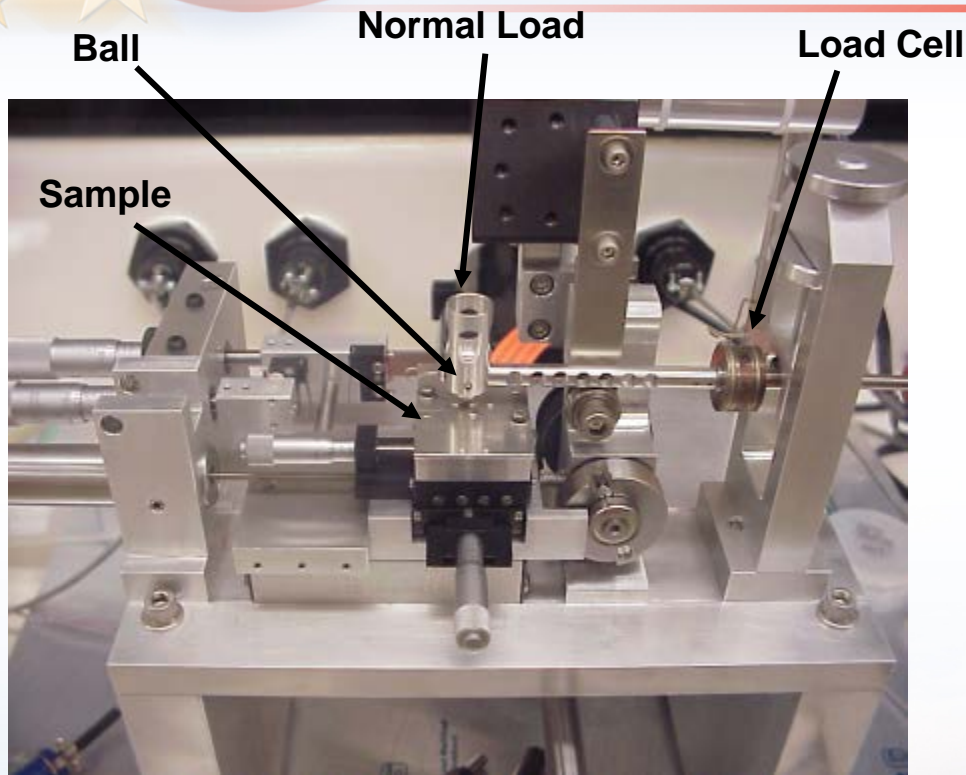
They form thin transfer films on the counterface



## Graphite

- 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.

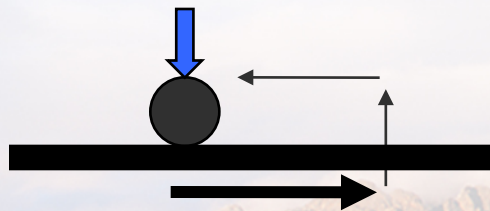
# Friction and Wear Measurements



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



Oxygen Analyzer  
Dew Point Measurement

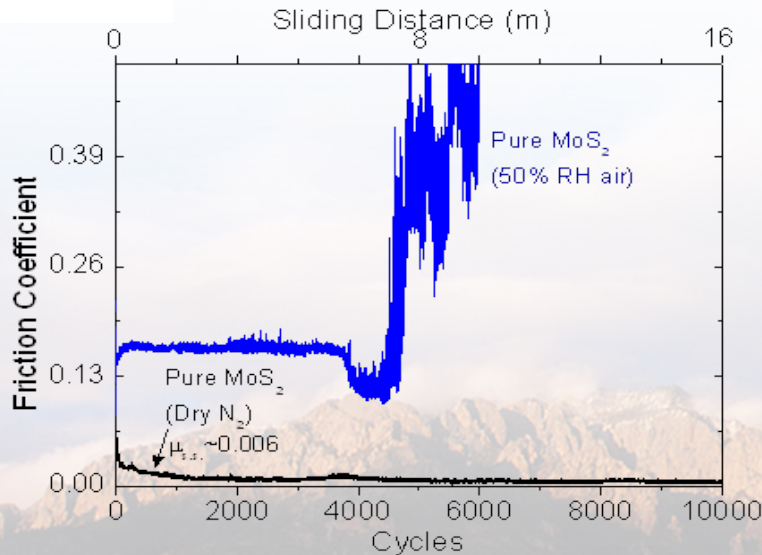
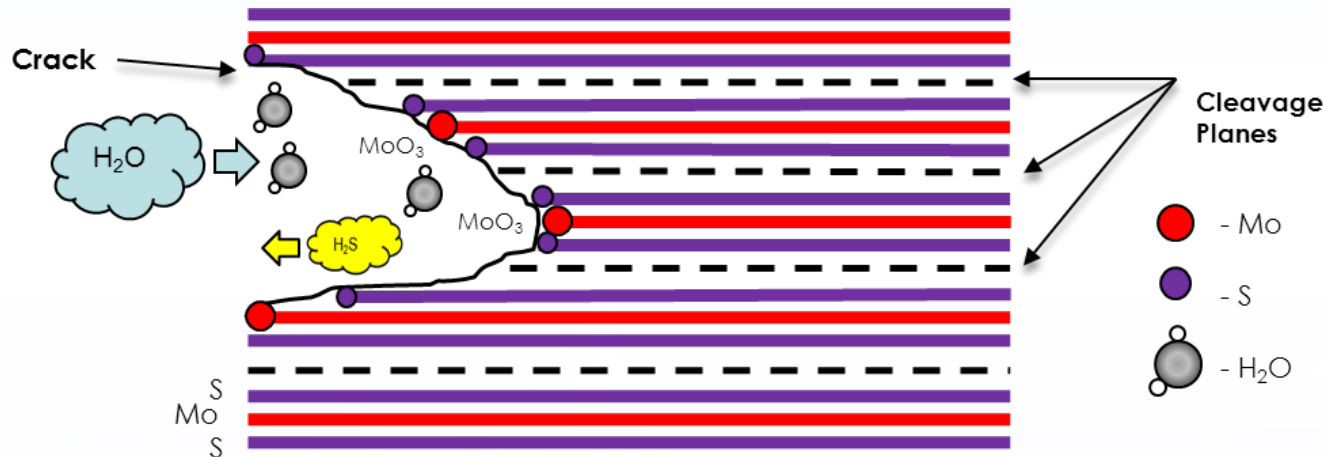
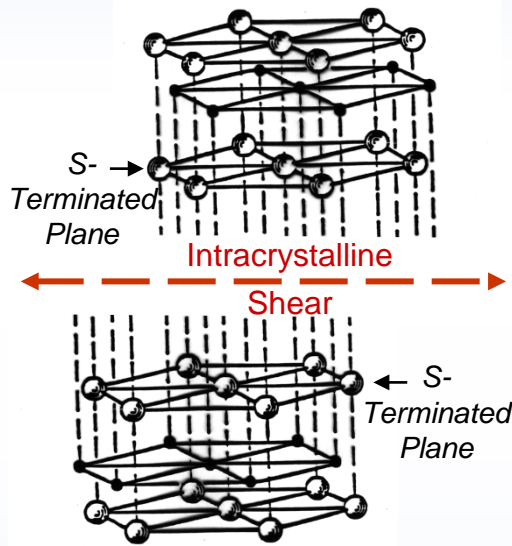


Linear Wear Tester  
(Ball-on-Flat configuration)

Environmental Control



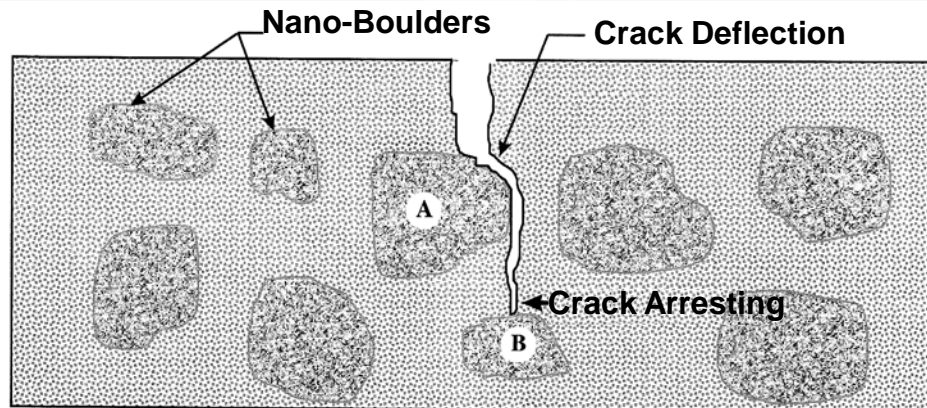
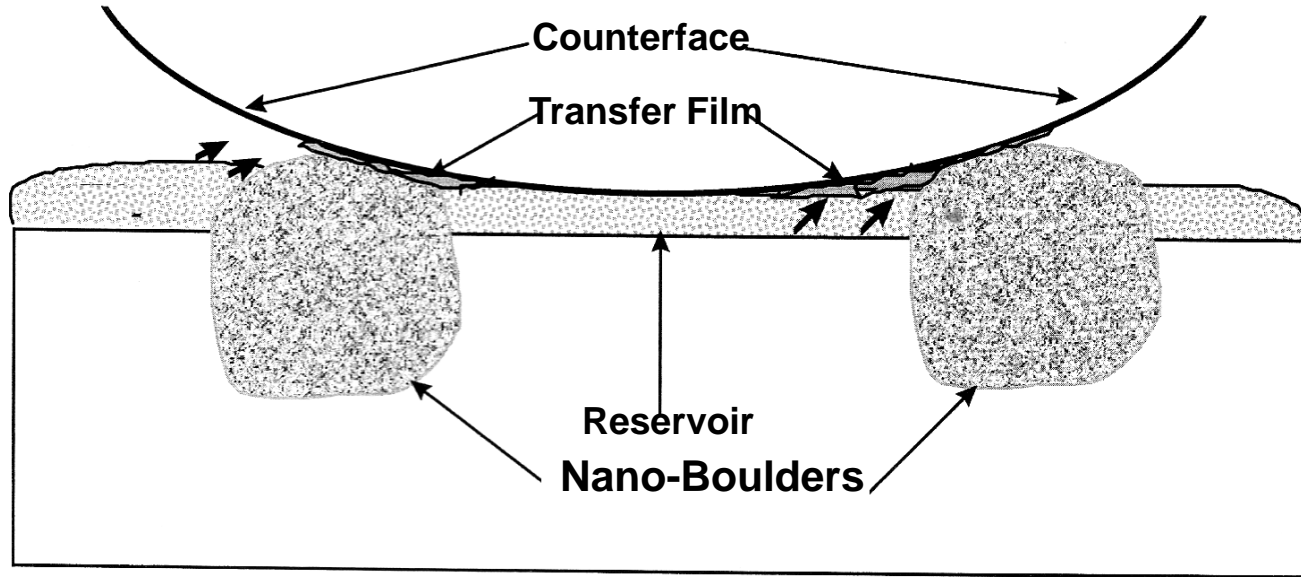
# Effect of humidity and water vapor on the friction behavior of MoS<sub>2</sub>



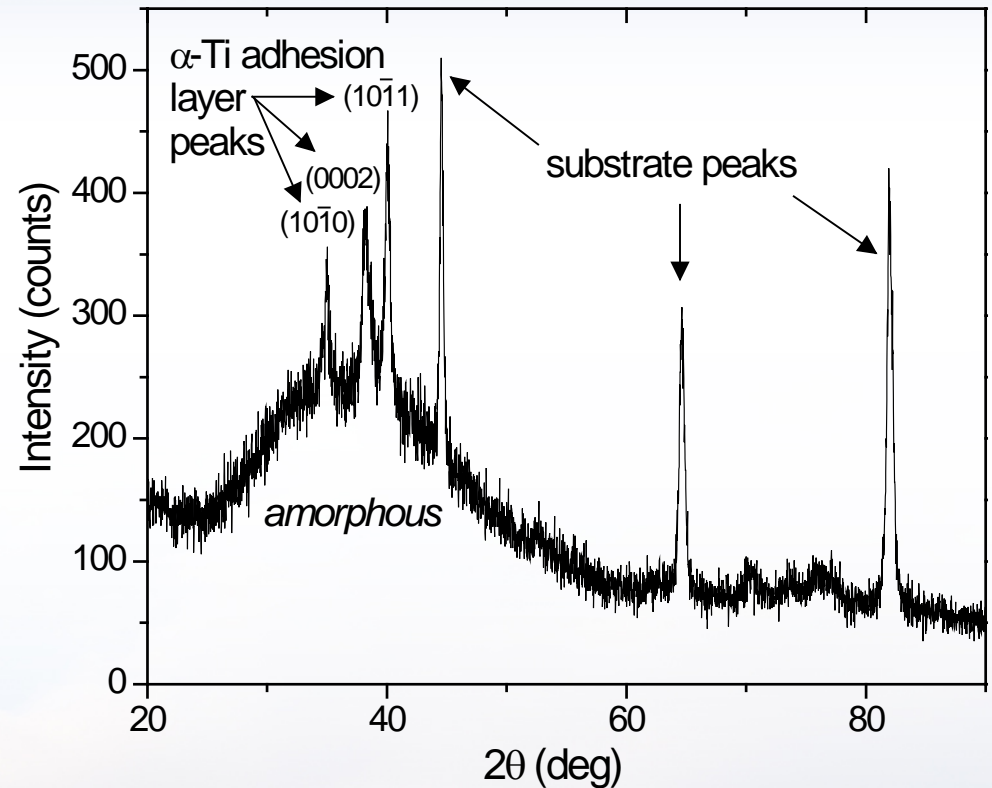
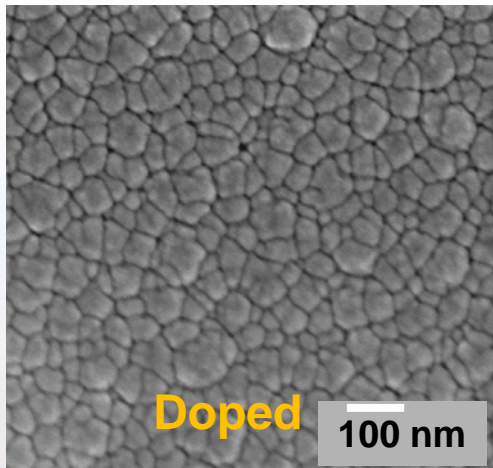
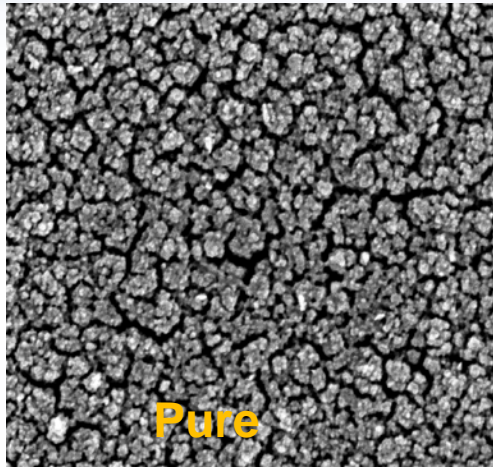
Reactions with water  
Tribo-oxidation (MoO<sub>3</sub> formation)  
Increase in the COF  
Reduced Wear Life



# Novel Concepts for Materials Synthesis



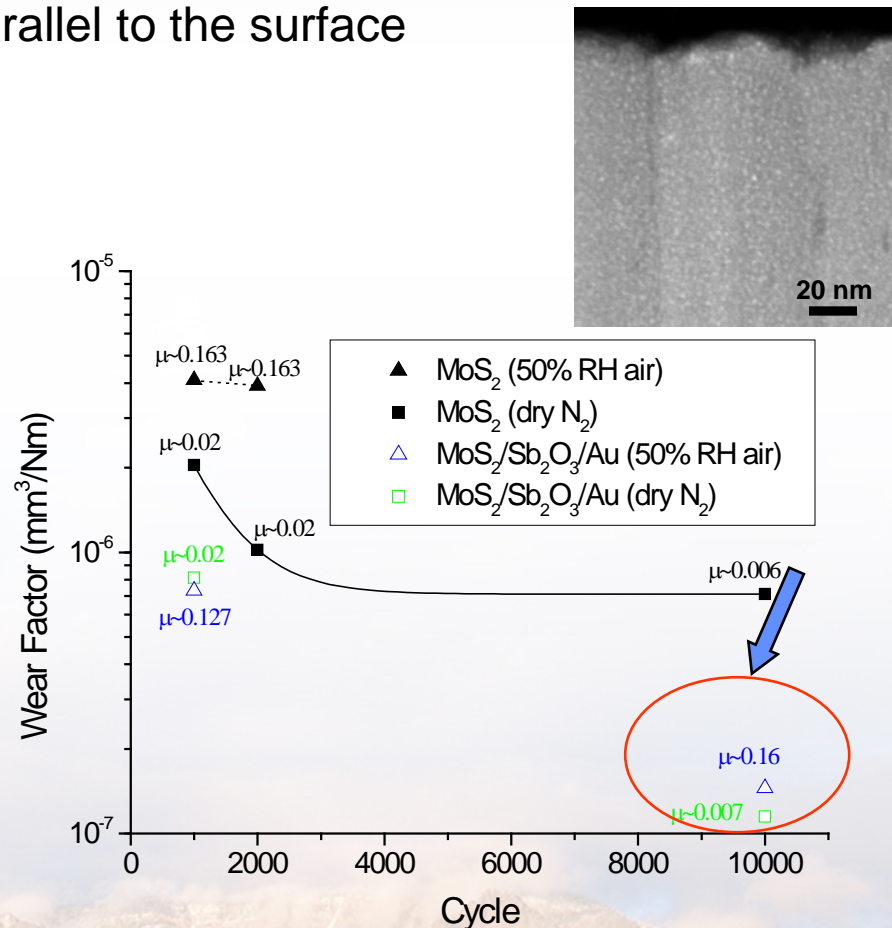
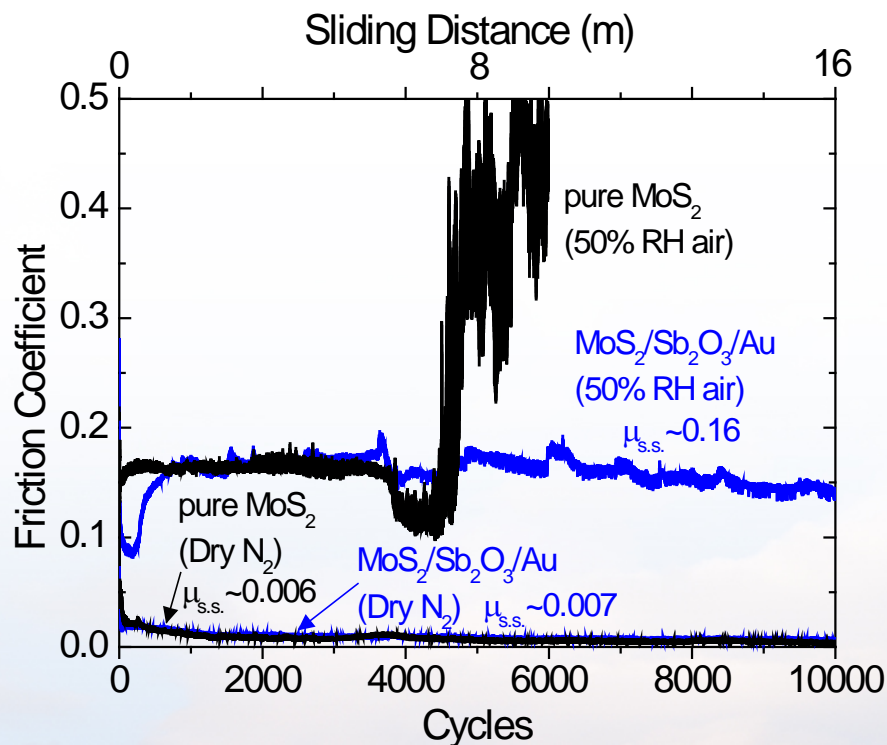
# Doped MoS<sub>2</sub> (Sb<sub>2</sub>O<sub>3</sub> and Au) from Tribologix



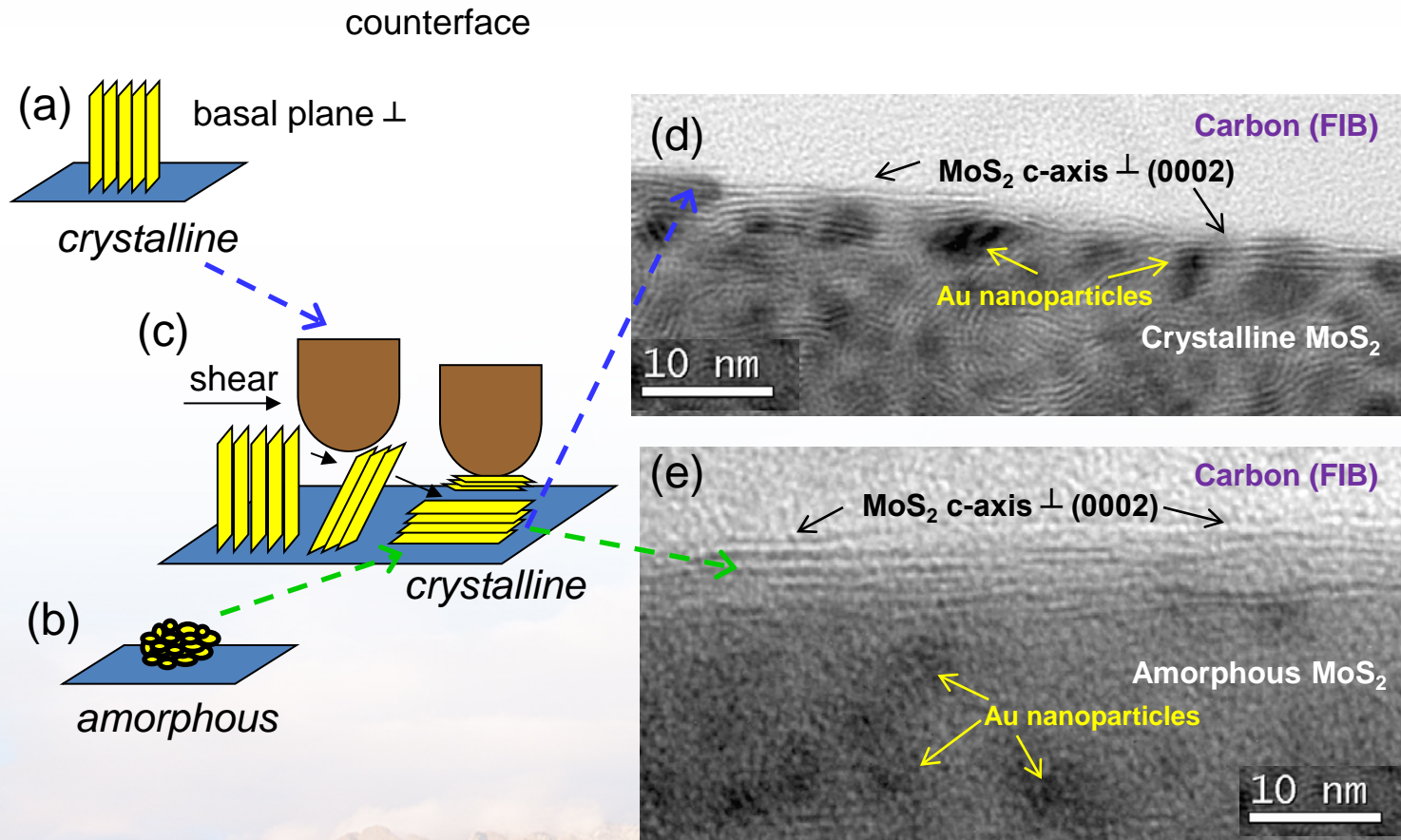
- Note the absence of peaks characteristic of any of the three constituent phases
- Instead there is a broad indicating the presence of an amorphous phase
- Doped films are much denser

# Friction and Wear of Doped and Undoped MoS<sub>2</sub>

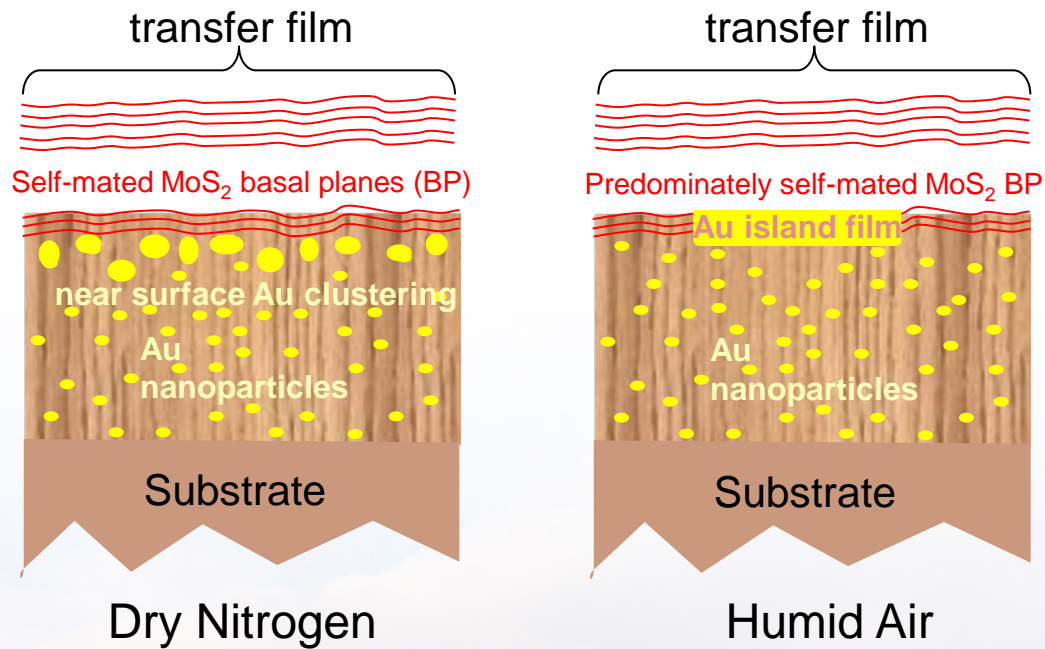
Whether the MoS<sub>2</sub> is in nanocrystalline form or amorphous, friction induces crystallization with basal planes aligning parallel to the surface



# Friction-induced crystallization and reorientation of basal planes



# Mechanisms of Friction

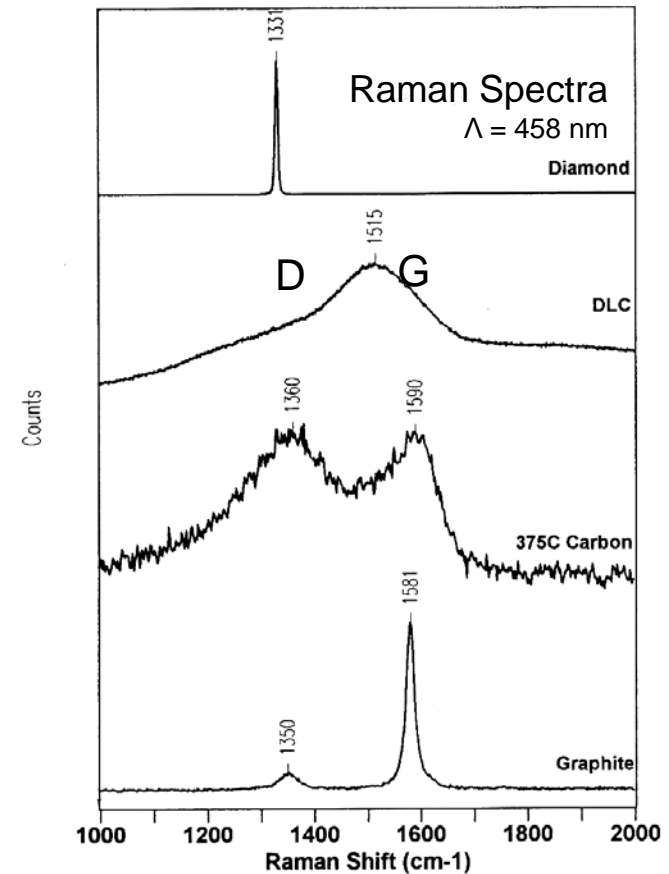
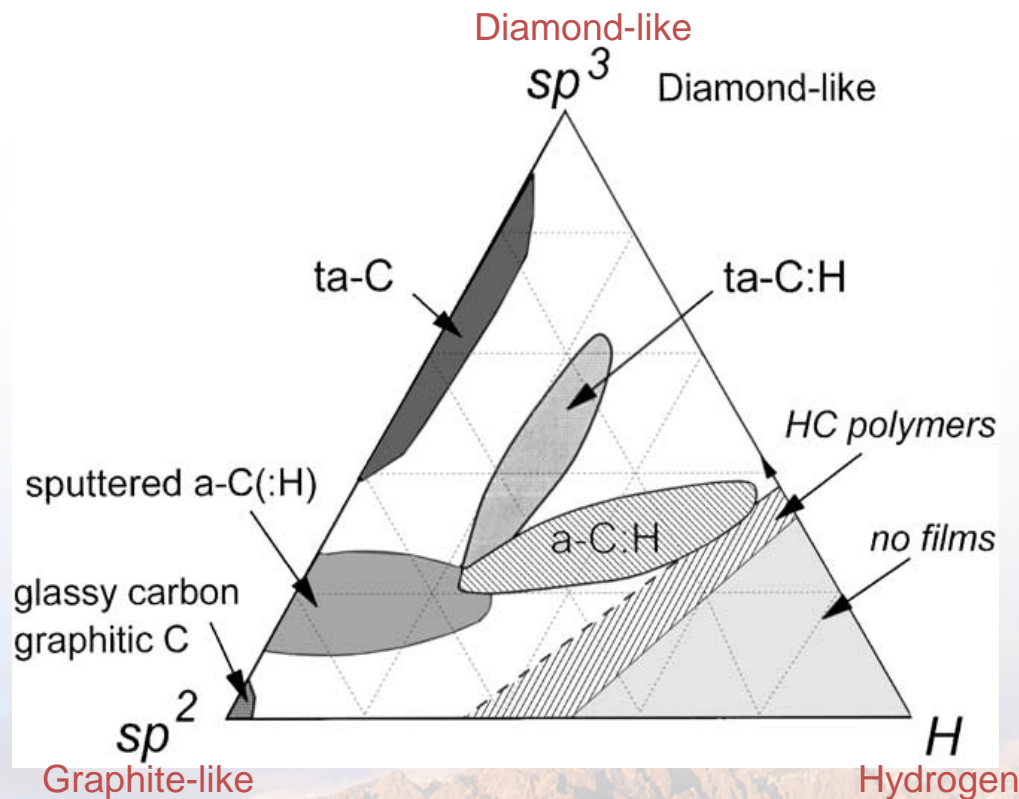




# **Diamond-Like Carbon**

# 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 can be amorphous (a-C) or hydrogenated amorphous carbon (a-C:H) (typically 10-50 atomic % H).



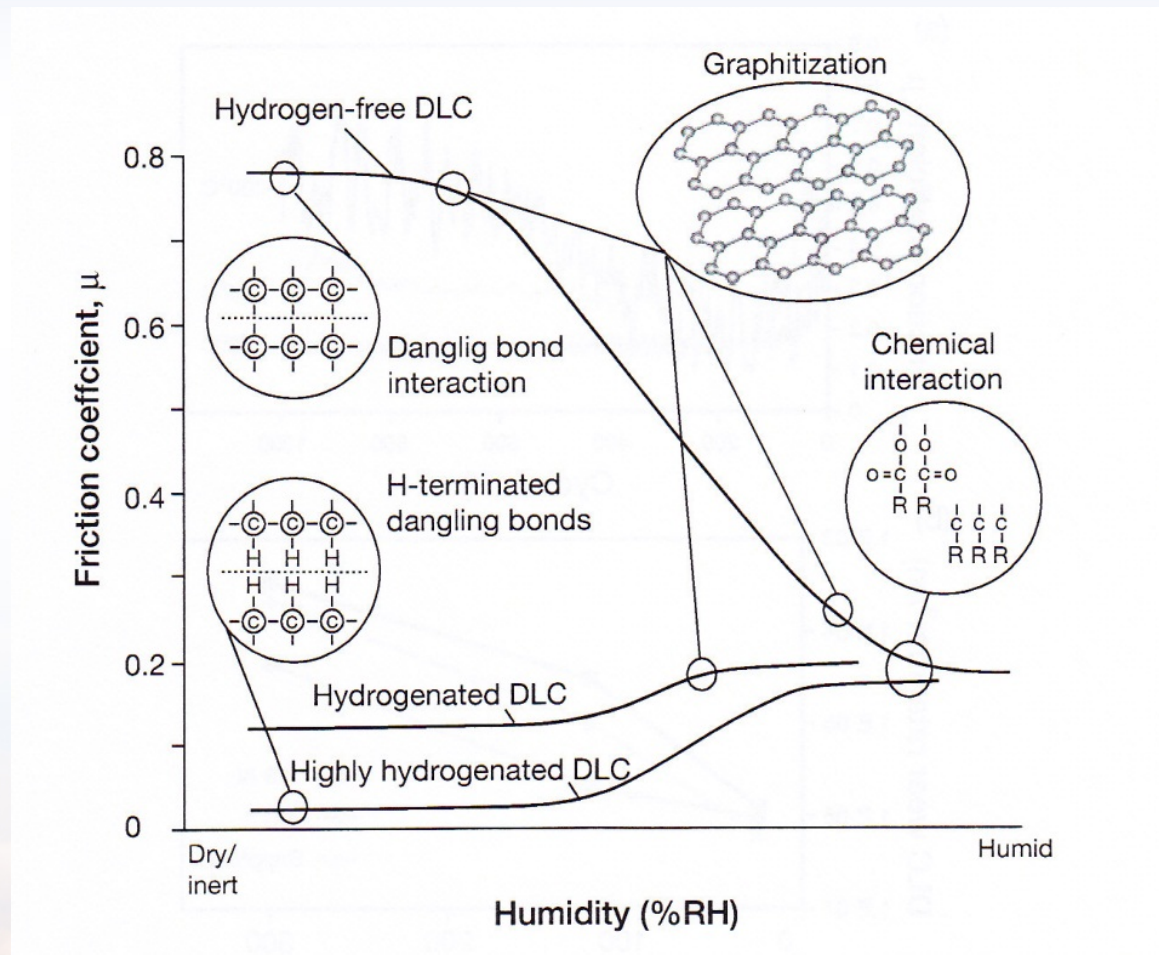
From J. Robertson (2002) *Mater Sci Eng R* 37: 129.

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.



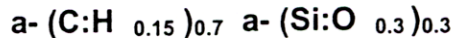
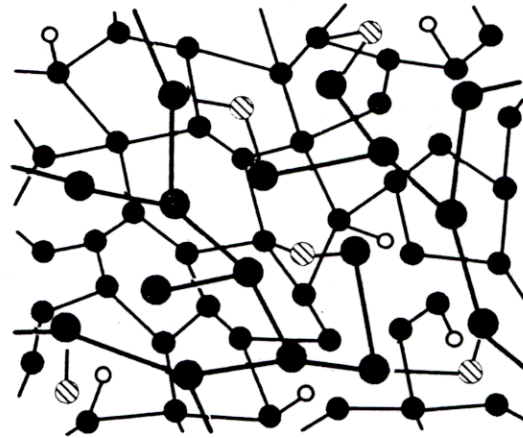
H. Ronkainen and K. Holmberg, "Environmental and Thermal Effects on the Tribological performance of Coatings", In: C. Donnet and A. Erdemir (eds.), *Tribology of Diamond-Like Carbon Films: Fundamentals and Applications*. Springer 2008



# Diamond-Like Carbon Nanocomposites

## Plasma Enhanced CVD

### Polyphenylmethylsiloxane 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 °C

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.

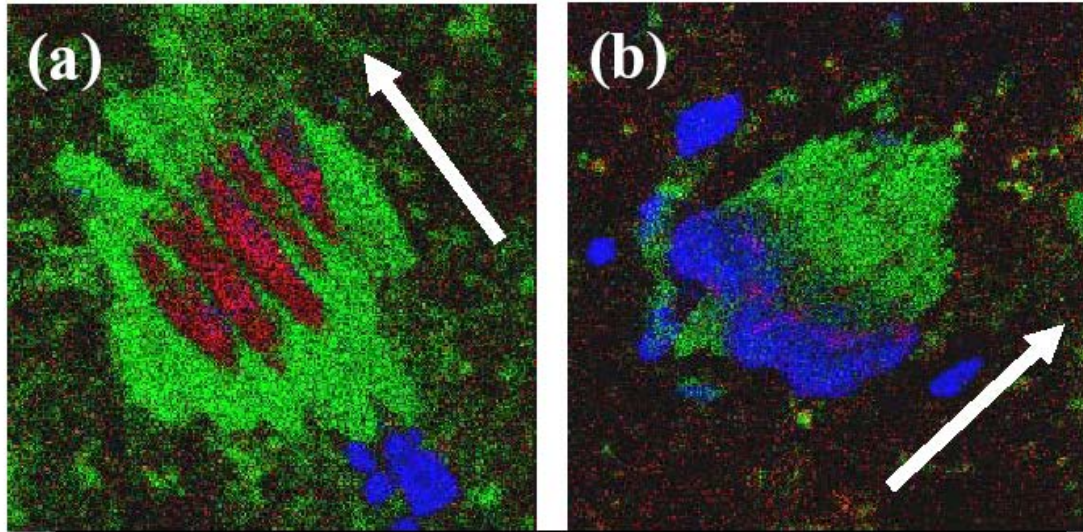


# ToF-SIMS of Transfer Films illustrating the Chameleon Nature

Humid Air ( $\mu\sim.2$ )

Dry Nitrogen ( $\mu\sim.02$ )

ToF-SIMS



Red:  $\text{SiO}_2$  ( $\text{O} + \text{Si} + \text{SiO}_2 + \text{SiO}_3$ )

Green: Long Range Carbon ( $\text{C}_1$  to  $\text{C}_4$  fragments)

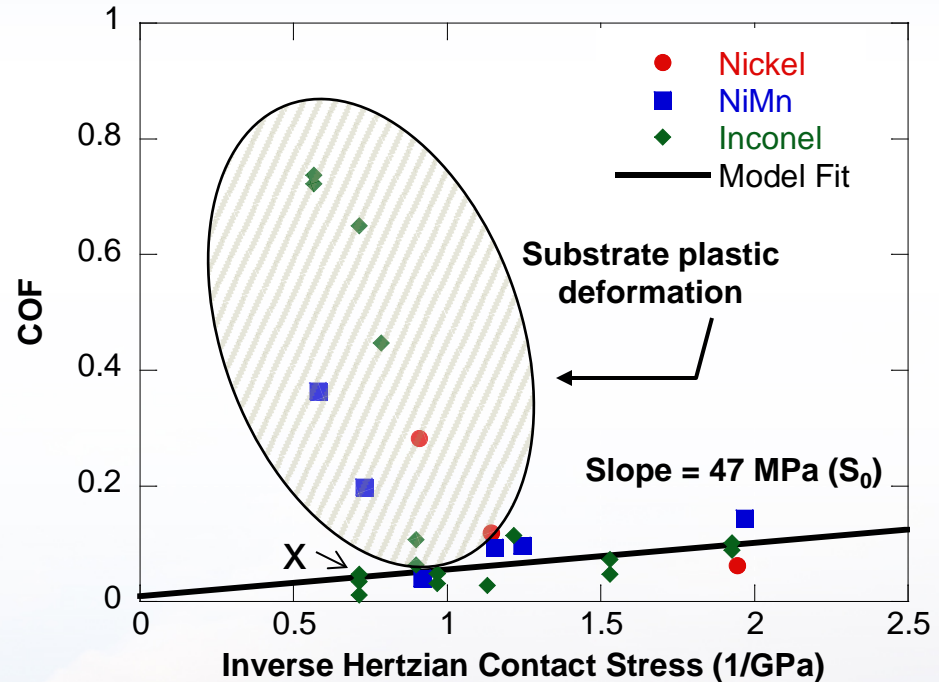
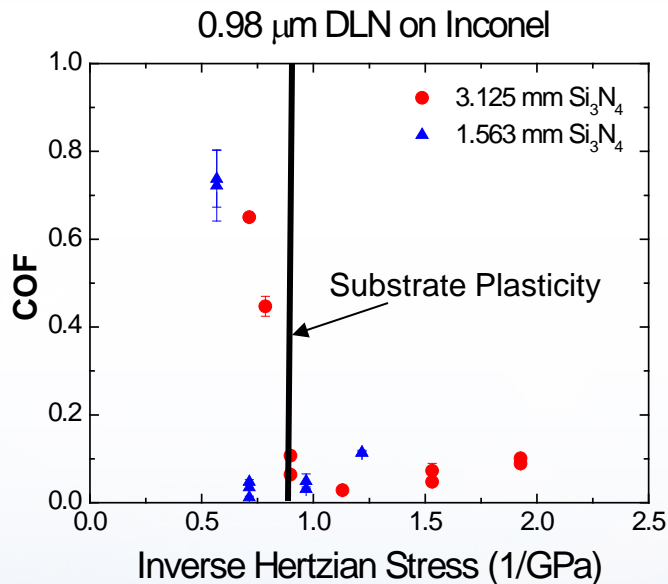
Blue: Hydrogenated Carbon ( $\text{CH} + \text{CH}_2 + \text{C}_2\text{H}$ )

78 MPa

9 MPa



# Deviations from Predicted Behavior

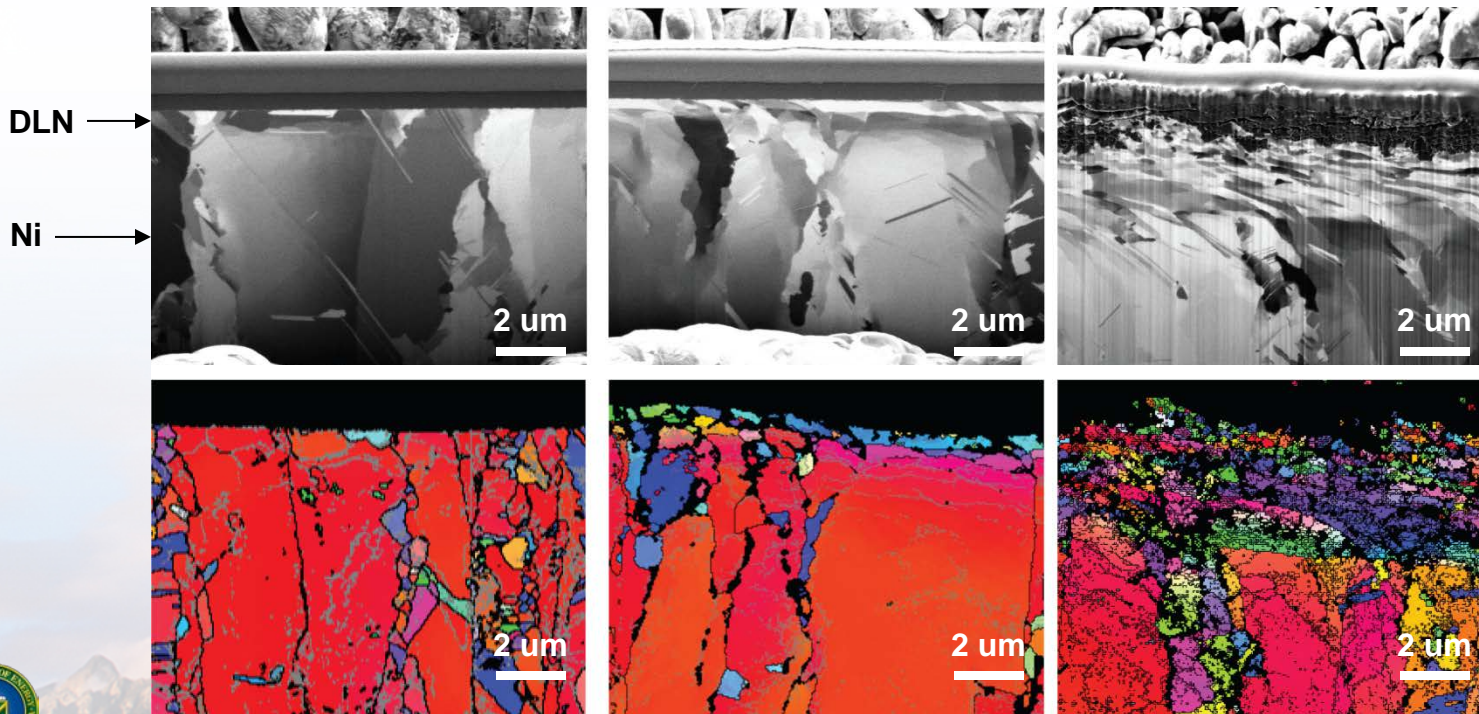
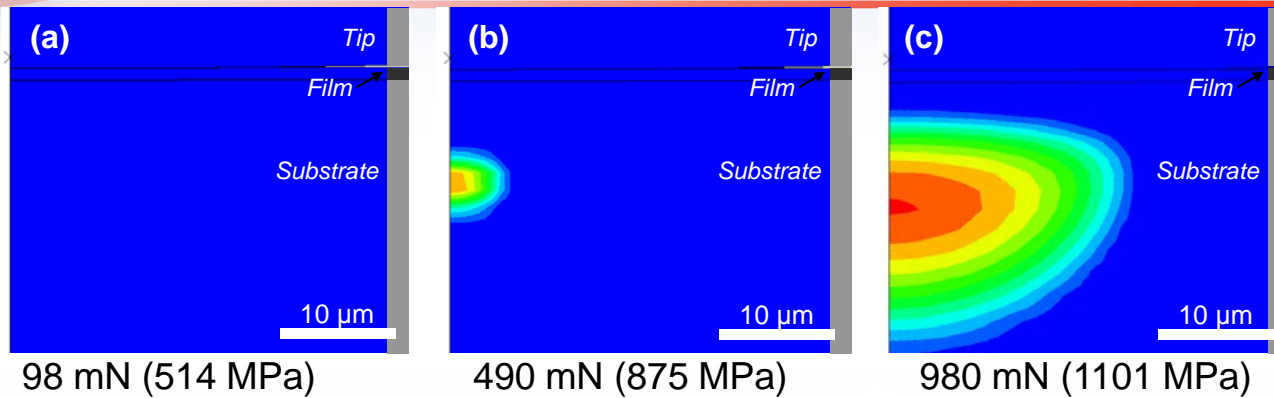


FEM predictions of substrate plastic deformation are in general agreement with observed deviations in Hertzian contact model

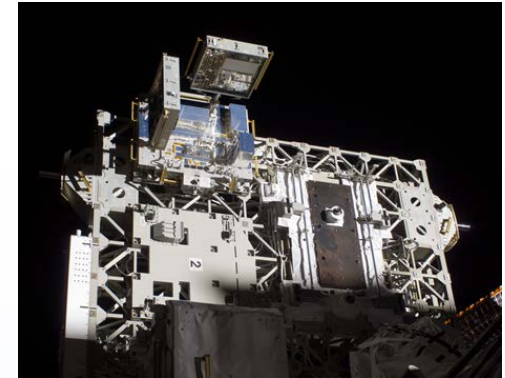
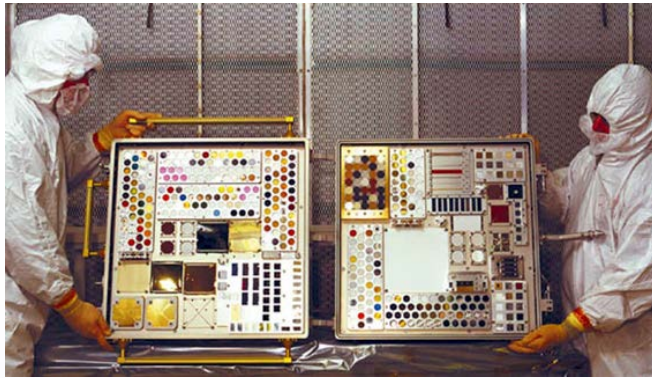
Multi-Layer Architectures may be necessary to mitigate substrate plastic deformation



# Friction Induced Plastic Deformation in the Substrate



# Space: Materials in Space Science Experiments (MISSE)

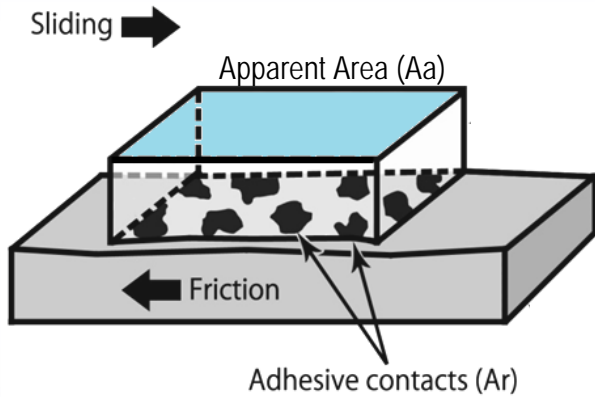


- Tribology samples launched into space on the Space Shuttle Atlantis (STS-129), November 16th, 2009
- Brought back on March 1, 2011 during STS-133 (shuttle Discovery)
- Post flight analyses provided valuable data on materials selection for future satellites.



# Balancing Fiction & Electrical Contact Resistance is Fundamentally Challenging

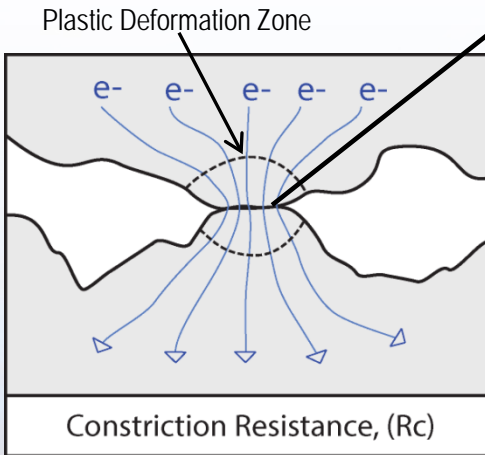
Real Area of Contact ( $A_r$ )  $\ll$  Apparent Area of Contact ( $A_a$ )



$$A_r = \mu + \text{Adhesive Wear} + R_c$$

Friction                      Adhesive Wear                      Constriction Resistance

$$\mu \rightarrow f(\text{Adhesive Strength } (S_0), A_r)$$



$A_r$  is a function of surface topography, applied load, and material properties ( $E$ ,  $H$ ,  $v$ )

- Friction and Constriction Resistance are fundamentally opposing phenomena
- Arriving the desired balance between these is the challenge

Archard, *Journal of Applied Physics* (1953) 24:981  
 R. Holm, *Electrical Contacts Handbook* (1958) Berlin: Springer-Verlag  
 Greenwood & Williamson, *Proc. Royal Society* (1966) A295:300  
 T.W. Scharf & S.V. Prasad, *Journal of Material Science* (2013) 48:511



# Electrical Contact Materials (Hard Au)

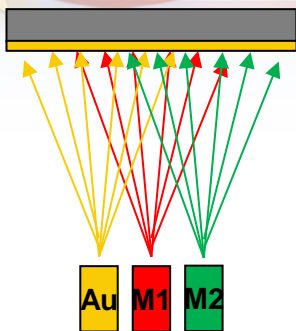
- Pure gold is soft (low yield point) and has unacceptable amount of friction and wear
- Gold is typically hardened with minute alloying of Ni or Co (referred to as hard gold) to achieve the desired balance between friction, wear and ECR
- Current practice is to apply hard gold by electrodeposition, per ASTM B488 and MIL-DTL-45204

*Nickel Underplating is used any time the substrate alloy contains Copper to prevent diffusion of Cu into Au coating.*

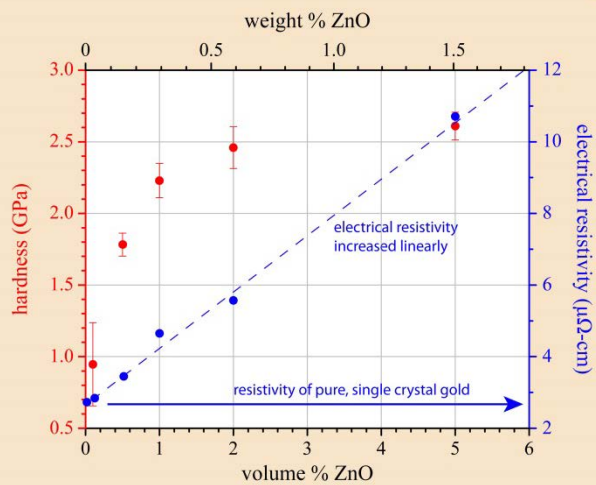
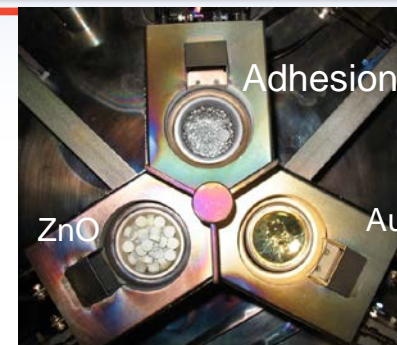
- Diffusion and segregation of hardeners and elements from “diffusion barriers” to the surface (ECR degradation)
- Limited electrochemistry (hardeners/diffusion barriers)
- Non-Technical issues...(OSHA and EPA regulations)



# Au-ZnO nanocrystalline coatings by e-beam evaporation



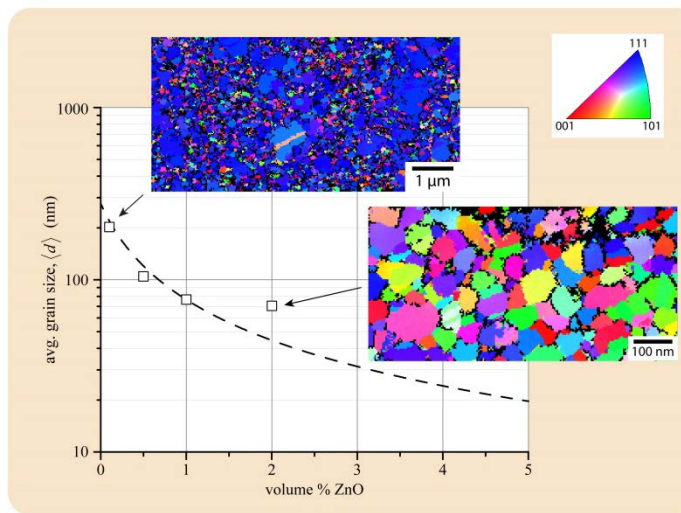
- Triad electron gun for E-beam evaporation
- Co-deposition of ternary alloy thin films
- Shutter in front of substrate for consistent composition
- Substrate rotation for improved uniformity
- Line of sight shields on QCMs eliminate cross-talk



Au nanocrystalline coatings are strengthened by reducing the average grain size below 100 nm by incorporating minute quantities of secondary ceramic phases (**Hall-Petch Strengthening**).

The secondary ceramic species are:

- insoluble in gold
- preferentially reside at grain boundaries (GBs), and cause the reduction in grain size and inhibition of crystallographic texture
- exhibit high thermal stability

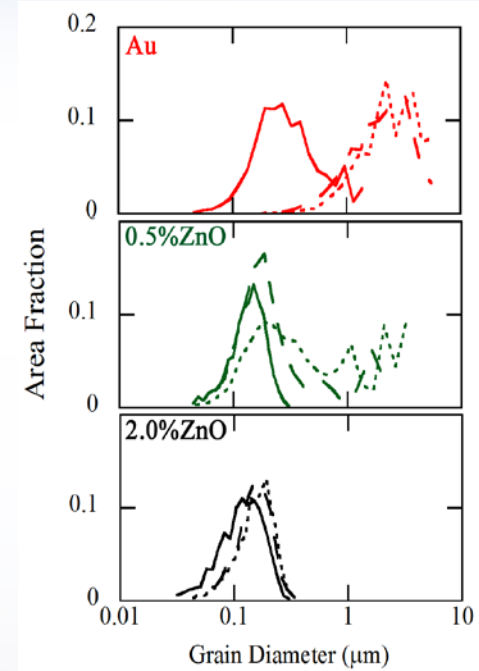
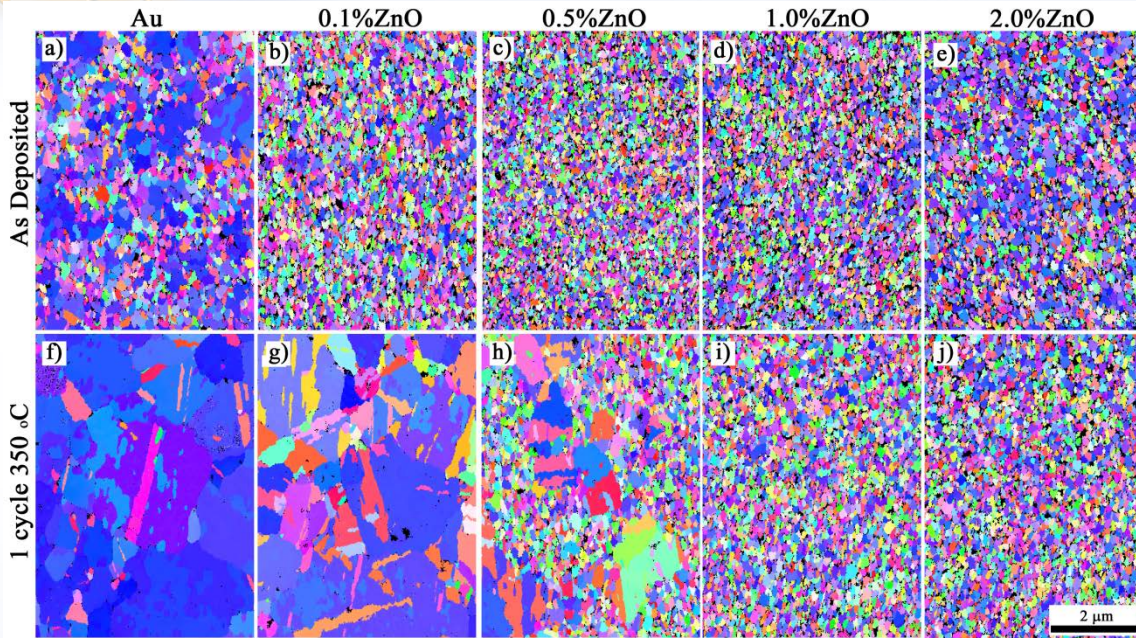


- The gold-ceramic nanocomposites exhibit superior electrical contact resistance and tribological behavior (friction and wear) to traditional electroplated hard gold.
- This class of materials is synthesized by e-beam evaporation, an **environmentally friendly synthesis route**.

US Patent -- *Wear-Resistant Nanocrystalline Hard Gold Coatings Synthesized by Electron Beam Evaporation* -- filed April, 2014



# Thermal Stability



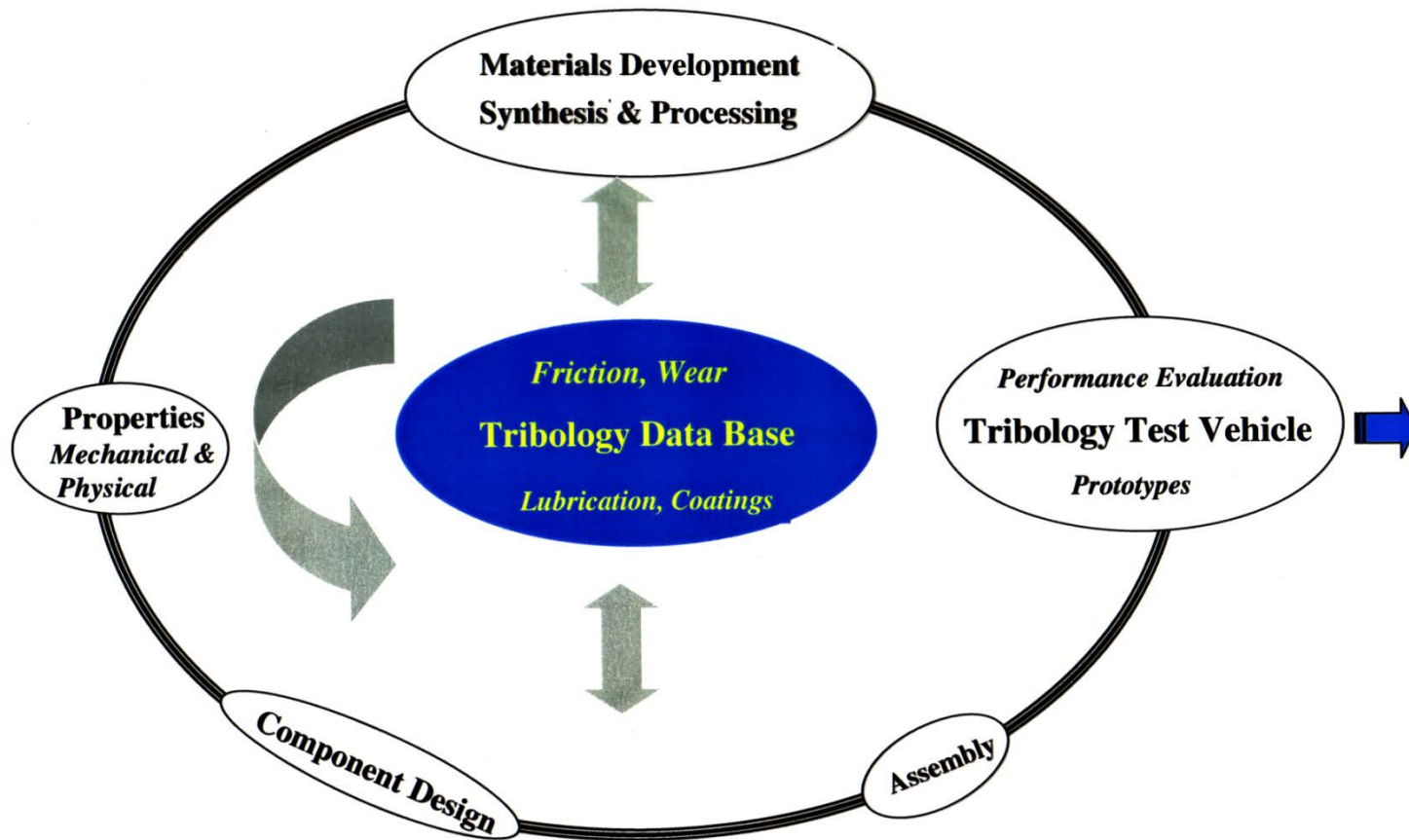
- Addition of ZnO to Au films improves thermal stability , and retains good electrical conductivity after annealing.
- The grain growth is effectively shut off at 350° C



# Concluding Thoughts



# Systems approach is an integral part of Tribology





# Acknowledgements to Collaborators

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