Designing Materials for Tribology

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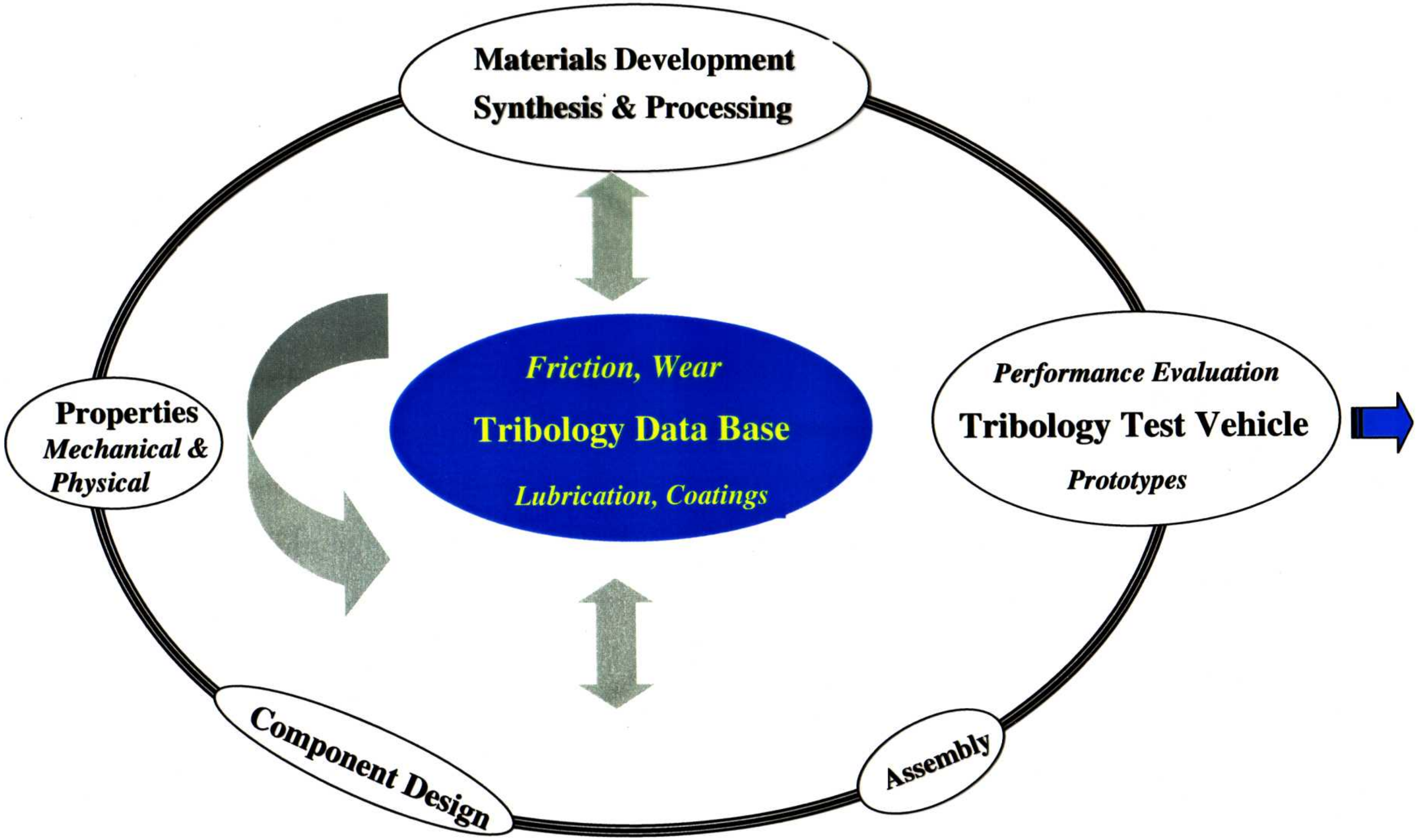
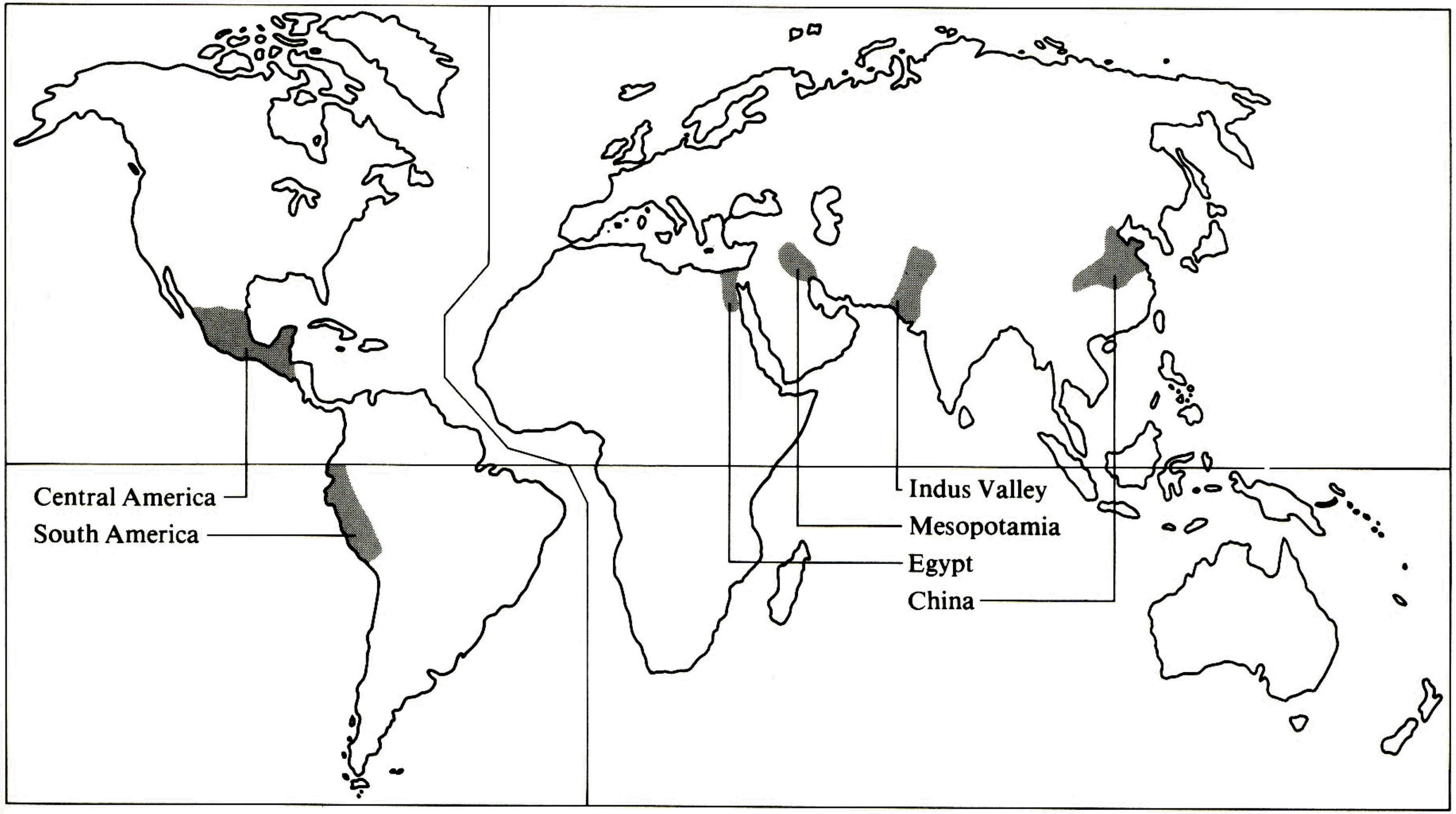
Materials Design for Tribology:; Why?

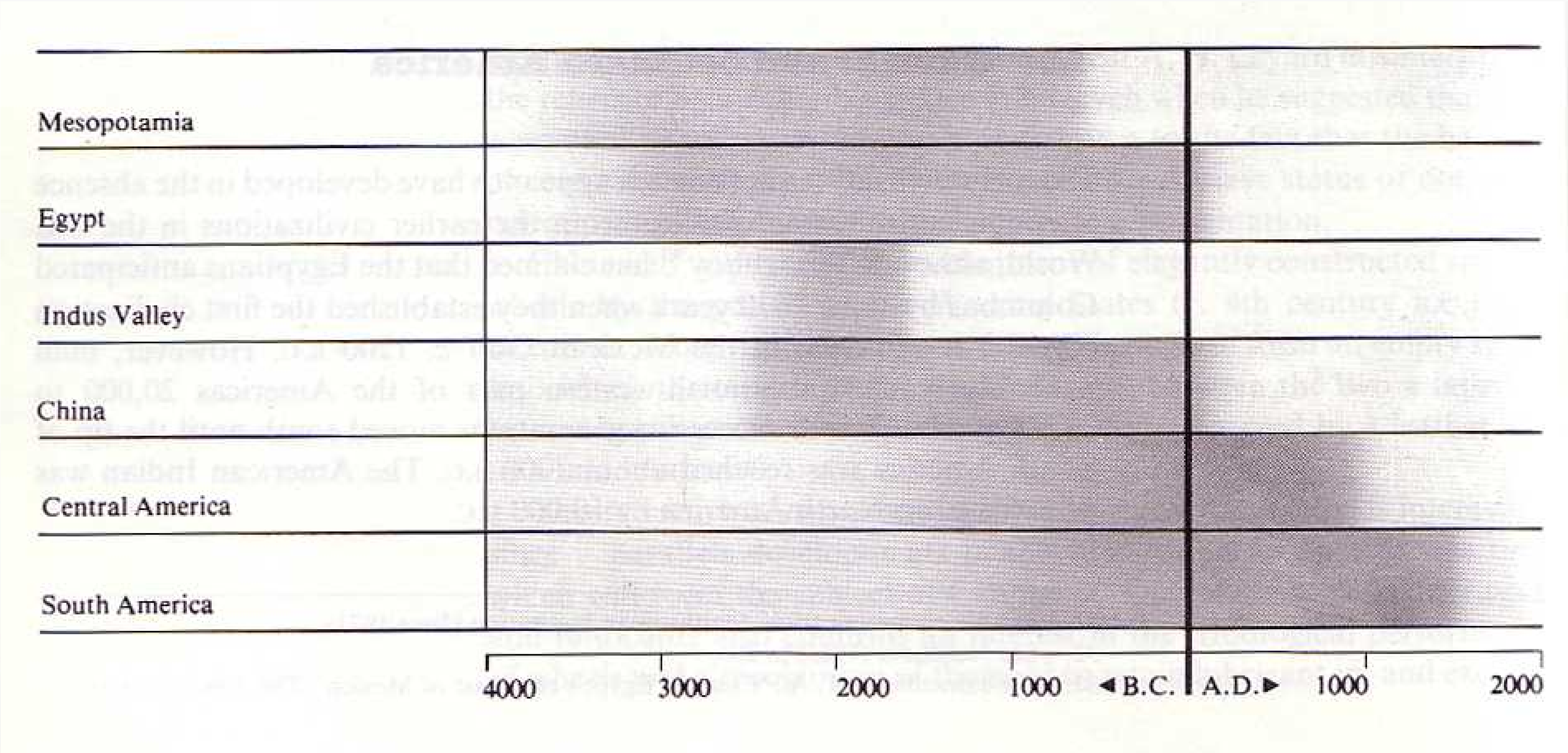


Systems approach is an integral part of Tribology

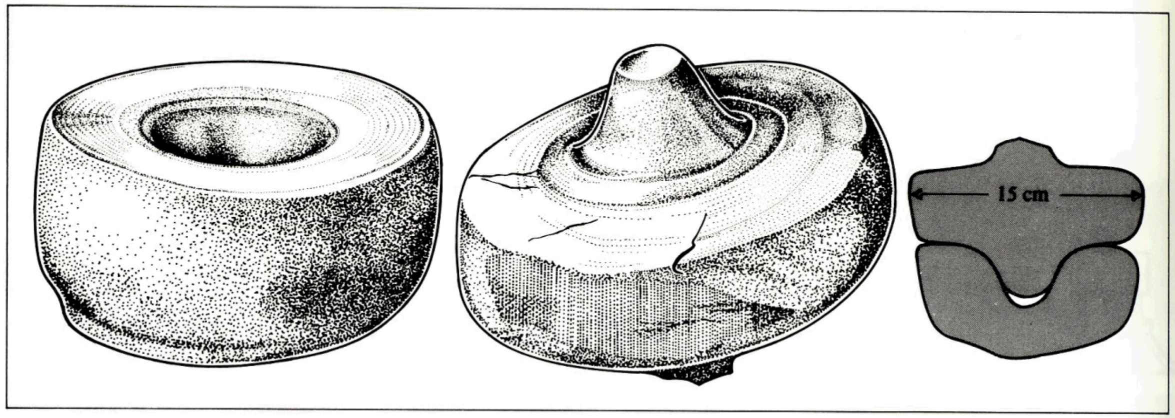
Early Civilizations Across the World



Approximate dates of the early civilizations

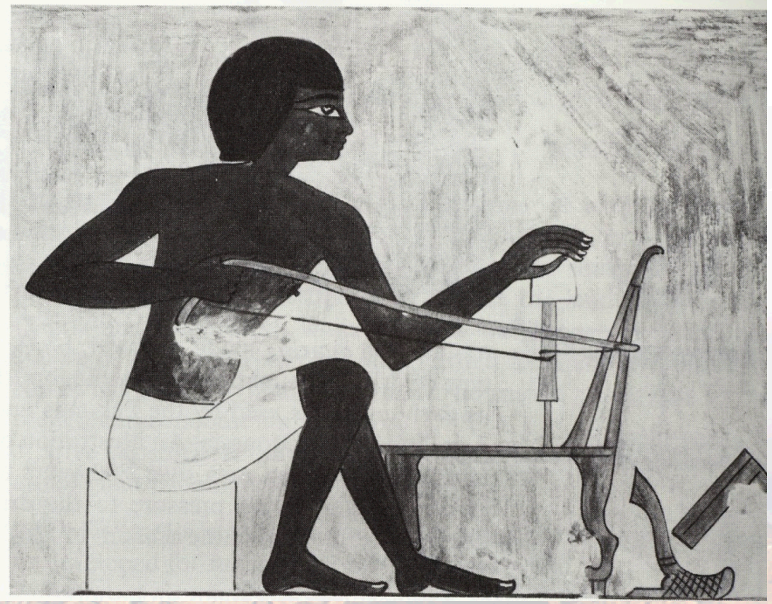


Tribological inferences from carvings

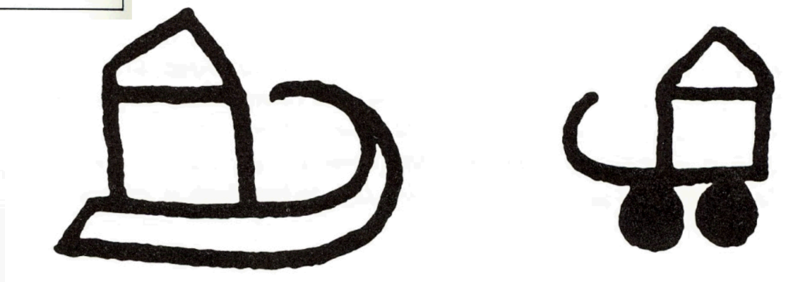


Potter's Wheel

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



Egyptians using a bow-drill

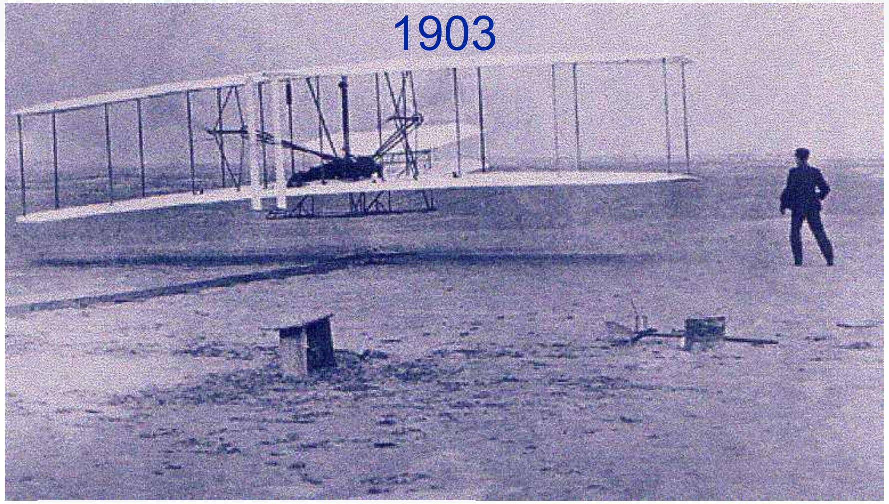


Sledge and wheeled vehicle (3000 B.C.)

Man on skis: Stone painting from Northern Norway

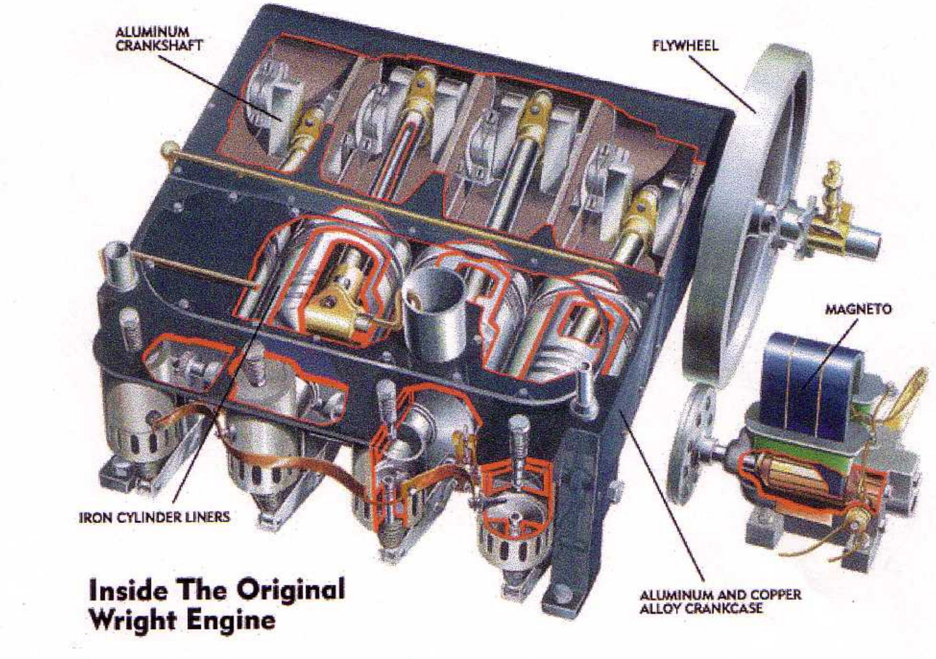
1900
Wright Cycle Company, W. Third Street, Dayton, Ohio

The Saga of Wright Brothers' Engine



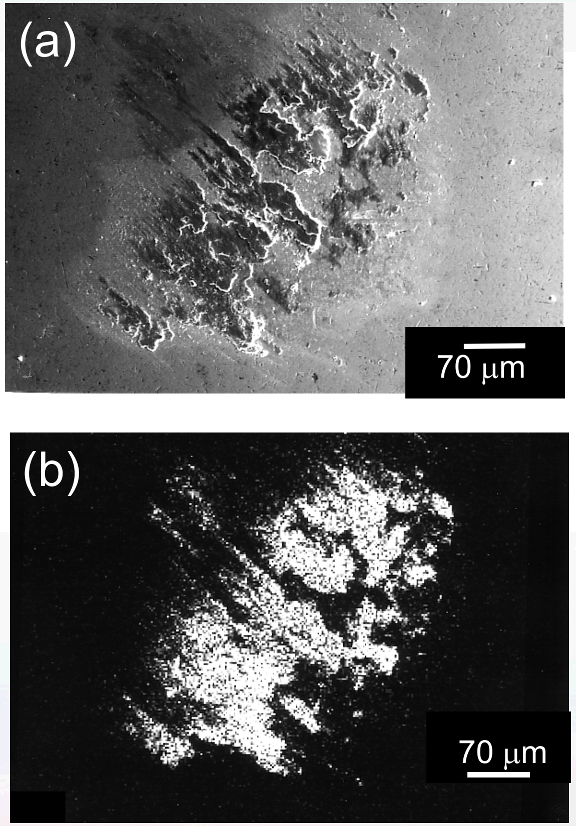
Mr. Charles Taylor (Mechanic) Considered replacing Cast Iron with Al-Cu

- 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.

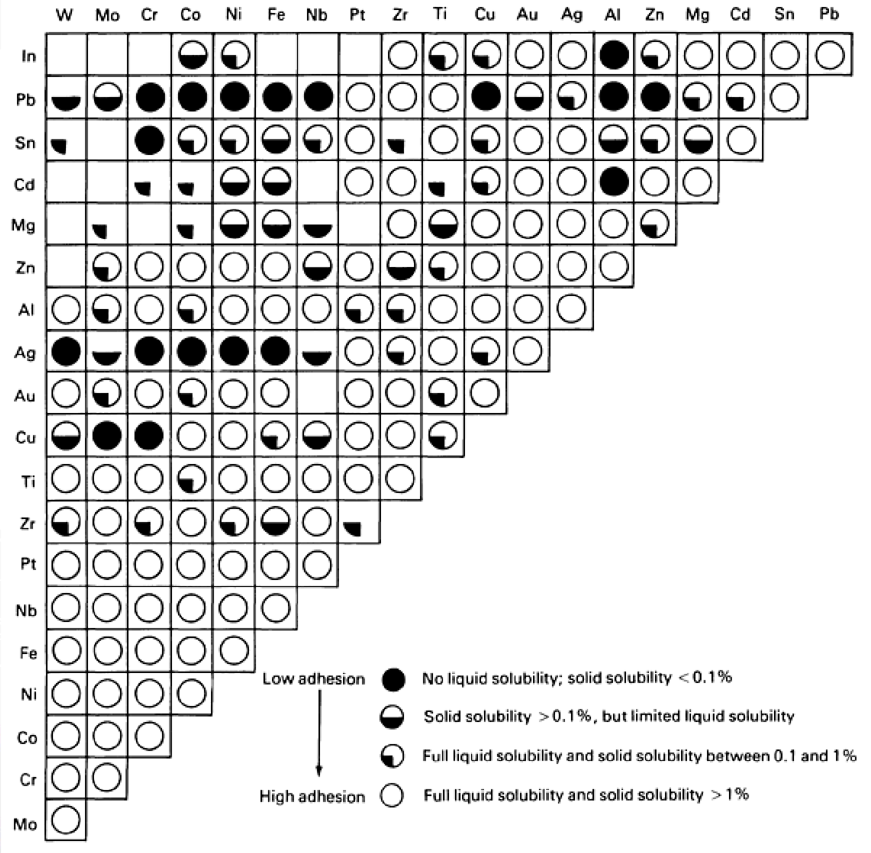
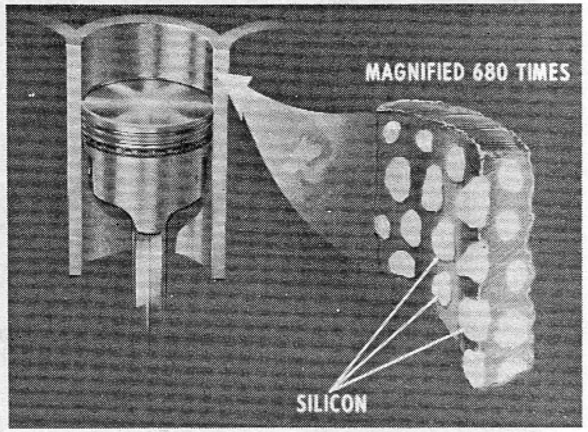


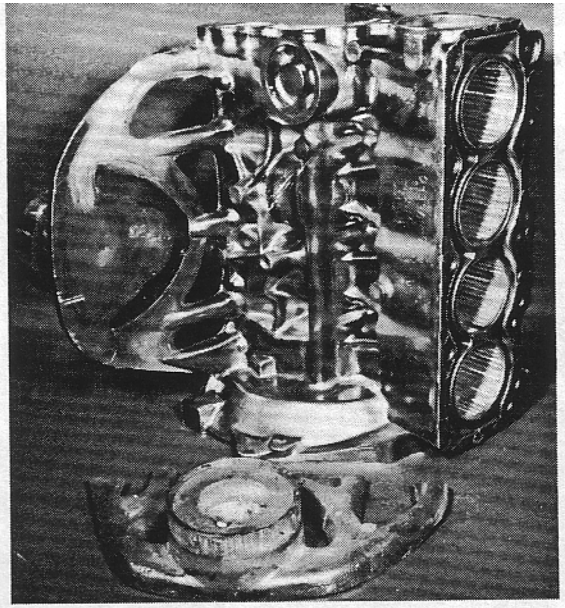
Chart indicates the degree of expected adhesion (and thus friction and wear) between the various metal combinations derived from binary equilibrium diagrams.

E. Rabinowicz (1971) ASLE Trans 14:198

The (Short) Legacy of the Vega Engine



Silicon surface cylinder bores

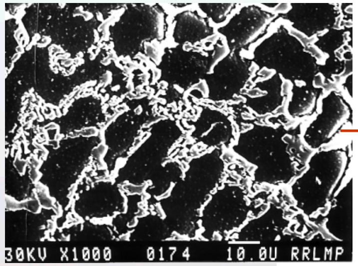

Vega engine block as removed from die

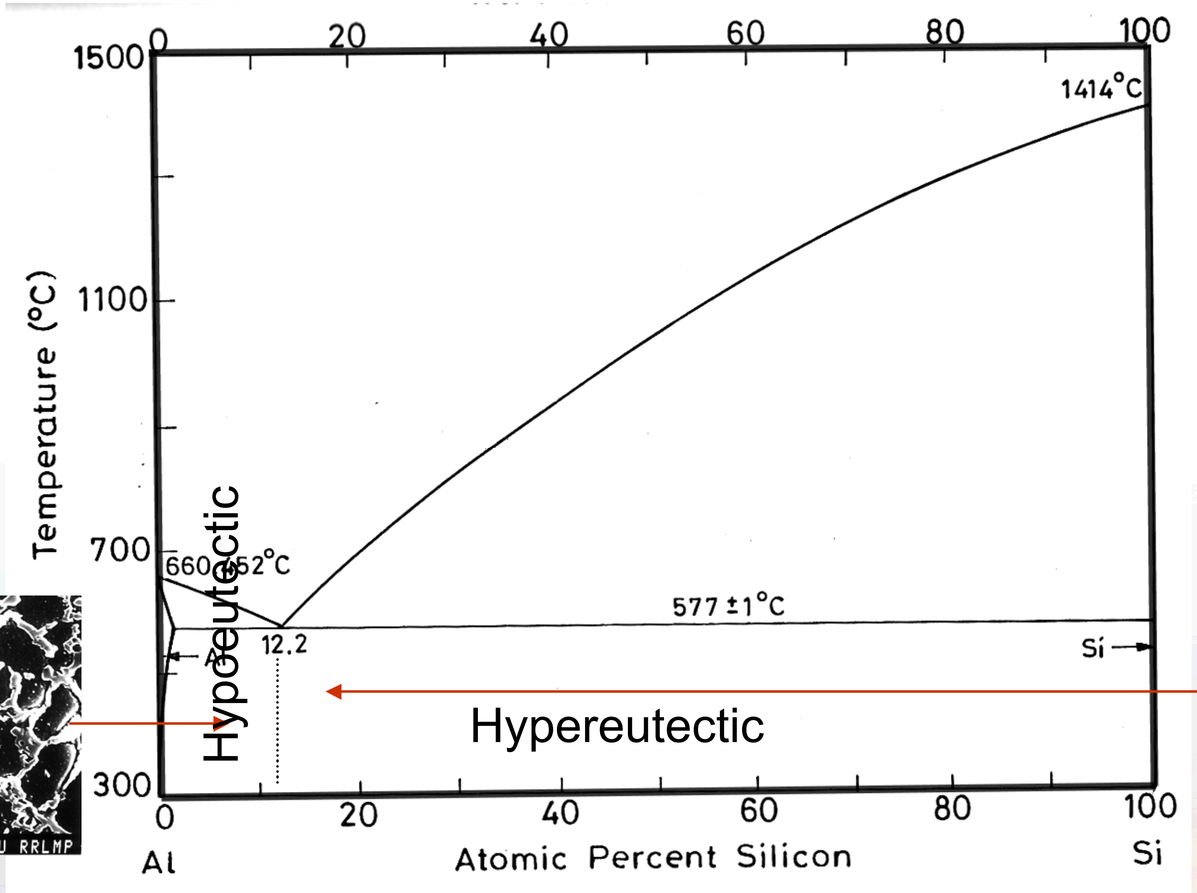
BASIC SPECIFICATIONS
VEGA 2300–140 cu in. Overhead Cam 4-cyl Engine

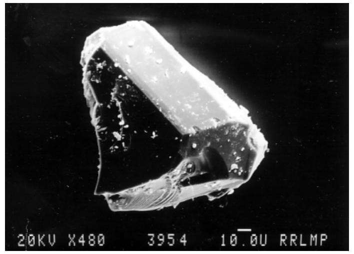
GENERAL	
Type	In-Line OHC 4-cyl (L-4)
Gross horsepower	
Standard engine	90 at 4600-4800
Optional engine	110 at 4800
Gross torque	
Standard engine	136 at 2400
Optional engine	138 at 3200
Compression ratio	8.00:1
Bore and stroke	3.501 × 3.625
Firing order	1-3-4-2
Engine installation angle	3 deg 50 min
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

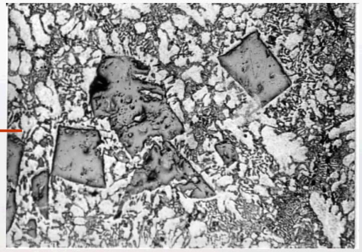
Both the eutectic and the primary Si have undesirable morphology



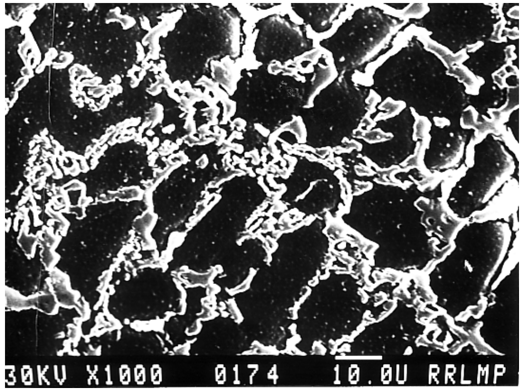
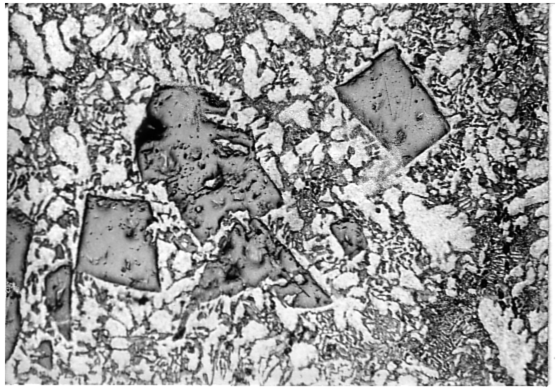
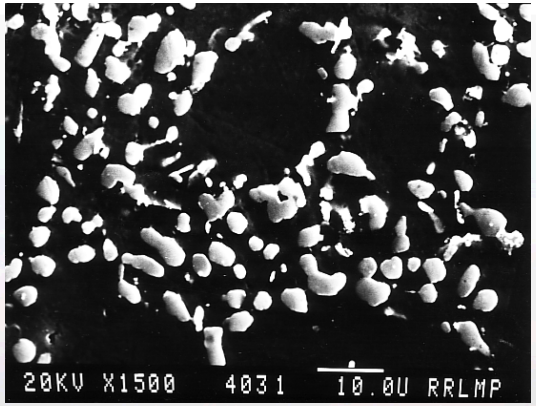
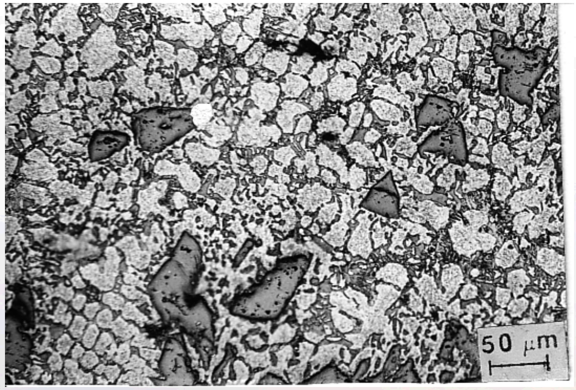




Silicon Debris
From Wear Test



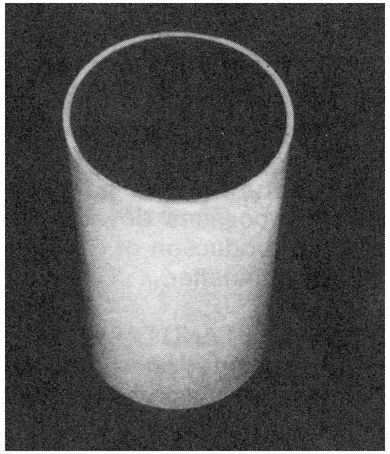
Microstructural Modification of Al-Si Alloys for improved wear resistance

	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.

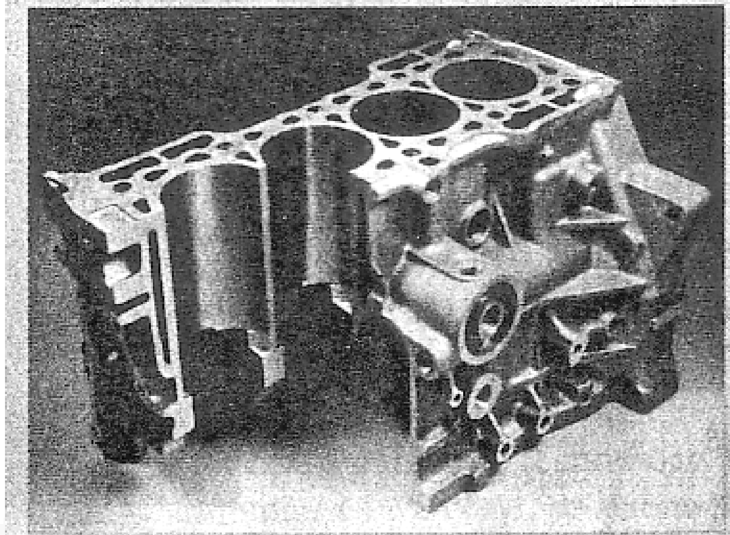
S. V. Prasad and R. Asthana, Tribology Letters, 17 (2004) 445-453.

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.

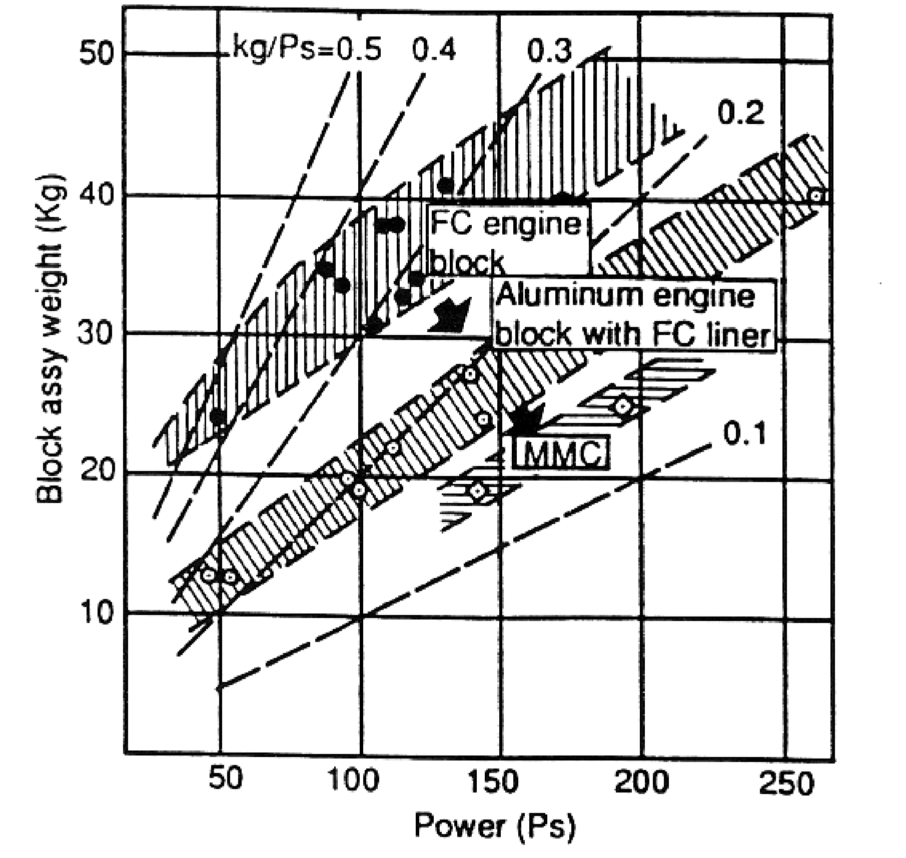
- Ceramic "preform" production
- Pressure casting process
- Honing

- 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

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

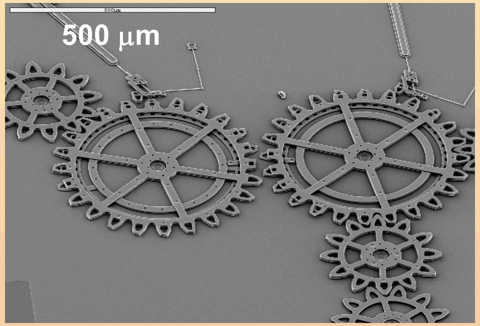
Relationship between Power and Engine Block Weight



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*

Harsh Environments



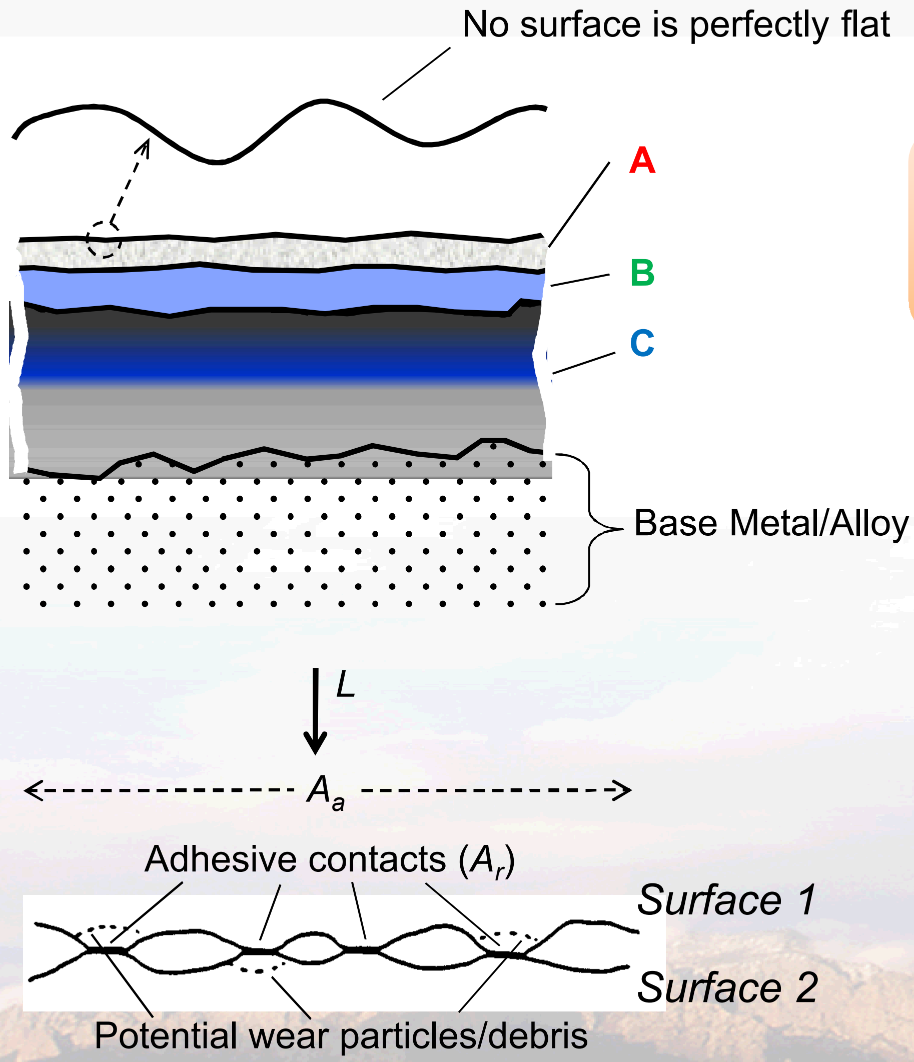
Energy and Communications

Outline

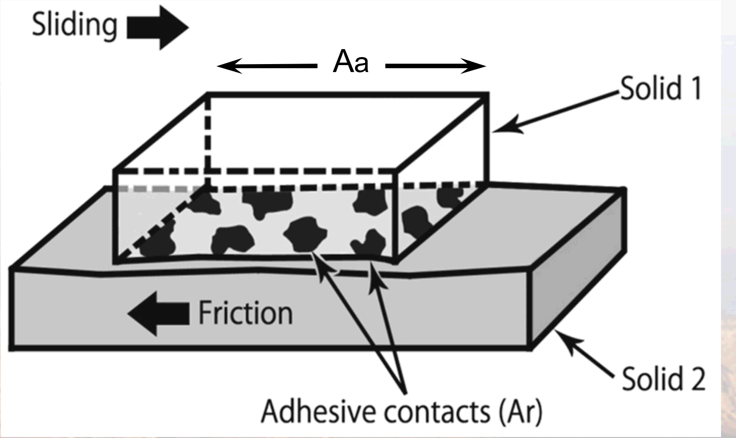
- Solid Lubricants
  - Transition Metal Dichalcogenides
  - Diamond-Like Carbon
    - Environmental Effects
    - Subsurface Deformation

Nature of Metallic Surfaces

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



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

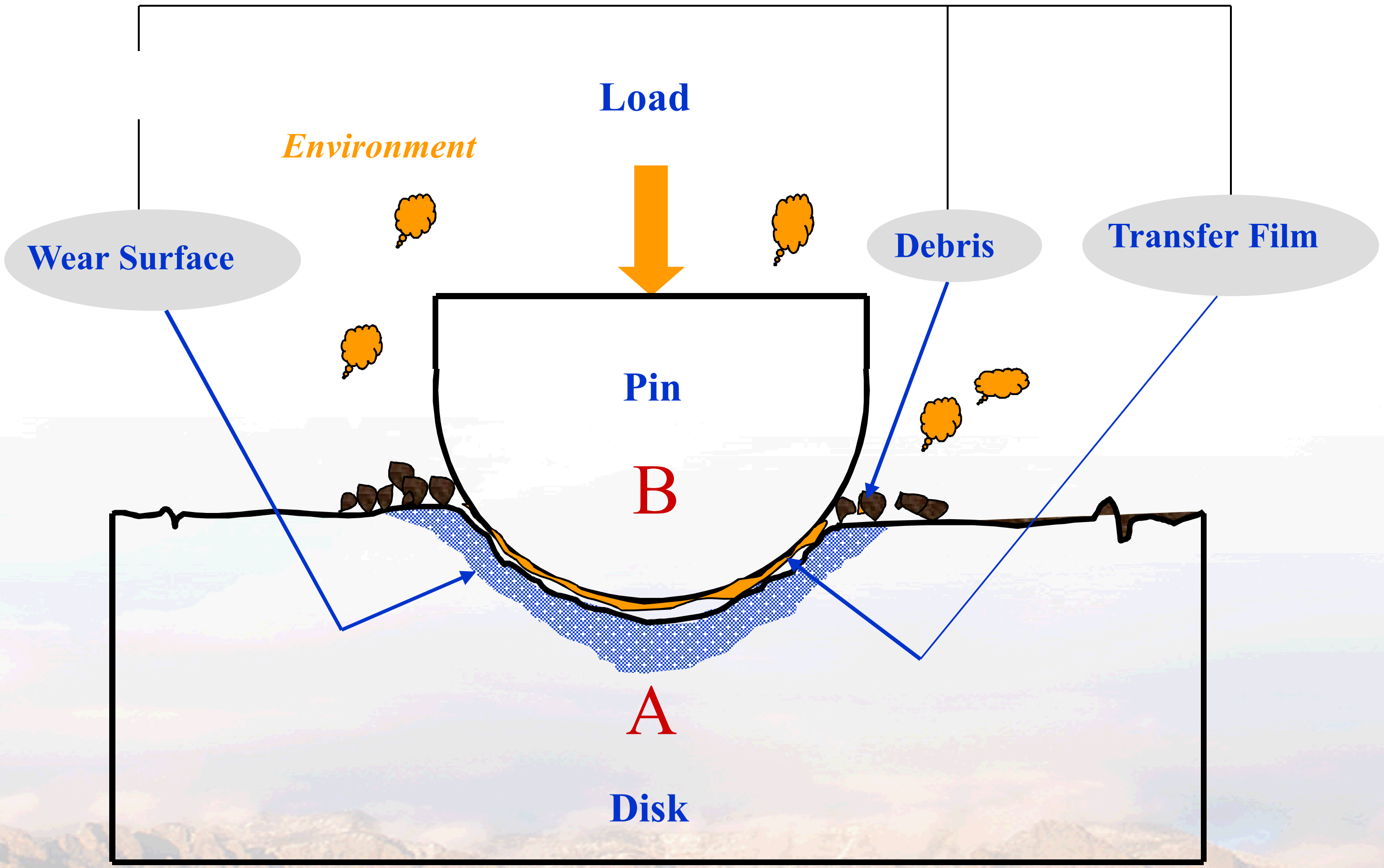


T.W. Scharf , S.V. Prasad, Journal of Material Science (2013) 48:511-531

Wear (Tribology) is a systems property

- *Engineering surfaces are never perfectly flat*
- *The real area of contact is a small fraction of the apparent area of contact*

- Plastic deformation
- Diffusion
- Tribochemistry
- Transfer Films
- Environmental Reactions



S. V. Prasad and K. R. Mecklenburg,, *Tribology Transactions* **39** (1996) 296-305.
T. W. Scharf and S. V. Prasad, J Mater. Sci. 48 (2013) 511–531
D. A. Rigney and J. P. Hirth, Wear 53 (1979) 345-70

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Evolution of Analytical Techniques

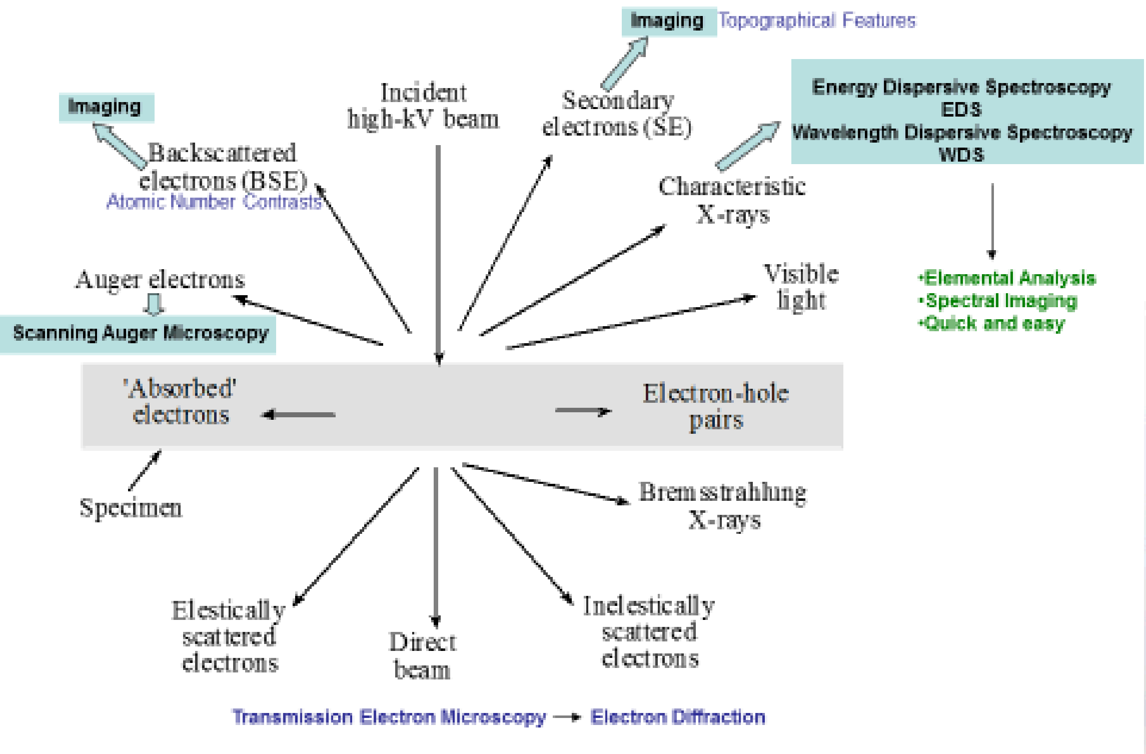
- Light Microscopy (Early Research)
  - Oblique Sectioning
  - *"Phase-Contrast Microscope*
- **Commercial Scanning Electron Microscopy**
  - Cambridge Stereoscan (1965)**
- Auger Electron Spectroscopy
- XPS
- Raman Spectroscopy
- ToF SIMS

Visualization/Resolution
Surface Chemical analyses

<u>Subsurfaces (Recent Advances)</u>

- **Focused Ion Beam Microscopy (2000)*****
- Transmission Electron Microscopy, TEM
- Electron Backscatter Diffraction, EBSD

Electron Microscopy

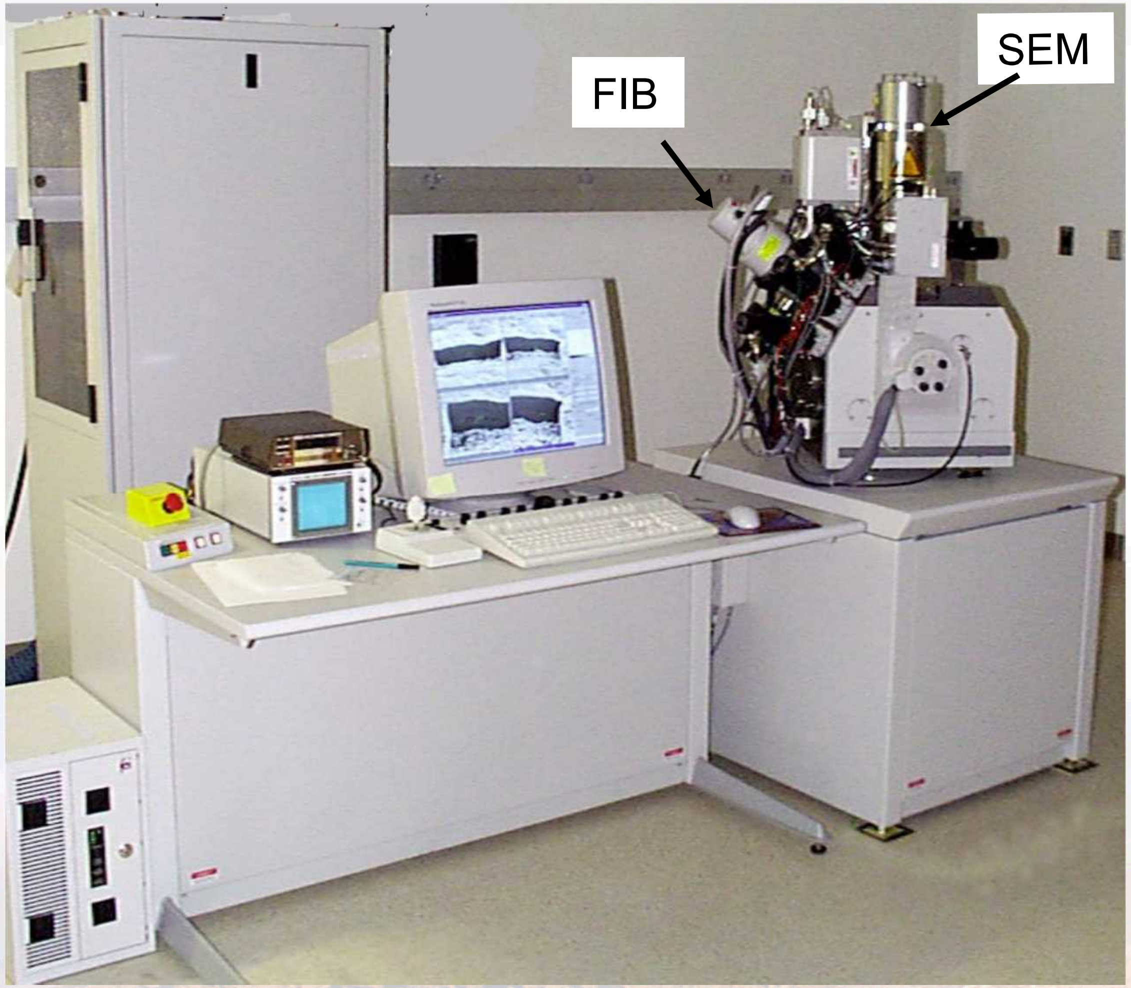


Focused Ion Beam Microscopes

Conventional Techniques

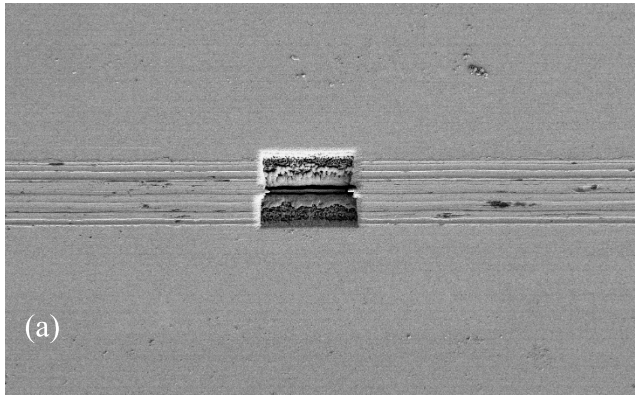
•Ion Milling (Dimpling)
•Electropolishing
•Ultramicrotomy

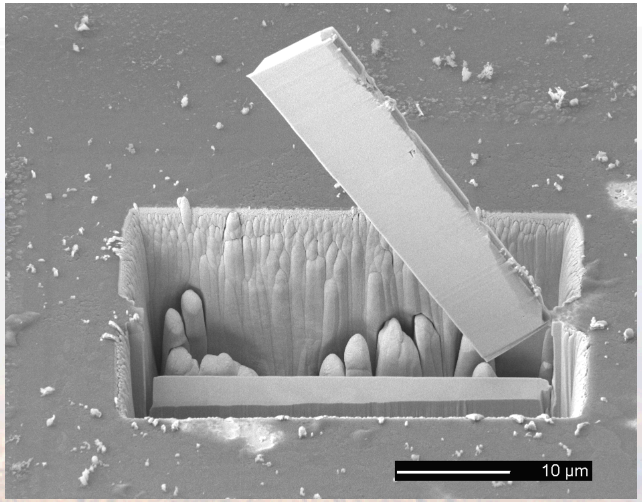
(-) (-) (-)
Not site specific



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

Sliding Direction





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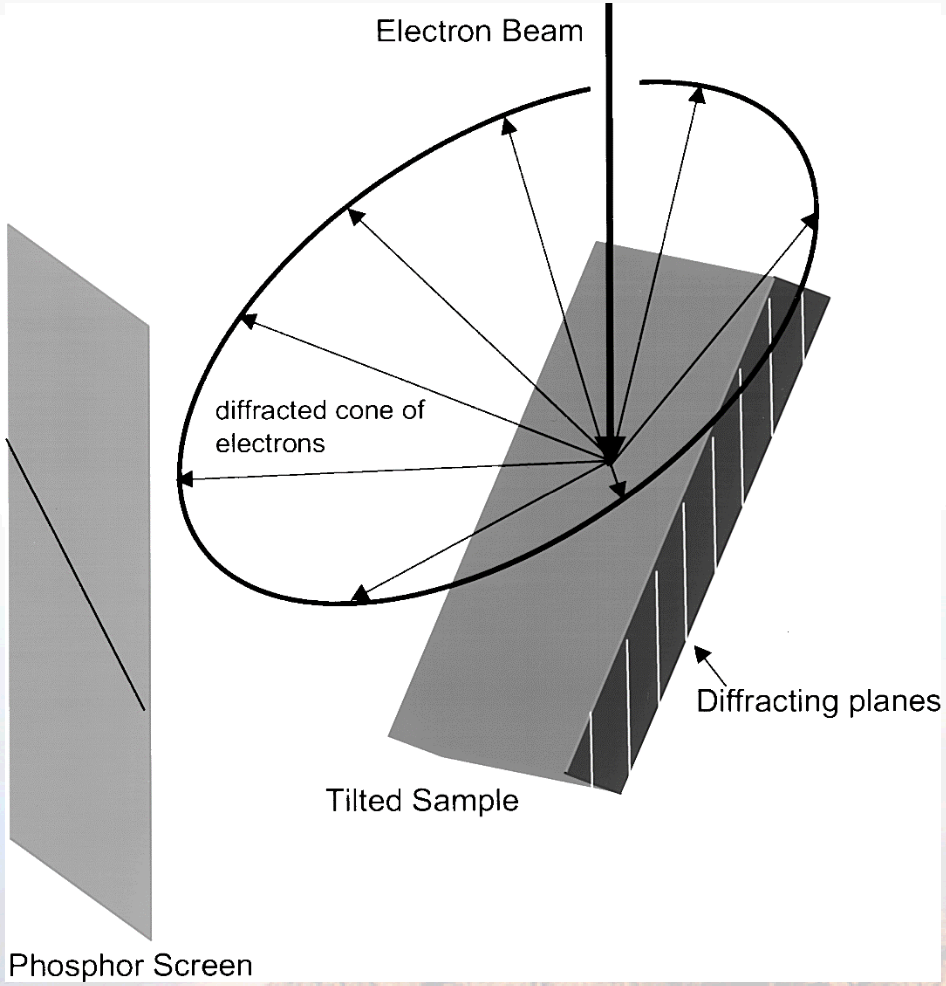
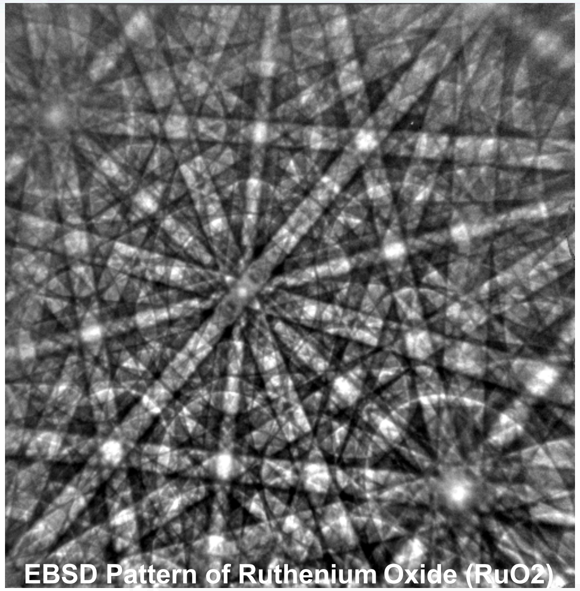
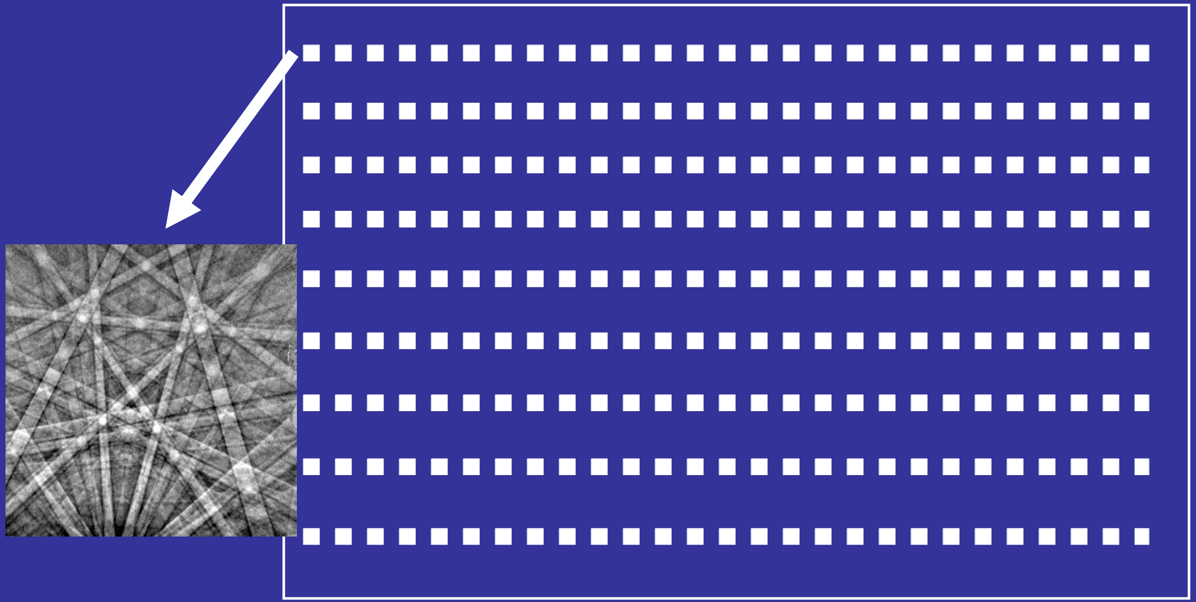
Electron Backscatter Diffraction (EBSD) in the SEM





ZnO Rods

Automated EBSD Pattern Indexing



SEM image with pixels for EBSD

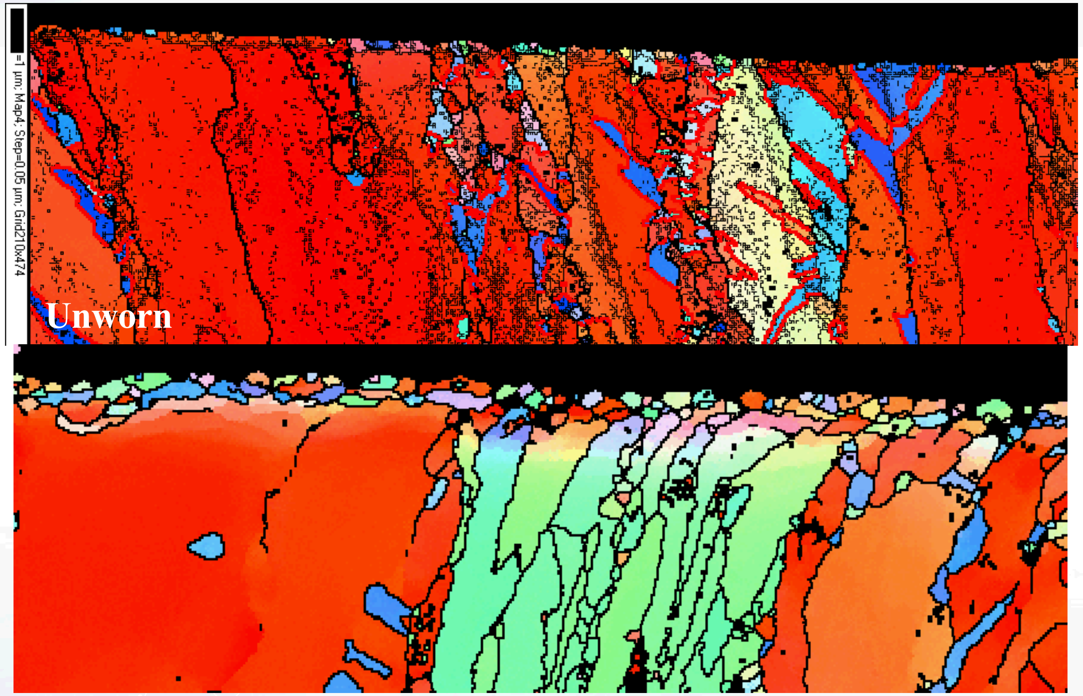
Step size dictated by microstructure and level of detail needed.

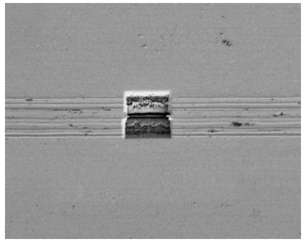
Minimum step size < 20nm! Backscattered
Minimum step size <2 nm in Transmission

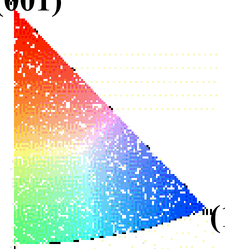
1. Scan area of interest pixel by pixel.
2. Collect EBSD pattern
3. Located 4 – 7 lines on pattern – Hough transform
4. Calculate angles between bands
5. Compare with known unit cells (short list)
6. Index pattern
7. Calculate orientation
8. Move to next pixel

Modern systems can do this up to 1000 times per second!

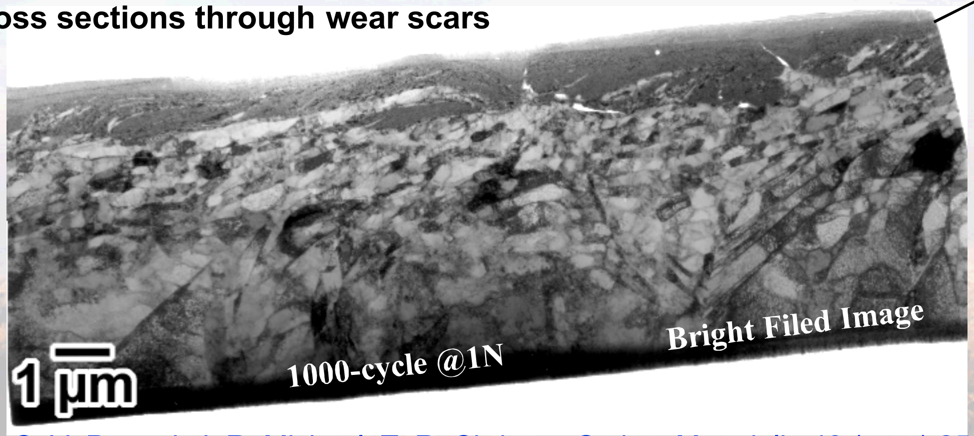
Visualization of suburface deformation: FIB, EBSD TEM

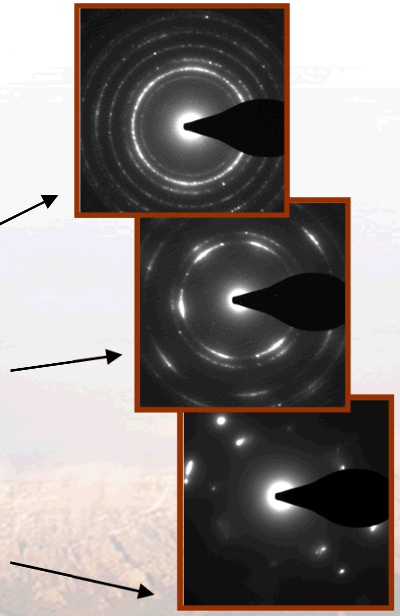






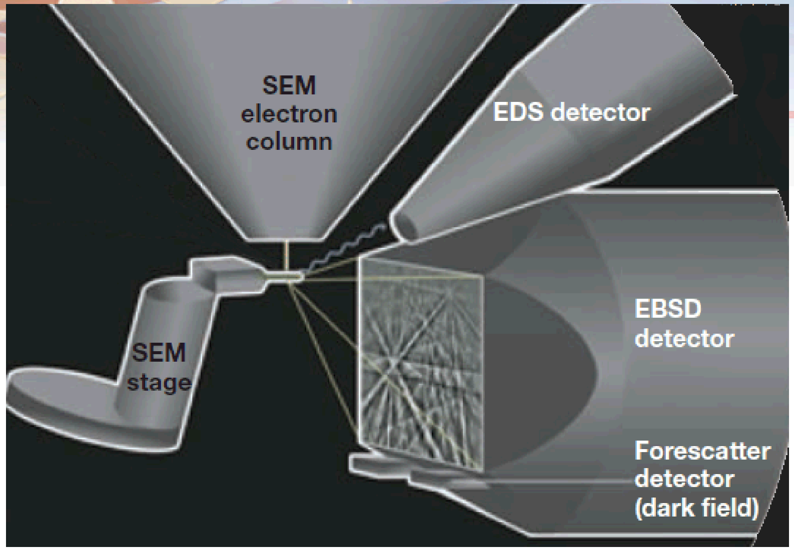
Cross sections through wear scars





S. V. Prasad, J. R. Michael, T. R. Christen, Scripta Materialia 48 (2003) 255

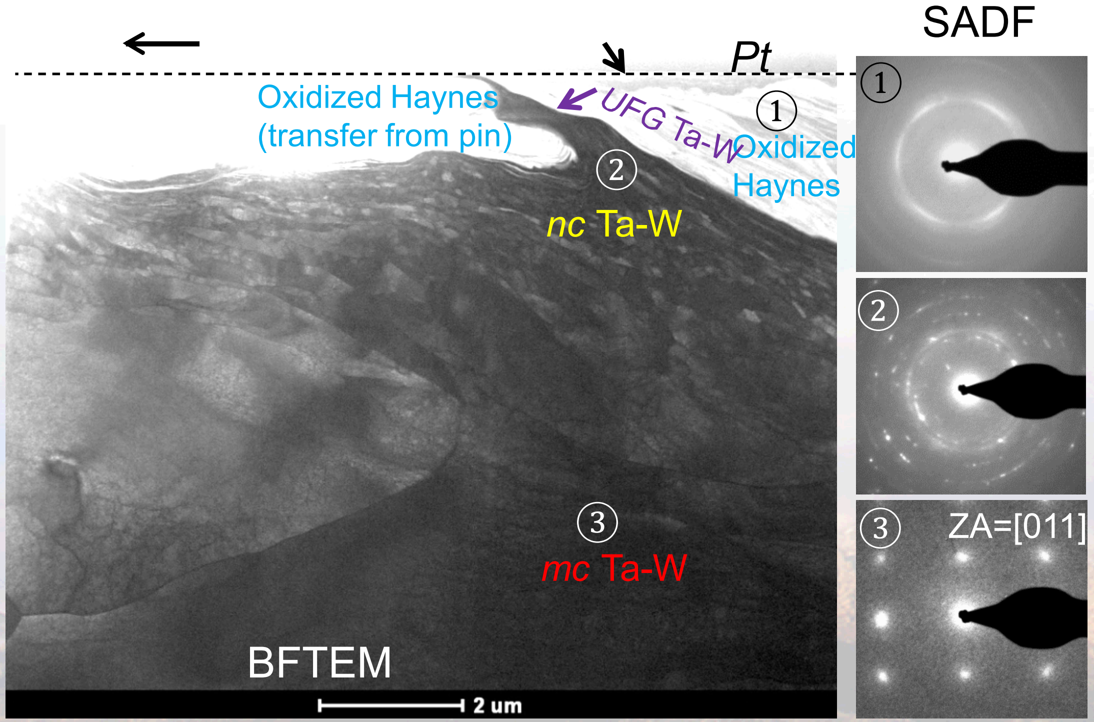
Transmission Kikuchi Diffraction (TKD)
(Haynes Alloy Pin on Ta-W Disk)

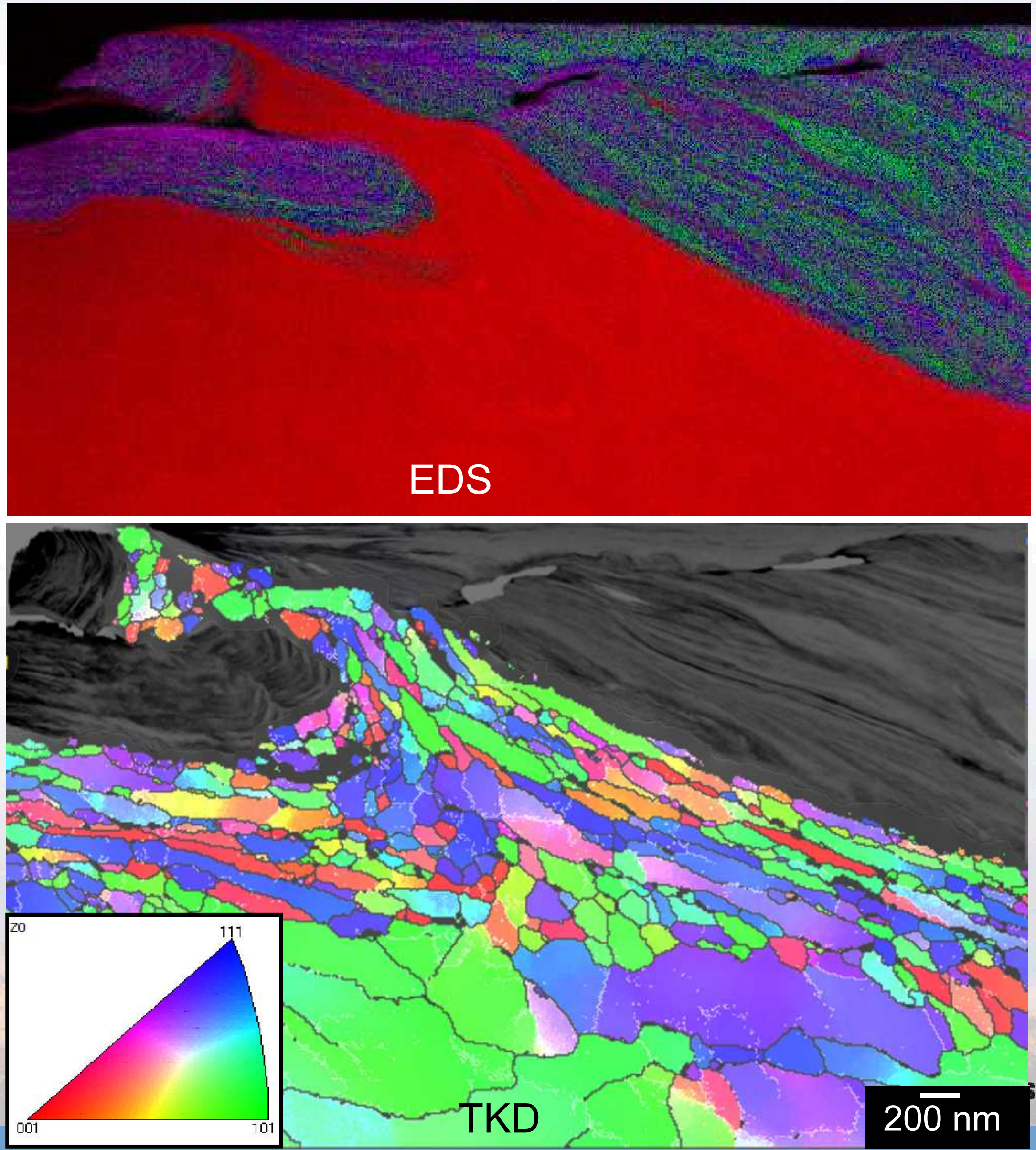


Higher resolution compared to EBSD
2 nm versus ~50nm

STEM to SEM

Visualization of grain orientation





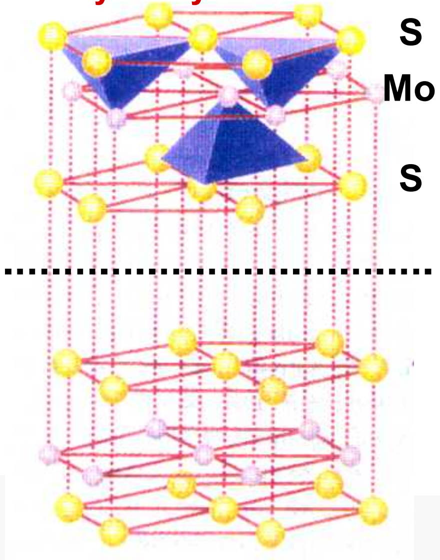
Solid Lubricants

- *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*

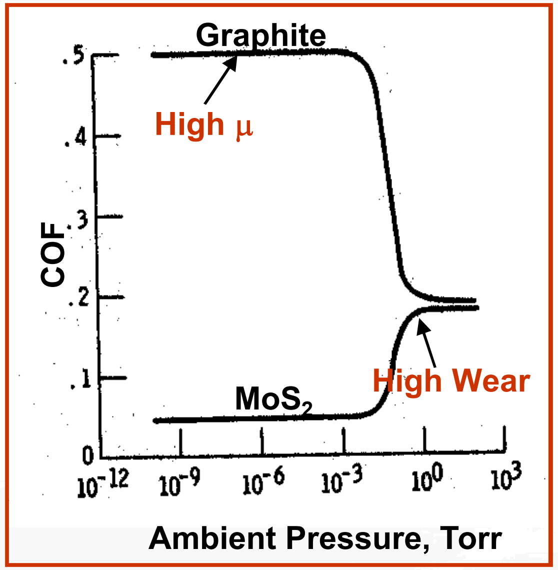
1. Carbon-based materials (graphite, DLCs, nanocrystalline diamond)
2. Transition metal dichalcogenides (MoS_2, WS_2)
3. Polymers (e.g., PTFE)
4. Soft Metals (Ag, Sn, Pb, In , Au)

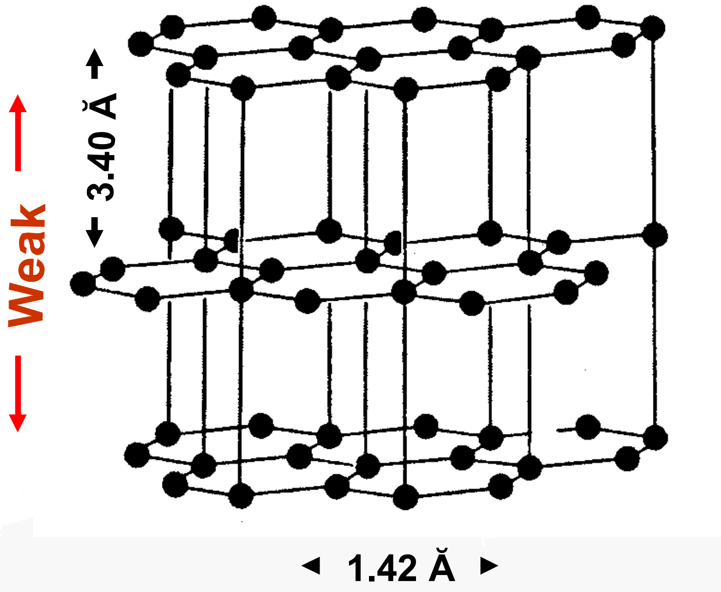
Classic Examples of Environmental Effects on Transfer Films & Friction

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



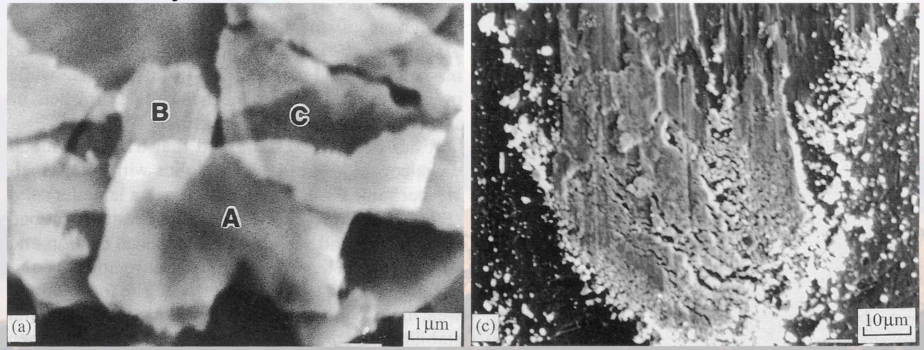
Mo/W Disulfide





Graphite

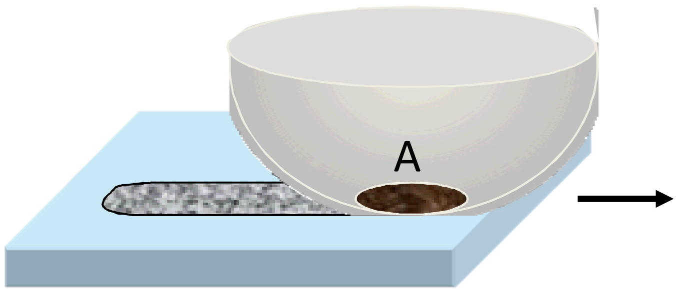
They form thin transfer films on the counterface



- 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

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')

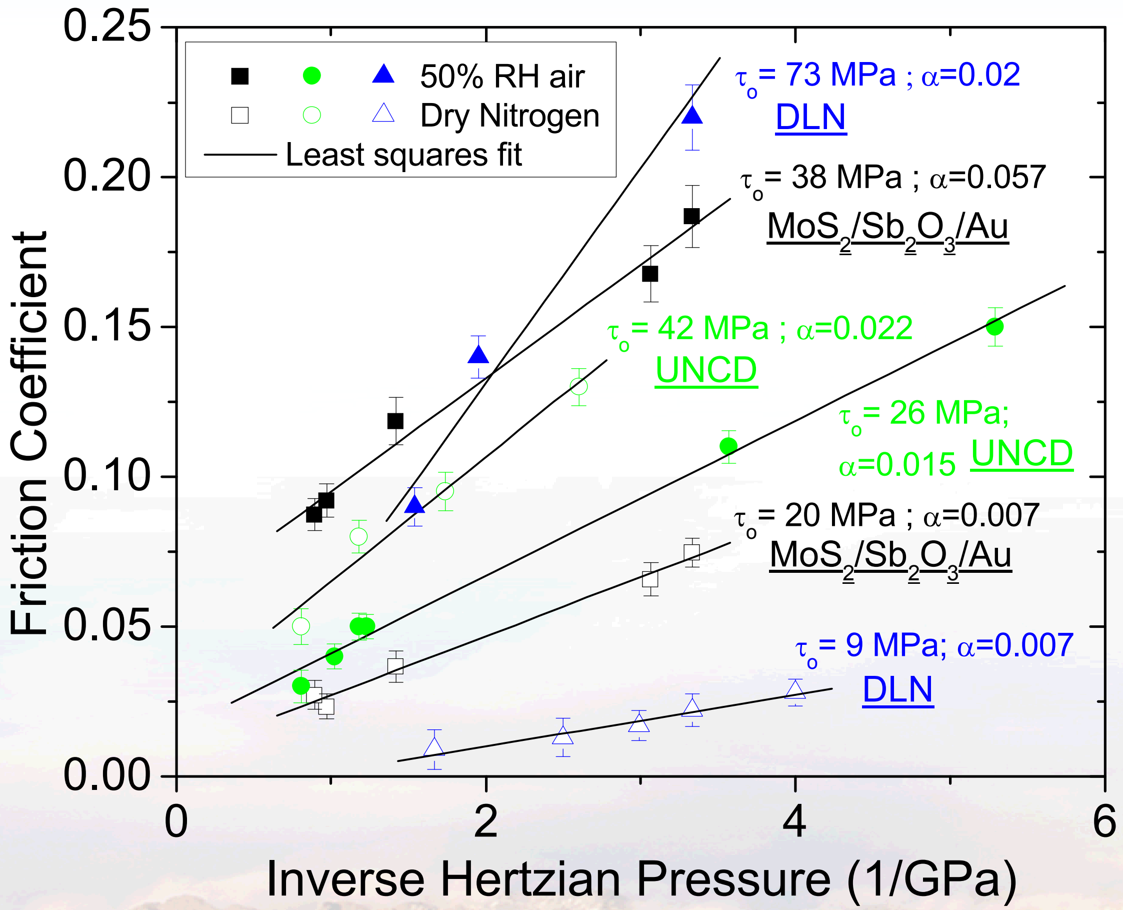
Friction is NOT independent of Load

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).

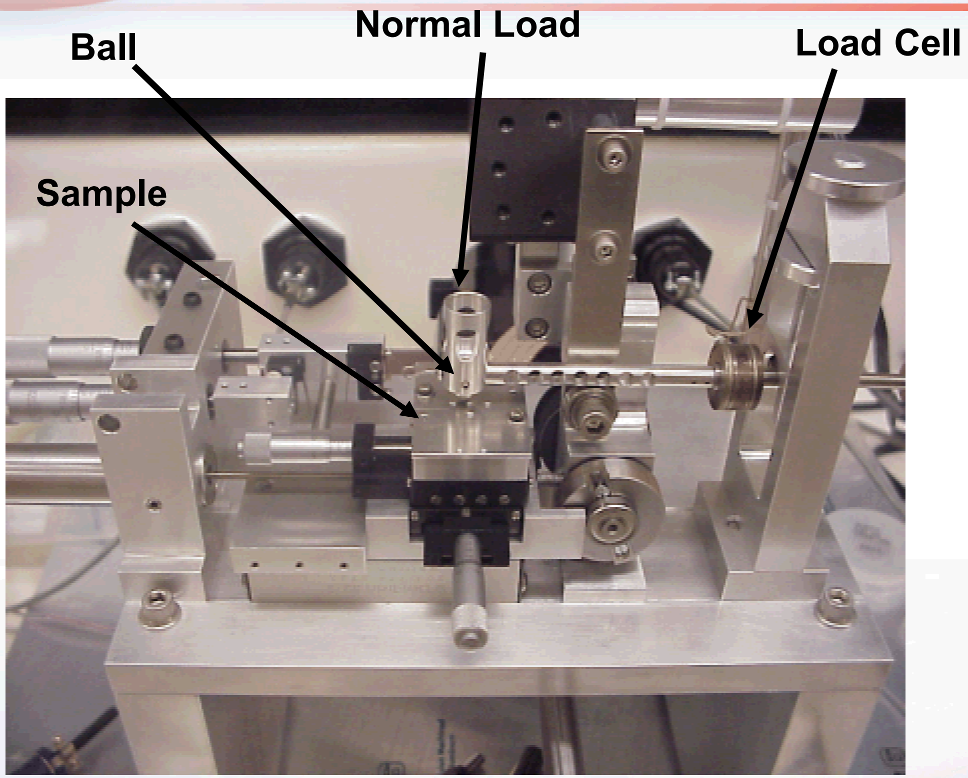
B.J. Briscoe and D.C.B. Evans, *Proc. R. Soc. Lond. A* 380, 398 (1982).

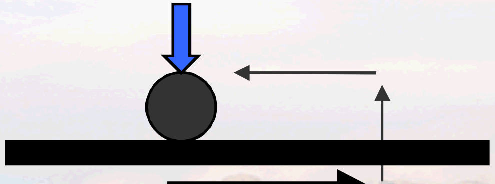
Inverse Hertzian Behavior— Non-Amontonian



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

Friction and Wear Measurements





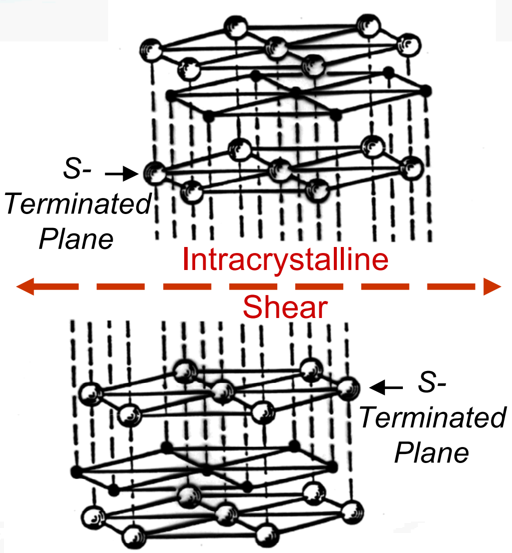
Linear Wear Tester
(Ball-on-Flat configuration)

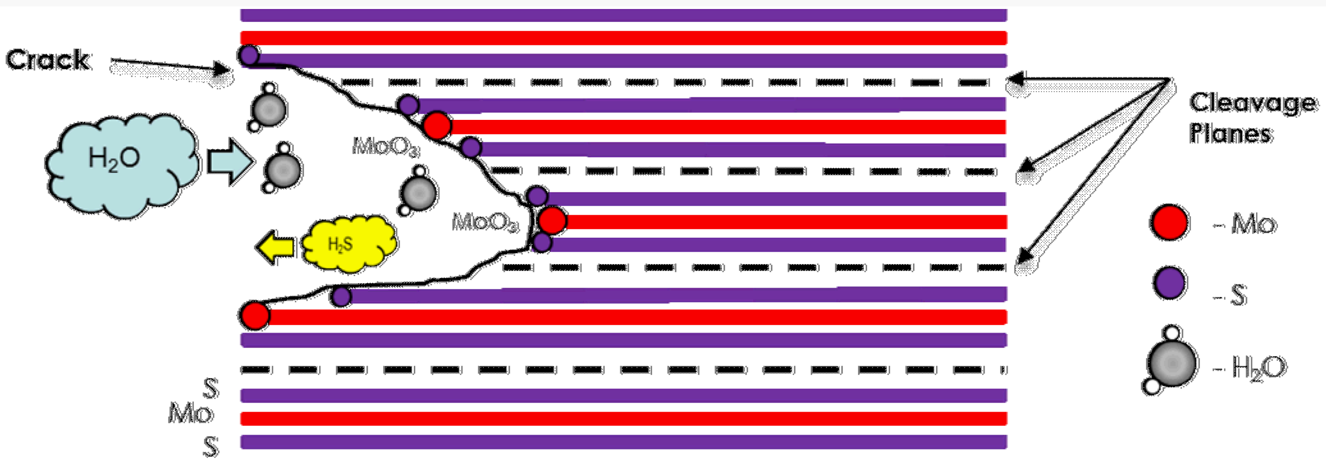
- Contact Pressures: 0.44 GPa to 1.7 GPa
- Environment: Dry Nitrogen; Air (50% RH)

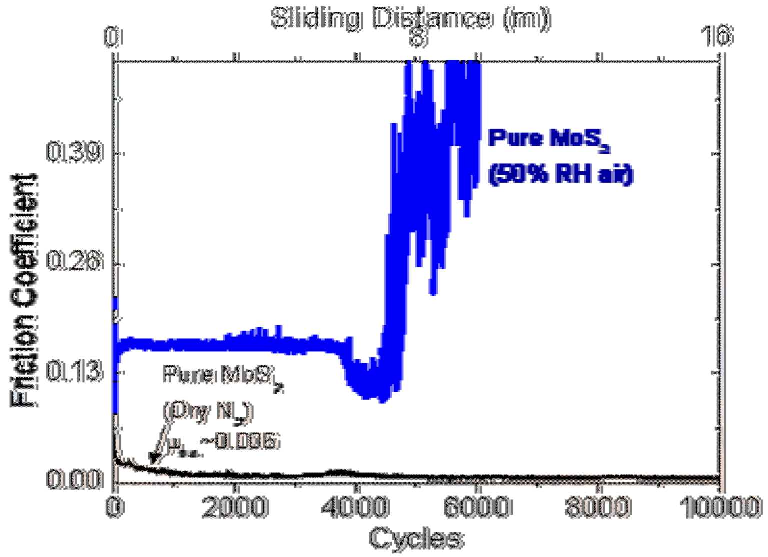
Oxygen Analyzer
Dew Point Measurement

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

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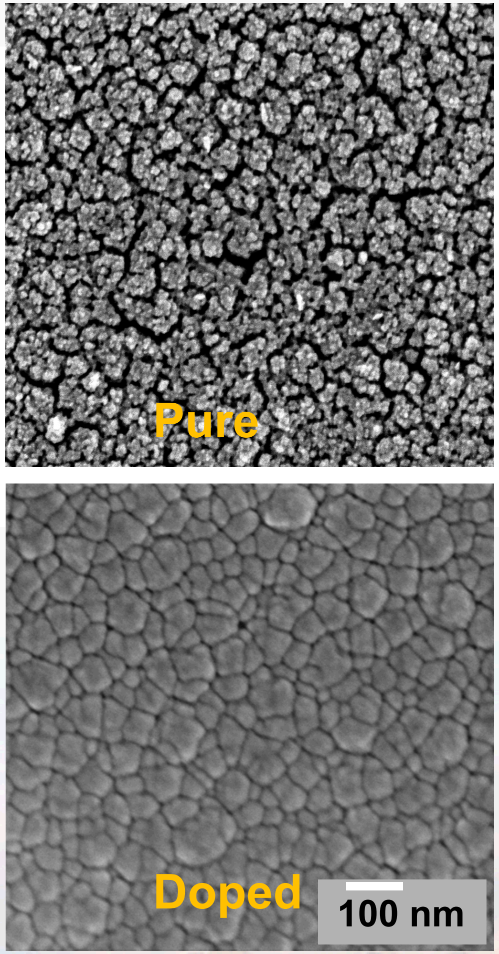
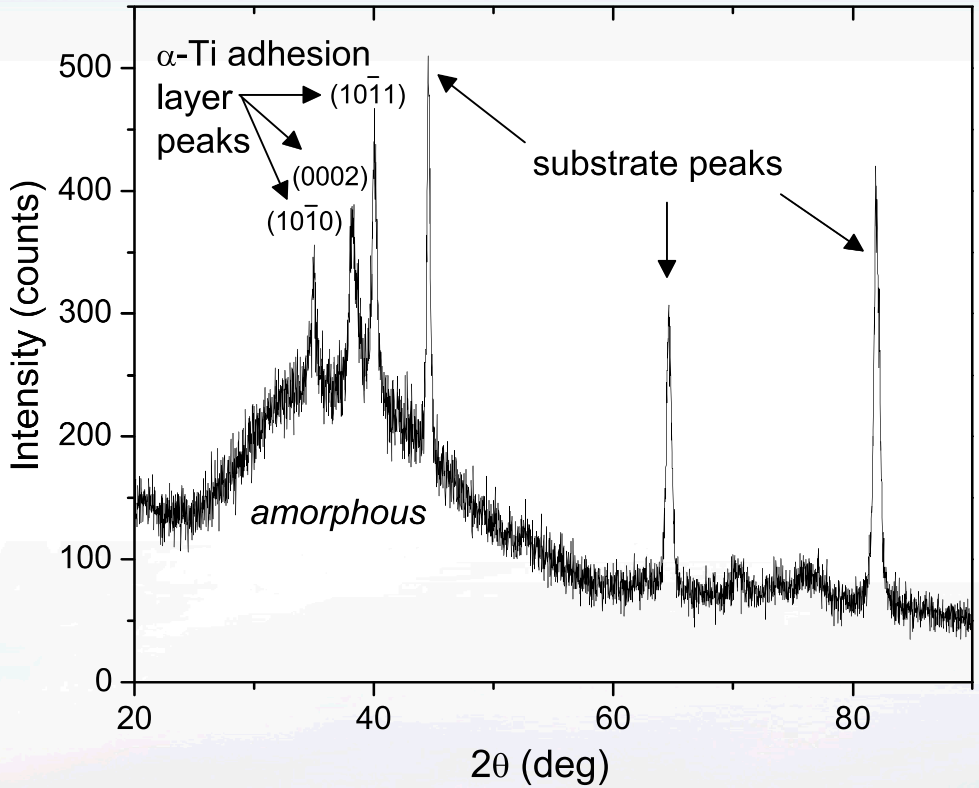
Doped MoS_2 (Sb_2O_3 and Au) from Tribologix



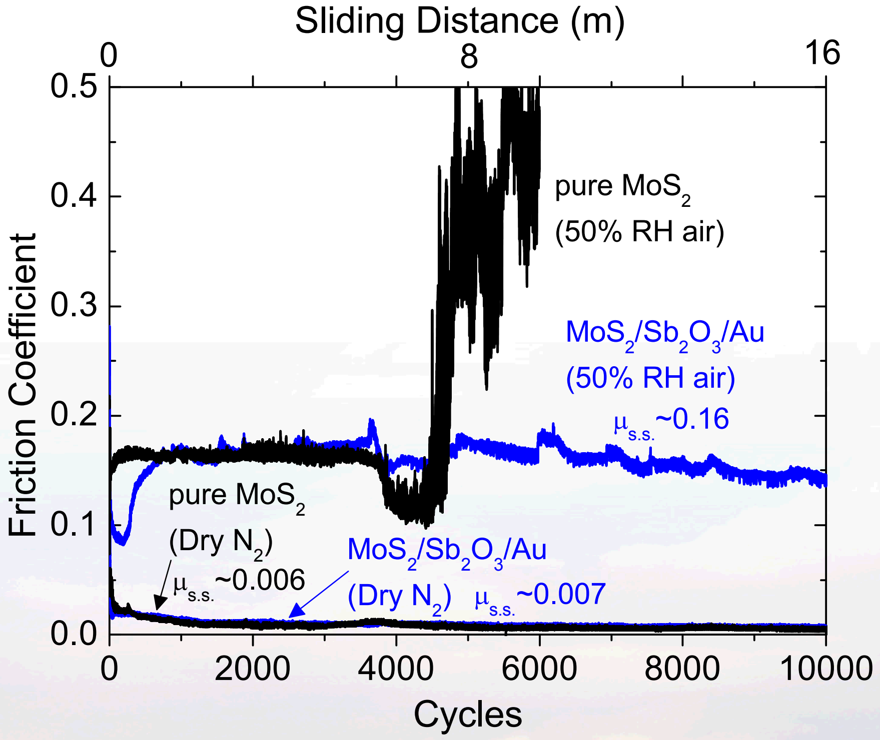


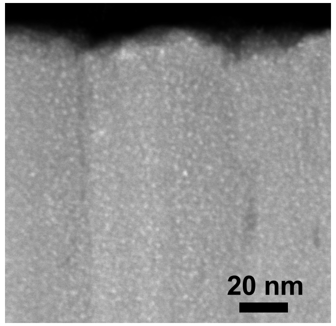
- Note the absence of peaks characteristic of any of the three constituent phases
- Instead there is a broad indicating the presence of an amorphous phase
- Doped films are much denser

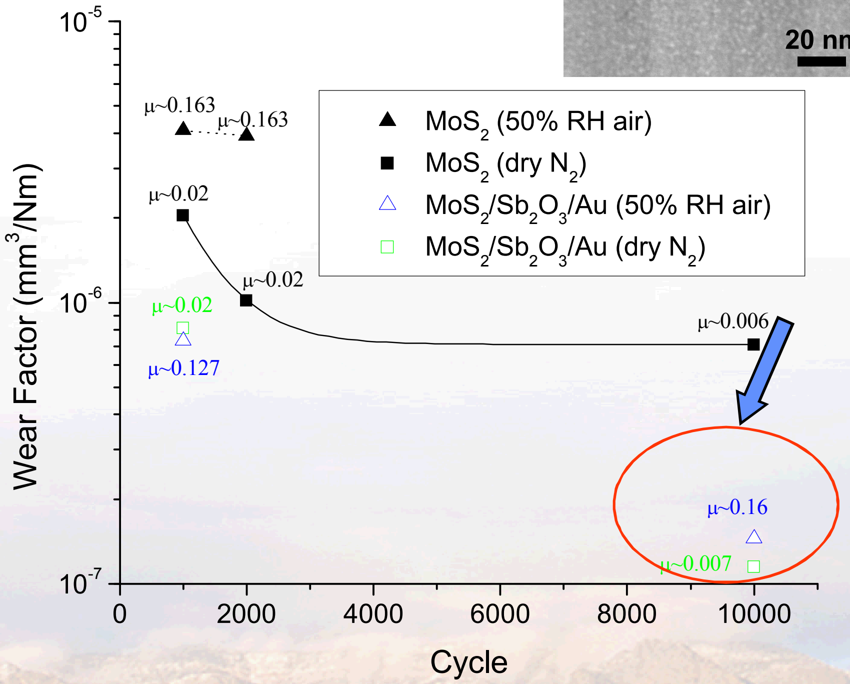
Sandia National Laboratories

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

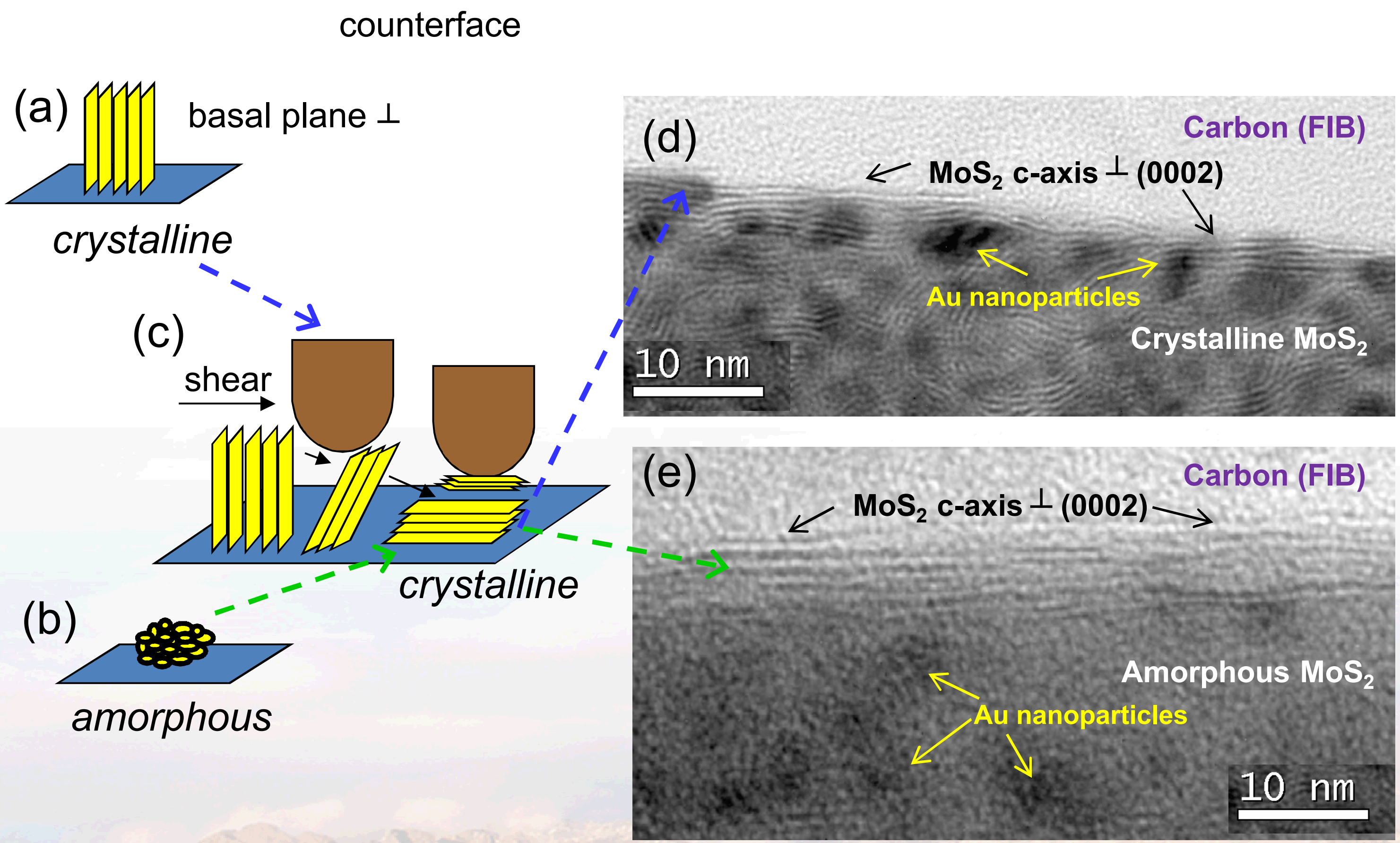




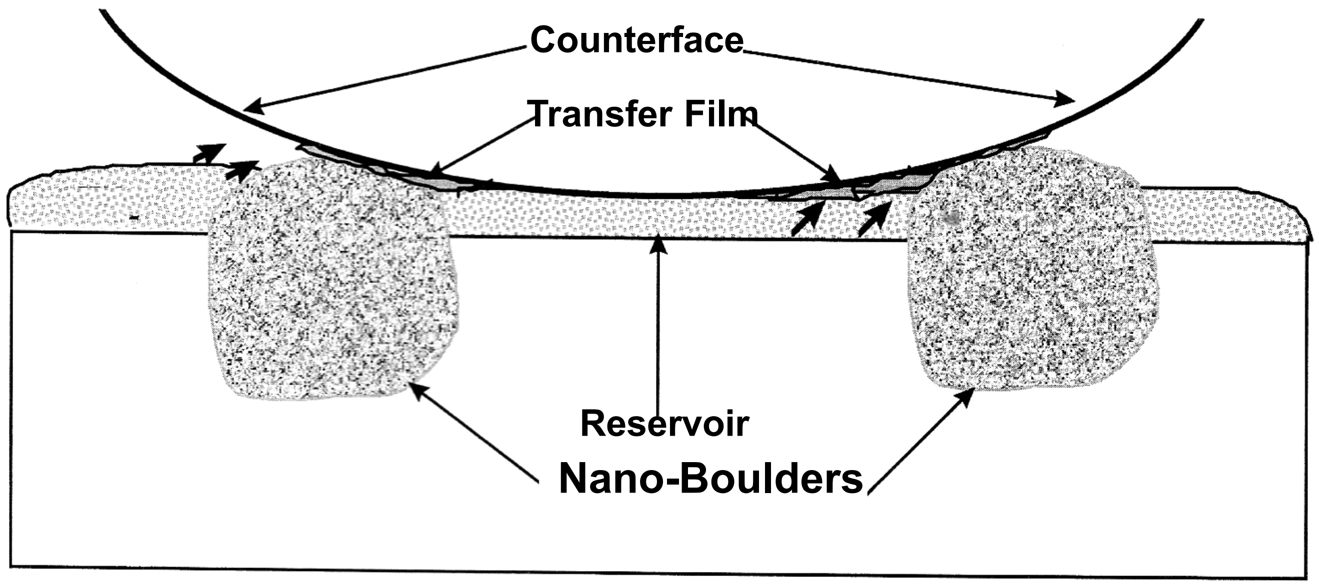


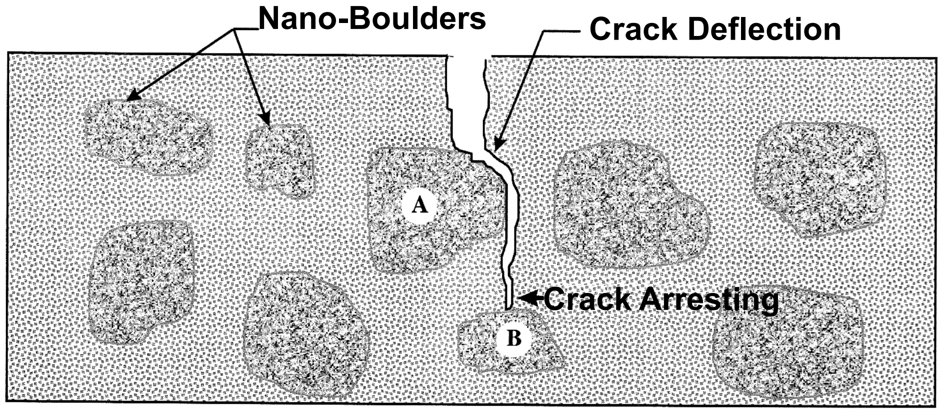
T. W. Scharf, P. G. Kotula and S. V. Prasad, Acta Materialia 58 (2010) 4100-4109

Friction-induced crystallization and reorientation of basal planes



Novel Concepts for Materials Synthesis



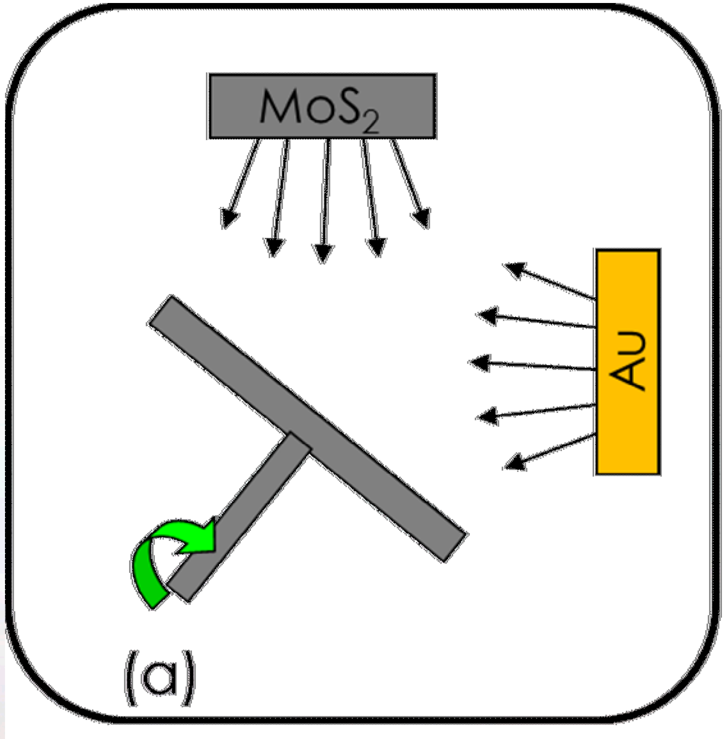


S. V. Prasad, N. T. McDevitt and J. S. Zabinski, Wear 230 (1999) 24-34

Sandia National Laboratories

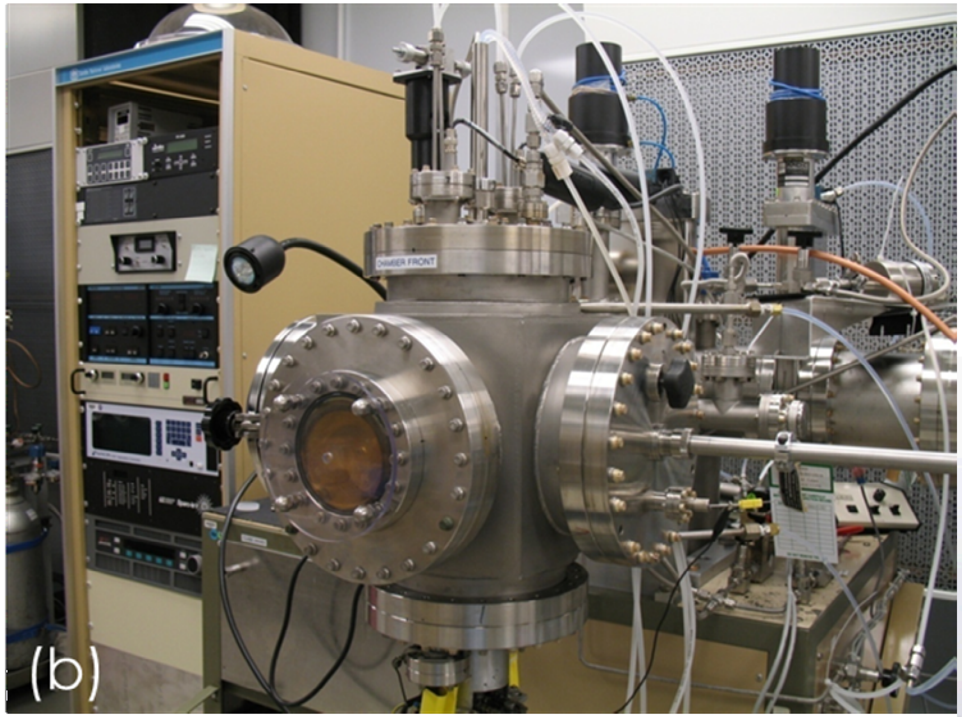
PVD-Co-Deposition for the Synthesis of MoS_2-Au Nanocomposites

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



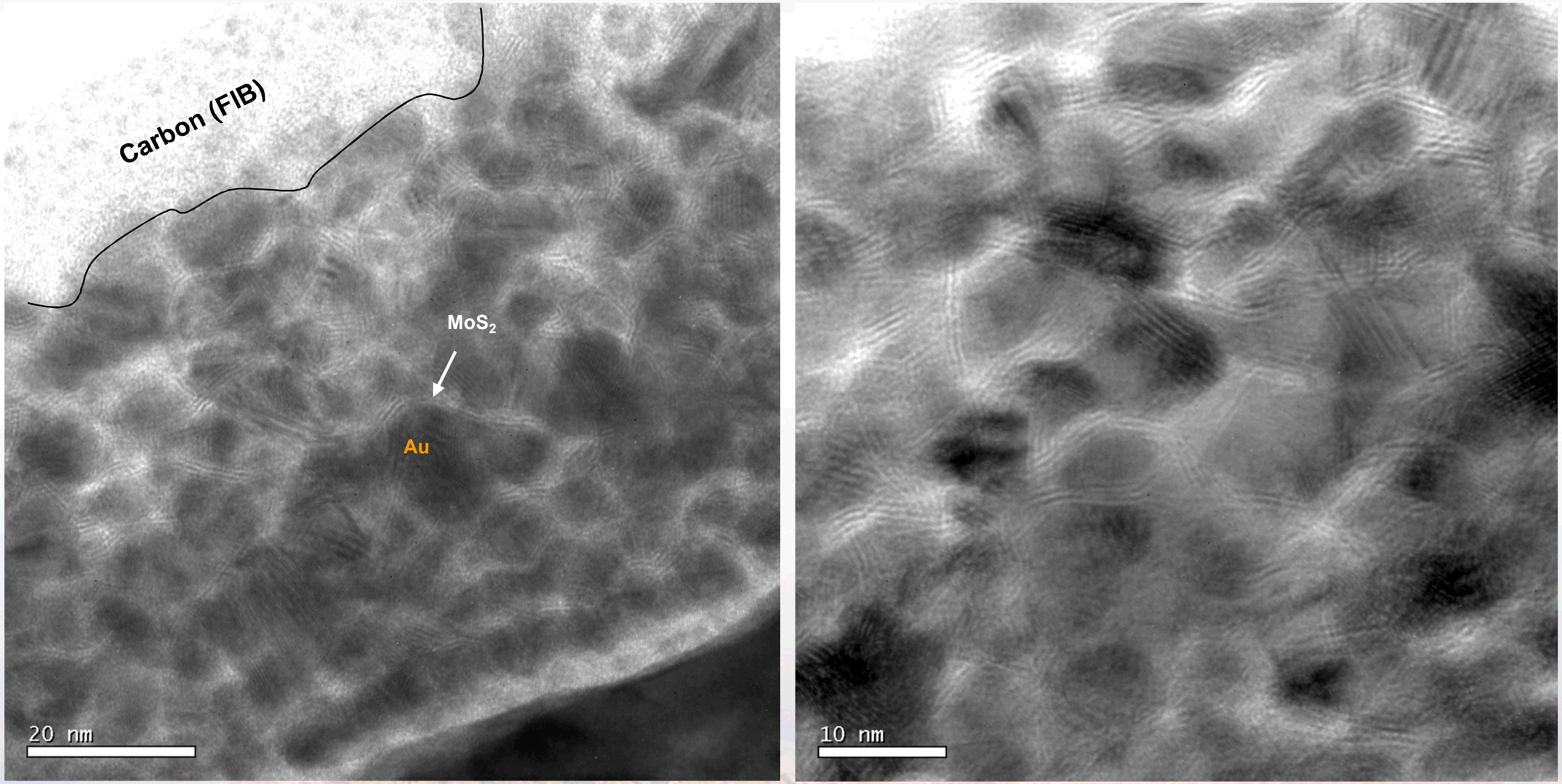
Independent rate control with stage rotation for uniformity

Experimental sputter co-deposition system used in this study



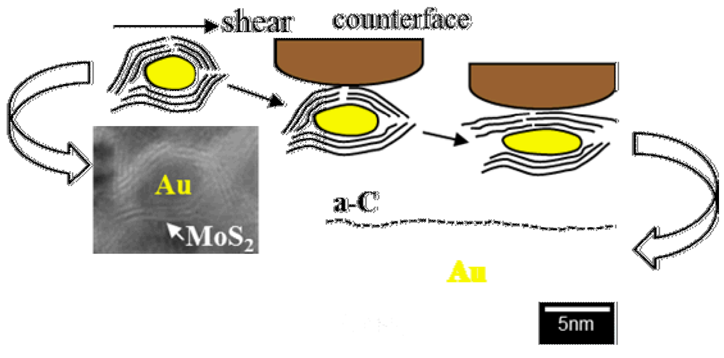
Independent QCM for rate monitor and control
Hot stage
DC Bias

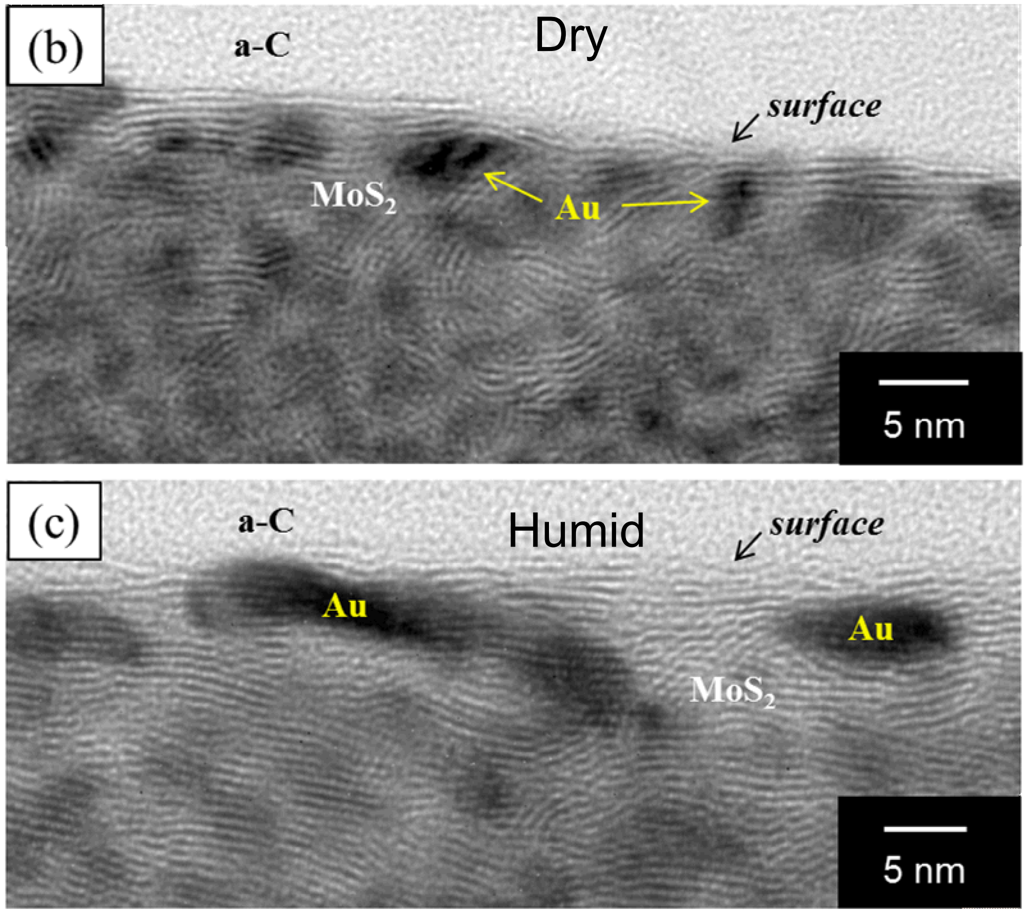
XTEM of MoS_2-Au nanocomposite grown at 200°C



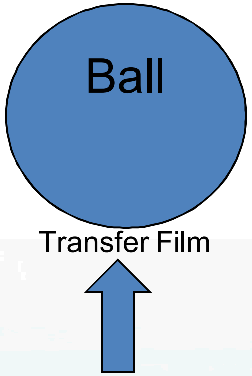
Nanocrystalline Au (~10 nm) core with MoS_2 basal planes encircling

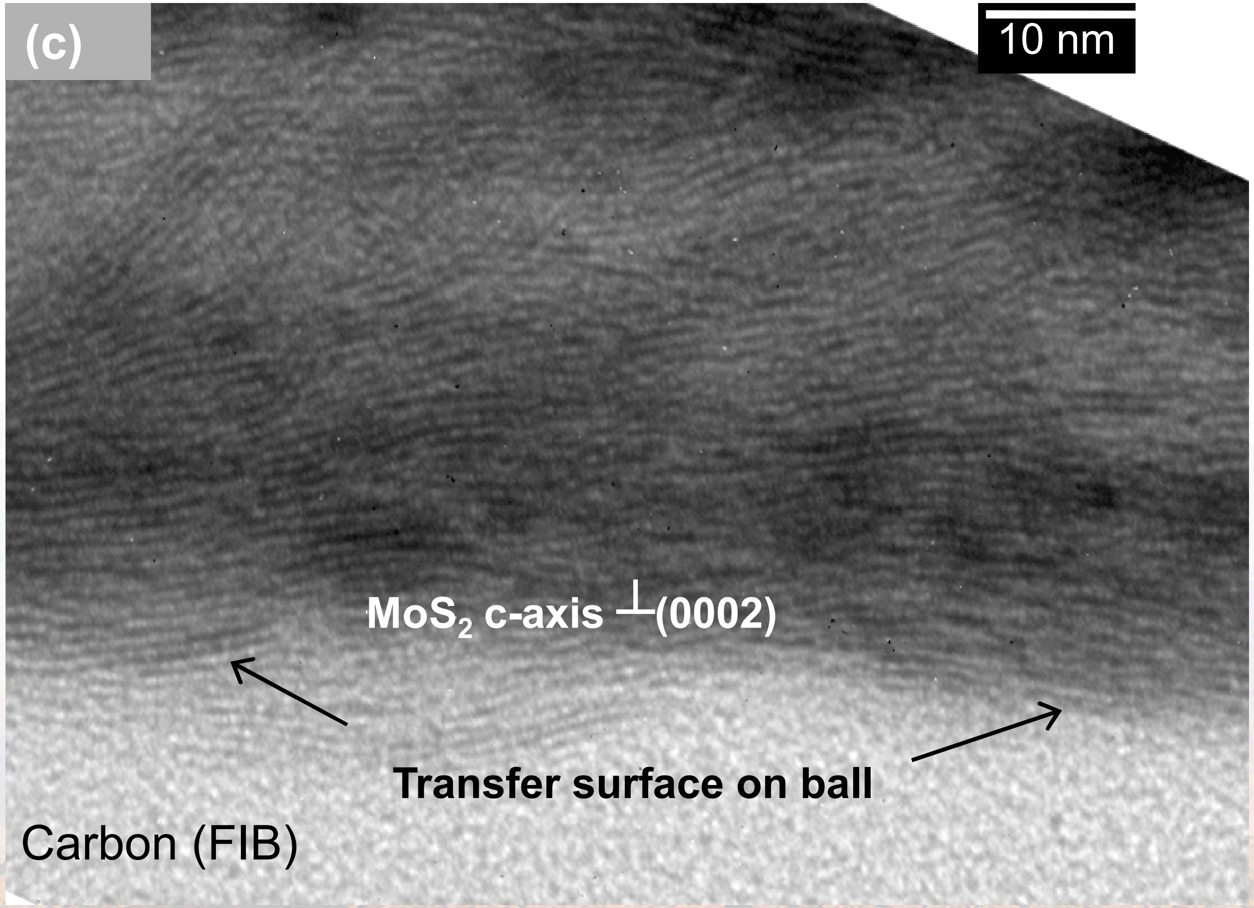
Shear-induced exfoliation of MoS_2 (0002) with basal planes parallel to the sliding direction





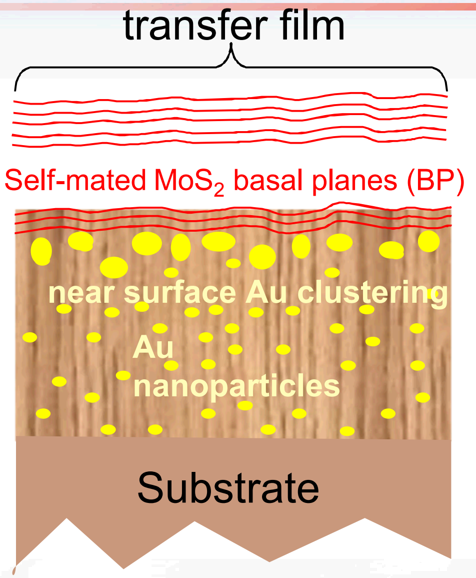
Cross-section of a Transfer Film
Air (50% RH)



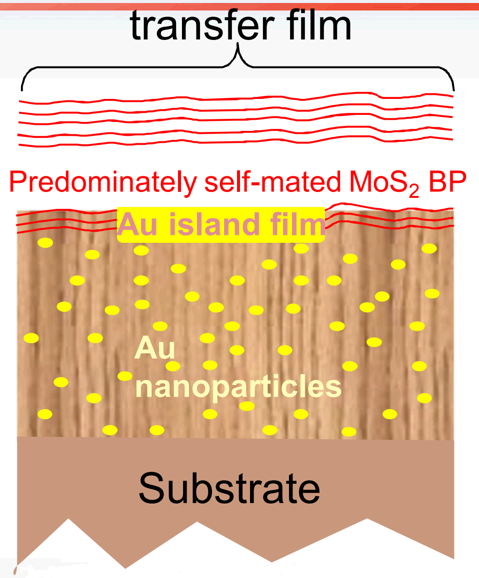


HRTEM

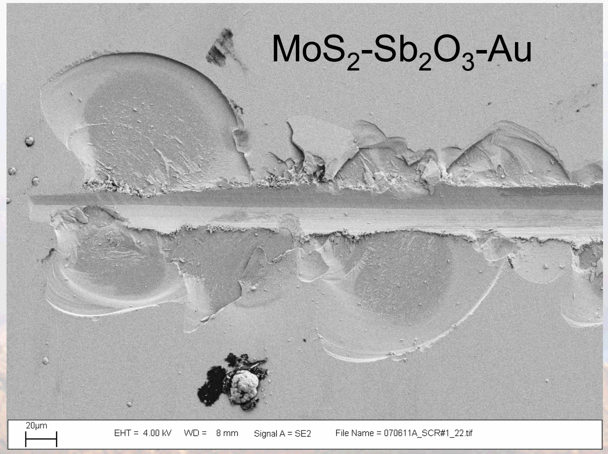
Mechanisms of Friction



Worn (dry nitrogen)



Worn (air with 50%RH)

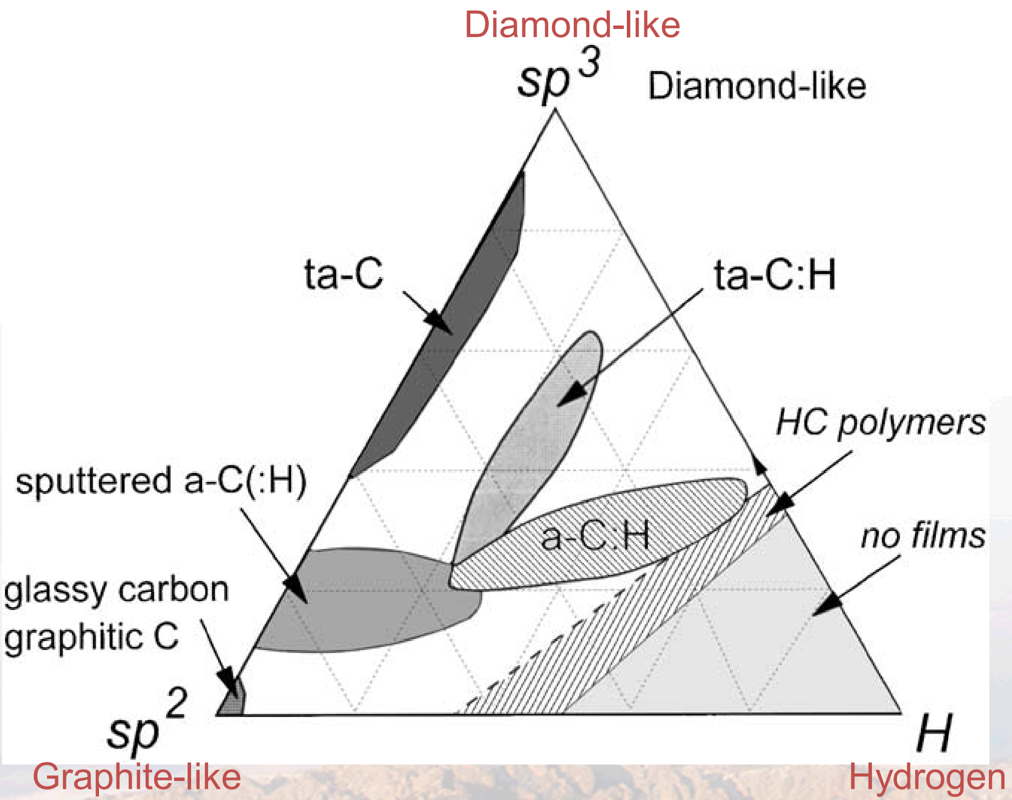


- Whether the MoS_2 is in nanocrystalline form or amorphous, friction induces crystallization with basal planes aligning parallel to the surface
- COF in air is higher but the wear rate is almost identical, indicating the environmental robustness of wear for the nanocomposite (MoS2/Sb2O3/Au) coating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

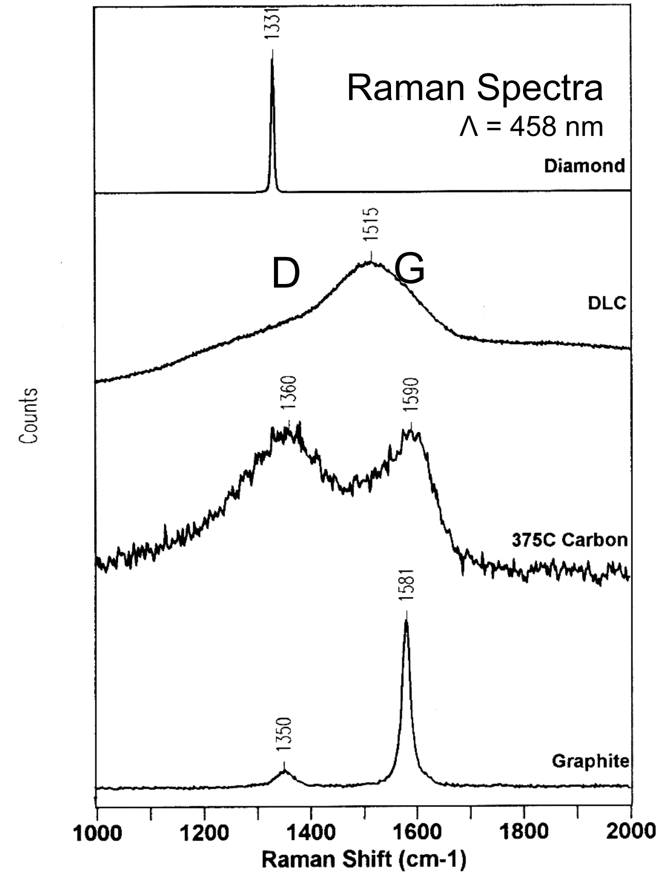
Diamond-Like Carbon (DLC)

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).



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

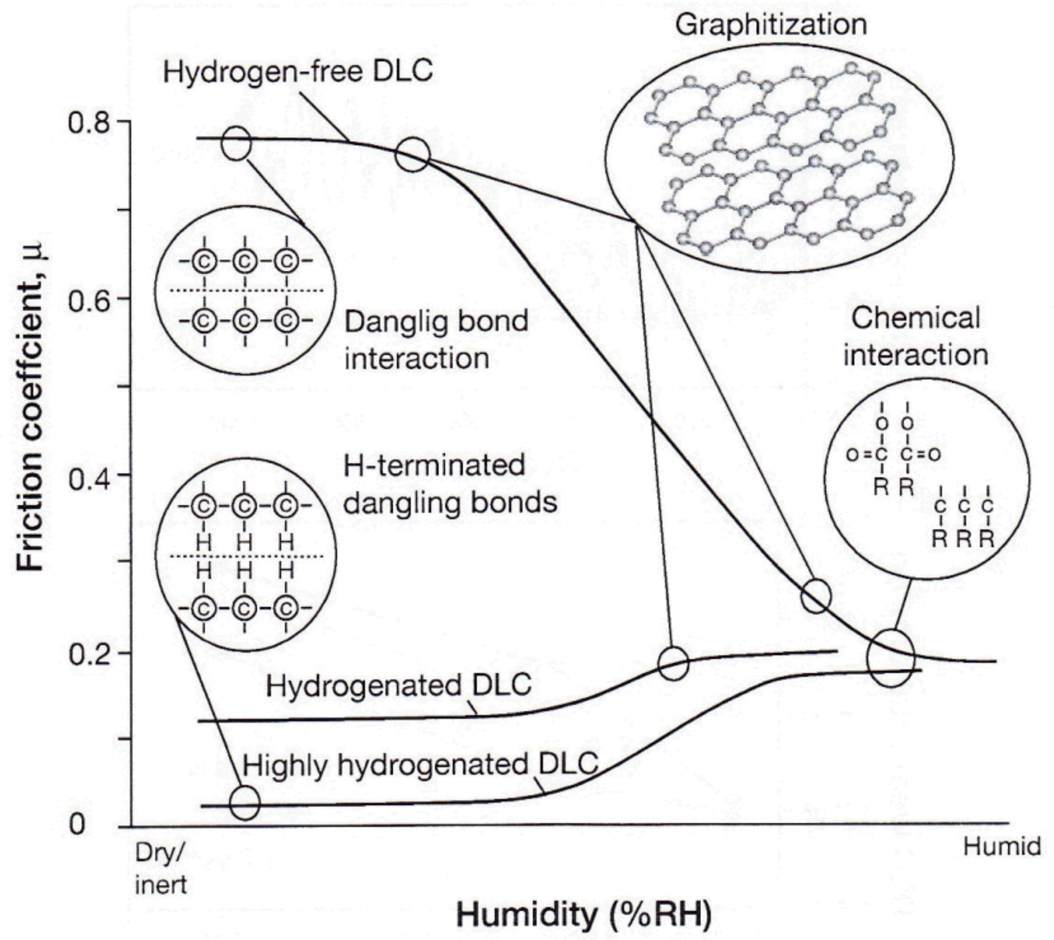


D. R. Tallant et. al, *Diamond and Related Materials* 4 (1995) 191-199

Sandia National Laboratories

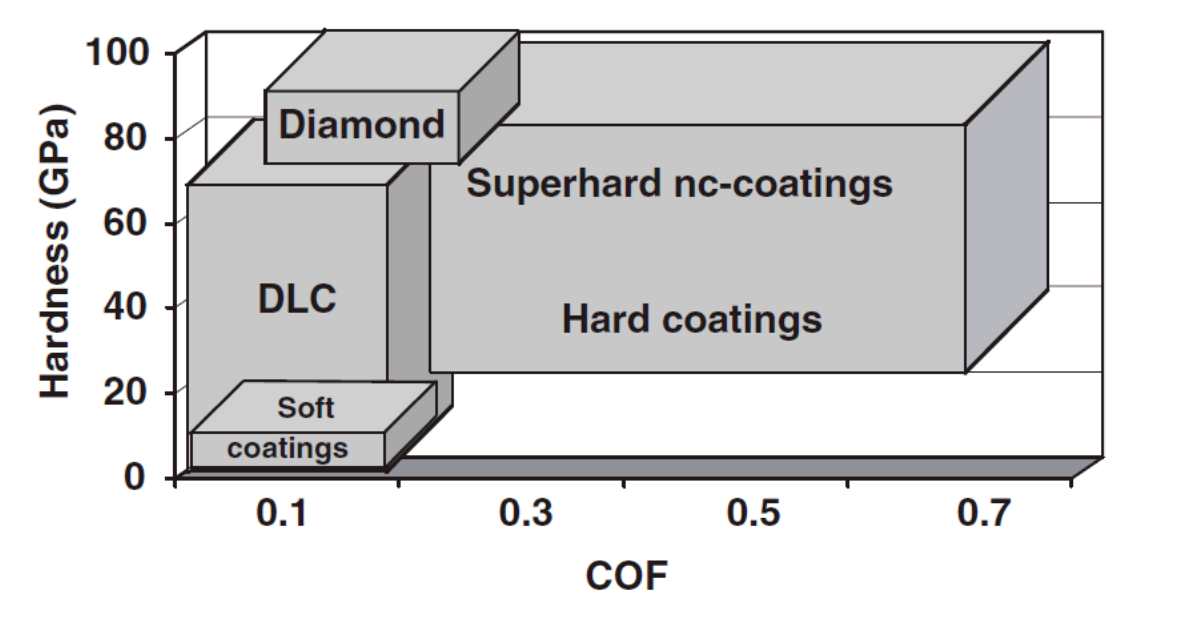
Synthesizing an Environmentally Robust DLC is Still a Challenge!

- 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



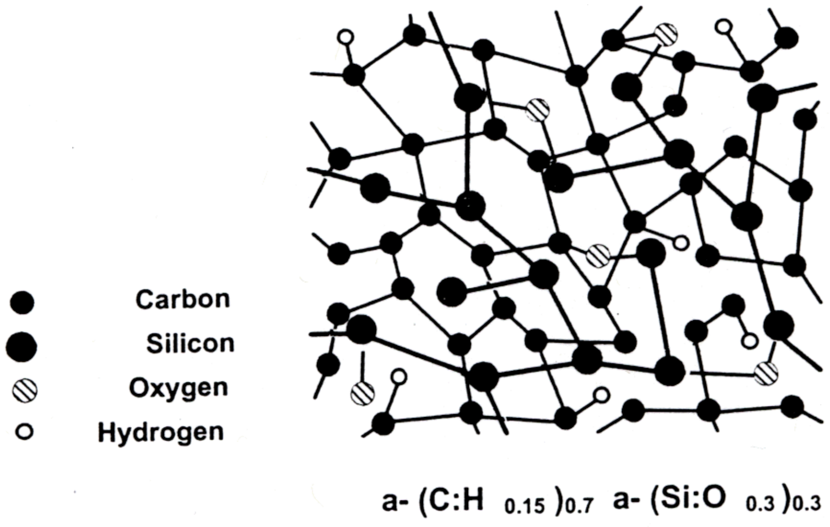
- DLCs exhibit the unusual combination of high hardness and elastic modulus in conjunction with low friction.
- This appears like an exception to the Bowden and Tabor Model which requires a low hardness for shear accommodation to achieve low friction.

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

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

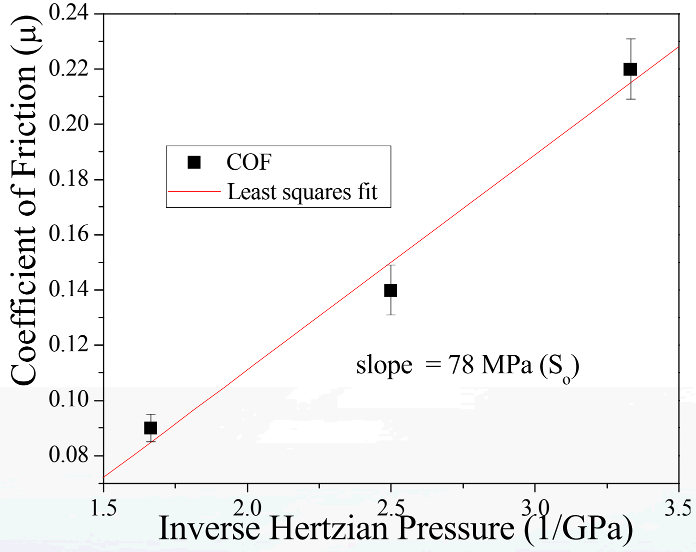
V. F. Dorfman, *Thin Solid Films*, 212 (1992) 267-273

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

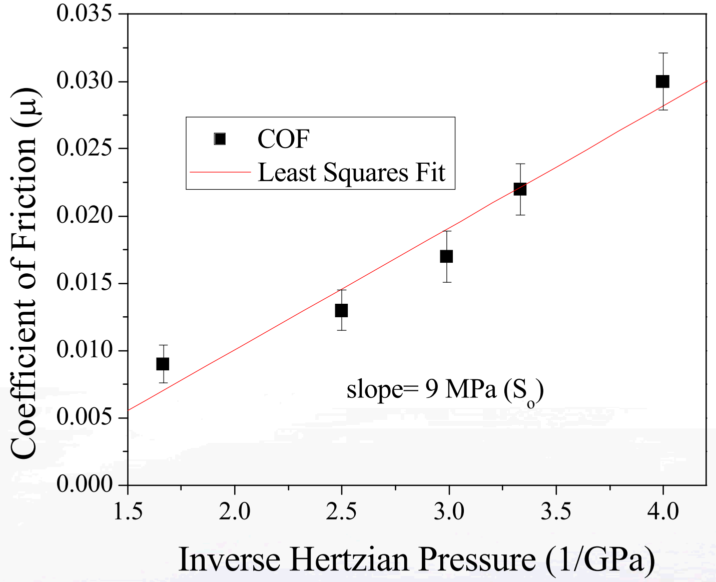
C. Venkatraman, C. Brodbeck and R. Lei, *Surface and Coatings Tech*. 115 (1999) 215-221.

The Friction Behavior is non-Amontonian

Air (50% RH)



Dry Nitrogen

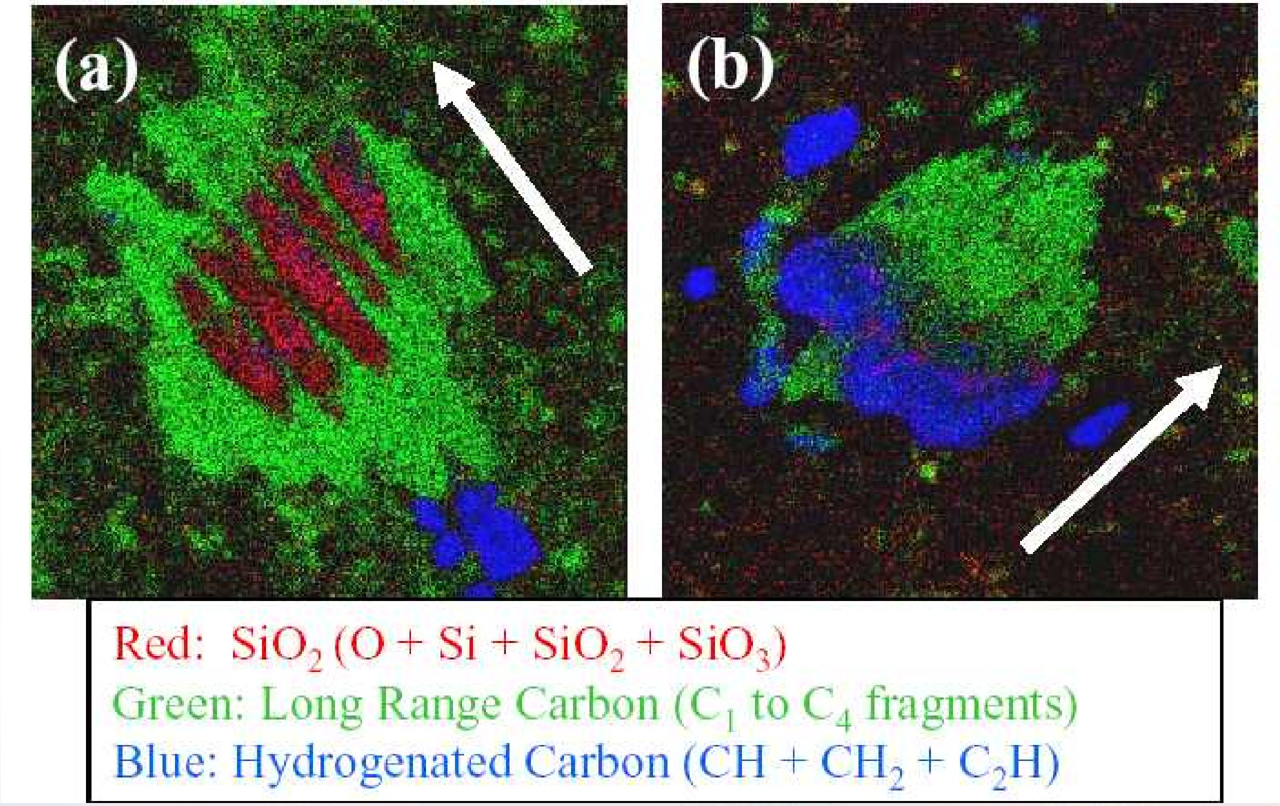


- Load Dependence
- Environmental Effects
- (Note the difference in the slopes)

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

ToF-SIMS of Transfer Films illustrating the Chameleon Nature

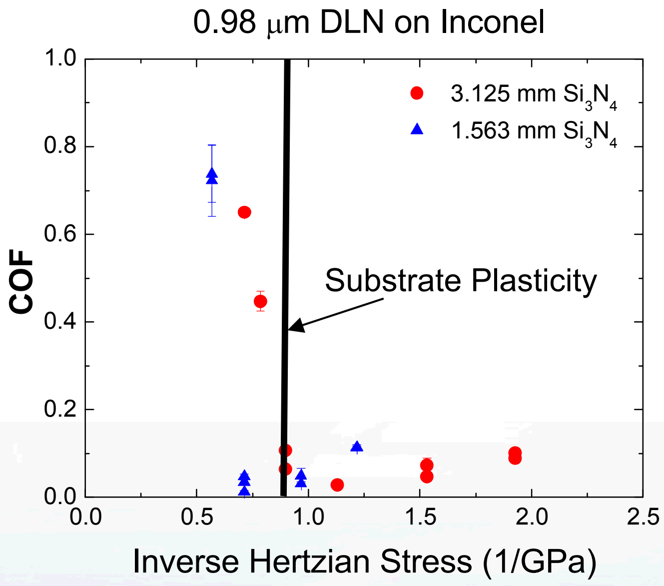
Humid Air (μ~.2) | Dry Nitrogen (μ~.02)

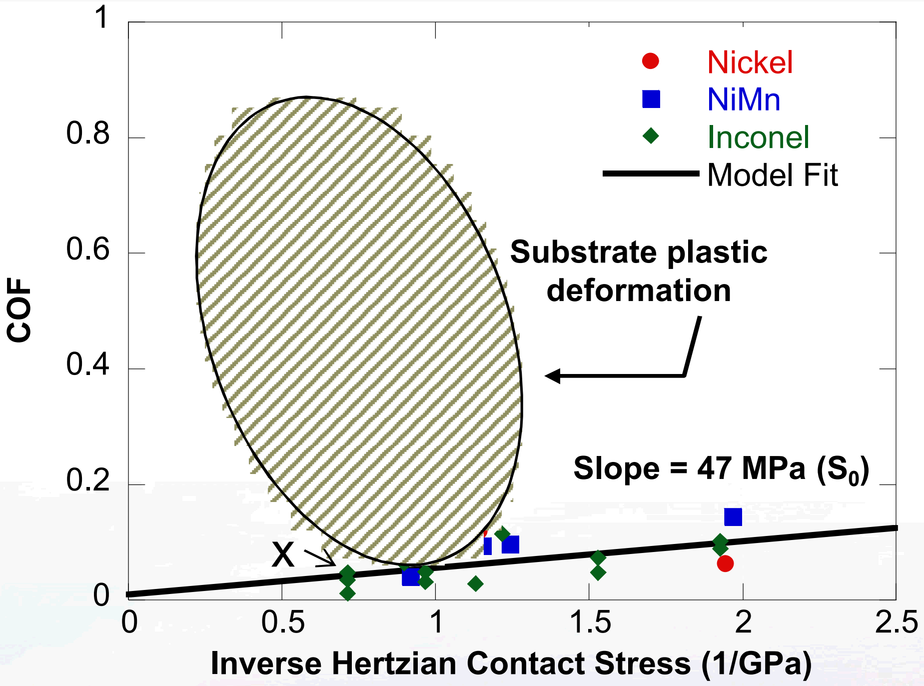


78 MPa | 9 MPa

ToF-SIMS

Deviations from Predicted Behavior



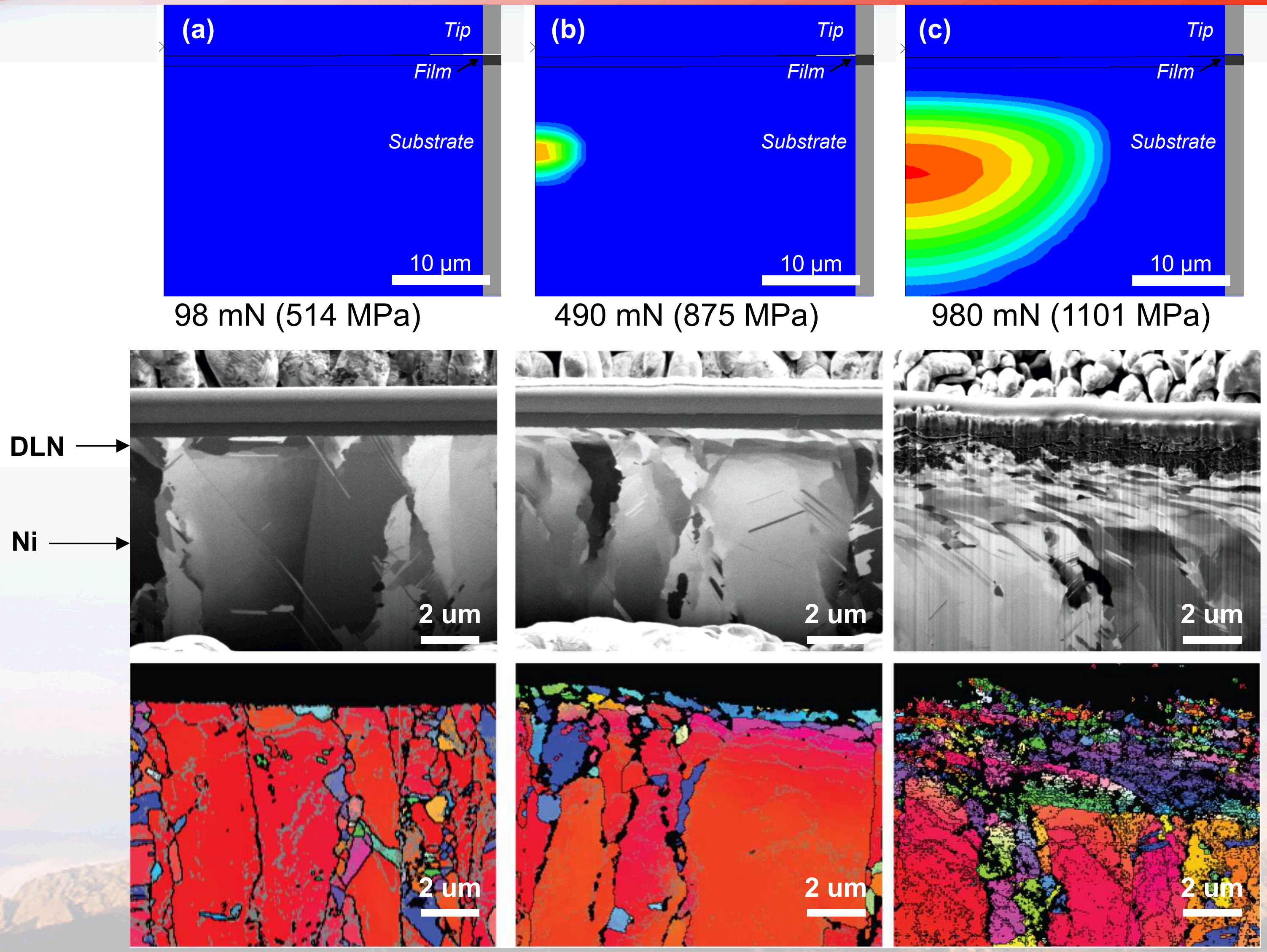


FEM predictions of substrate plastic deformation are in general agreement with observed deviations in Hertzian contact model

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

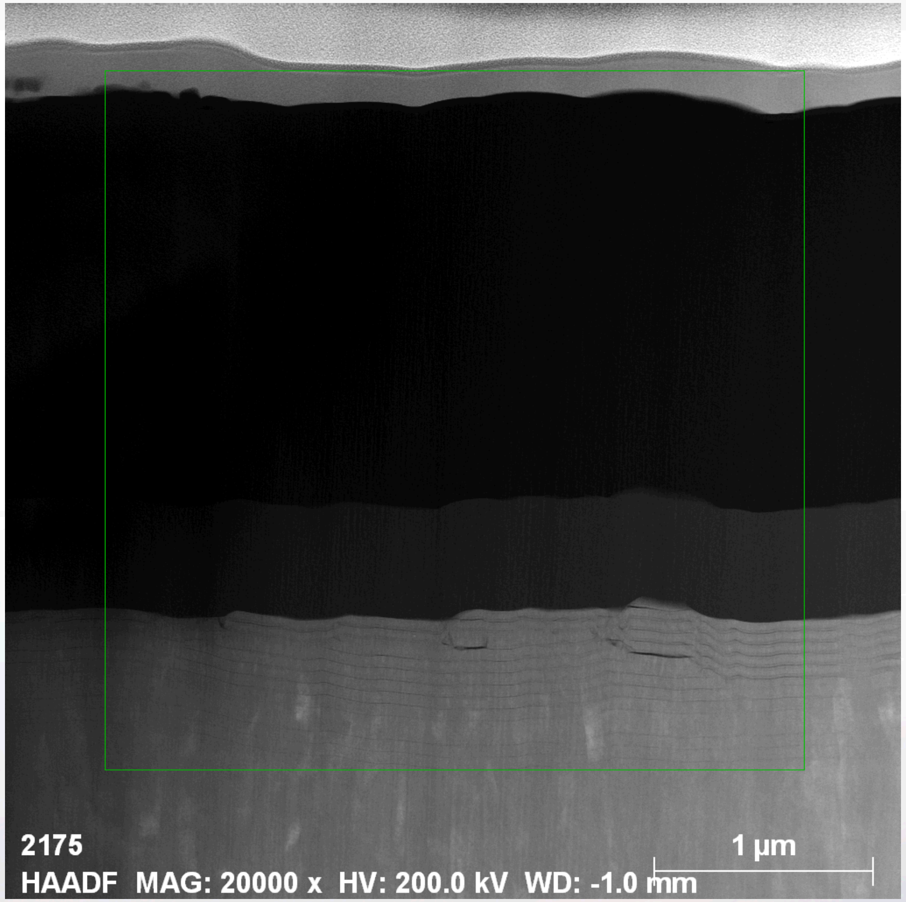
J.M. Jungk, J.R. Michael and S.V. Prasad, Acta Materialia, (2008) 56: 1956-1966.

Friction Induced Plastic Deformation in the Substrate

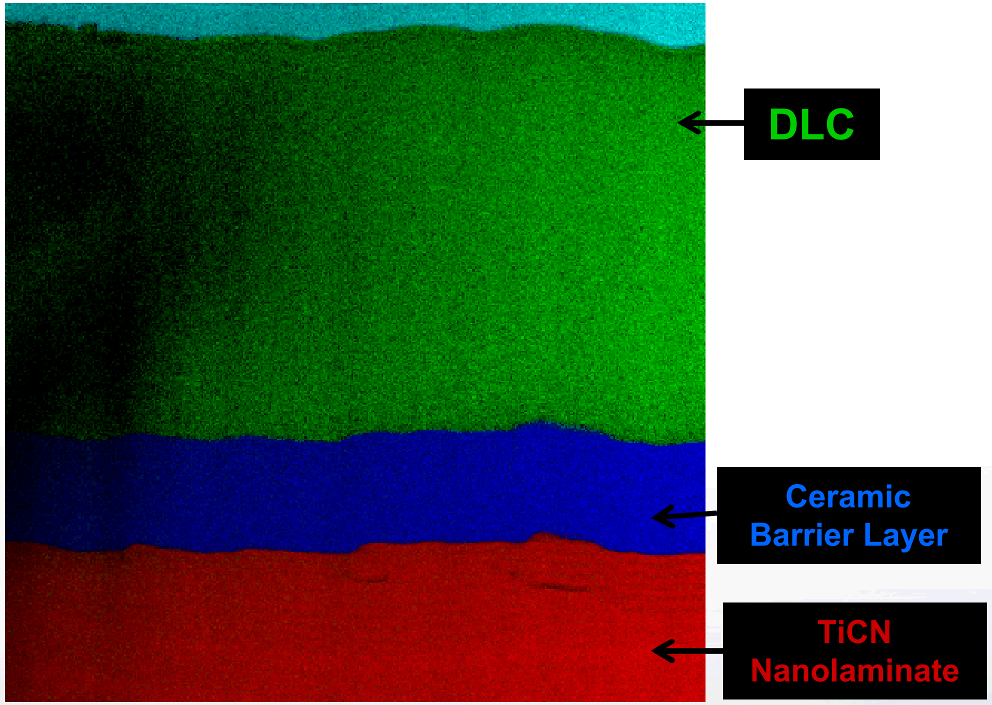


S.V. Prasad, J.R. Michael T. R. Christenson, Scripta Materialia, 48 (2003) 48

Multilayer Coatings: Adhesion, Load Bearing, Diffusion Barrier



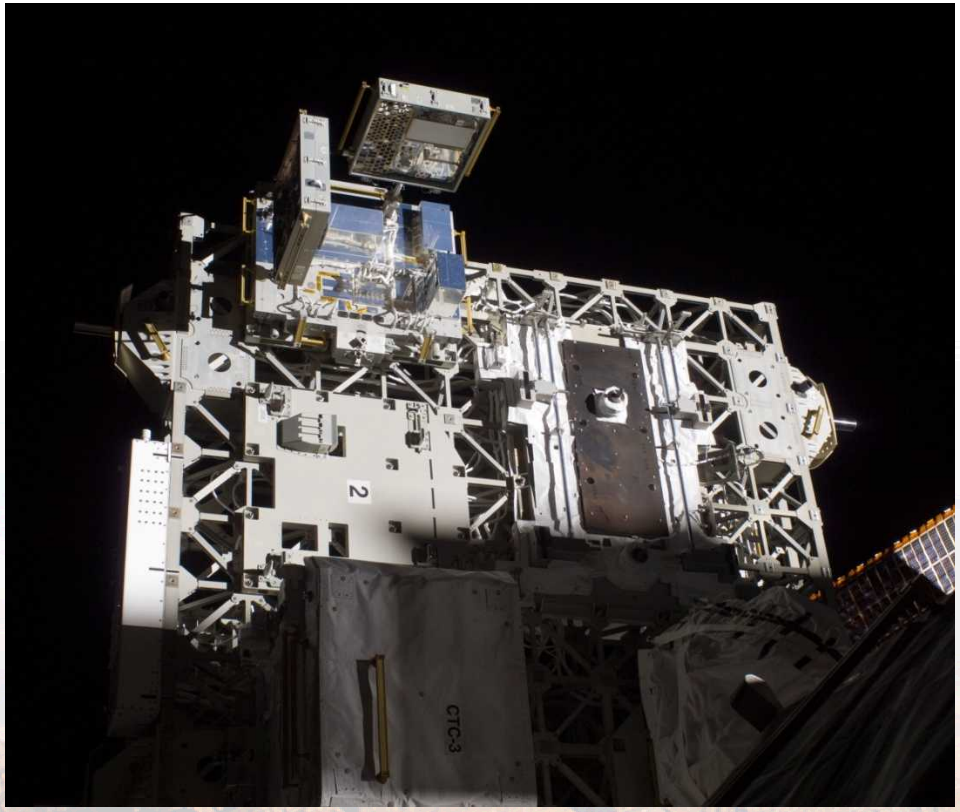
Micro-cracks between nanolaminate layers

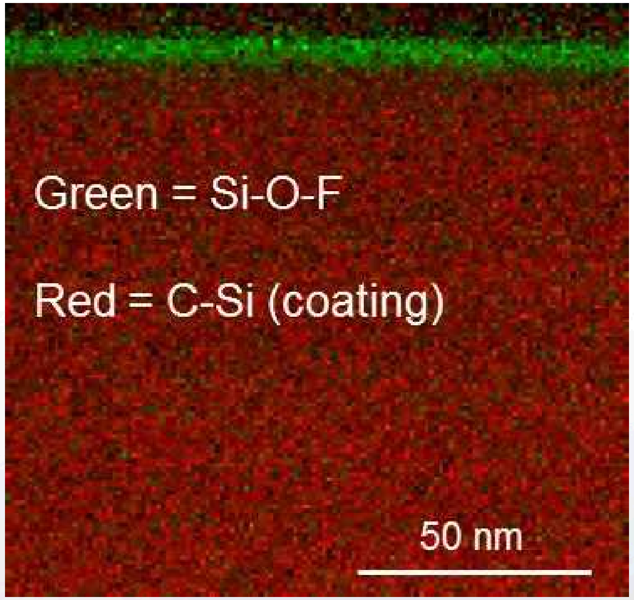


Robust Barrier

MISSE-7

Materials on the International Space Station Experiment





DLC post-MISSE (FIB)

Advanced analytical techniques are essential for assessing the materials aging and reliability

M. T. Dugger, T. W. Scharf and S. V. Prasad, “Materials in Space: Exploring the Effect of Low Earth Orbit on Thin Film Solid Lubricants” ADVANCED MATERIALS & PROCESSES 32 • MAY 2014

Concluding Thoughts

- Materials designed for friction and wear mitigation, commonly referred to as tribological materials, must also meet mechanical and physical property requirements. This balance makes it very challenging from a practical design perspective .
- Avoid using metals/alloys that are prone to galling (Rabinowicz's Compatibility Chart)
- 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
- The DLN and MoS_2-bsed composites are two examples of Nanostructured materials that provide some degree of environmentally robustness.
- Introduce multilayer coatings if subsurface plastic deformation cannot be avoided.
- Use systems approach for the design of tribological contacts.

Acknowledgements to Collaborators

- Ron Goeke (Thin Films)
- Paul Kotula (TEM)
- Joe Michael (EBSD)
- Mike Dugger (Tribology)
- Tony Ohlhausen (ToF-SIMS)
- John Jungk (FEM)
- Rand Garfield (Tribology Support)
- Michael Rye, Gary Bryant (FIB)
- Bonnie McKenzie (SEM)

- Tom Scharf (U of North Texas)
- Matthew Brake, Rice U
- 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)

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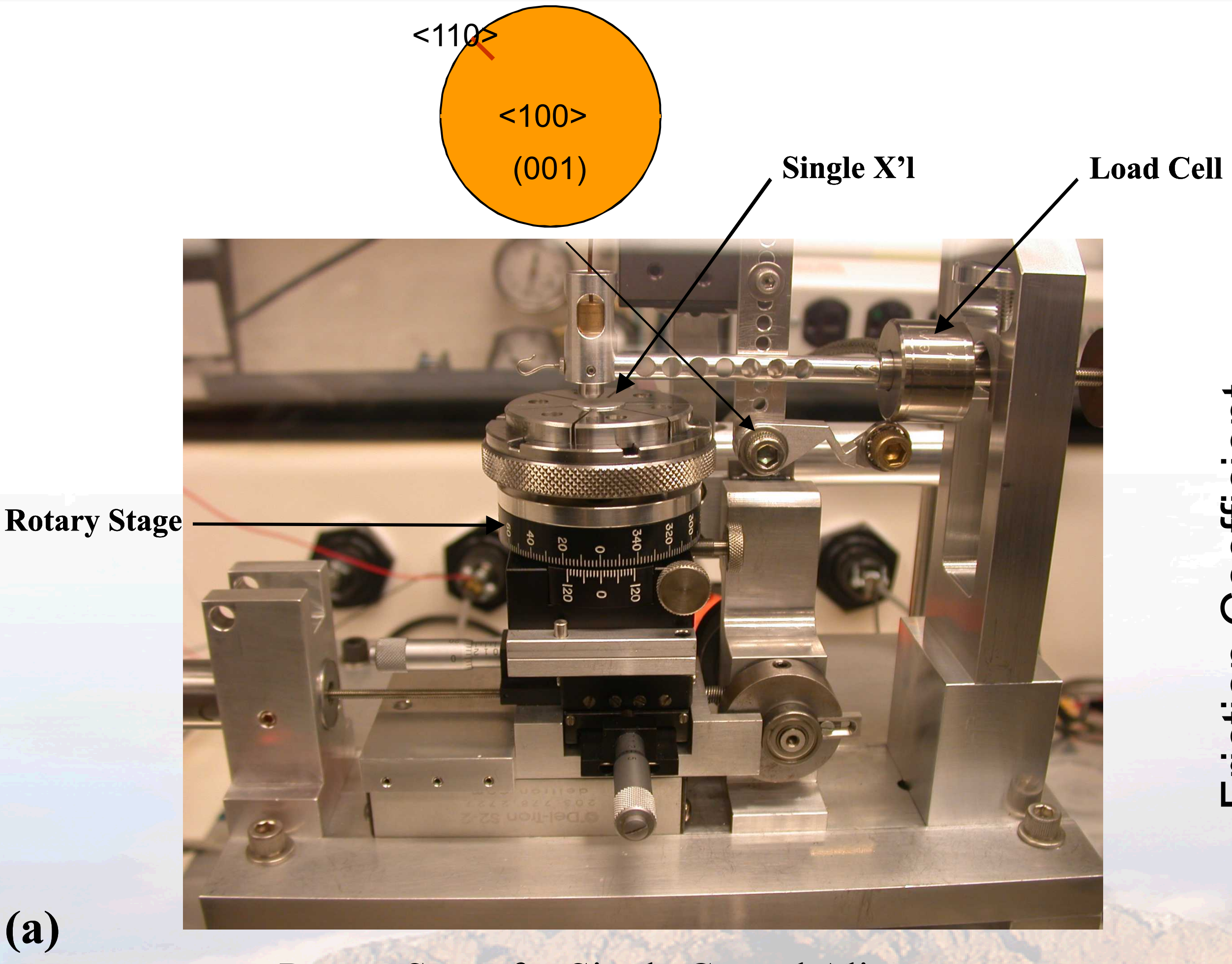
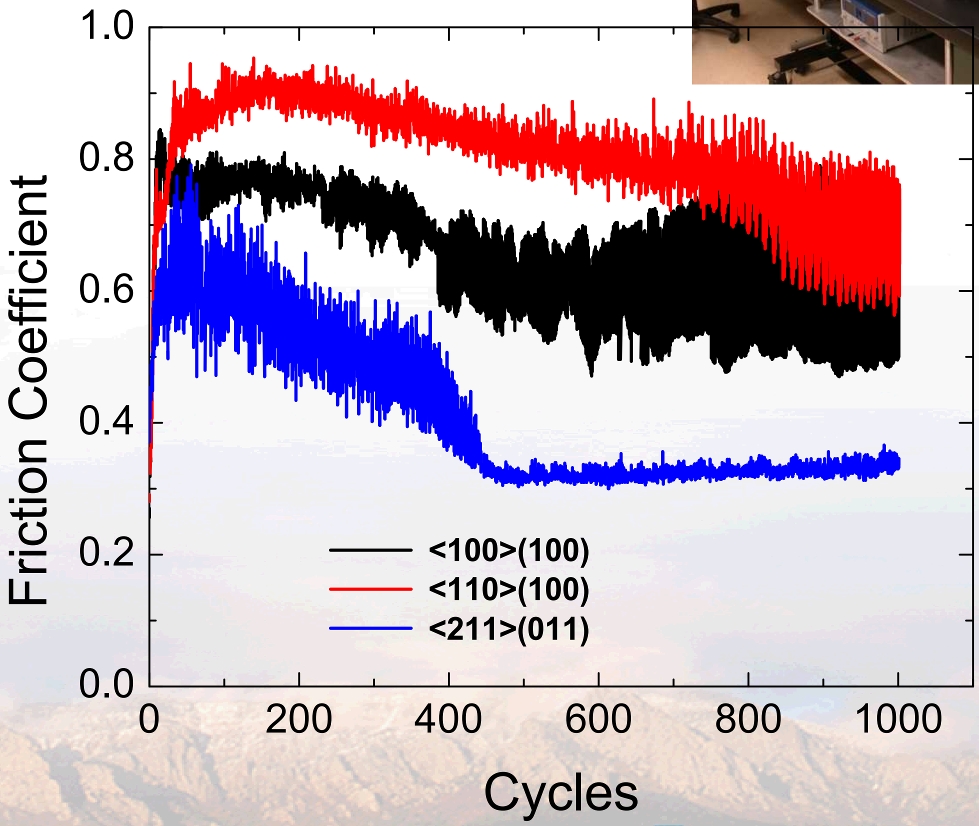
Back-Up Slides

Single Crystals

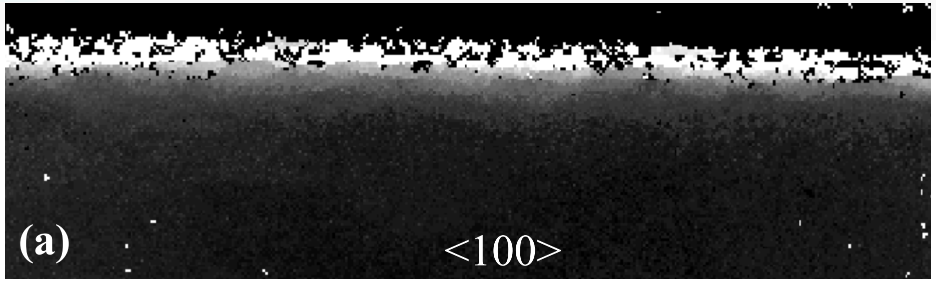
Measurements in specific crystallographic directions

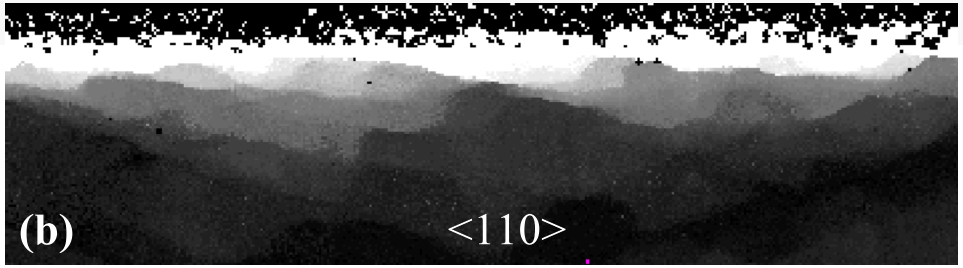


Rotary Stage for Single Crystal Alignment



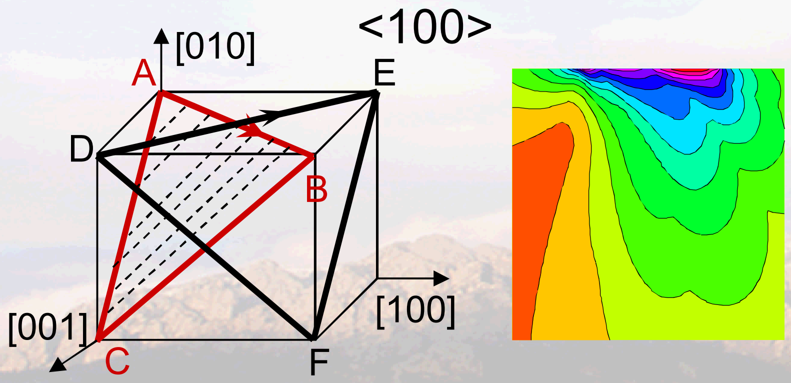
Depth of deformation is related to crystallography

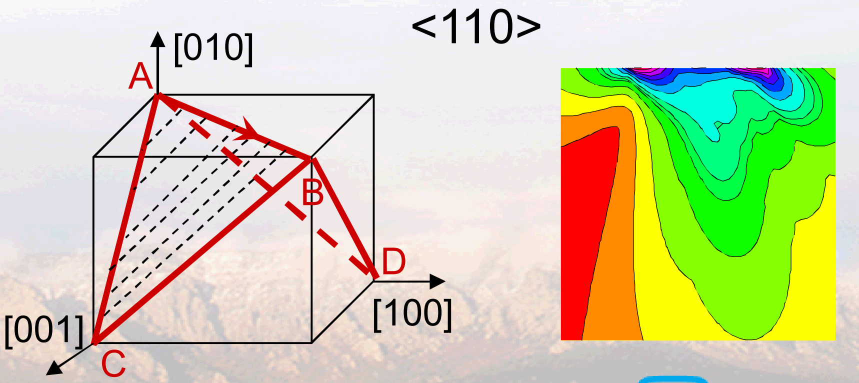




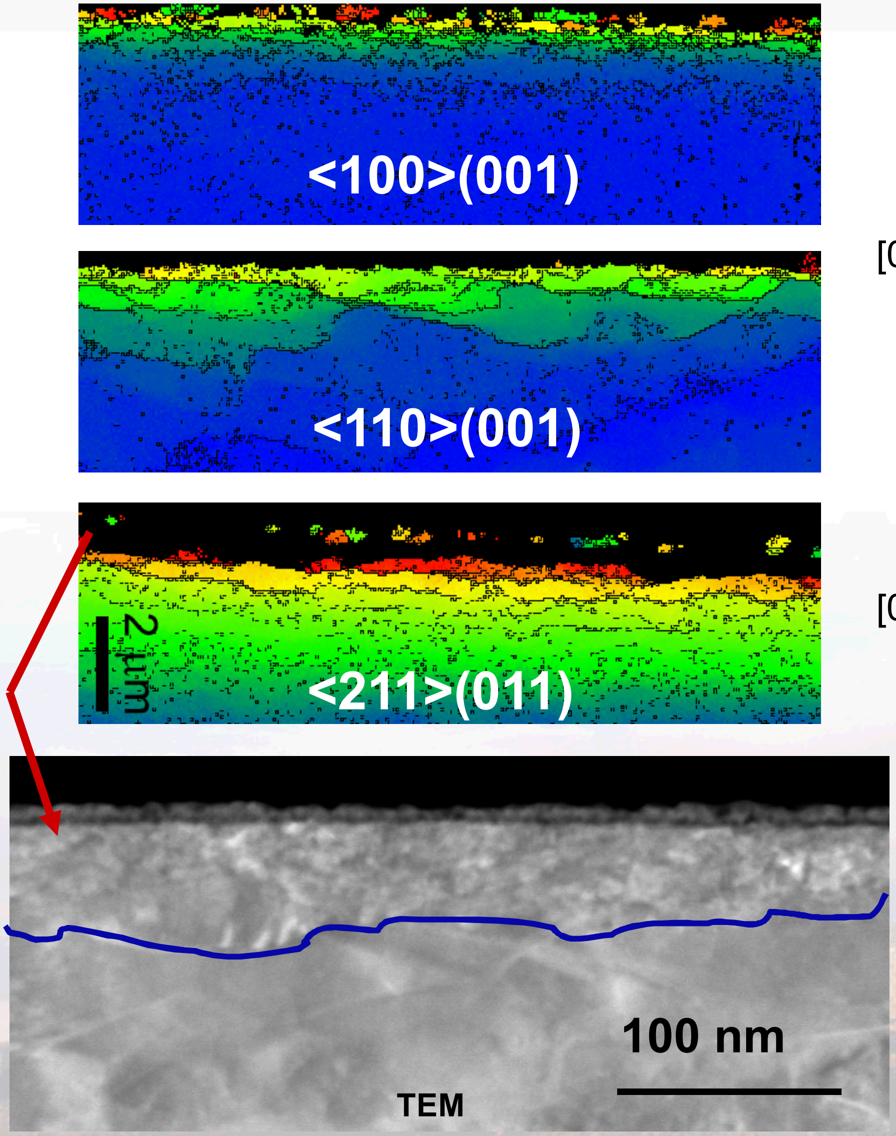
Maps showing the orientation changes relative to undeformed regions on (100) crystal surface. Brighter color represents larger orientation change. The magnitude of orientation change was about 6º total in for the friction track in the <100> direction and about 13 º for the track in <110> direction.

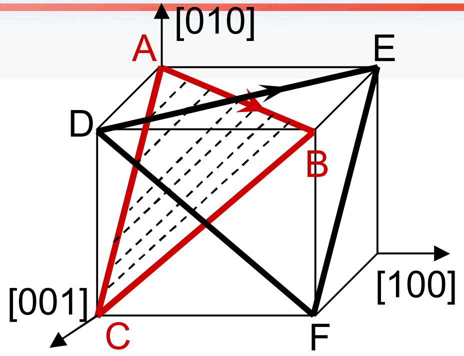
Slip system orientations show intersecting slip systems for <100> wear (ABC plane in AB direction, and DEF in DE), but not for <110> (ABC in AB and ABD in AB), suggesting more hardening for <100>. Color maps of resolved shear stress from analyses of plastic deformation show the strong asymmetry induced by sliding (as opposed to static) contact.



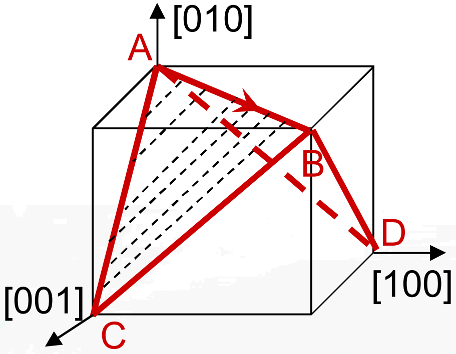


Depth of deformation is related to crystallography

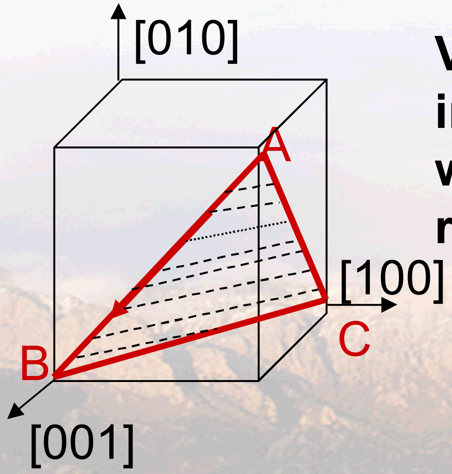




Strong dislocation interactions- high work hardening



Weak dislocation interactions- low work hardening



Very weak dislocation interactions- low work hardening – rapid recrystallization

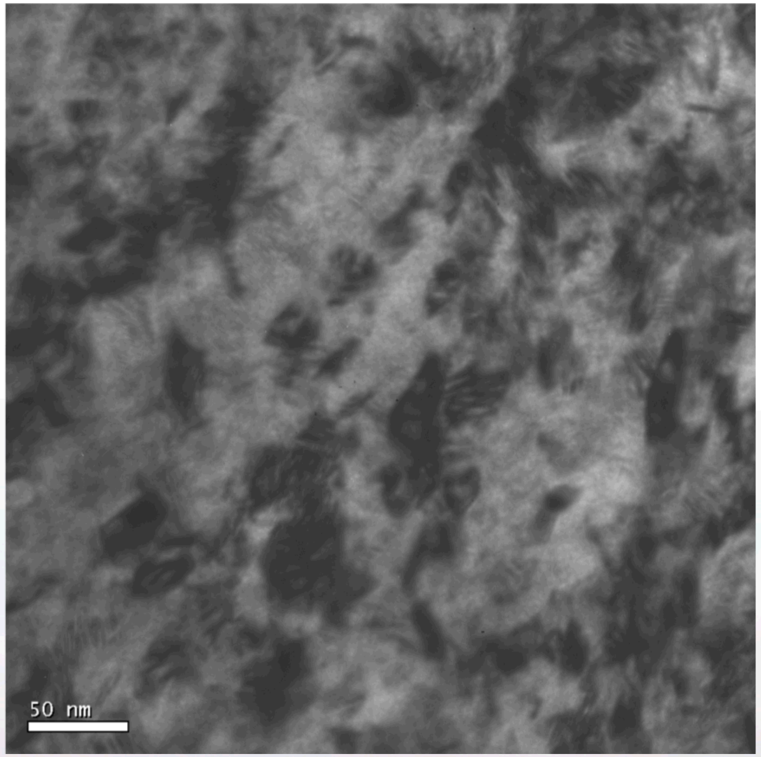
Nanocrystalline Metals

- Hall-Petch Effect
- In the ultrananocrystalline regime, grain boundary processes are known to dominate the deformation behavior, resulting in reduction of yield strength with grain size: ~20 nm or below.
- Is there such a “cross-over” with friction-induced deformation?

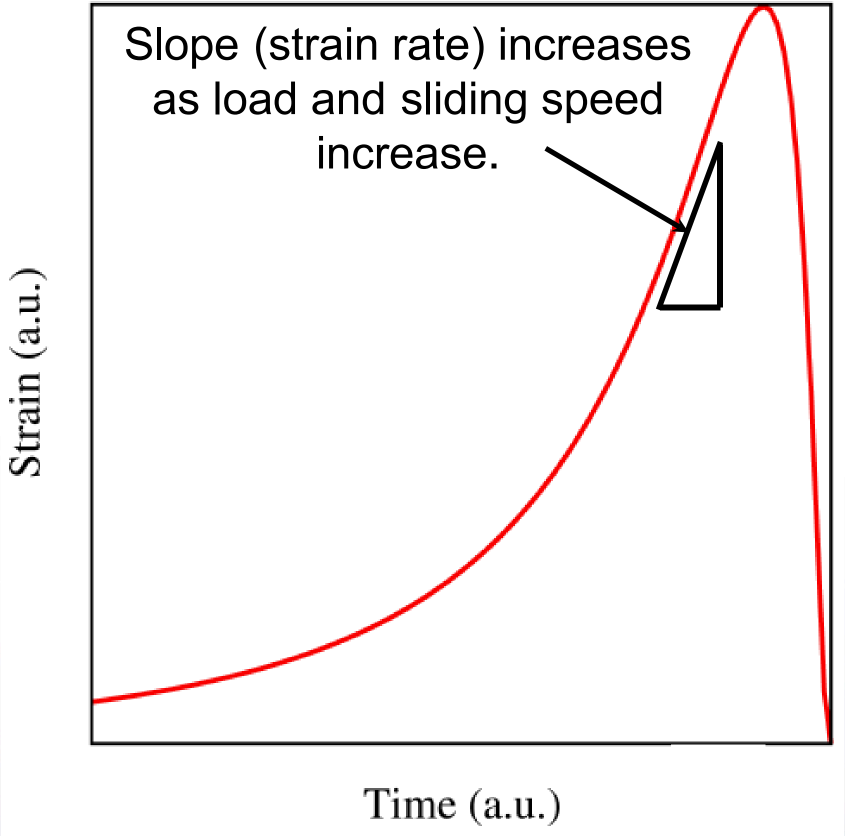
S. V. Prasad, C. C. Battaile and P. G. Kotula, *Scripta Materialia* **64** (2011) 729-732.
H A. Padilla, B. L. Boyce, C. C. Battaile and S. V. Prasad ,, *Wear* **297** (2013) 860-871
C. C. Battaile, B. L. Boyce, C. R. Weinberger, S. V. Prasad, J. R. Michael and B. G. Clarke, *Acta Materialia* **60** (2011) 1712-1720

Nanocrystalline Ni Films

Load and sliding speed dictate subsurface strain rate

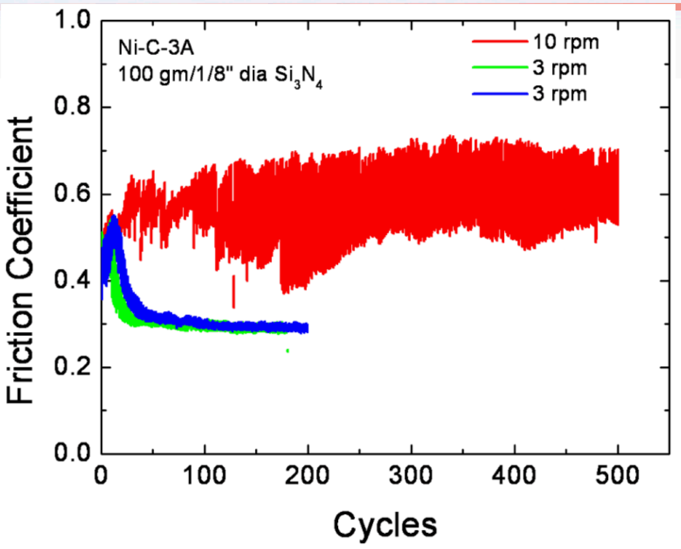


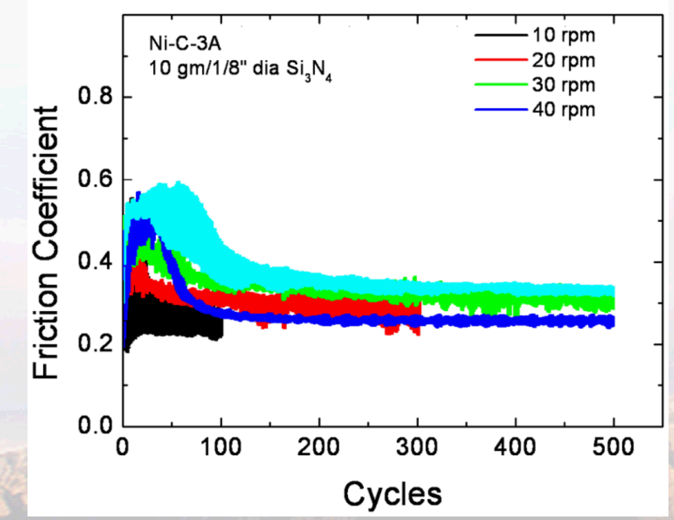
Bright-field TEM image



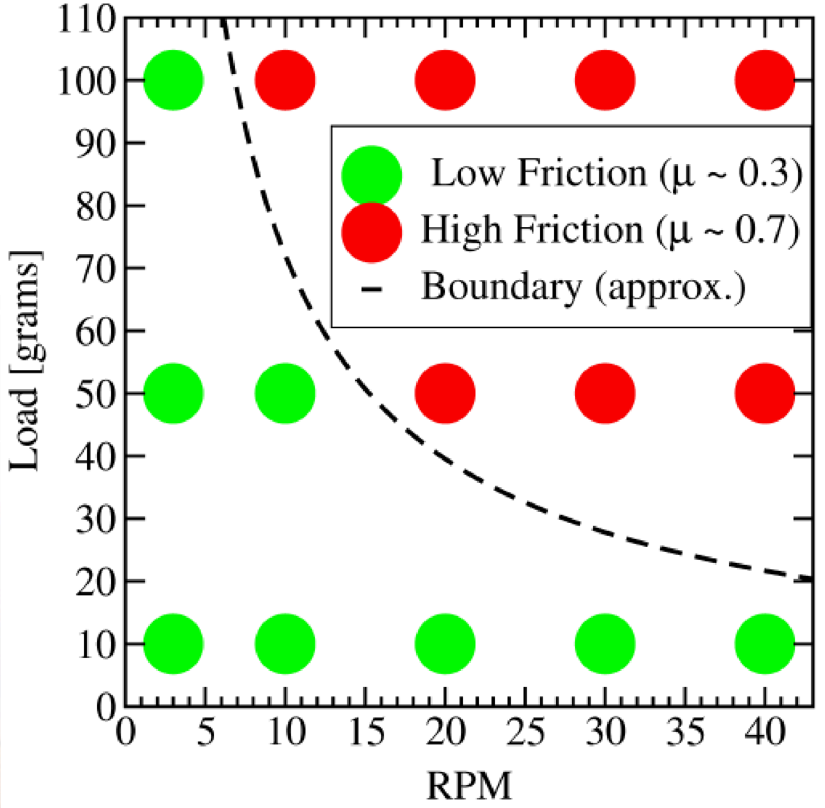
Schematic of the strain history experienced by the material below the worn surface.

Yes, there is: But it is Strain Rate sensitive





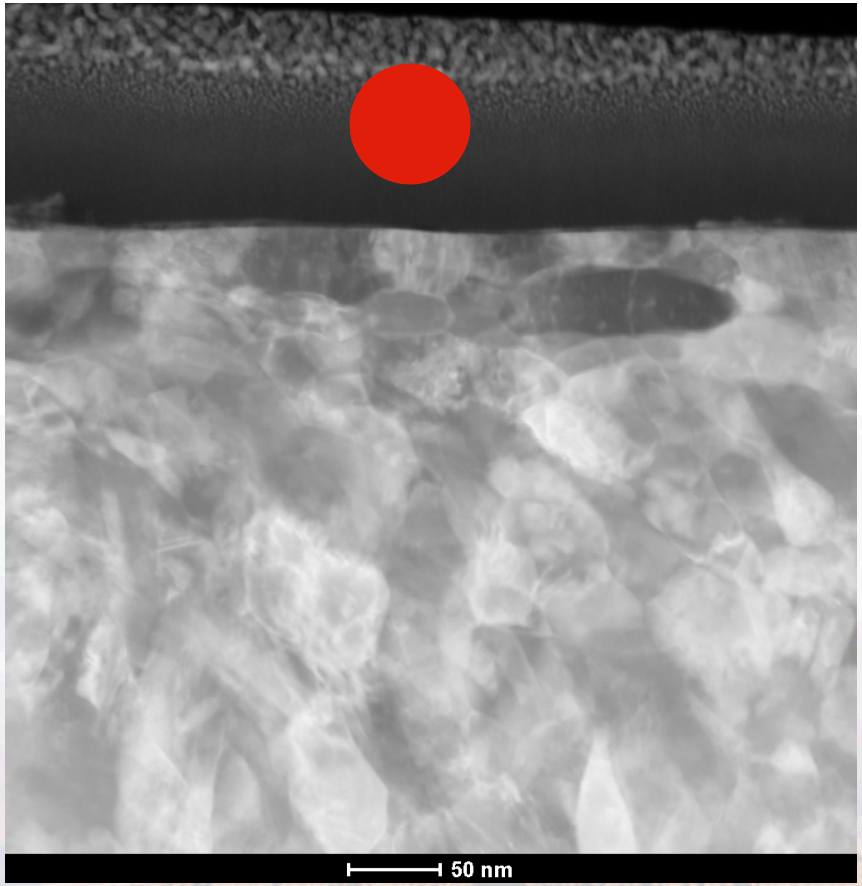
Transition to low friction shows a clear dependence on strain rate.



S. V. Prasad, C. C. Battaile and P. G. Kotula, *Scripta Materialia* **64** (2011) 729-732.

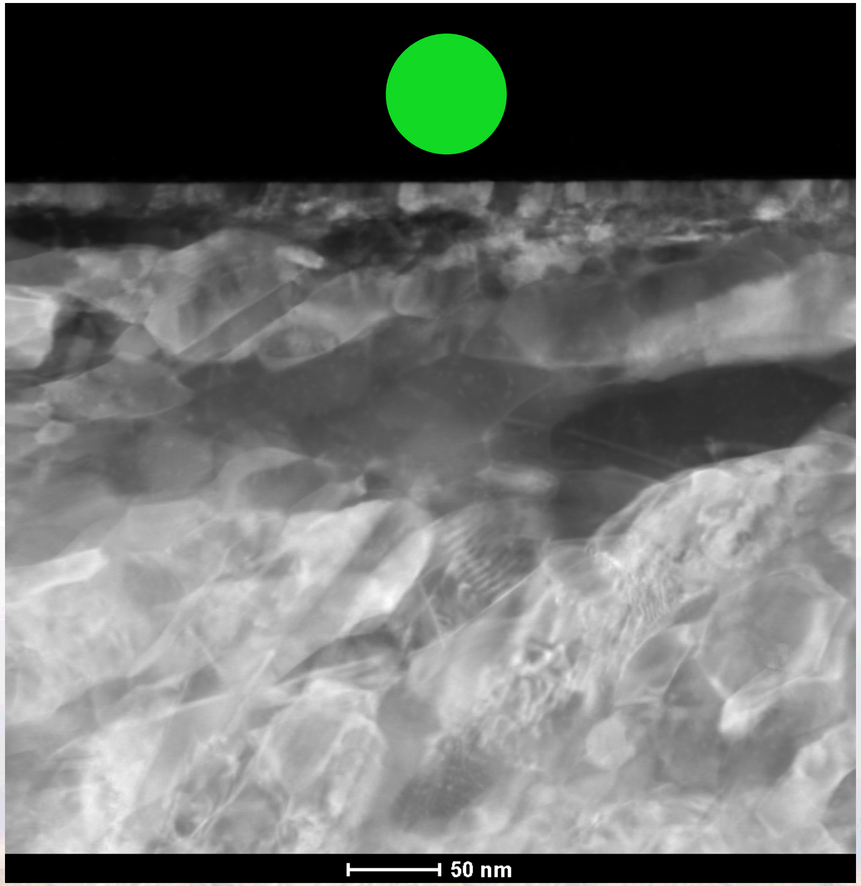
Comparison of Subsurfaces: High Friction (Red) and Low friction (Green)

Ni-C-3A #1 051201G Track 14, 100g, 20rpm, 600cycles



No Zone 1

Ni-C-3A #1 051129B Track 3, 100g, 3rpm, 200cycles



Zone 1 Present

Annular DF STEM Images

S. V. Prasad, C. C. Battaile and P. G. Kotula, *Scripta Materialia* **64** (2011) 729-732.

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Stable Ultrananocrystalline Layers

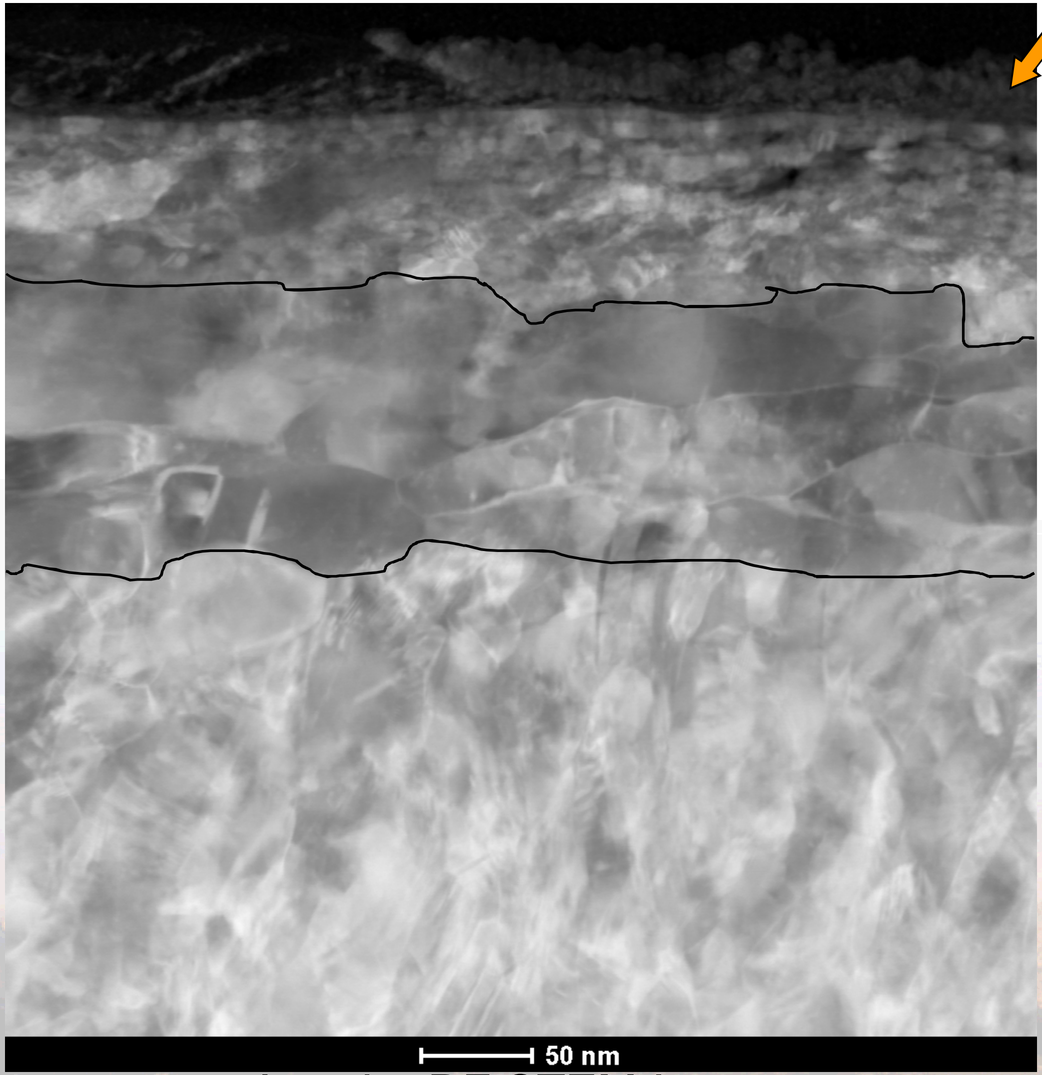
Zone 1
Ultra Nanocrystalline

Zone 2
Grain Growth (dynamic recrystallization?) + Texture

Zone 3
Bulk

Annular DF Image

Ni-3C-A1 #1 051202D Track 19, 10g, 20rpm, 600cycles



Zone 1+

Annular DF STEM Image

S. V. Prasad, C. C. Battaile and P. G. Kotula, *Scripta Materialia* **64** (2011) 729-732.

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