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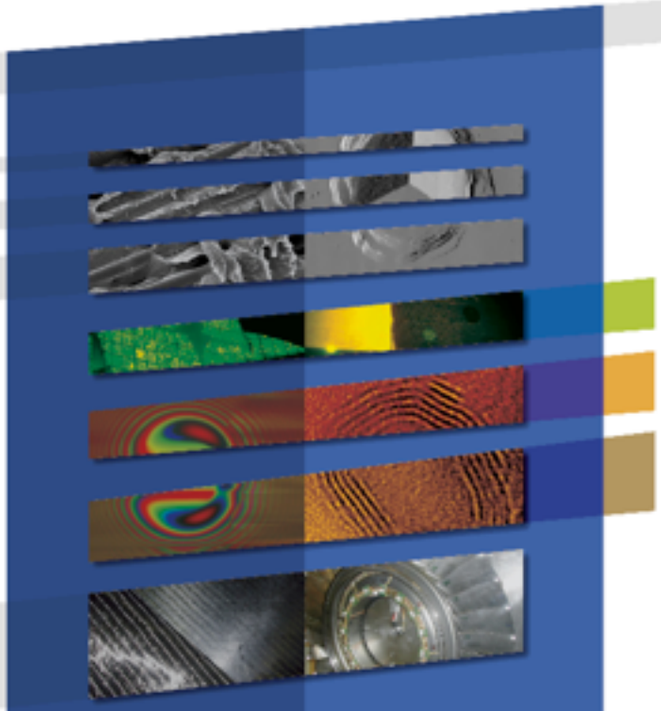
Laboratoire de Tribologie et Dynamique des Systèmes

2023 Summer School: Tribology and Surfaces Interactions
July 3rd-7th, 2023 – Visp, Switzerland



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LTDS UMR 5513
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Surfaces & Friction

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Introduction

- ***Tribology:***

  science of ***contact***, ***friction***, ***wear*** and ***lubrication***

  Probably the key of most ancient techniques
  (stone tools, fire, wheel…)
  yet a very recent science: « Tribology » invented in 1956…

- Solids are contacting through their ***surfaces***, forming a ***sliding interface***

- The surfaces' interactions are thus controlling/affecting the ***friction*** (and wear) between solids

Summary

- **Dealing with surfaces…**
  - What is a « surface »? How to describe it?
  - What are the key properties of a surface?
  - How to characterise a surface?

- **Influence of surfaces on friction**
  - What is « Friction »?
  - How can friction be affected by surfaces?
  - How to study surface-related friction phenomena?

- **Case-study**
  - Solid lubrication processes of Diamond-Like Carbon

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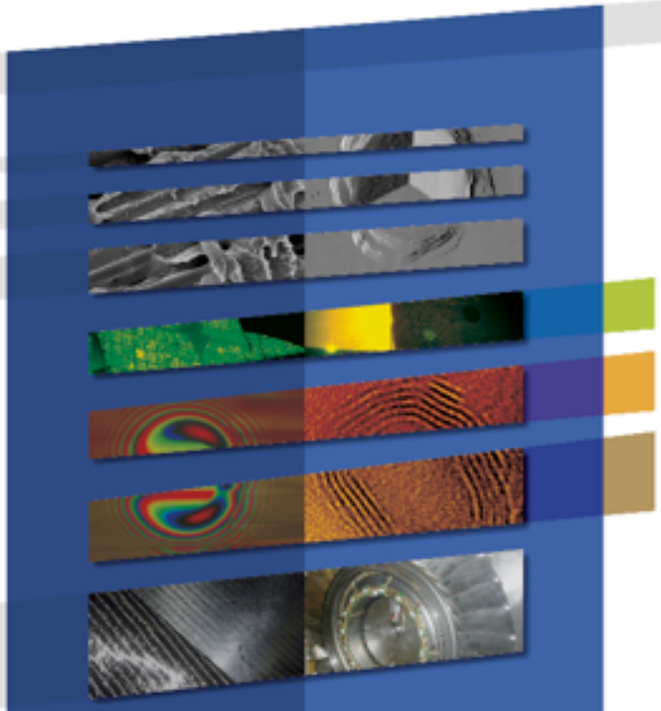

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Surfaces & Friction

Dealing with surfaces…

Part 1

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What is a surface?

« God created solids, but the devil made their surfaces »

(Gott schuf das Volumen, der Teufel die Oberfläche)

Wolfgang Pauli

Interface between two phases
(or between a phase and vacuum)

- Surface = discontinuity of matter!

- Describing the solid before considering its surface!
  - How atoms stay together: chemical bonds
  - Strongly dependent on the material considered:
    metal, ceramic, polymer…
  - Key-role of the structure of matter at larger scales (nm → µm)

Cohesion of solids

Cohesion of solid: interactions between atoms or molecules

"Strong" interactions inside molecules or solids,
"Weak" interactions between molecules or solids

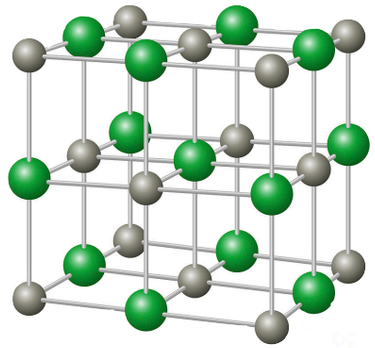
- **Chemical bonds:** electron charge distributions of the atoms (atomic orbitals) is completely changed
- **Physical "bonds":** atoms/molecules remain distinct entities
- Yet physical binding may be quite strong as well…

Cohesion of solids: chemical bonds

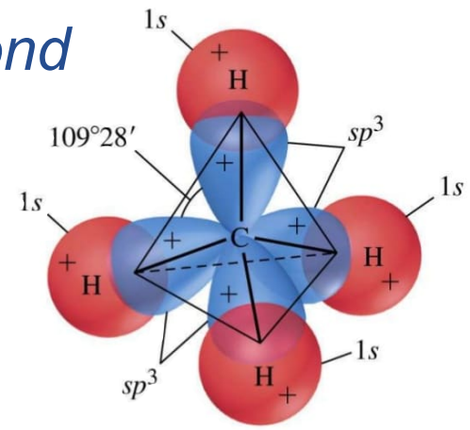
- **Strong chemical bonds:** atomic interactions through electrons (change in shape and occupation of atomic orbitals)

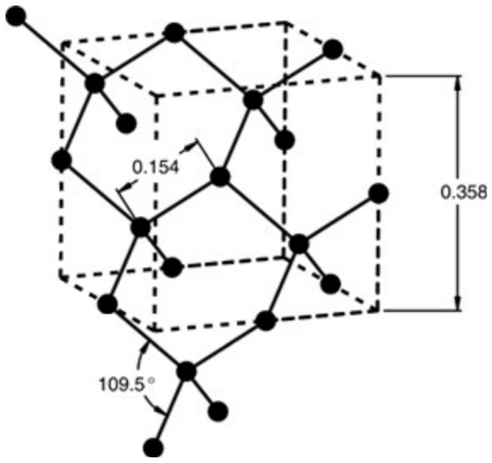
  - **Ionic bond:** exchange of electrons between two atoms
    Example: Sodium Chloride (salt!)

$$Na + Cl \rightarrow Na^{+} + Cl^{-} \rightarrow NaCl$$



  - **Covalent bond:** sharing of electrons between two atoms
    Example: Methane CH_4 or Diamond





  - **Metallic bonding:** bonding electrons are delocalised over a lattice of atoms, creating a « gas of electrons »
    The behaviour of this gas and its interactions with the lattice controls the metal properties

Cohesion of solids: intermolecular forces

- **Intermolecular bonding:** involves electrostatic interactions between atoms and/or molecules
  - **Involving charged atoms/molecules:** Charge-charge interactions (*Coulomb forces*) or charge-dipole interactions
  - **Involving polar molecules:** Dipole-dipole, dipole-charge or dipole-induced dipole interactions (*Van der Waals forces*)
    - Polar molecules: distribution of charges within the molecule
    - Dipoles may be inherent to the structure of a molecule, or may be induced by the surrounding environment
- Depending on the type of interactions involved, **different strengths and ranges** will be observed…

The key-role of defects

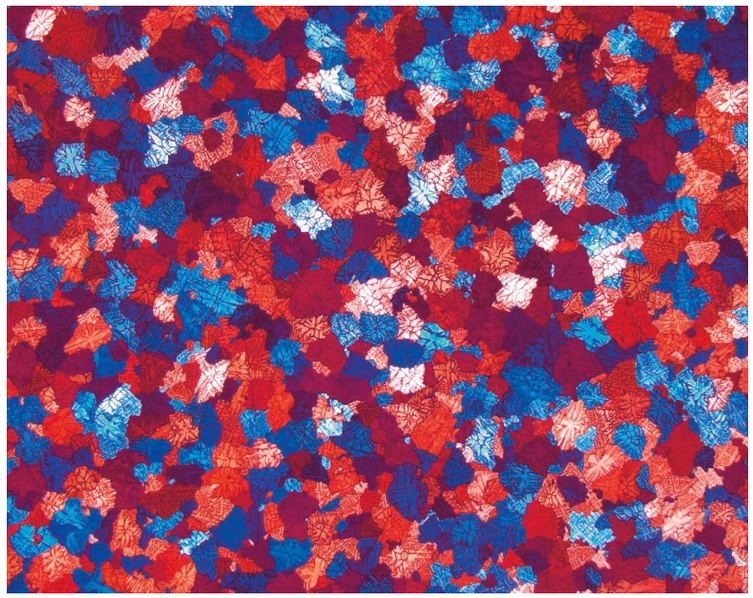
- Solids are the result of a fabrication process - **they can't be perfect!**

- Several types of defects can be found in crystalline materials:
  - Point defects (0D): vacancies or impurities (solid solutions)
  - Line defects (1D): dislocations
  - Planar defects (2D): grain boundaries
  - Bulk defects (3D): voids or precipitates

- All these defects may affect the properties of the solid, especially hardness (while elastic modulus is controlled by interatomic or intermolecular forces)

The key-role of microstructure

- Many engineering materials are alloys
- They consist in an assembly of grains, with different orientations, that might be of different phases
- The nature, size and distribution of these phases control the mechanical behaviour of the material: hardness, toughness…

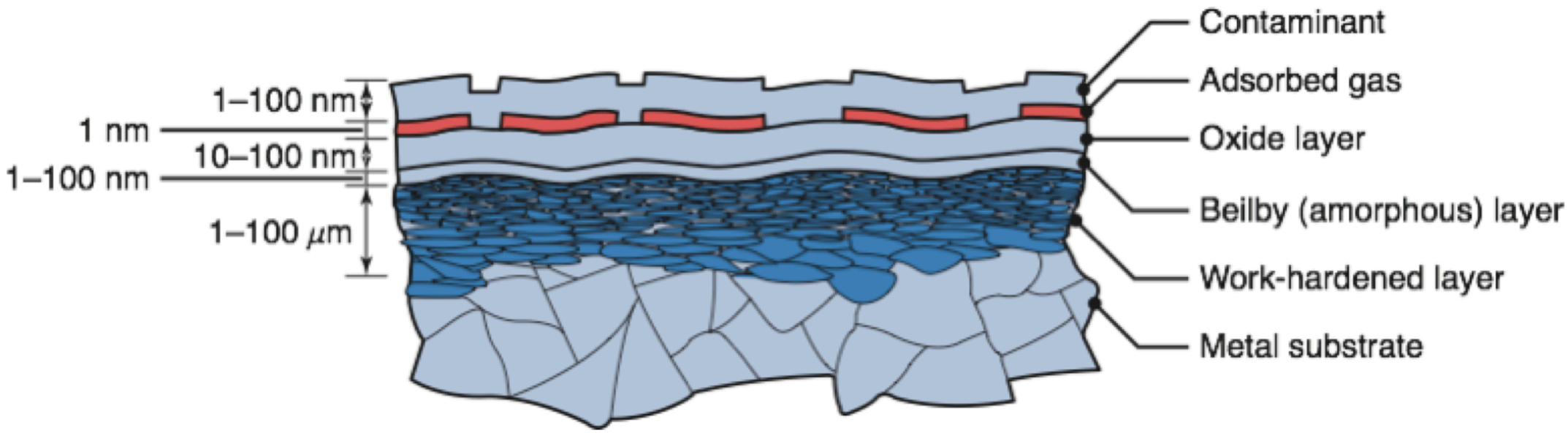


- Study of microsctrure:
  - Diffraction (XRD) for cristallography
  - Microscopy on cross-section (optical or electron: SEM), EBSD
  - X-Ray or TEM tomography

Describing a solid surface

- Machining process or fabrication process lead to gradients in the microstructure: *e.g.* change in grain size close to the surface…

- Since the surface is an interface with the environment, chemical reactions may occur at the surface: oxide layers, adventitious carbon…

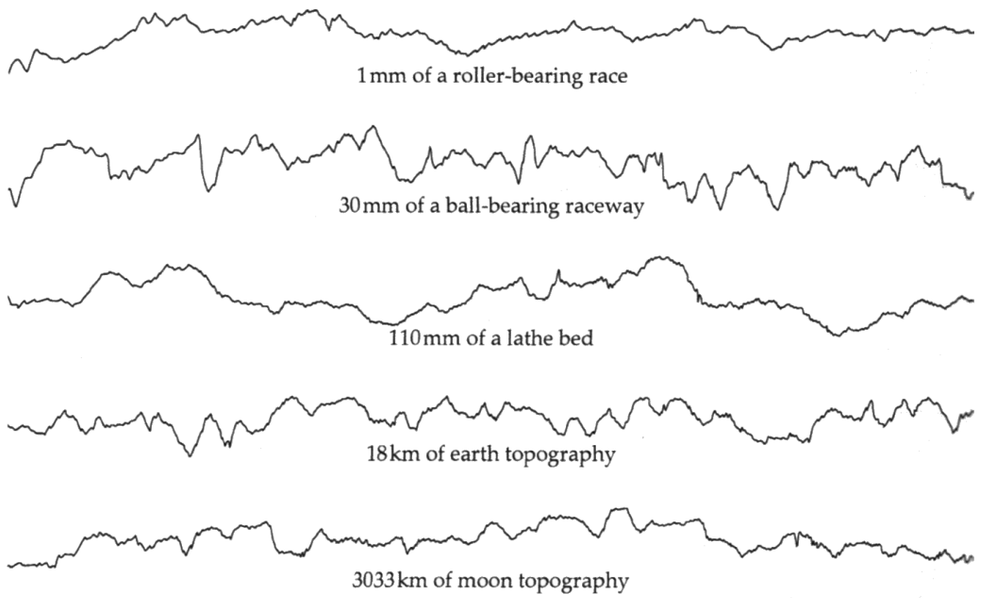


- Even for monocrystalline solids, the edges of a periodic lattice are not favorable: promote “surface reconstruction”

→ always some roughness!

Investigating surface topography

- Surfaces always exhibit some roughness…
- Critical role of the considered scale:



- The probe size is thus critical – Many techniques available!
  - Tactile profilometry: from simple stylus to Atomic Force Microscopy (AFM)
  - Laser beam profilometry
  - Optical methods: interferometric microscopy, confocal microscopy…

- Don’t forget to look at surface morphology!
  (e.g. optical or electron microscopy)

Investigating surface topography

- Parameters describing the surface:
  - Height characteristics
    - Arithmetical mean height

$$R_a = \frac{1}{L}\int_0^L |z| \, \mathrm{d}x$$

    - Root mean square roughness

$$R_q = \sqrt{\frac{1}{L}\int_0^L z^2 \, \mathrm{d}x}$$

    - Maximum peak to valley, skewness (asymmetry), kurtosis…
  - Spatial characteristics
    - Autocorrelation function, Power spectral density function…
  - Multiscale characterisation
    - Fourier transformation, wavelet transformation…

Investigating surface chemistry

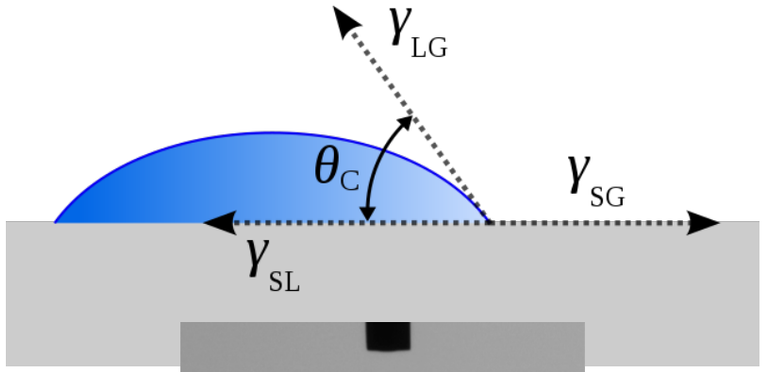
- Knowing the composition and/or chemistry of a surface is critical for understanding its properties

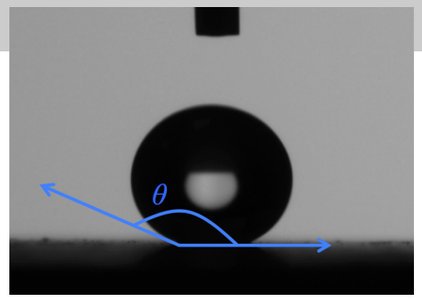
- Many surface characterisation techniques are available:
  - SEM coupled with EDX (Energy Dispersive X-ray spectroscopy)
  - Vibrational spectroscopies: Raman, FTIR…
  - Glow Discharge Optical Emission Spectroscopy (GDOES)
  - Secondary Ion Mass Spectrocopy (SIMS), static (ToF-SIMS) or dynamic
  - X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectrocopy (AES)
  - Electron Energy Loss Spectroscopy (EELS) in transmission or reflection

Surface energy

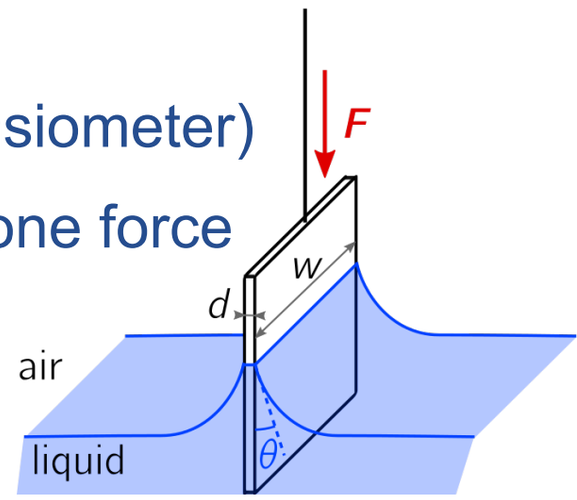
- Surface energy corresponds to the **disruption of interatomic or intermolecular bonds** due to the surface creation
- Equivalence between surface energy (J/m²) and surface tension (N/m):
  Increasing the size of a surface corresponds to the work of a force

- ***Measuring surface energy:***
  - **Contact angle measurements**
    - Liquid droplet on a surface
    - Young's equation: $\cos\theta_c = \dfrac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$
    - Work of adhesion: $W_{adh} = \gamma_{LG}\left(1 + \cos\theta_c\right)$





  - **Surface tension measurements** (Wilhelmy plate tensiometer)
    - Immersion of a plate with measurement of undergone force
    - $\gamma = \dfrac{F}{l\cos\theta}$, where l is the perimeter



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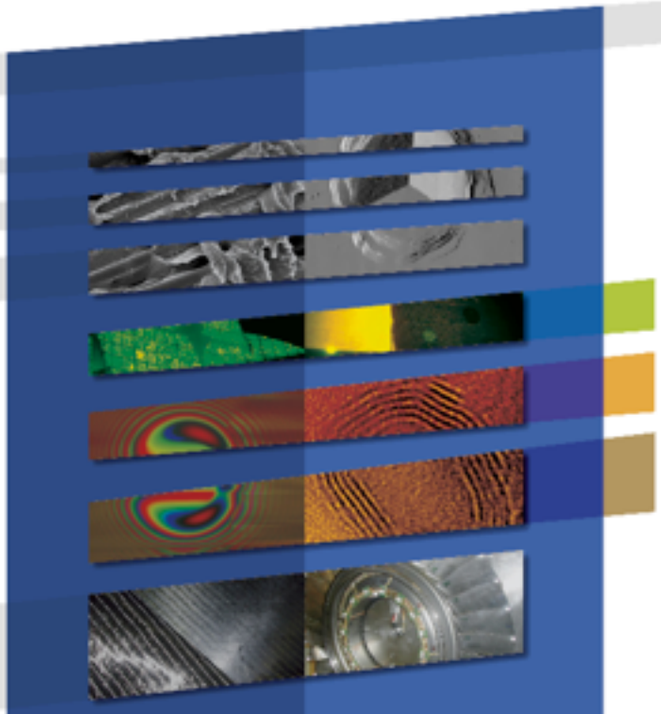

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Surfaces & Friction

Influence of surfaces on friction

Part 2

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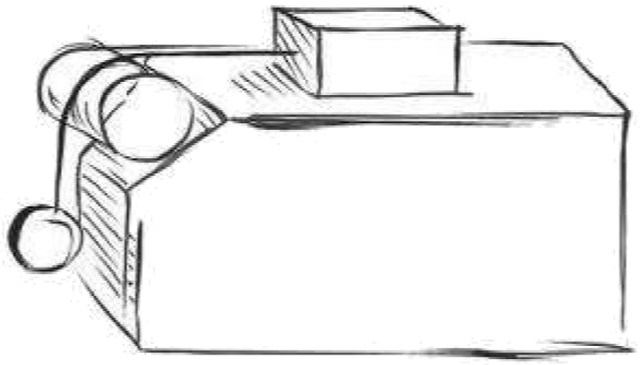
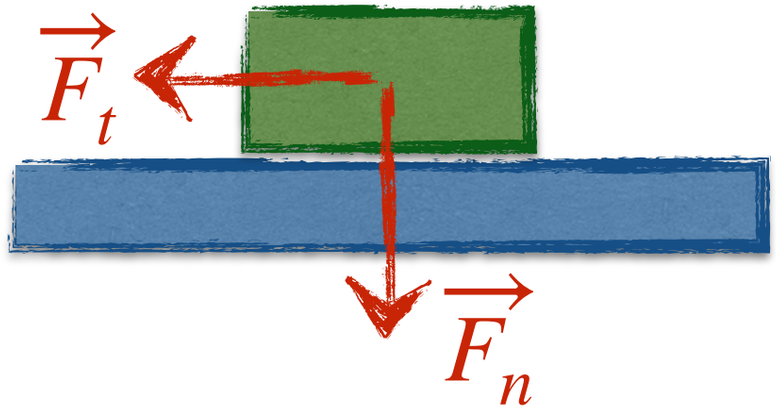
Defining friction…

Friction: the force resisting to relative motion between solids





- **Early laws of dry friction** - Da Vinci, Amonton, Coulomb
  - *Friction force is proportional to load*
  - *Friction force is independent of contact area*
  - *Friction force is independent of sliding velocity*

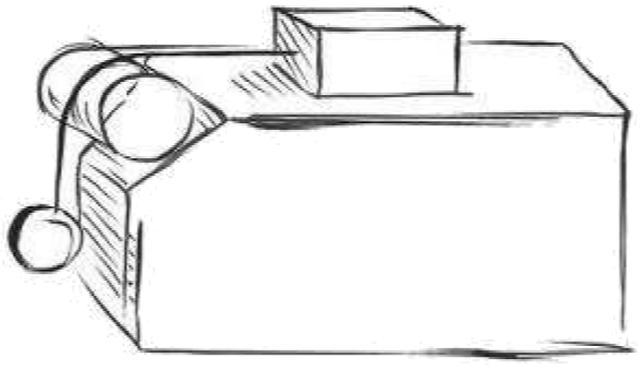
- Definition of the **coefficient of friction** μ

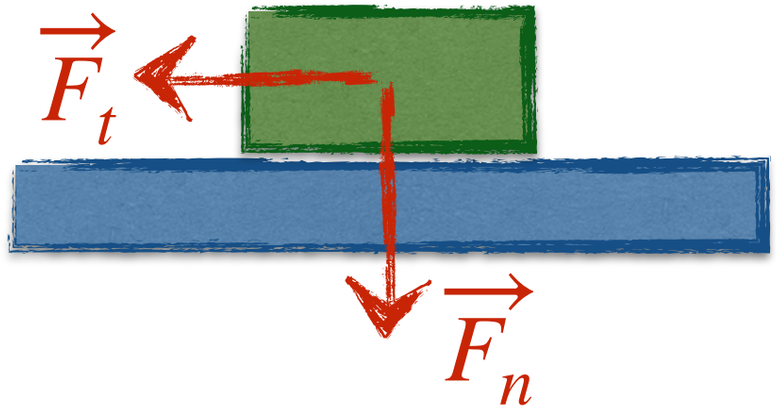
  Ratio of the tangential force to the normal force:

$$\mu = \frac{F_t}{F_n}$$

Defining friction…

Friction: the force resisting to relative motion between solids





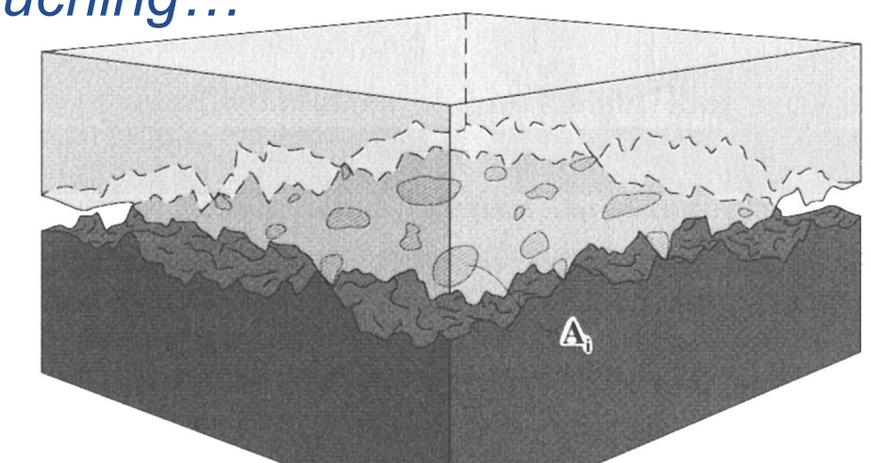
- **Early laws of dry friction** - Da Vinci, Amonton, Coulomb
  - *Friction force is proportional to load*
  - *Friction force is independent of contact area*
  - *Friction force is independent of sliding velocity*

- No effect of **apparent contact area**!

  Due to roughness, only asperities are touching…

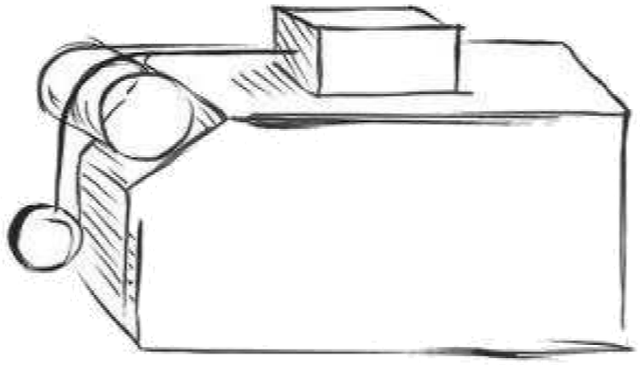
  Real vs. apparent contact area

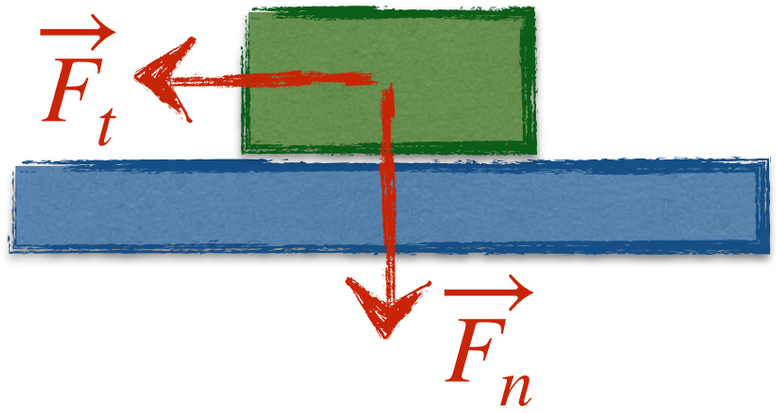
$$A_r \neq A_{app}$$



Defining friction…

Friction: the force resisting to relative motion between solids





- **Early laws of dry friction** - Da Vinci, Amonton, Coulomb
  - *Friction force is proportional to load*
  - *Friction force is independent of contact area*
  - *Friction force is independent of sliding velocity*

- No velocity effect proposed, but:

  Static friction ⩾ Sliding friction (or “kinetic” or “dynamic”)

  Static friction: maximum friction force before sliding occurs

The challenge of lubrication: Velocity accommodation

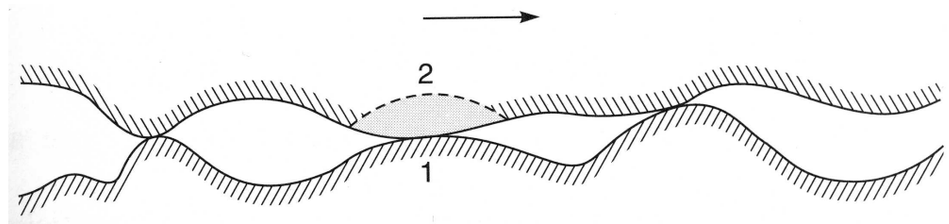
- **Lubrication with oils or liquids:** a fluid film separates the solids, allowing an easy shear of the sliding interface
  - **Hydrodynamic lubrication:** thickness of the fluid film is large compared to the surface roughness
  - **Elasto-hydrodynamic lubrication** (EHD or EHL): elastic deformation of solid surfaces, creating
  - **Mixed Lubrication:** some asperity contact, but part of the load is carried by the fluid
  - **Boundary lubrication:** most of the load is carried by contacting asperities, which are surrounded by the fluid

- **Solid lubrication:** a material (often a coating) provides an easy shear of the sliding interface

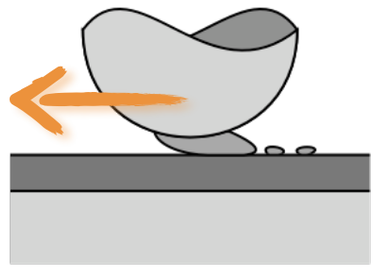
Velocity accommodation in “dry” contacts

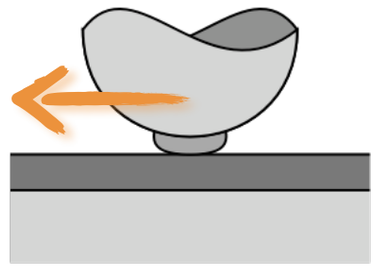
- In “dry” or “solid” contacts, when solid asperities interacts, **shear occurs where it’s easier**!

- In case of seizure, breaking of **adhesive junctions**
  - at initial interface (1)
  - inside the weakest material (2) (depending on hardness and brittleness)



- With solid lubricants, shearing of **interfacial films**:
  - “Intrafilm flow” or “interfilm sliding”

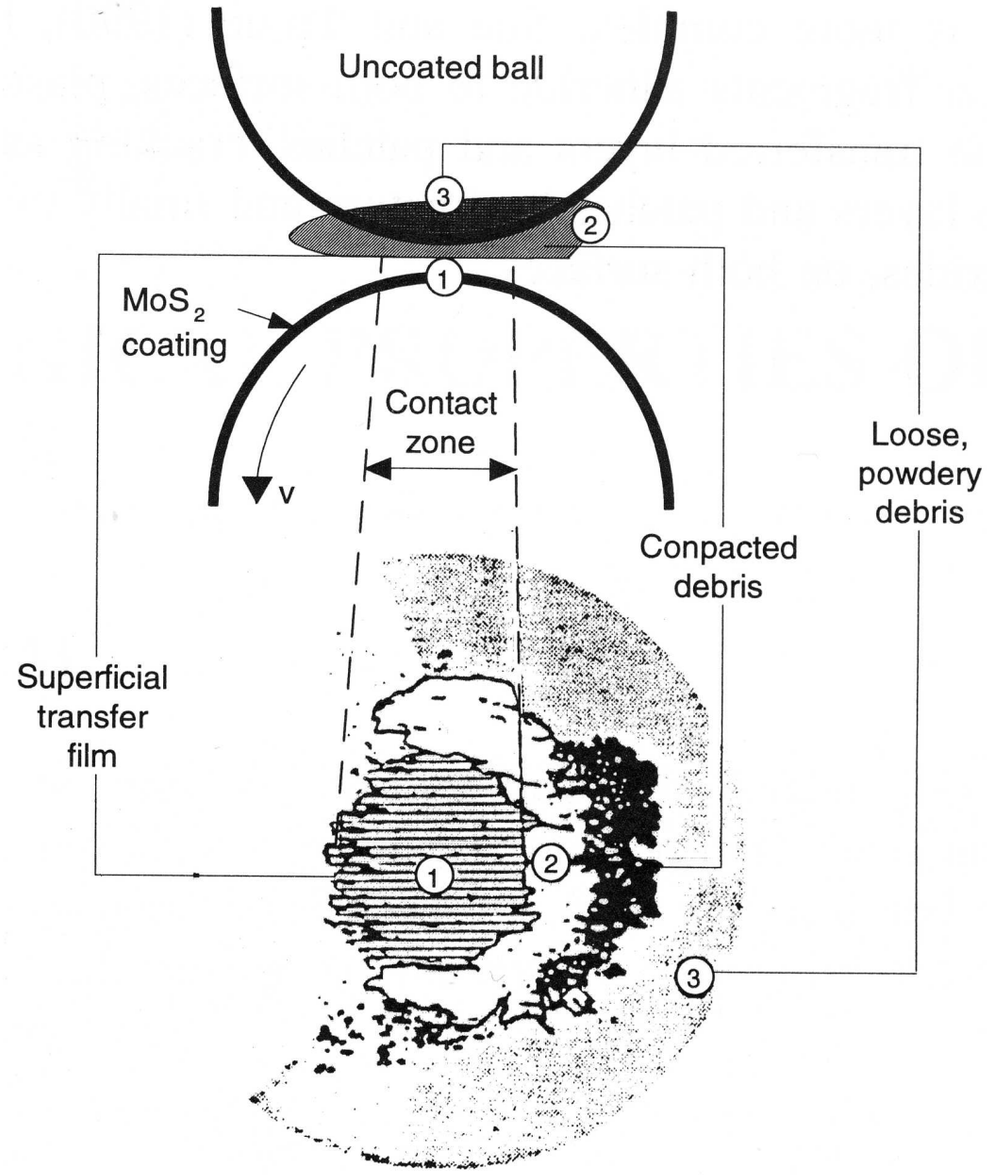




- General case: shearing of debris or trapped particles → **third body concept**

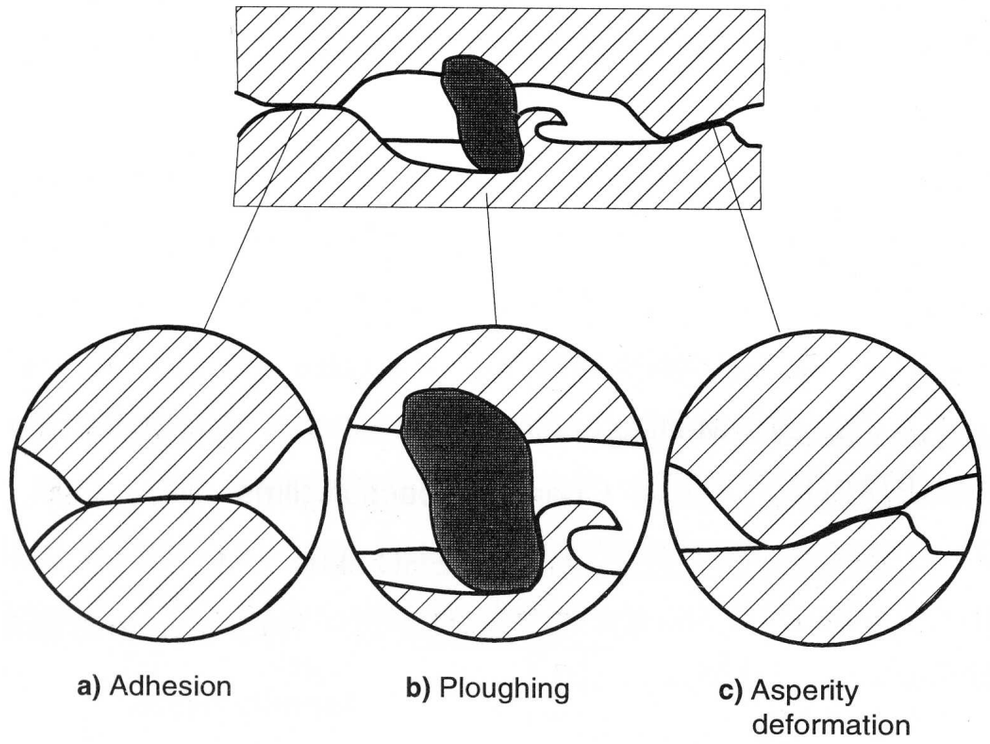
What may be found in a “dry” contact?

- Flow from one solid to the other
- Compaction of wear debris
- Build-up of « tribofilms » or « transfer layer »
- Chemical reactions between contacting bodies or with the environment



Origins of friction force

- Contributions to the friction force *(Bowden & Tabor)*:



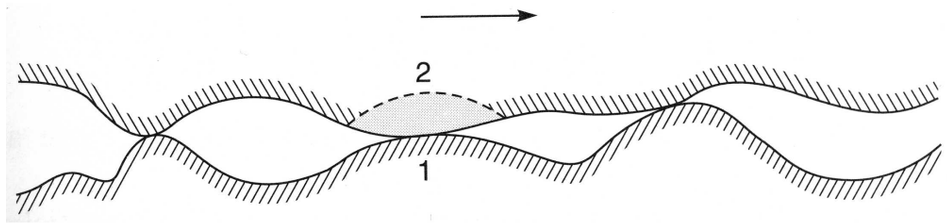
- Adhesion: shearing of adhesive junctions

  $F_{adh} = A_r \cdot \tau$, with A_r: real contact area, τ: interfacial shear strength

- Plastic deformations
  - Macroscopic: ploughing - abrasion of the softer body
  - Microscopic: plastic deformation of contacting asperities

Dry friction of metals: adhesion

- Adhesive phenomena between asperities *(Rabinowicz)*



  - Release of adhesive junctions:
    - Controlled by surface energy → strength of interface
    - Controlled by hardness → strength of asperities

  - Empirical formula based on experimental results:

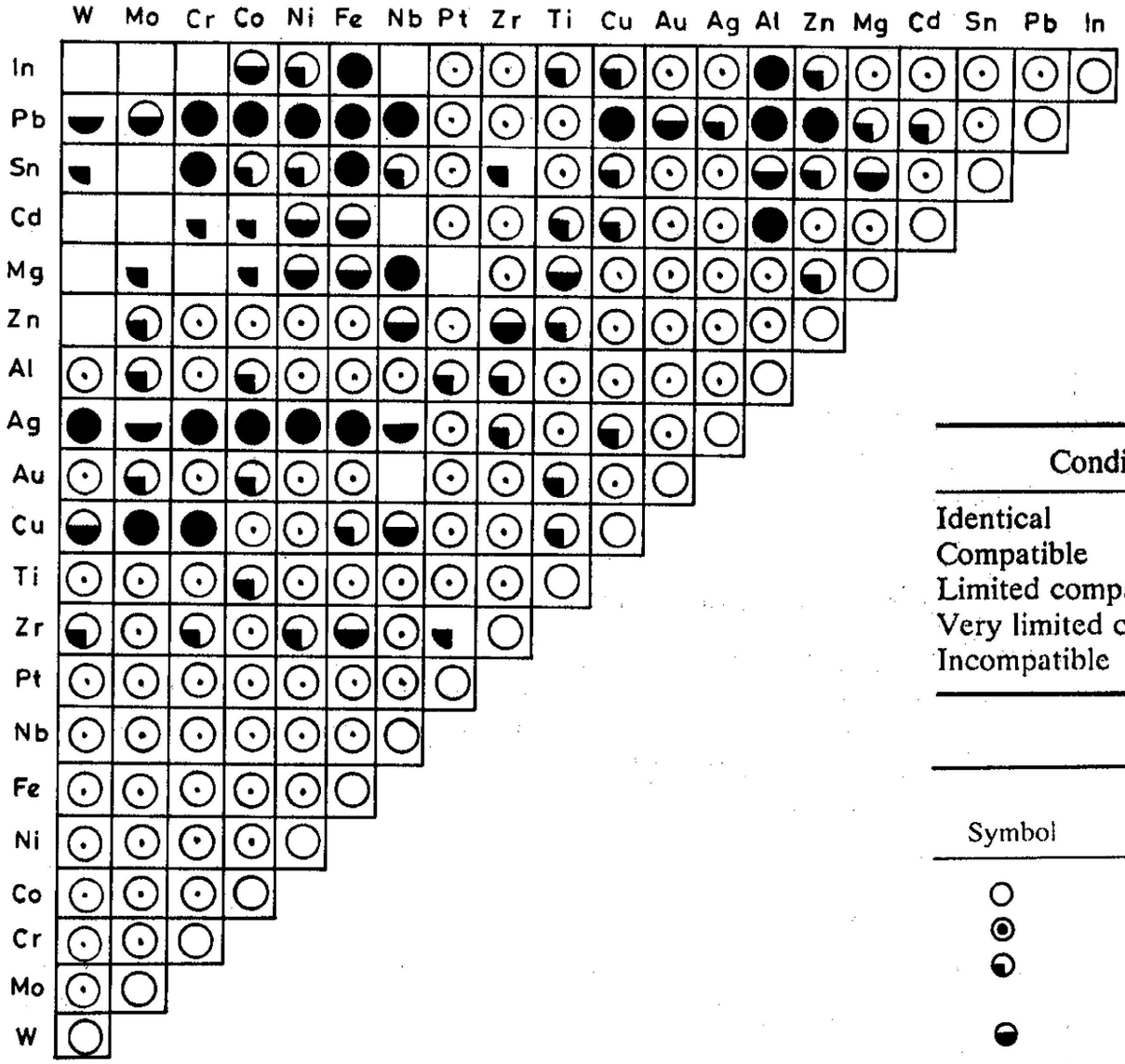
$$\mu \simeq 0.3 + C_1 \frac{W_{12}}{H}, \text{ with } W_{12} = C_2 \left(\gamma_1 + \gamma_2\right)$$

$$\mu \simeq 0.3 + C_1 C_2 \frac{\gamma_1 + \gamma_2}{H}$$

W_{12}: work of adhesion – γ_1, γ_2: surface energies
C_1: geometrical constant – C_2: miscibility constant
H: hardness of softer body

Dry friction of metals: adhesion

- Adhesive phenomena between asperities *(Rabinowicz)*



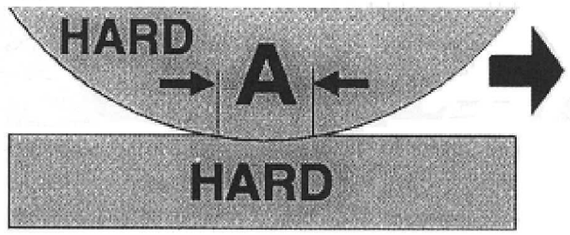
$$\mu \simeq 0.3 + C_1 C_2 \frac{\gamma_1 + \gamma_2}{H}$$

Condition	Symbol	Measured value of C_2
Identical	○	1.00
Compatible	◉	0.50
Limited compatibility	◔	0.32
Very limited compatibility	◒	0.20
Incompatible	●	0.125

Symbol	Metallurgical solubility	Metallurgical compatibility	Sliding compatibility	Anticipated wear
○	100%	Identical	Very poor	Very high
◉	Above 1%	Soluble	Poor	High
◔	0.1–1%	Intermediate soluble	Intermediate	Intermediate
◒	Below 0.1%	Intermediate insoluble	Intermediate or good	Intermediate or low
●	Two liquid phases	Insoluble	Very good	Very low

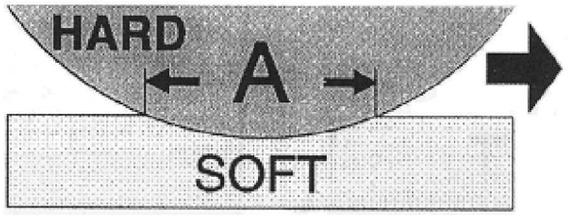
Controlling dry friction: solid lubrication

- How to reduce dry friction of metals? *(Bowden & Tabor)*
  - Soft metal film – Playing with A_r & τ in $F_t = A_r \cdot \tau$



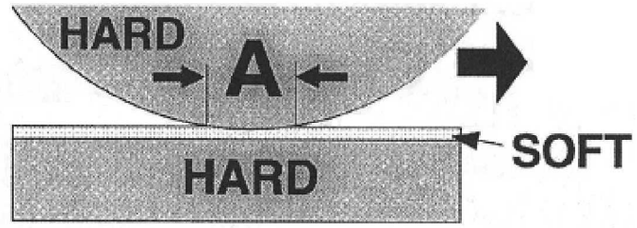
τ high

A_r small



τ small

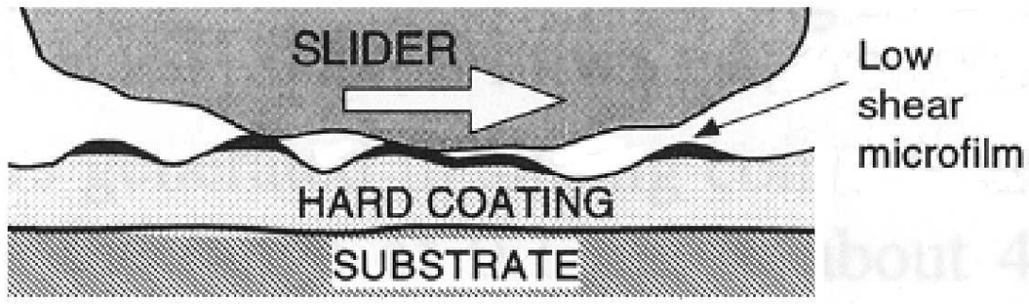
A_r high



τ small

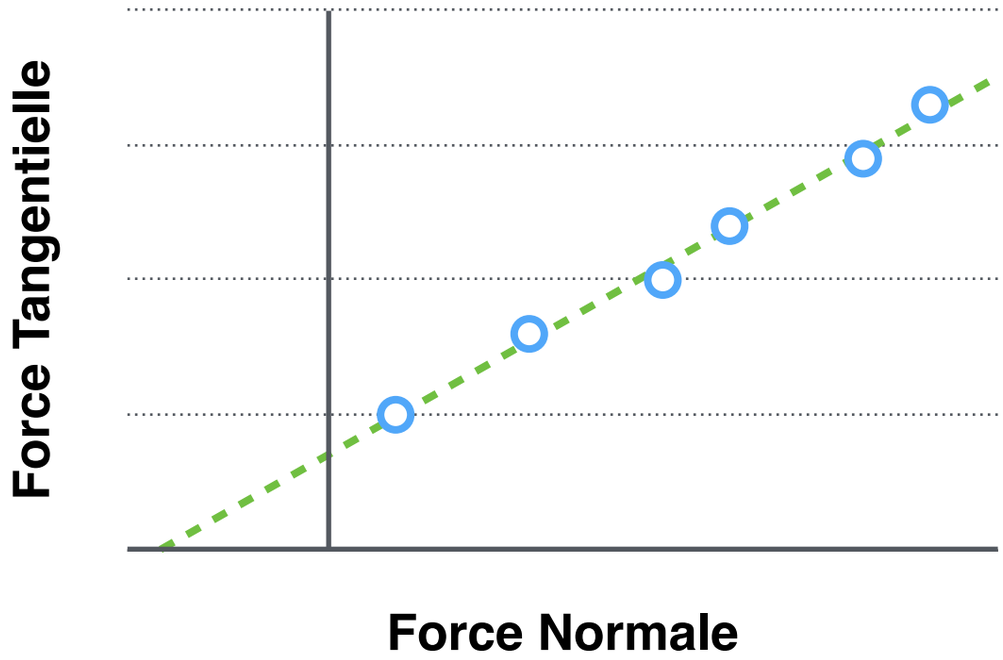
A_r small

- General case with solid lubricants *(Holmberg & Matthews)*
  - Soft thin coating providing easy shear
  - Hard and stiff substrates (or underlayers)



The limits of Coulomb's law

- Friction force is not always proportional to load: $\mu \neq \frac{F_t}{F_n}$



- Example: affine behaviour
  - $F_t = \mu \cdot F_n + F_{t_0}$: Threshold in interfacial shear strength?
  - $F_t = \mu \left(F_n + F_{n_0} \right)$: Adhesive forces added to normal force?

The limits of Coulomb's law

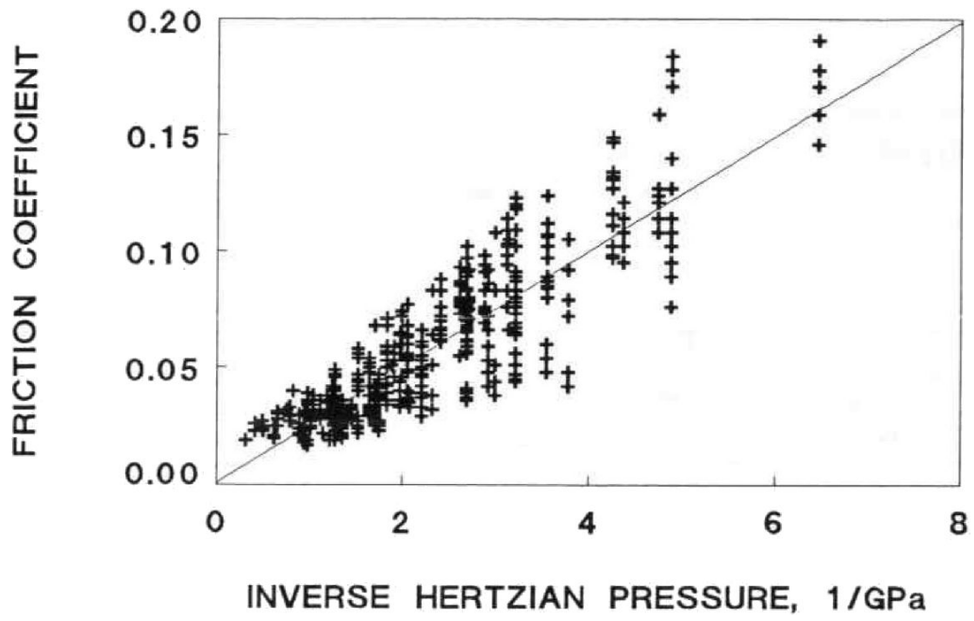
- Both tangential & normal force are proportional to contact area

$$F_t = A_r \cdot \tau \text{ and } F_n = A_r \cdot P$$

$$\mu = \frac{F_t}{F_n} = \frac{\tau}{P}$$

- If μ is changing with normal load, or contact pressure P, then it means that τ depends on contact pressure P

Example with MoS_2 solid lubricant coatings



e.g. $\tau = \tau_0 + \alpha P$ implies that $\mu = \frac{\tau_0}{P} + \alpha$ *(Singer)*

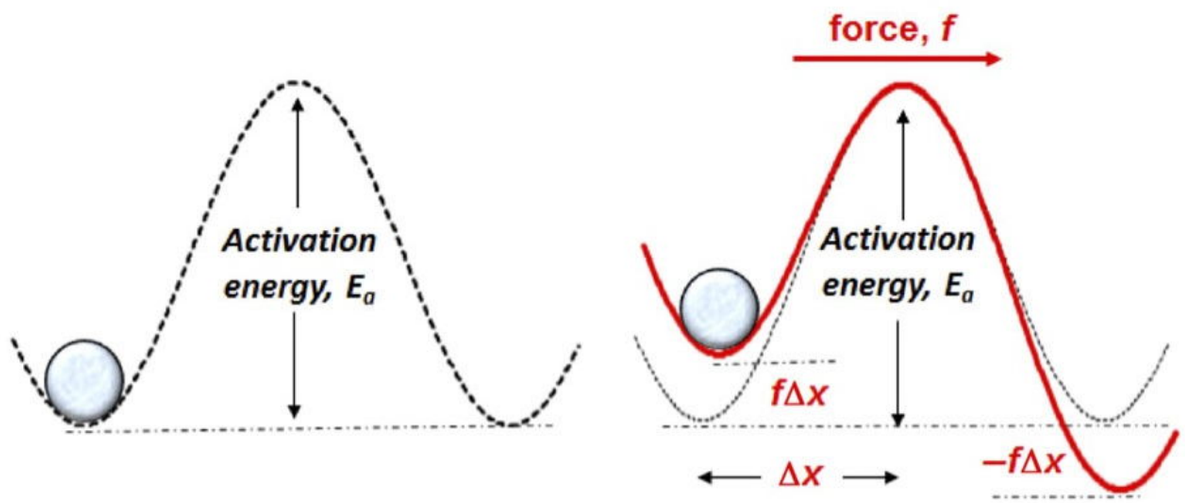
Key role of interfacial material

- Critical parameters controlling dry friction:
  - ***Shear strength of interface:*** τ
    Depends on the nature of interfacial material
  - ***Load carrying capacity of the substrates:*** P
    Elastic deformation as well as roughness affect the contact pressure

- The nature, composition and properties of the interfacial material are thus critical for understanding friction and its evolution!

Friction-induced chemical changes: Tribochemistry

- Producing new compounds through chemical reactions require energy. Several ways to provide the energy:
  - Photon activation: photochemistry
  - Electrical activation: electrochemistry
  - **Thermal activation: thermochemistry**
  - **Stress-induced activation: mechano-chemistry**

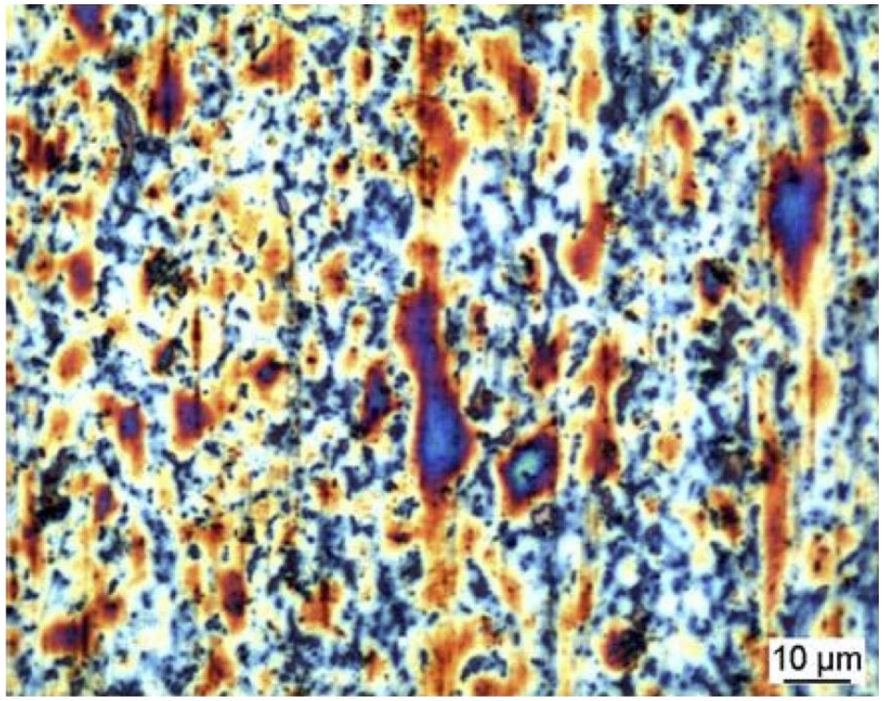


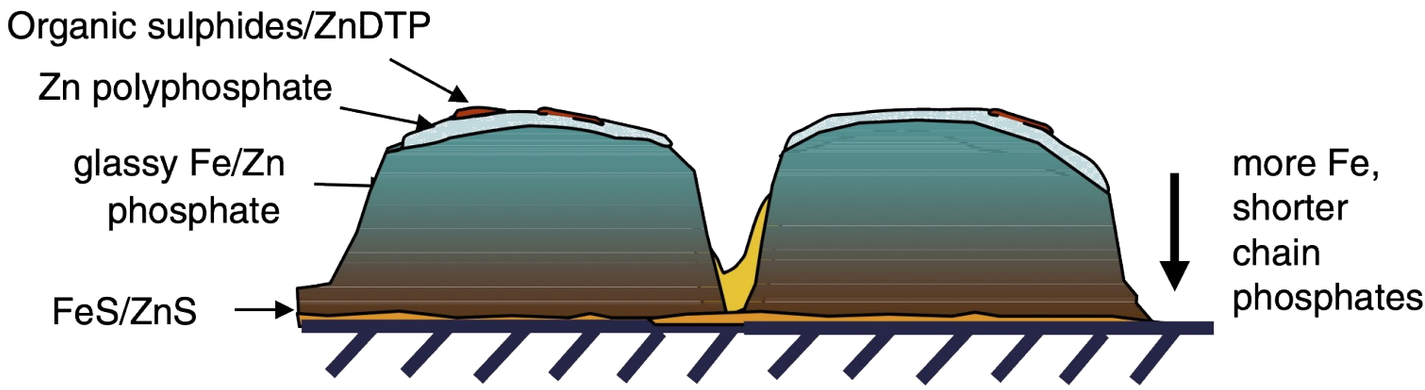
- *Contacts are « chemical reactors » where reactions may take place between the counterfaces and/or with the environment*

Friction-induced chemical changes: Tribochemistry

- Tribochemistry: some specificities though!
  - Reacting species must be “close enough”
  - Stress distribution in a real contact is highly heterogeneous
  - Nature of reaction products will affect tribological response

⇒ **Complex structure of the “tribofilms” with lateral and vertical gradients**

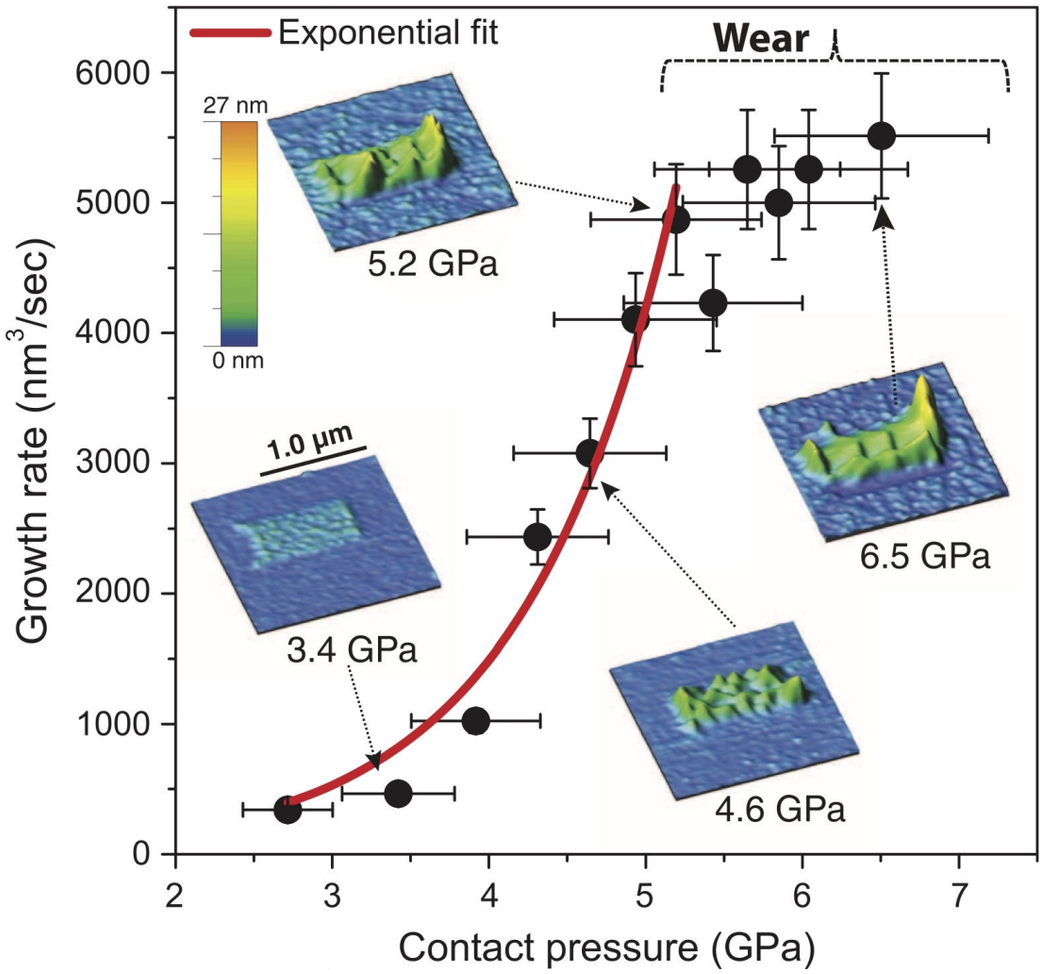


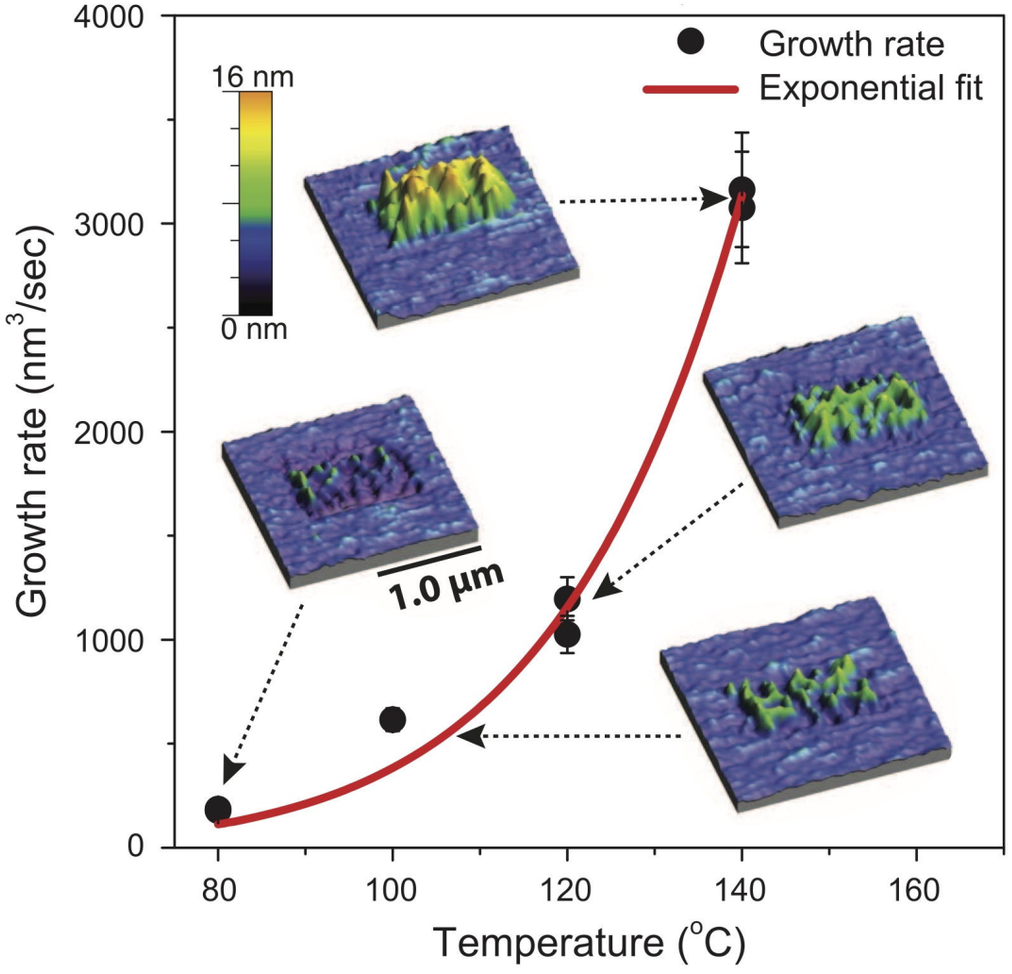


Example of tribofilm growth on steel from an anti-wear lubricant additive, Zinc dialkyl-dithiophosphate (ZDDP or ZnDTP)

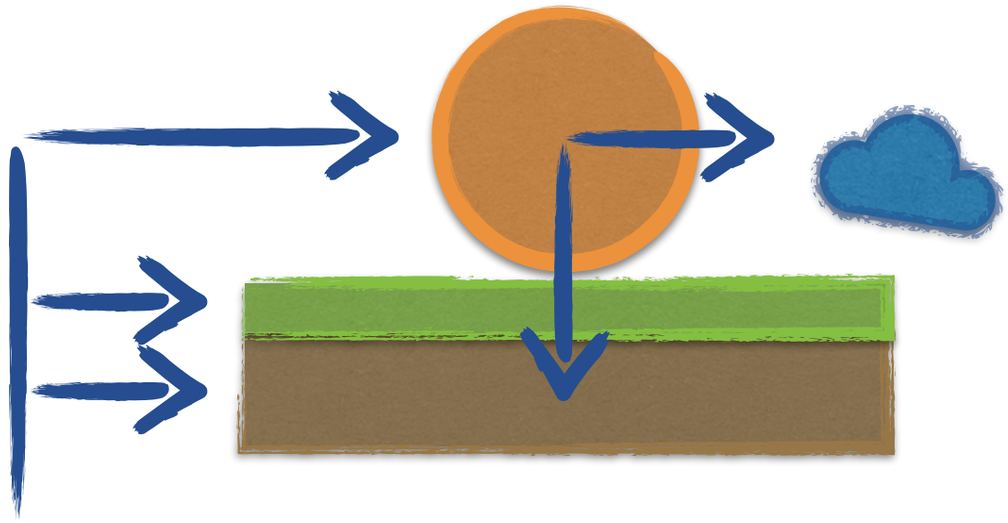
Friction-induced chemical changes: Tribochemistry

- Competition between stress activation and catalysis
  - Due to wear, new surfaces are exposed: “nascent surfaces”
  - Presence of metal or oxides may affect chemical processes
  - Yet experiments with Atomic Force Microscopy (AFM) clearly evidence a stress and temperature activation





Key tribological parameters



Intrinsic parameters: Materials

- **Surfaces & interfaces**
  - Composition & chemistry
  - Roughness
- **Coatings**
  - Composition & chemistry
  - Structure & thickness
  - Adhesion to substrate
  - Mechanical properties
- **Substrates**
  - Composition & chemistry
  - Structure
  - Mechanical properties

Extrinsic parameters: System

- **Contact parameters**
  - Geometry & applied forces
  - Contact pressure
- **Kinematic parameters**
  - Nature of relative motion
  - Speed, length
  - Frequency of exposure
- **Environmental parameters**
  - Nature & pressure of gases or presence of liquid
  - Temperature
  - External solid particles

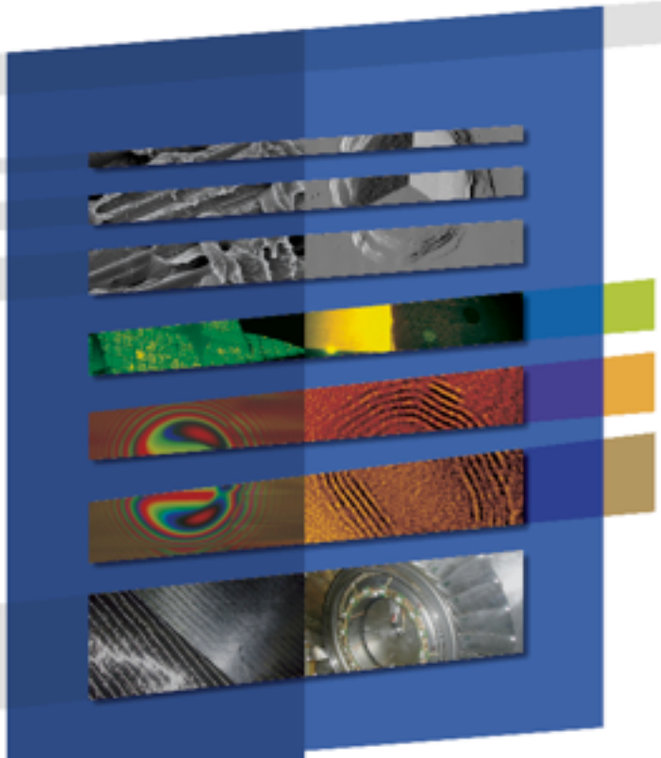
Adjusting contact severity…

- **Geometry**
  - Point contact / Line contact / Surface contact
  - Increasing apparent contact area
  - Decreasing contact pressure
- **Applied force**
  - Affects contact area and pressure
  - Contact computations: Hertz, K.L. Johnson…
  - Maximum stress beneath the surface
- **Sliding velocity / contact frequency**
  - Contact temperature
  - Kinetics of tribochemical reactions
- **Environment**
  - Nature & reactivity of the environment
  - Imposed temperature

Playing with kinematics…

- Different **type of motion**: linear, rotating / continuous or reciprocating
- **Dwell time**: time between passes – may affect chemical reactions with environment
- **Kinematic lengths** of both counterparts: asymmetric nature of most tests!
  - ***Linear ball-on-flat case***
    - Distance traveled by a point on the ball: $L_{ball} = l \cdot N$
    - Distance traveled by a point on the flat: $L_{flat} = 2a \cdot N$
    - With $2a = 100\ \mu m$ & $l = 5\ mm$, ratio: $\frac{L_{ball}}{L_{flat}} = \frac{l}{2a} \simeq 50$
  - ***Rotating ball-on-disk case***
    - Distance traveled by a point on the ball: $L_{ball} = 2\pi R \cdot N$
    - Distance traveled by a point on the flat: $L_{flat} = 2a \cdot N$
    - With $2a = 100\ \mu m$ & $R = 15\ mm$, ratio: $\frac{L_{ball}}{L_{flat}} = \frac{2\pi R}{2a} \simeq 1000$

LTDS
Laboratoire de Tribologie et Dynamique des Systèmes



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http://ltds.ec-lyon.fr

Surfaces & Friction

Solid lubrication processes of Diamond-Like Carbon

Part 3

Member of UNIVERSITÉ DE LYON

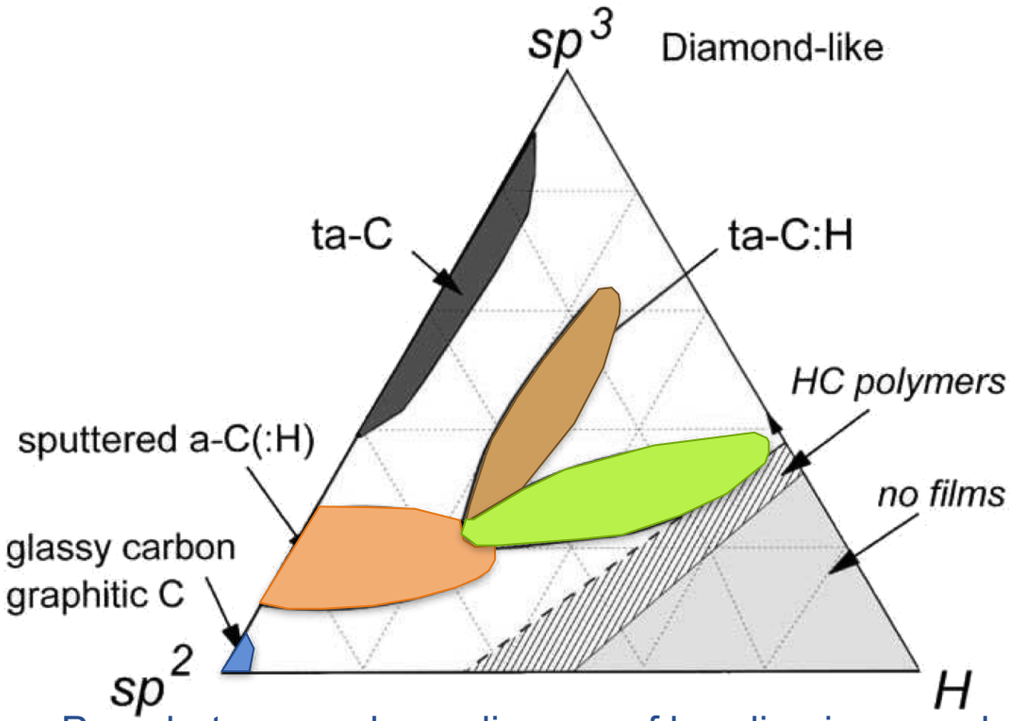
Solid lubrication processes of Diamond-Like Carbon

- **Introduction to DLC coatings**
- **Role of surface chemistry**
- **Role of surface topography**
- **Interactions with environment**
- **Discussion & summary**

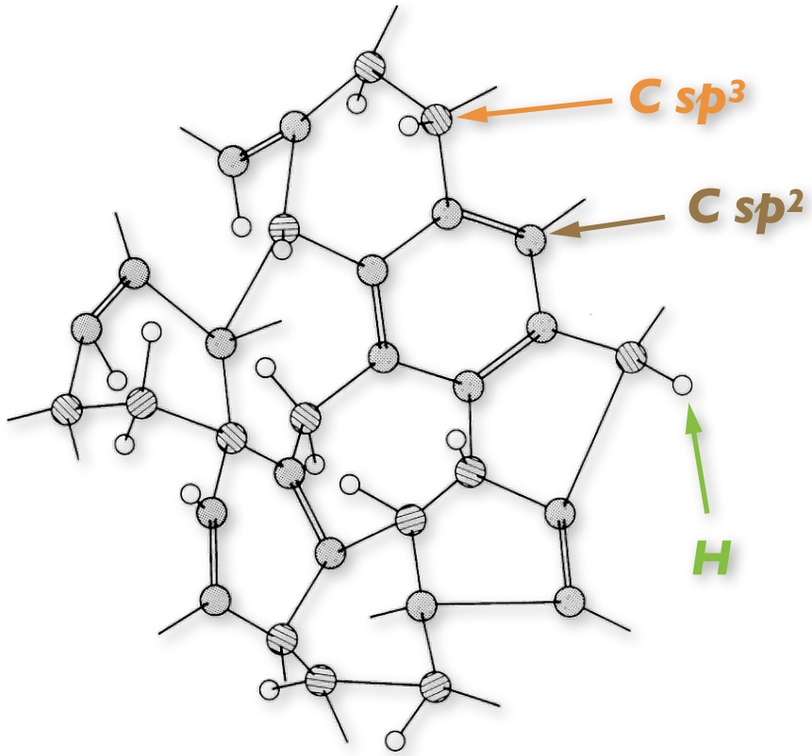
Diamond-Like Carbon: Popular tribological coatings…

- DLC: a family of hard amorphous carbon films
- Provide low friction and wear:
  good performances as solid lubricants
- Many industrial applications…

… An amorphous carbon structure…



Pseudo-ternary phase diagram of bonding in amorphous carbon-hydrogen alloys
Robertson et al. (1997)



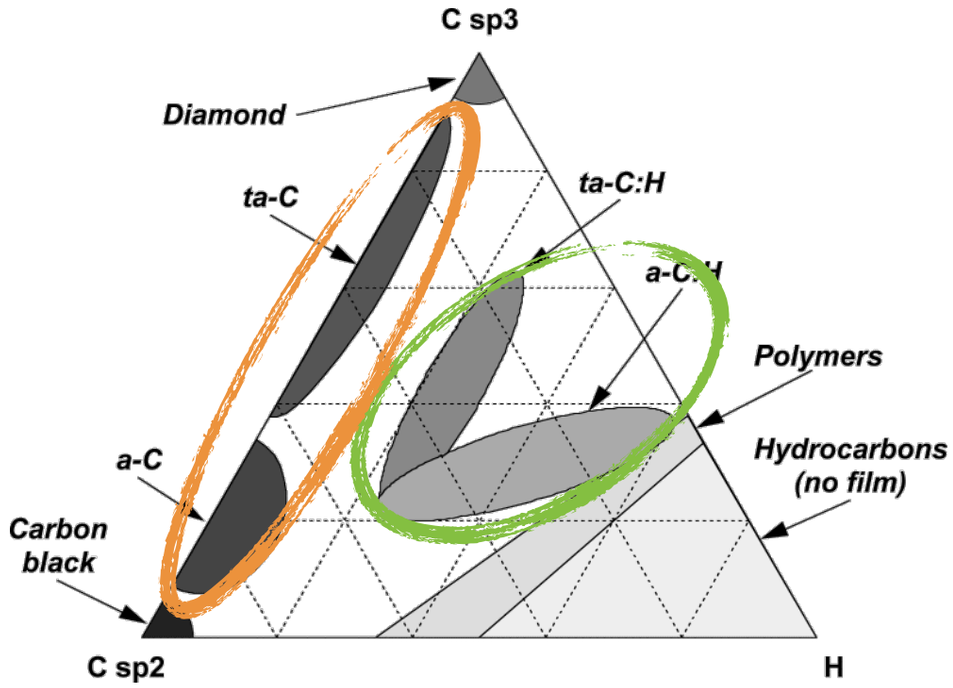
Random covalent network model of hydrogenated amorphous carbon films
Angus et al. (1992)

- Metastable amorphous DLC structure:
  - "Random Covalent Network" of sp^2 C, sp^3 C, H
    … with defects: dangling bonds, entrapped H_2 or CH_4…
  - Clustering of sp^2 C: aromatic rings (6-fold C rings)
    … with defects: 5- or 7- fold rings (non planar clusters…)
  - Graphite is the stable form of carbon,
    but high disorder may hinder long-range ordering

… With versatile properties…

- **Large variety of DLC coatings:**
  many different structures & compositions
  depending on deposition process …
  ⇒ wide range of properties

  - ***Physical Vapor Deposition*** (PVD)
    for hydrogen-free a-C and ta-C
  - ***Chemical Vapor Deposition*** (CVD)
    for hydrogenated a-C:H and ta-C:H

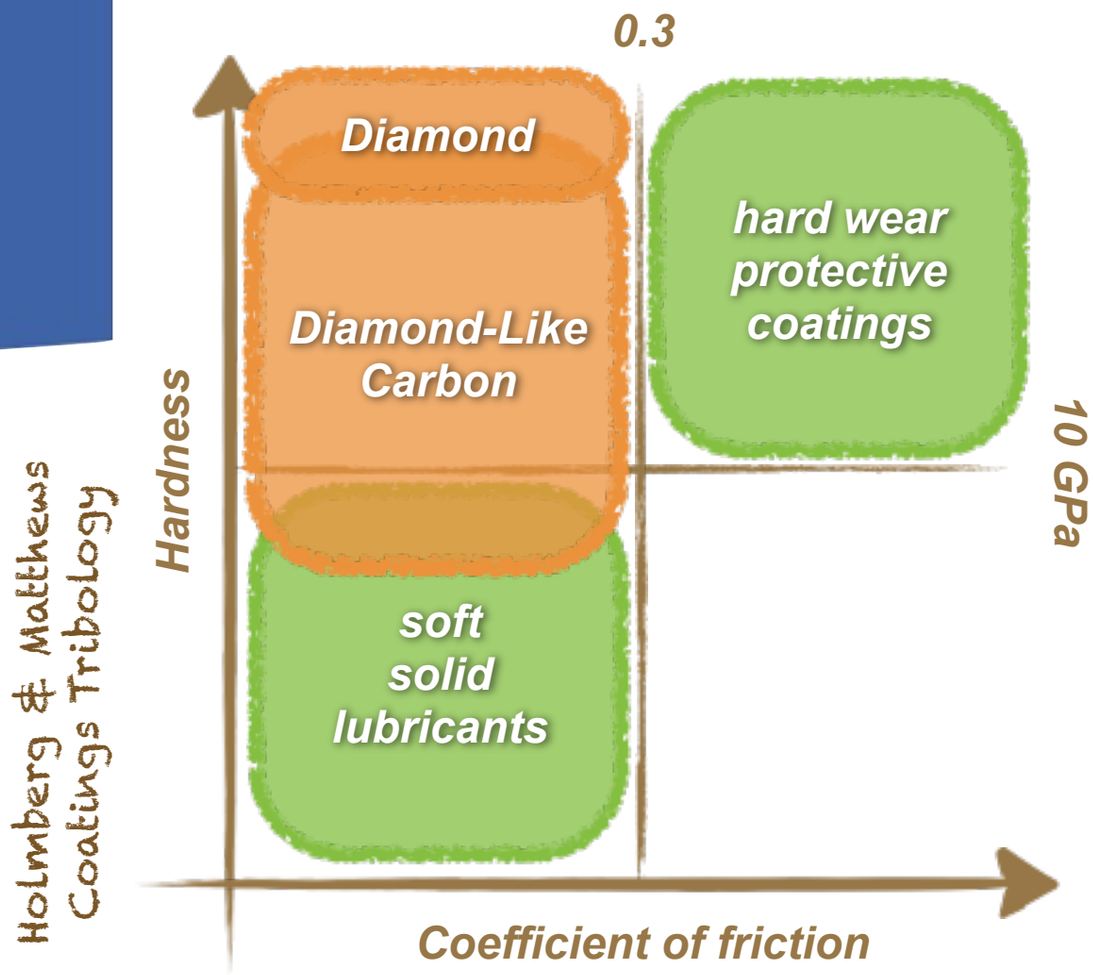


Hydrogen content	< 1 to > 50 at.%
Percentage of sp^3	20 to 90%
Optical gap	0.4 to 4 eV
Compressive stress	up to few GPa
Surface energy	< 20 to > 60 $mN.m^{-1}$
Thermal stability	up to ~300°C

	a-C	a-C:H	ta-C	ta-C:H
Hardness (GPa)	10 - 20	2 - 30	25 - 70	25 - 60
Elastic modulus (GPa)	150 - 200	50 - 250	200 - 650	150 - 300
H/E ratio	0.08 - 0.1	0.1 - 0.16	0.1 - 0.2	0.16 - 0.2

- As hard or harder than steel or most metallic substrates
- Comparable or lower elastic modulus (except high sp^3 content ta-C)
- Higher H/E ratio (~ strain to failure)

… But a tribological paradox!



- ***Archard's law***
  The harder the more wear-resistant
  Nitrides, carbides, ceramic coatings

$$V_{worn} = \frac{k}{H} \cdot F_n \cdot L$$

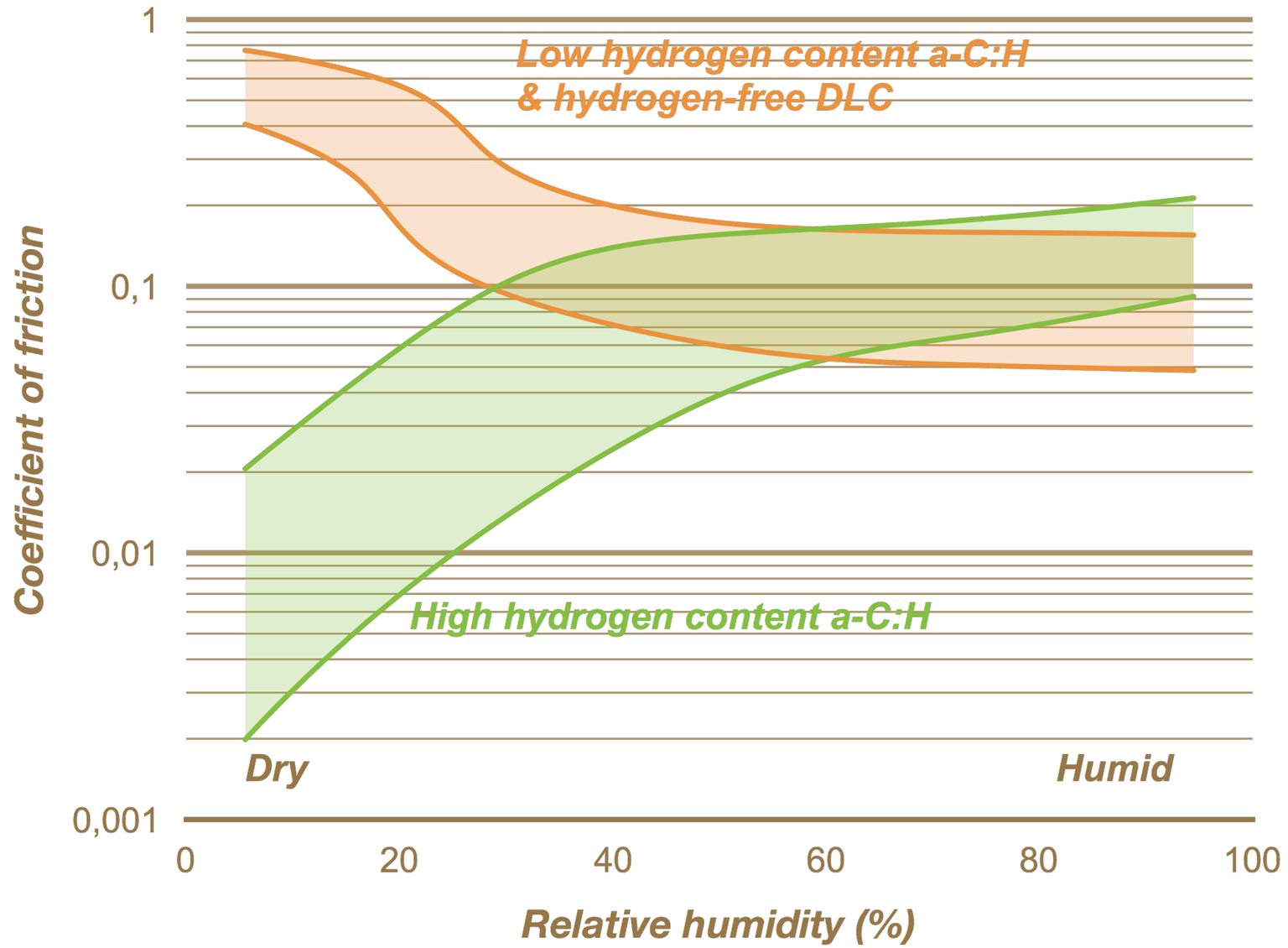
- ***Bowden & Tabor***
  Easy shear thin film trapped between hard and stiff substrates
  Soft metals, lamellar solids…

$$F_t = A_r \cdot \tau$$

How can DLC be both hard and easy to shear?

… Yet some limitations!

- Strong sensitivity to environment and coating composition!
- Versatility of the tribological performance…
  …dependence on deposition process parameters



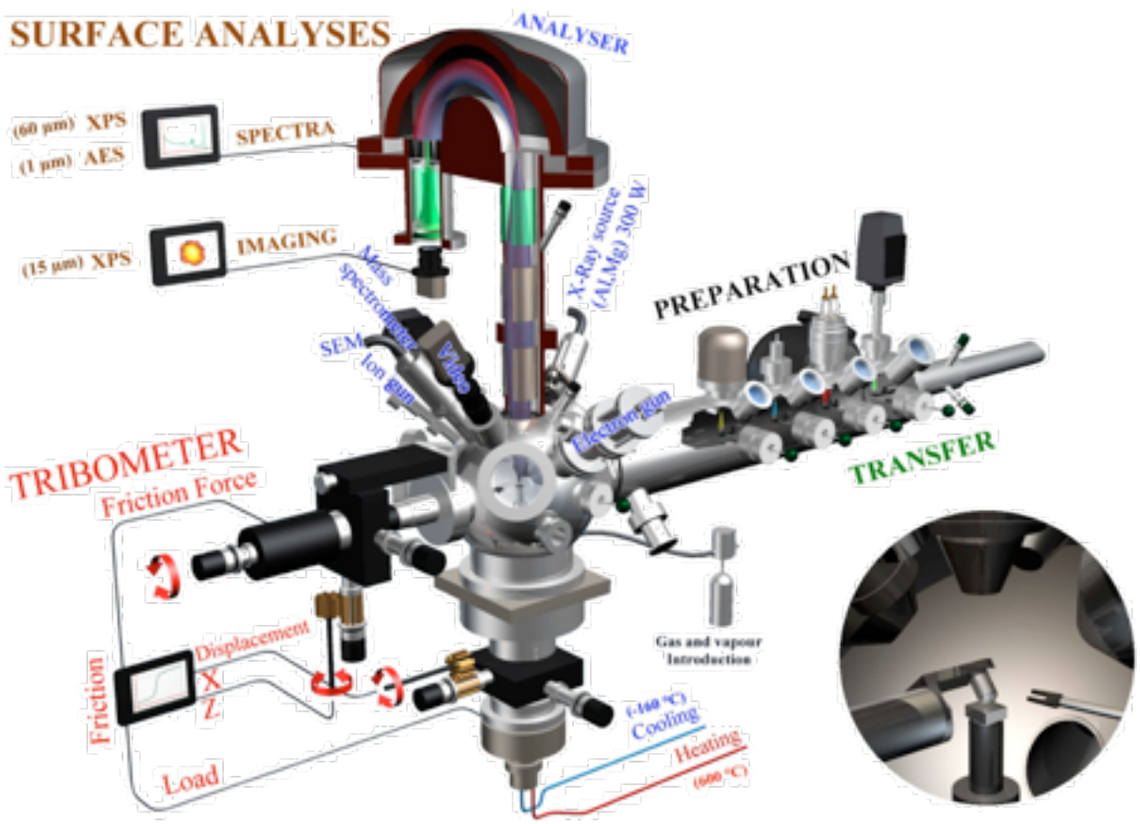
Solid lubrication processes of Diamond-Like Carbon

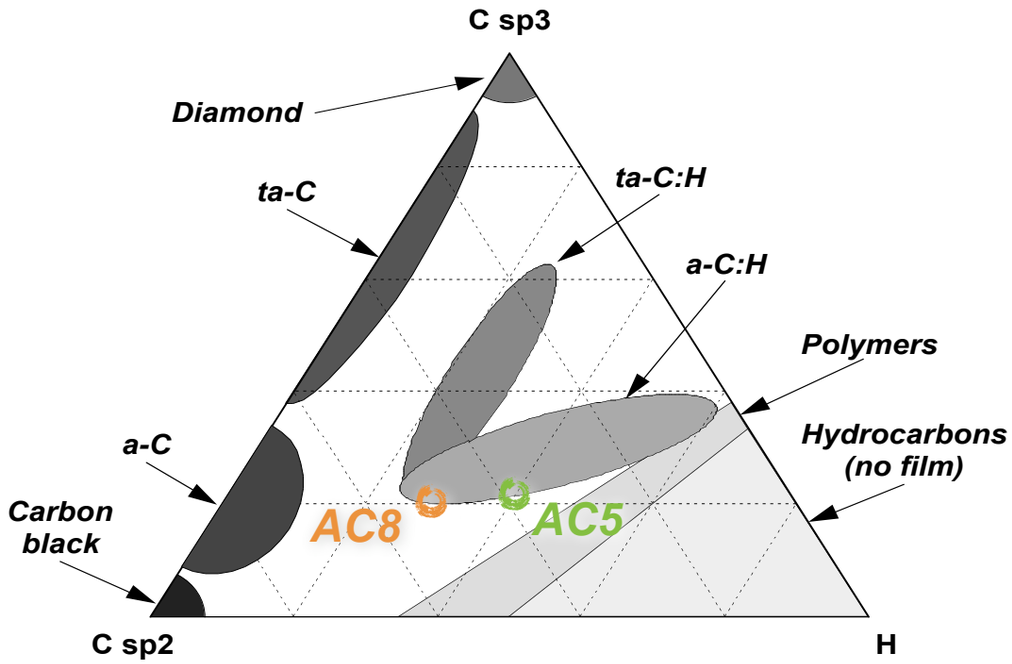
- Introduction to DLC coatings
- **Role of surface chemistry**
- Role of surface topography
- Interactions with environment
- Discussion & summary

Tribological experiments on "model" DLC

Analytical UHV tribometer

Linear reciprocating motion
DLC (1 µm) on Si(100)
Environment: UHV (<10^{-6} Pa) or pure gases
Sliding speed: 0.5 mm/s
Pin material: 52100 bearing steel
Pin radius: 8 mm
Normal force: 3-5 N
Max. Hertz pressure: ~550 MPa
Contact width ~100 µm
Macroscopic contact

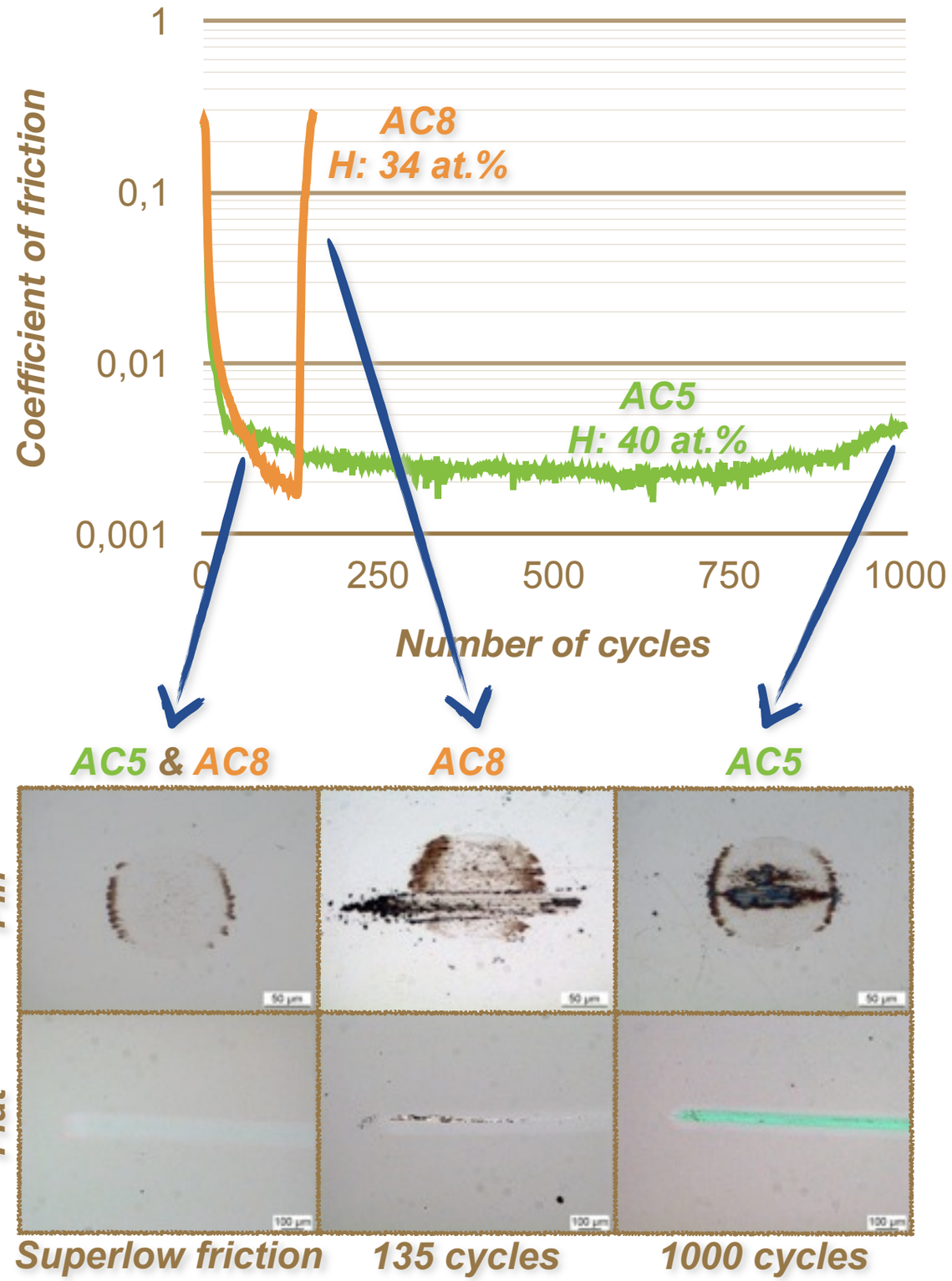




dc-PECVD	AC8	AC5
Precursor	C_2H_2	C_2H_2
Flow rate	10 sccm	10 sccm
Pressure	100 mTorr	200 mTorr
Bias voltage	-800 V	-500 V
Carbon content	66 at.%	60 at.%
C sp^3	*30%*	*35%*
C sp^2	*70%*	*65%*
Hydrogen content	34 at.%	40 at.%
Free H (FTIR)	*43%*	*27%*
Free H (NMR)	*7%*	*2%*
Hardness	10.5 GPa	7.5 GPa
Elastic modulus	80 GPa	62 GPa

Donnet & Grill, Surf. Coat. Technol. 1997
Donnet et al., J. Appl. Phys. 1999
Bec et al., Phil. Mag. 2006

Friction of a-C:H in UHV



Comparison of these 2 a-C:H films

AC8: 34 at.% of H – ***AC5:*** 40 at.% of H

Superlow friction is achieved
(μ < 0.01)

For ***AC8***, **drastic friction increase**
occurs after few tens of cycles
(> x100)

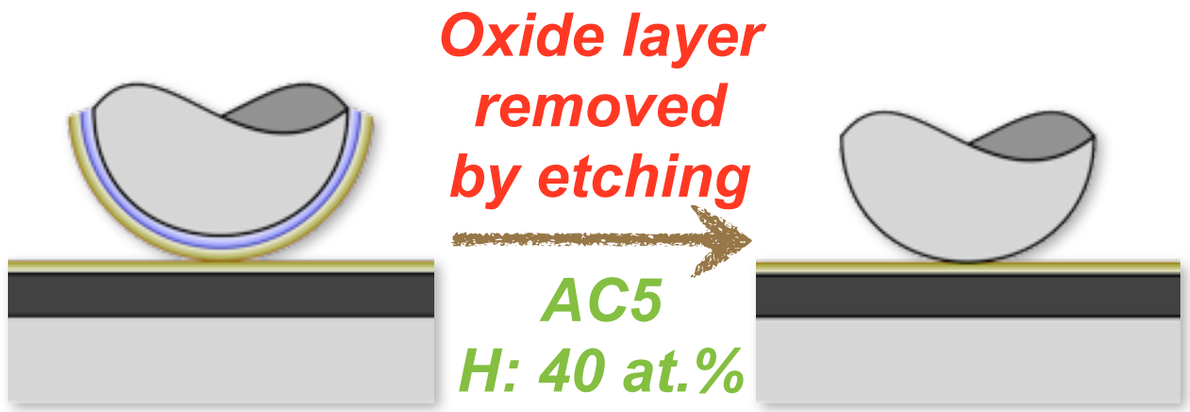
For ***AC5***, **small friction increase**
occurs after few hundreds of cycles
(< x10)

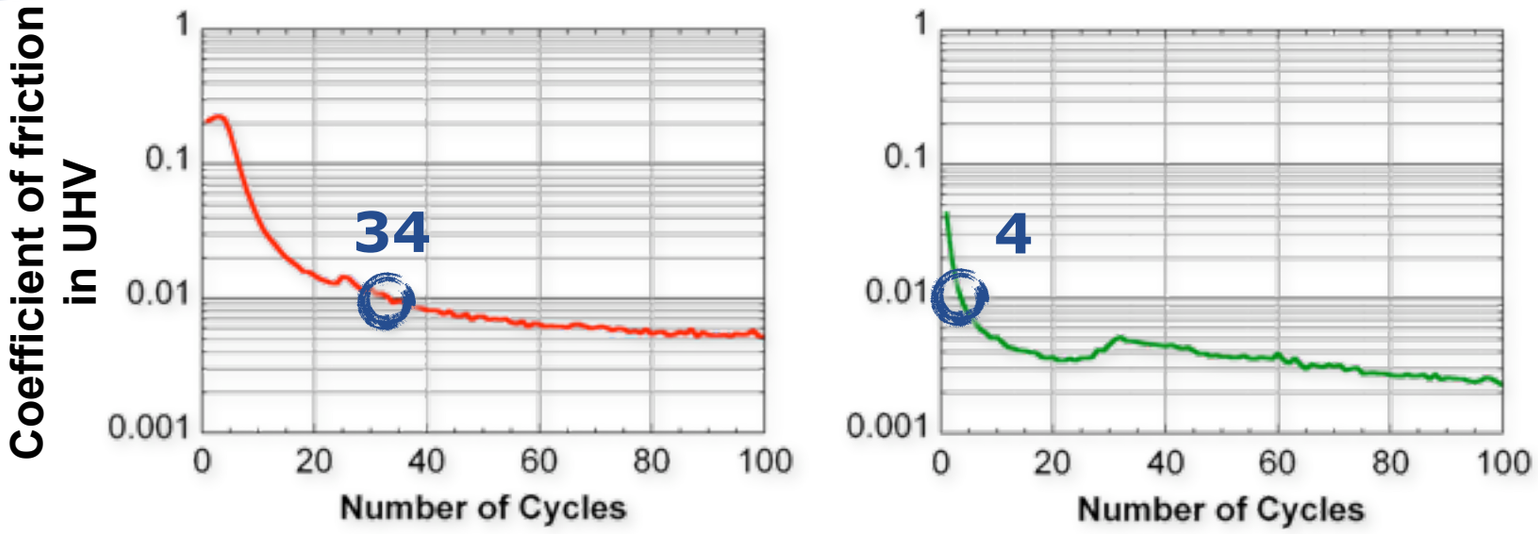
Tribofilm is formed during running-in

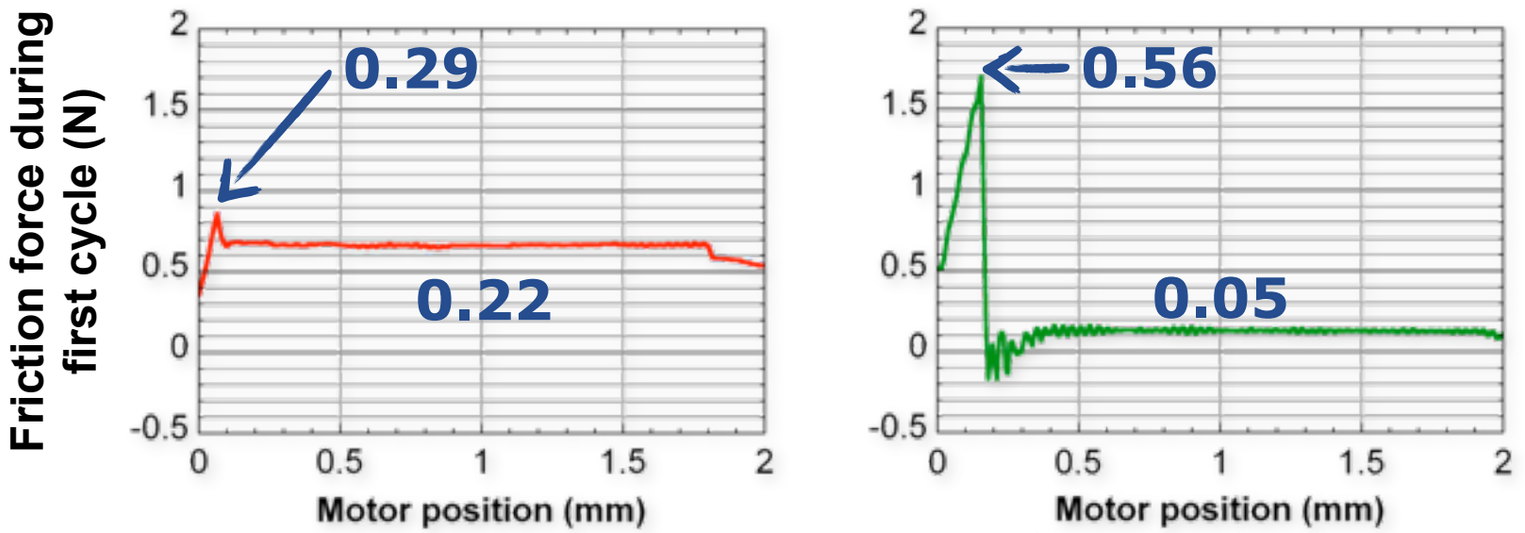
Drastic friction increase correlated
with ***removal of tribofilm***

Key-role of hydrogen content?

Surface chemistry & tribofilm build-up







"Tribofilm"

Interfacial material on counterface could be different from initial a-C:H

≠ "Transfer film"

Removal of iron oxide

↓

Strong adhesion

↓

Faster tribofilm build-up

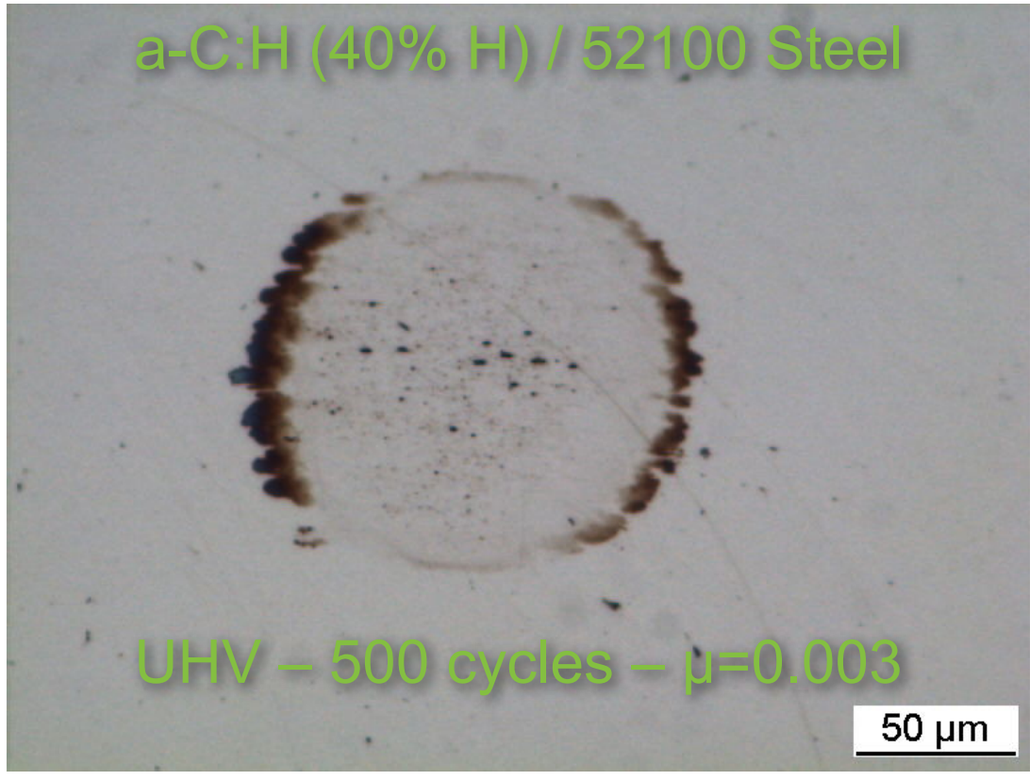
↓

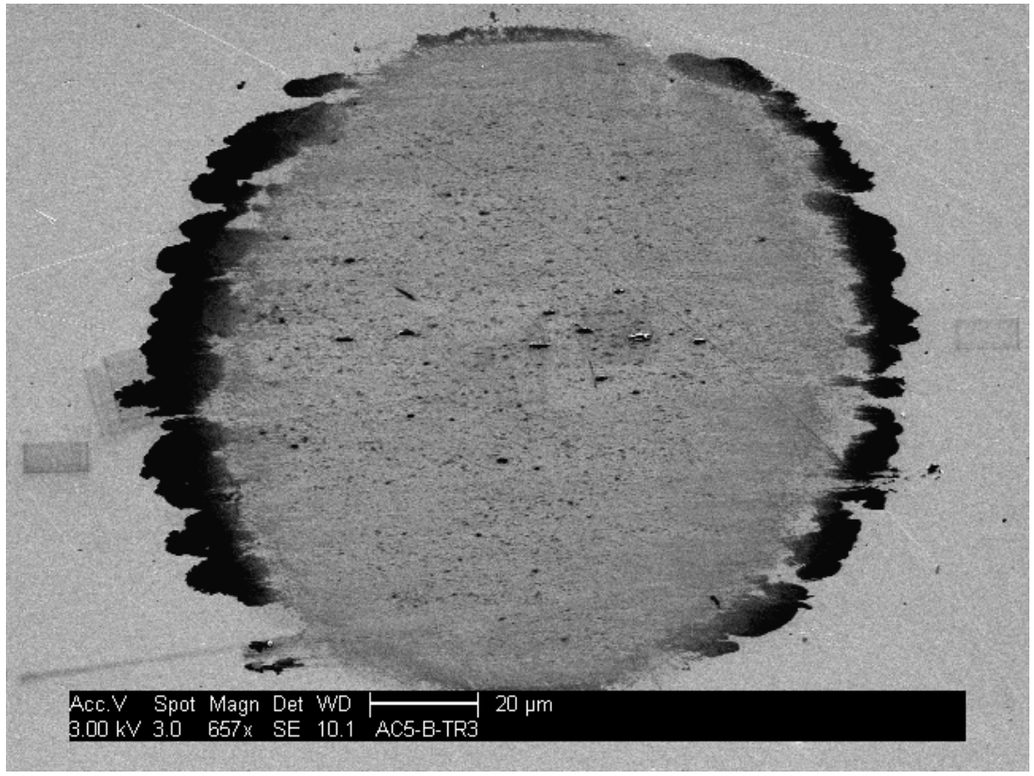
Faster friction decrease

Fontaine et al., Thin Solid Films 482 (2005) 99.

Key role of tribofilm build-up

- Tribofilm grown on metallic counterface



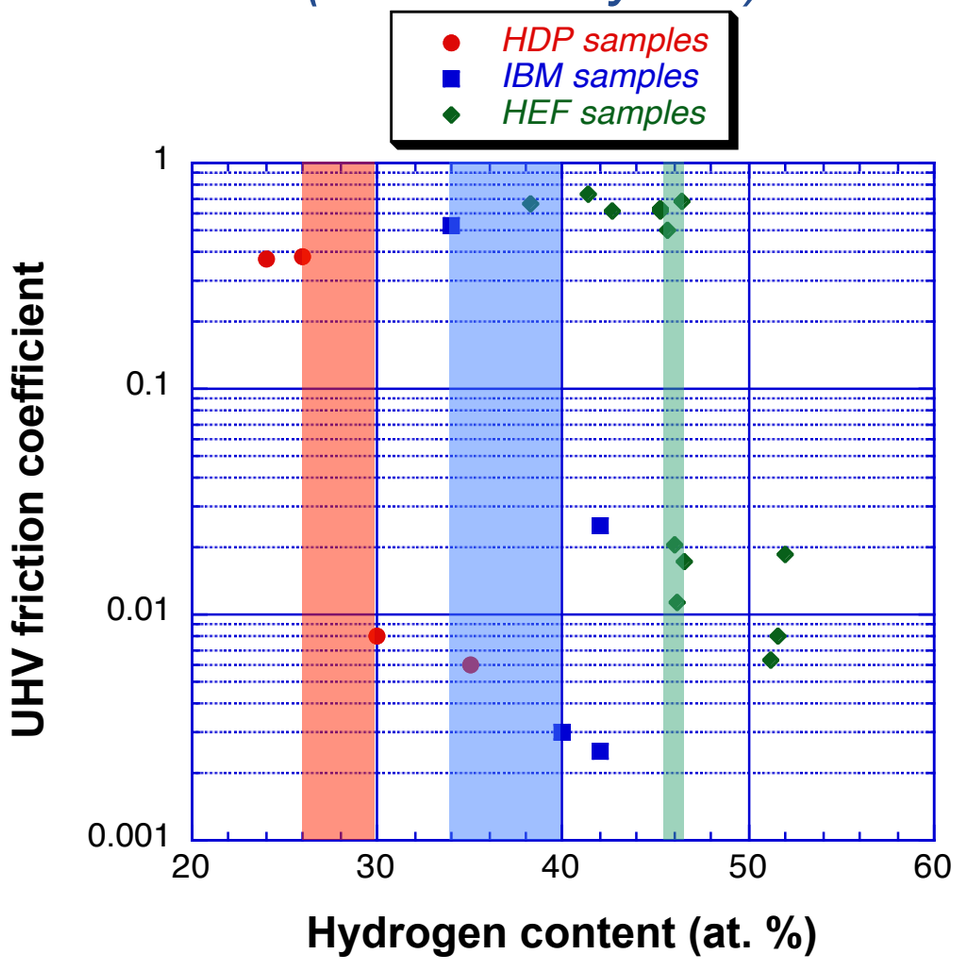


- Weak interactions between carbon-based sliding surfaces
  - Reduced adhesion if enough hydrogen on the surface? (or “passivating” species)
  - Avoiding strong bonds: covalent or metallic

Critical surface coverage by hydrogen?

- ***Surface coverage by Hydrogen*** would explain superlow friction of a-C:H under ultra-high vacuum?

"Stabilized" UHV friction coefficient (after 500 cycles)



3 different PECVD processes

HDP: *rf-PECVD from $C_2H_2 + H_2$*

IBM: *dc-PECVD from C_6H_{12} or C_2H_2*

HEF: *dc-PECVD from C_2H_2*

(PVD Ti-based underlayers)

HDP: 26-30 at. %

IBM: 34-40 at. %

HEF: ~ 46 at. %

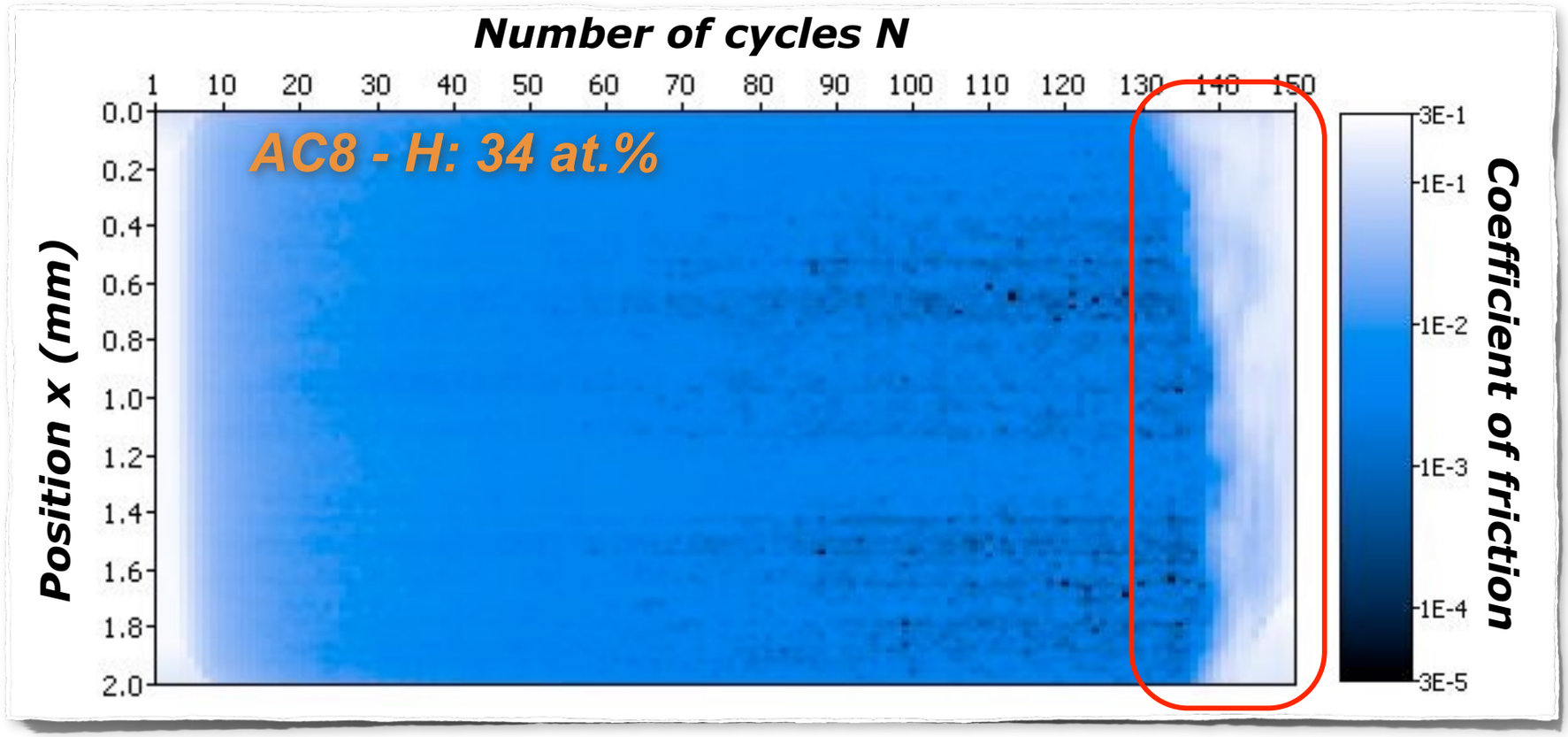
Threshold in hydrogen content depends on deposition process

How could we have similar hydrogen coverage with such different hydrogen contents?

Loss of superlow friction…

Triboscopy: "friction maps"

Friction as a function of position and number of cycles



Loss of "superlow" friction:

- Start at localized points of the wear track
- Quickly extends to an entire cycle

⇒ ***due to adhesive phenomena***

The key-role of adhesive phenomena

- **Positive role** of adhesive phenomena:
  → promote tribofilm build-up and friction reduction

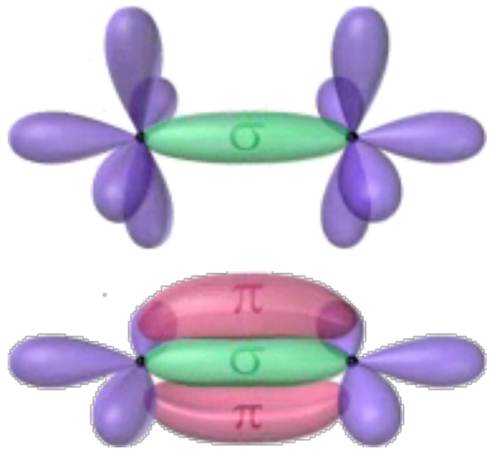
- **Negative role** of adhesive phenomena:
  → may lead to drastic friction increase

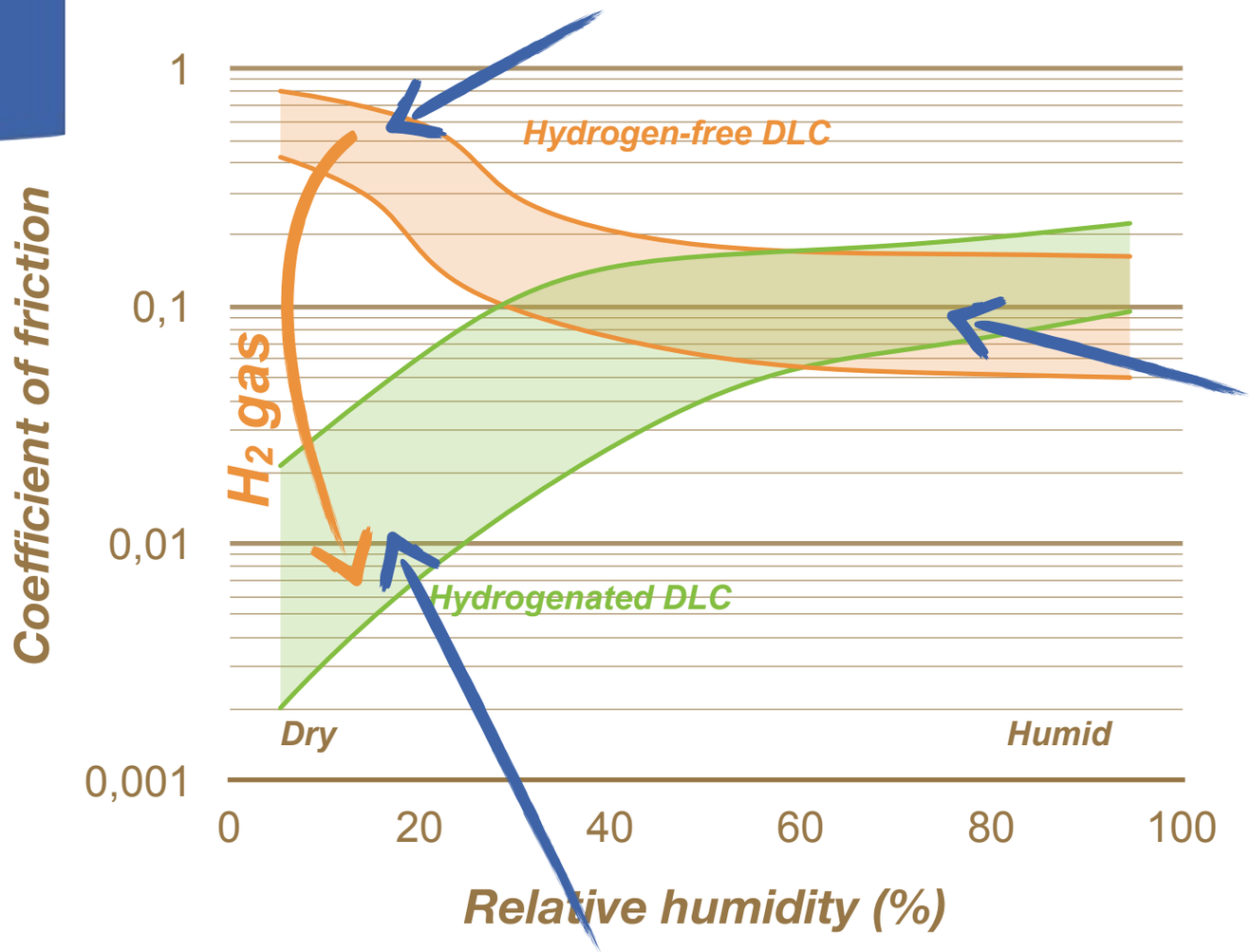
- **Adhesion** seem to control the friction of DLC
  → related to surface chemistry?

Surface chemistry & adhesion

Strong adhesion

- “Dangling” σ bonds
- π orbitals interactions? Metallic bonding?





Intermediate adhesion

Critical role of water vapor

- Hydrogen bonding ?
- Capillarity ?

Weak adhesion

- Hydrogen-terminated surfaces
- Van der Waals interactions

Solid lubrication processes of Diamond-Like Carbon

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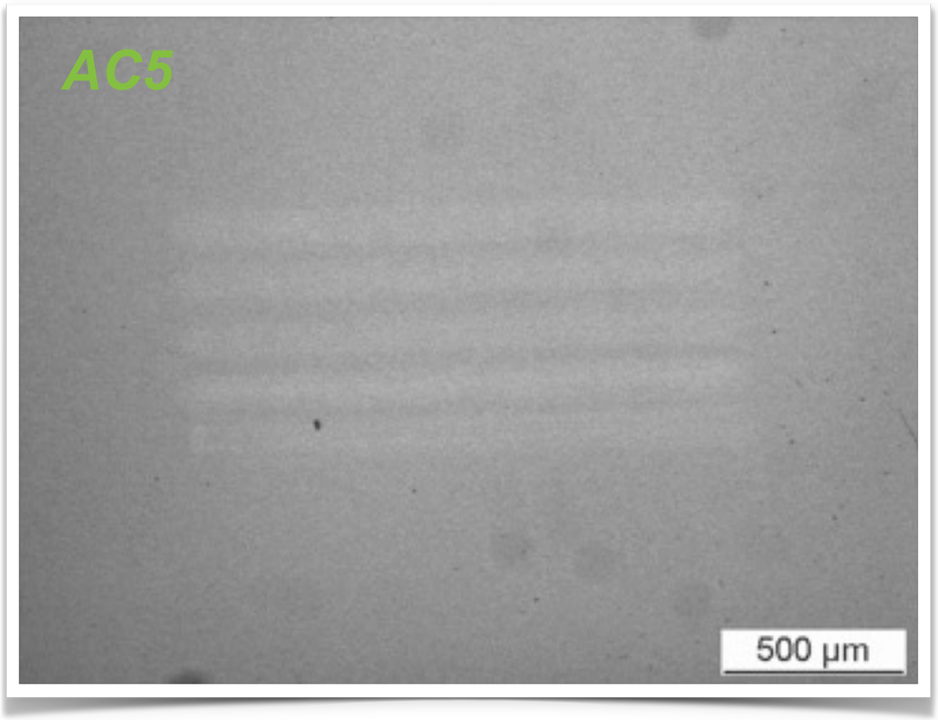
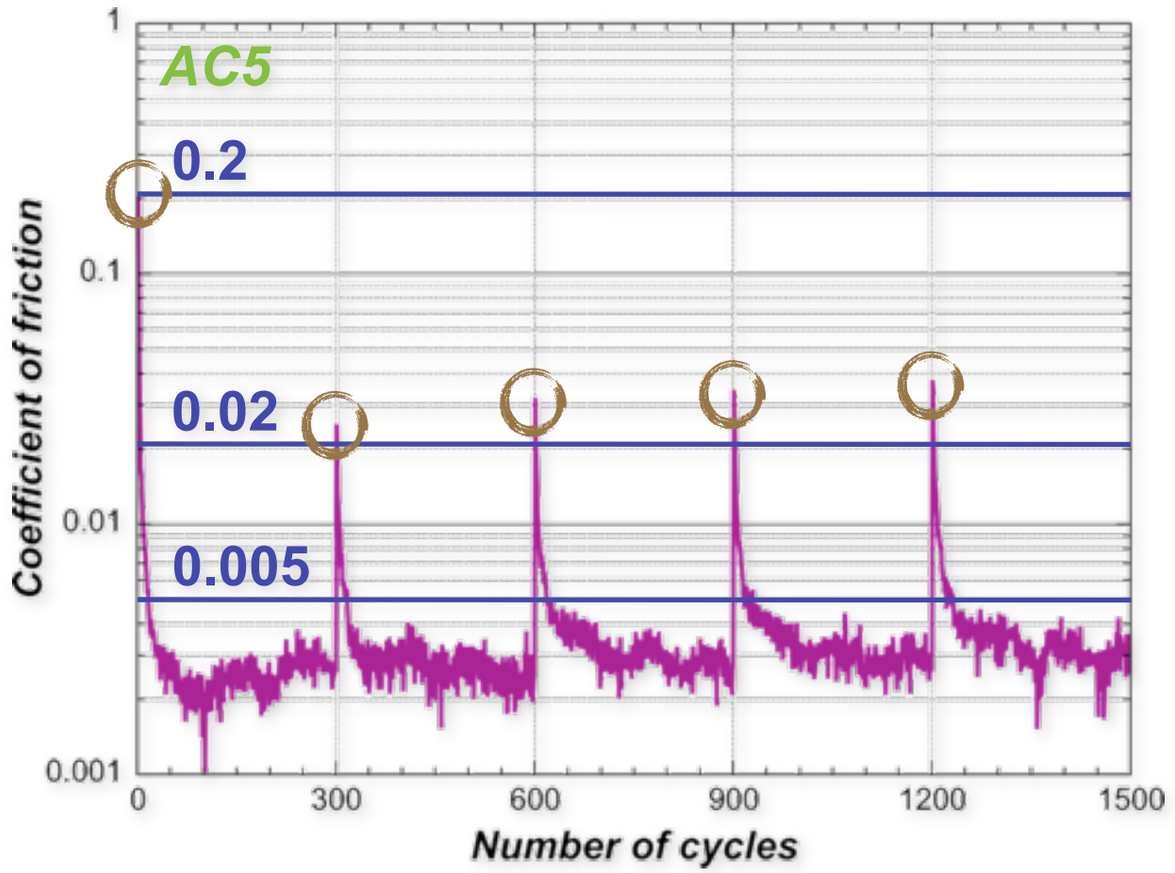
A closer look at running-in…

Running-in: only due to tribofilm build-up?

UHV friction experiments with :

- *5 different positions on the DLC coated flat*
- *Same position on the steel pin*
- *300 cycles at each flat position*





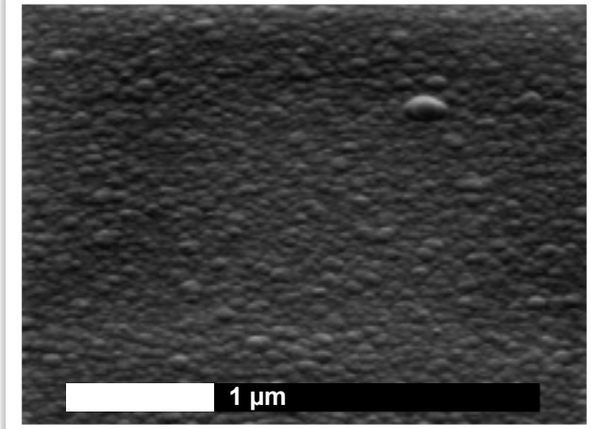
Systematic running-in from > 0.02 during > 15 cycles…

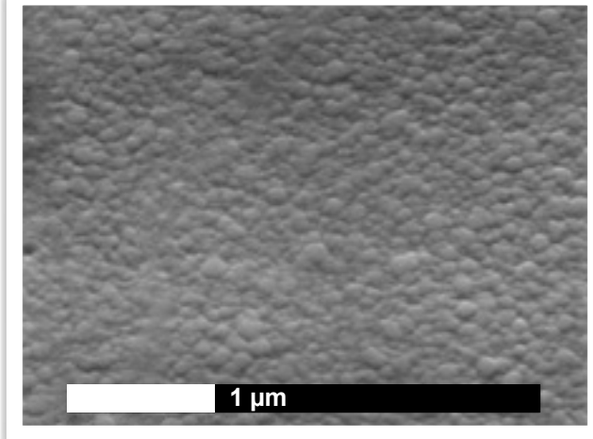
Something has to change on DLC surface!

Investigating surface morphology

AC5
0 cycles

R_a = 2.7 nm
R_q = 3.4 nm





AC5
500 cycles

R_a = 1.4 nm
R_q = 1.9 nm

μ ≃ 0.25

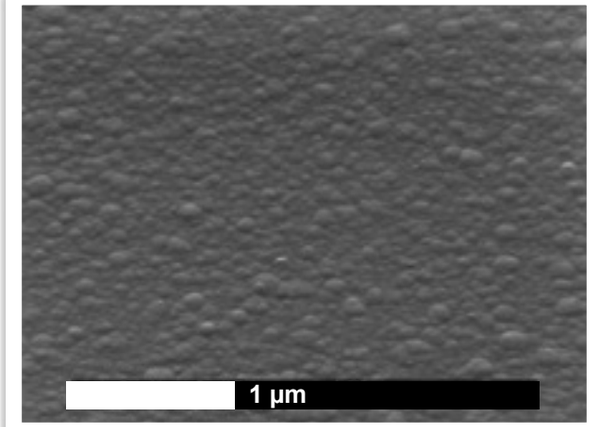
Before friction

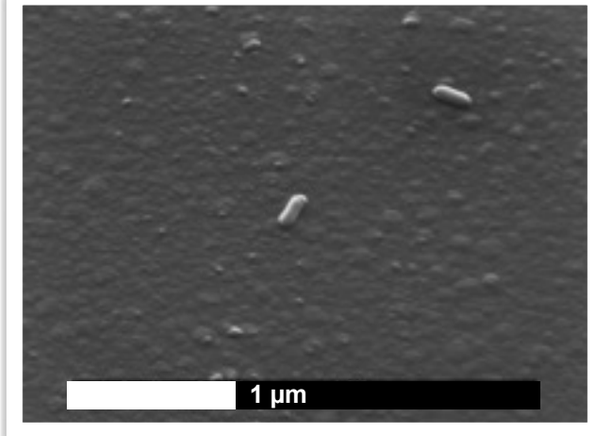
Superlow friction

μ ≃ 0.003

AC8
0 cycles

R_a = 1.8 nm
R_q = 2.4 nm





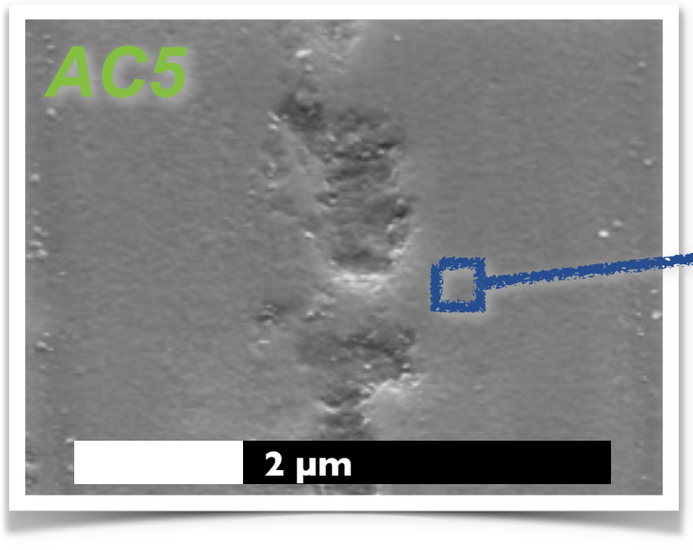
AC8
80 cycles

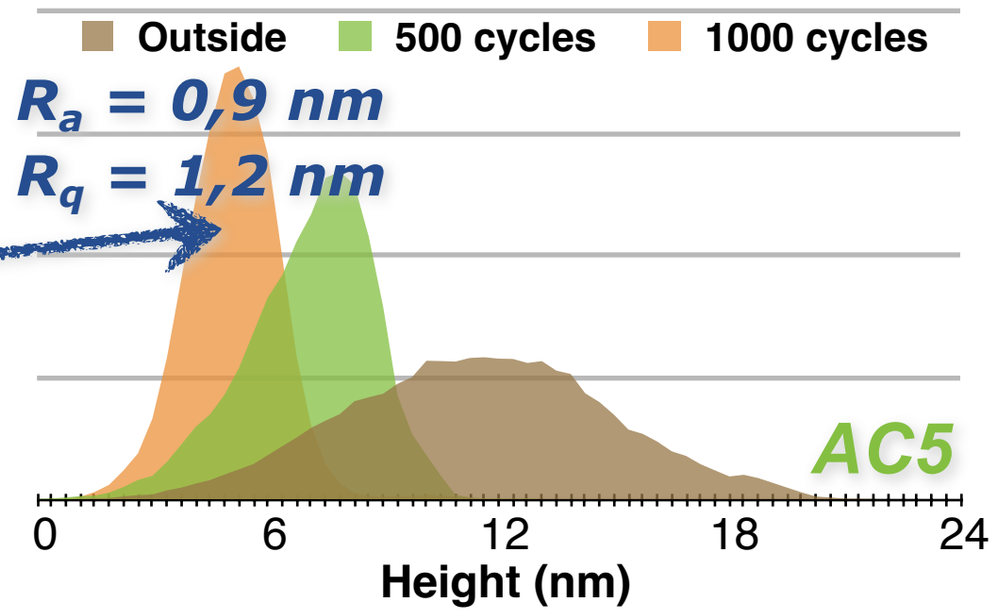
R_a = 1.3 nm
R_q = 1.6 nm

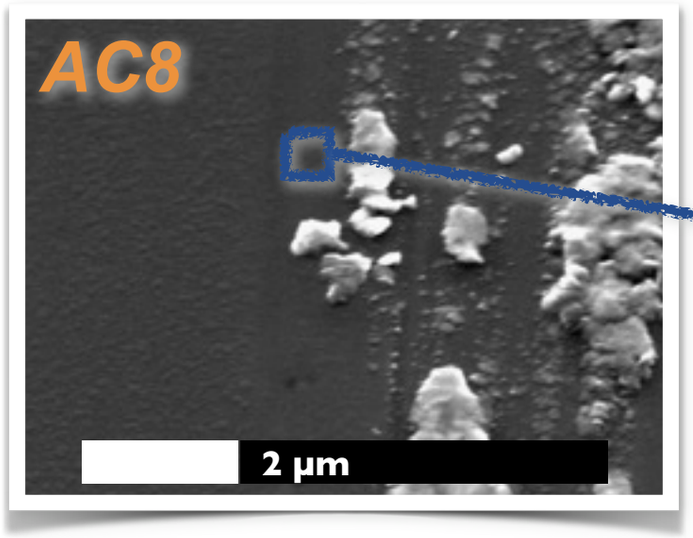
- Topography observed by SEM and measured by AFM
- Both samples exhibit **roughness at nanoscale**
- Partial wear of asperities is necessary to reach superlow friction
- Wear of **AC8** asperities seems faster than **AC5**

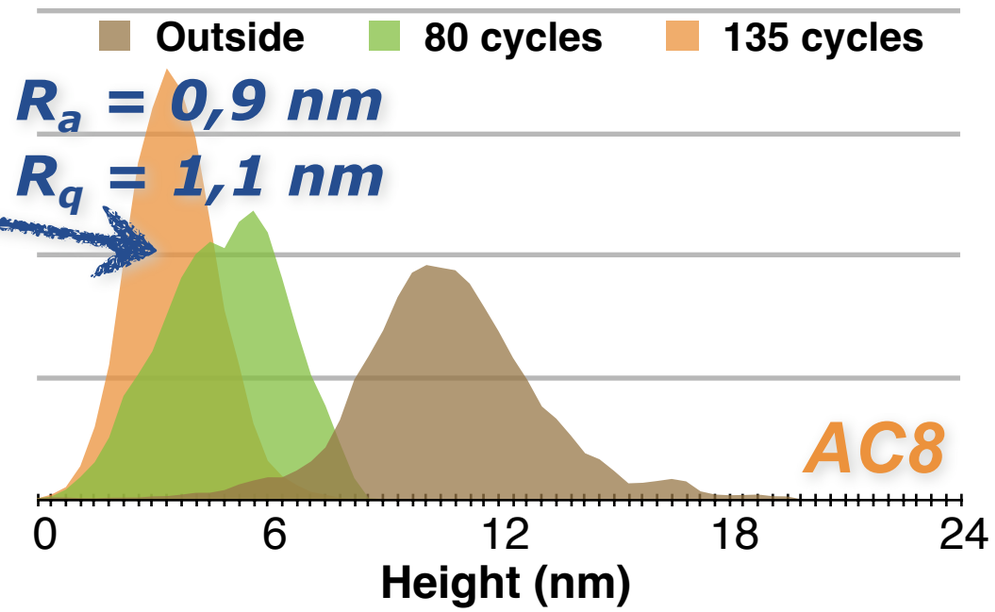
Surface smoothening & adhesion

What happens near the high friction areas?









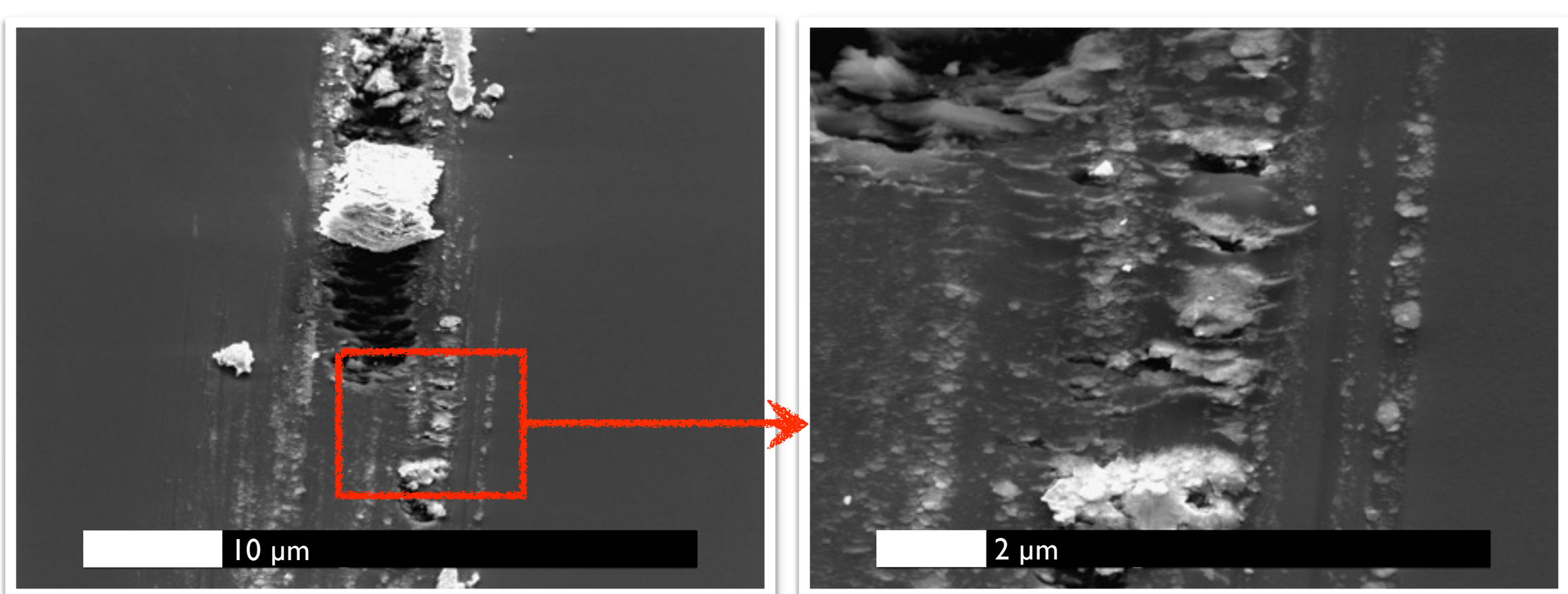
Smoothening of nanoscale roughness leads to ***large adhesive phenomena***

Why such different friction evolution between these two coatings?

Consequences of adhesion

SEM / EDX observations of wear tracks on the AC8 flat:

- *Iron is transferred to the DLC surface (in high friction zones)*
- *Some cracks can be found in the DLC around transferred iron particles*
- *Deep grooves are then formed from these “adhesive junctions”*
- ***Adhesion is clearly controlling the loss of superlow friction for AC8***

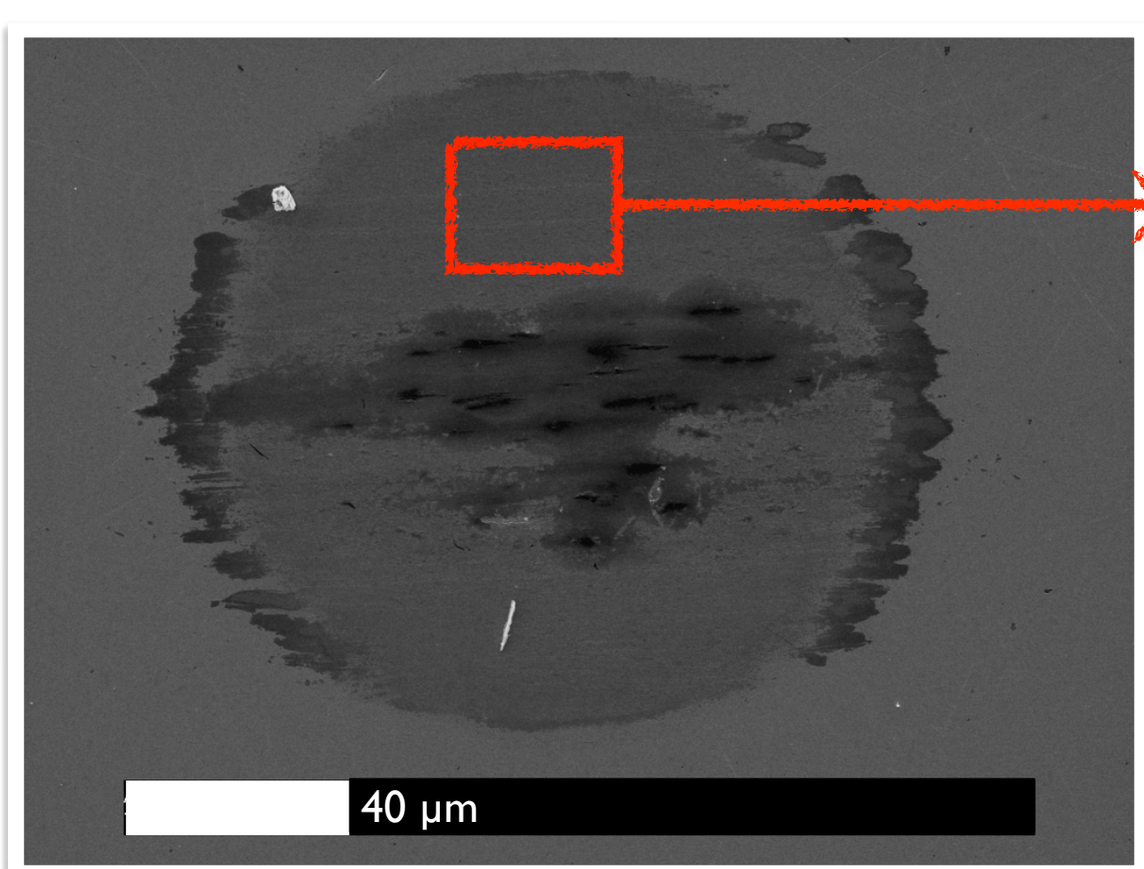


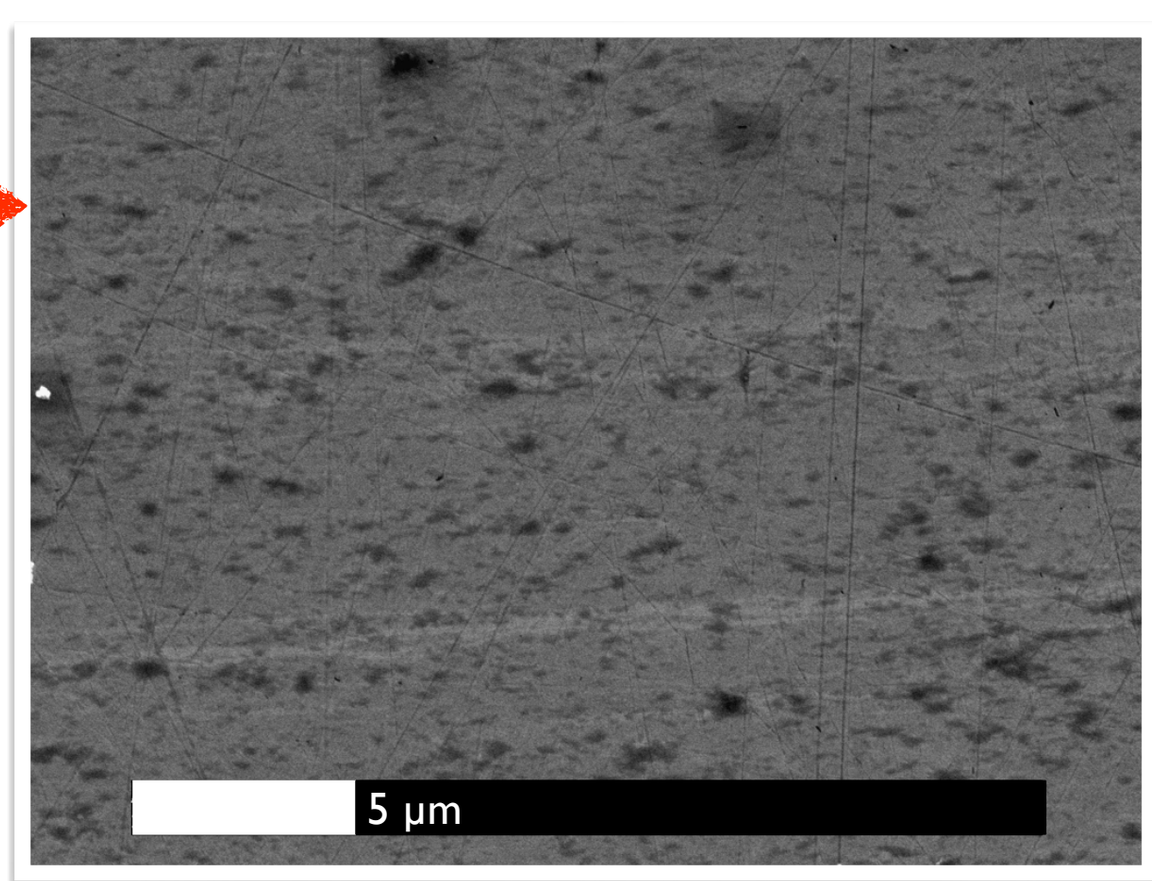
AC8 - 34 at.% H

Consequences of adhesion

SEM / EDX observations of tribofilm on counterface of AC5:

- *Tribofilm doesn't appear to be continuous!*
- *Many "dots" of carbon-based materials are covering the steel surface*
- *Much thicker tribofilm is found in high friction areas*
- ***Growth of tribofilm results from the release of adhesive junctions***

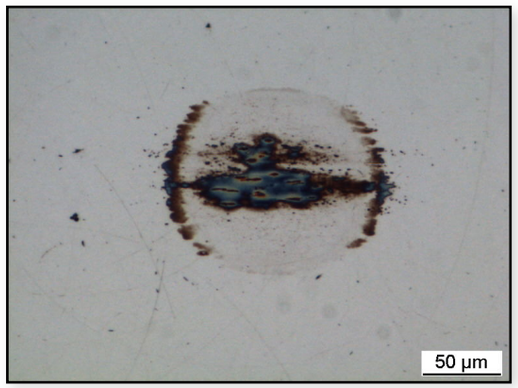




AC5 - 40 at.% H

Key-role of mechanical properties

Mechanical properties of DLC control how adhesive junctions will break :



SOFTER AC5 :

H = 7.5 GPa

Viscoplasticity: 6.8 10^{-2}

Adhesion

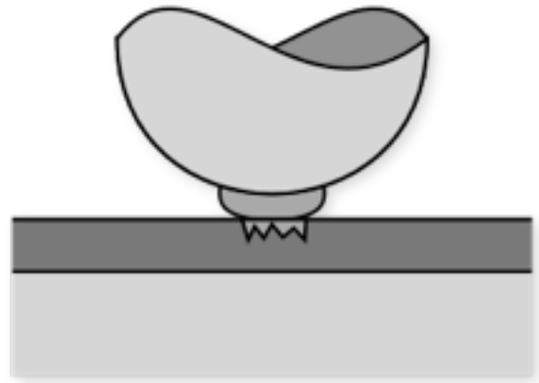
↓

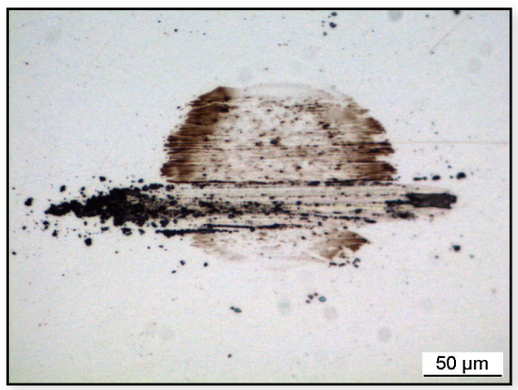
Transfer of DLC to steel pin

thicker tribofilm

↓

Preserving **low friction**





HARDER AC8 :

H = 10.5 GPa

Viscoplasticity: 1.4 10^{-2}

Adhesion

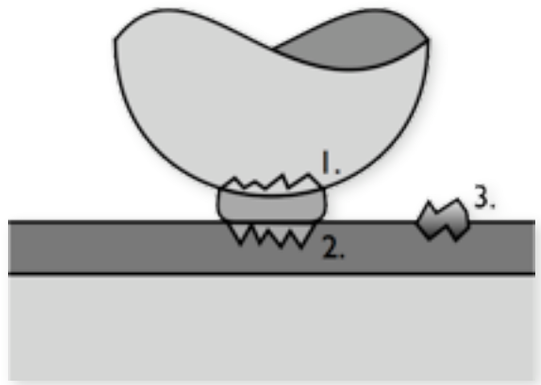
↓

Transfer of steel to DLC flat

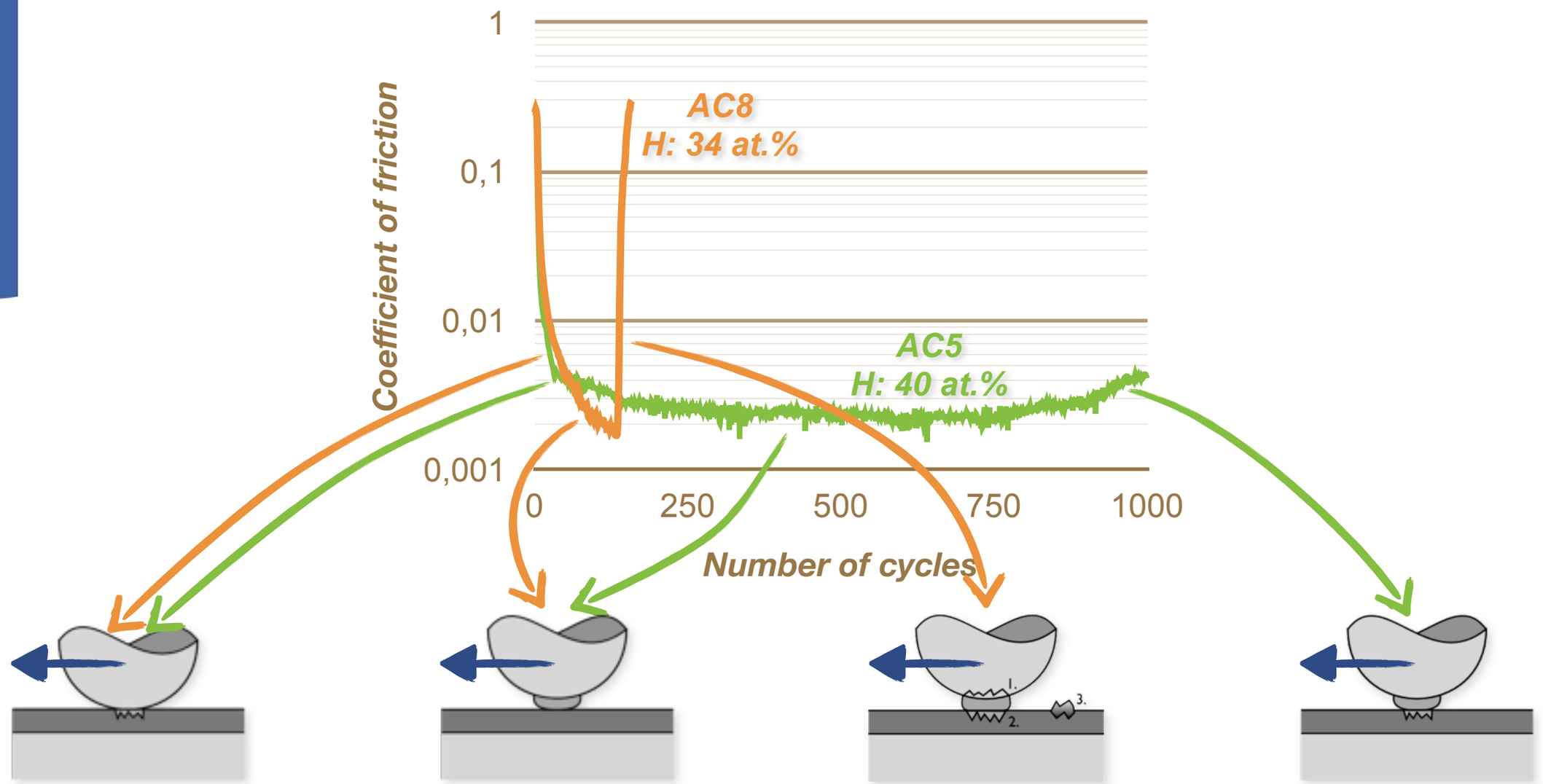
Tribofilm removal

↓

Leading to **high friction**



Solid lubrication process of DLC



Small adhesive junctions
⇒
Tribofilm build-up

Surface “passivation”, few small junctions
⇒
Interfilm sliding

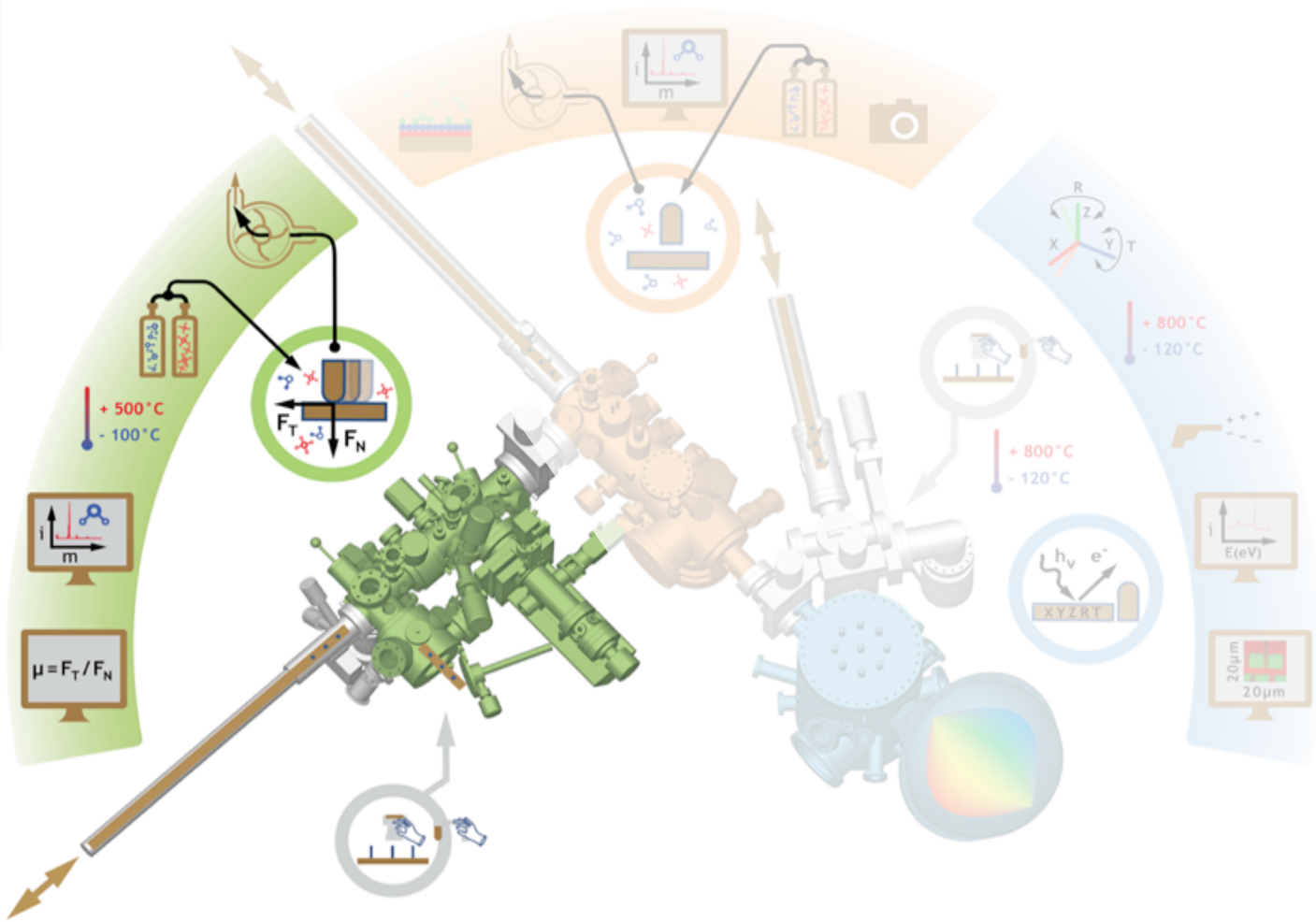
Large adhesive junctions
⇒
Tribofilm removal

Large adhesive junctions
⇒
Wear of DLC

Solid lubrication processes of Diamond-Like Carbon

- Introduction to DLC coatings
- Role of surface chemistry
- Role of surface topography
- **Interactions with environment**
- Discussion & summary

Environment-controlled experiments on SiO_x-DLC



Si wafer coated with a-C:H:Si:O

C: 57±3 at.% H: 34±3 at.%
Si: 6±1 at.% O: 3±1 at.%

Fraction of sp^2-bonded C:
54±2% *(NEXAFS)*

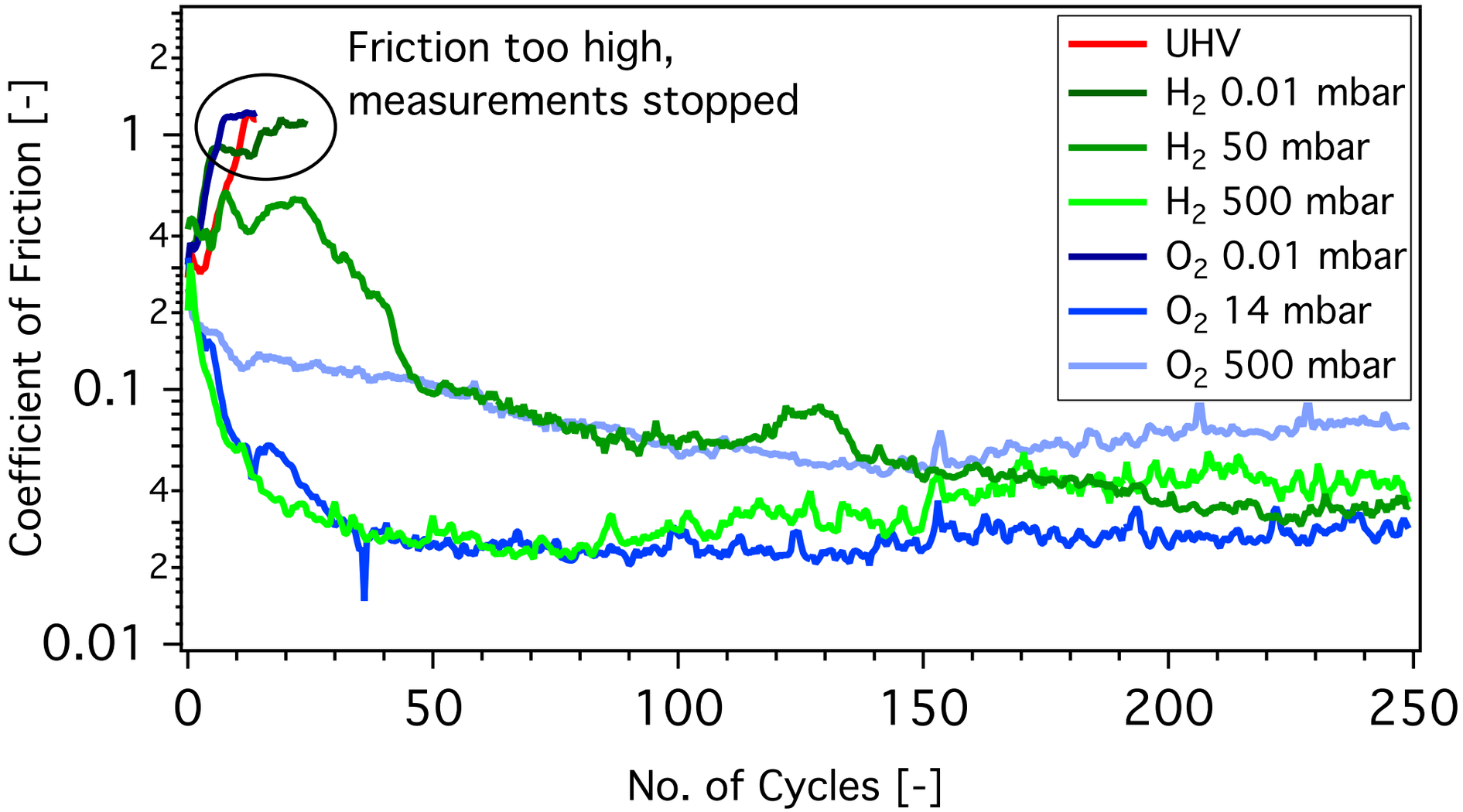
Thickness: 1.9±0.1 µm
Roughness (rms): 1.4±0.1 nm
(over 5x5µm²)
H = 10 GPa – E* = 140 GPa

Experimental conditions

Materials: ***Steel pin, Si-coated flat***
Experiments under O_2:
0.01 mbar up to 1000 mbar
Experiments under H_2:
0.01 mbar up to 2000 mbar

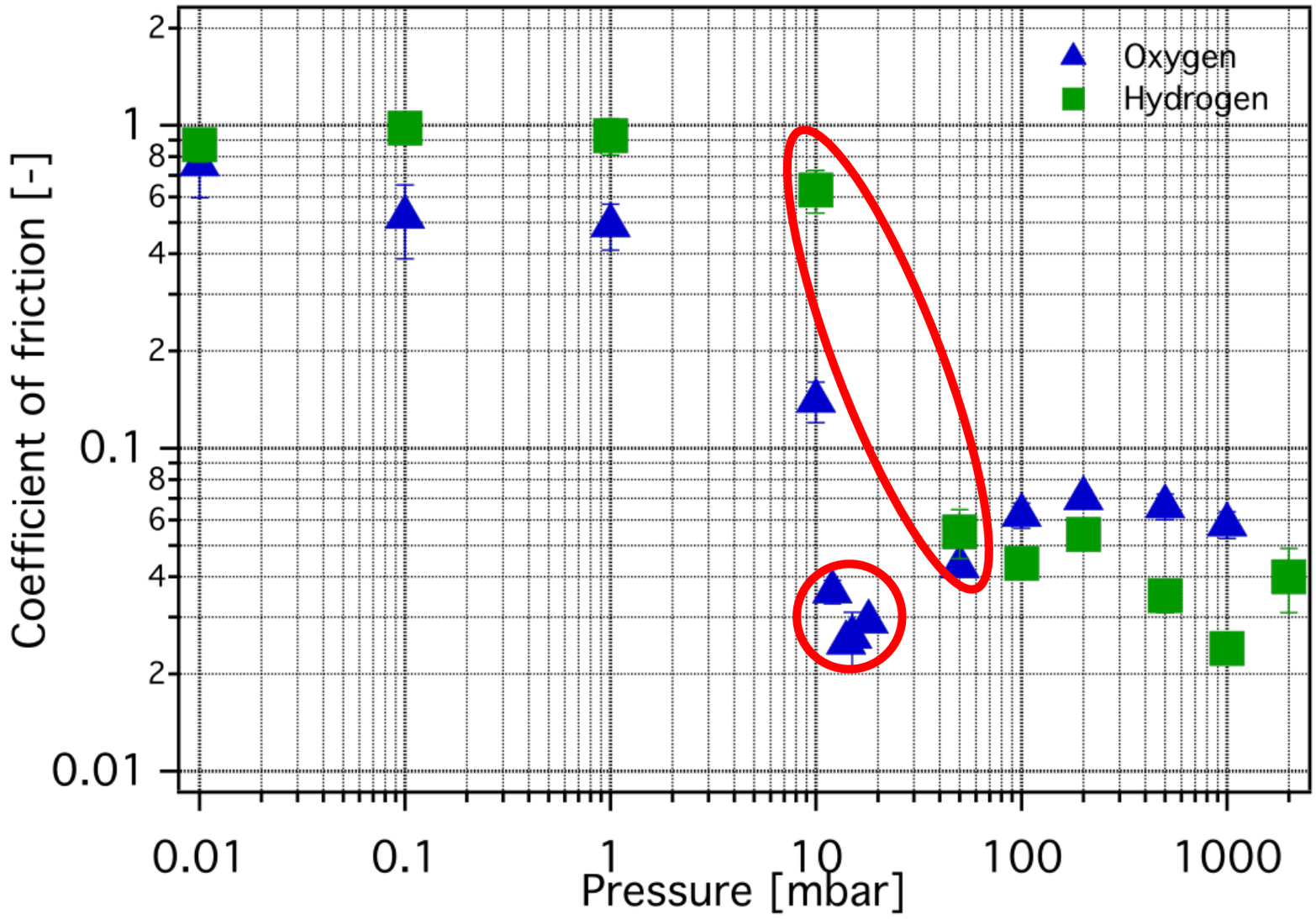
Pin diameter:	8 mm
Sliding Speed:	0.5 mm/s
Applied load:	3 N (≈ 430 MPa)
Track's length:	2 mm

Friction evolution in H_2 & O_2



- HV and low gas pressure: ***very high friction***
- With higher pressures of O_2 or H_2: ***lower friction***
- Computing an average coefficient of friction

Threshold in gas pressure to achieve low friction



- Clear **threshold** between high and low friction
- At least 14 mBar of O_2 or 10 to 50 mBar of H_2 is required

Transfer phenomena triggered by gas pressure

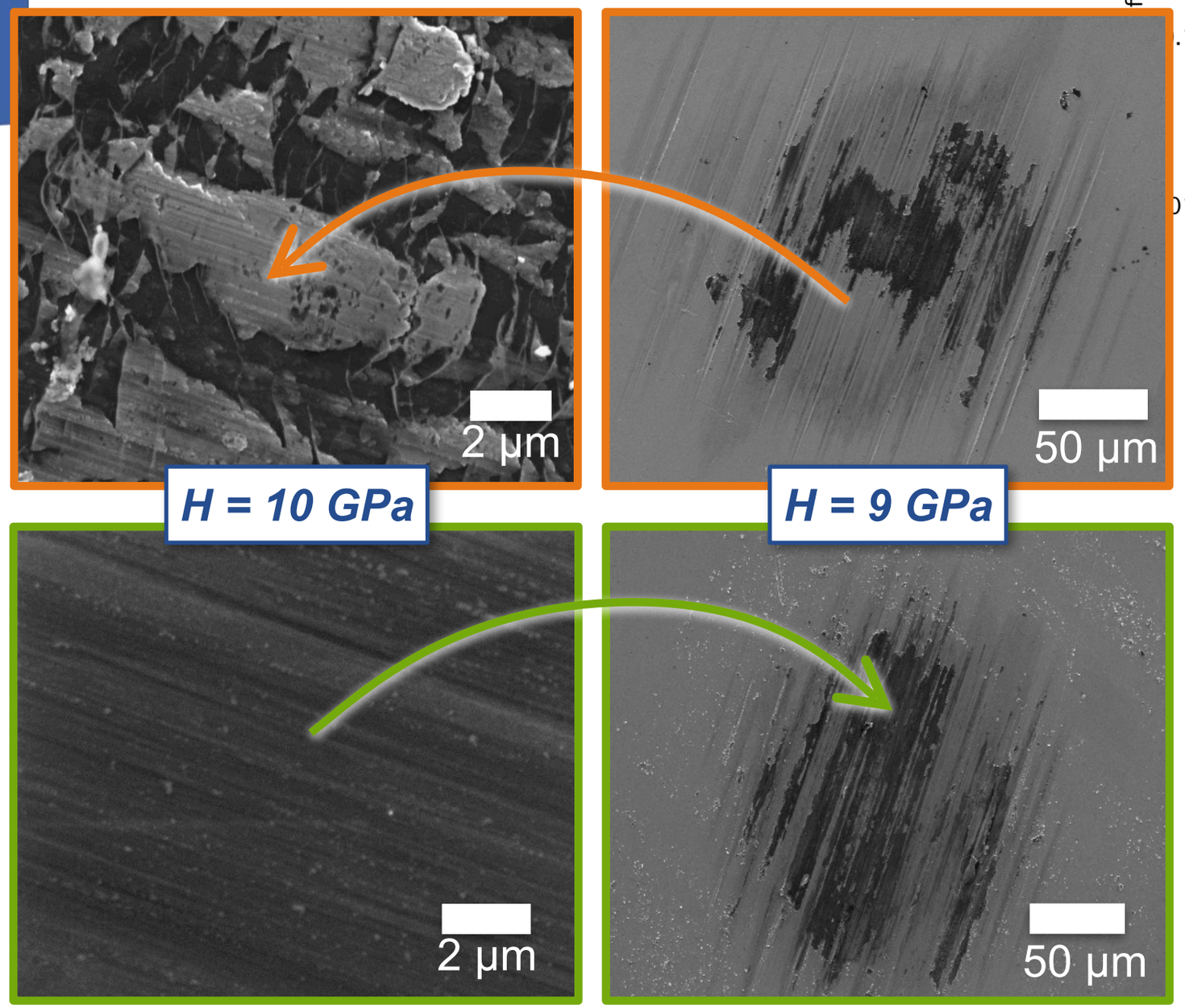
SEM observation of wear tracks

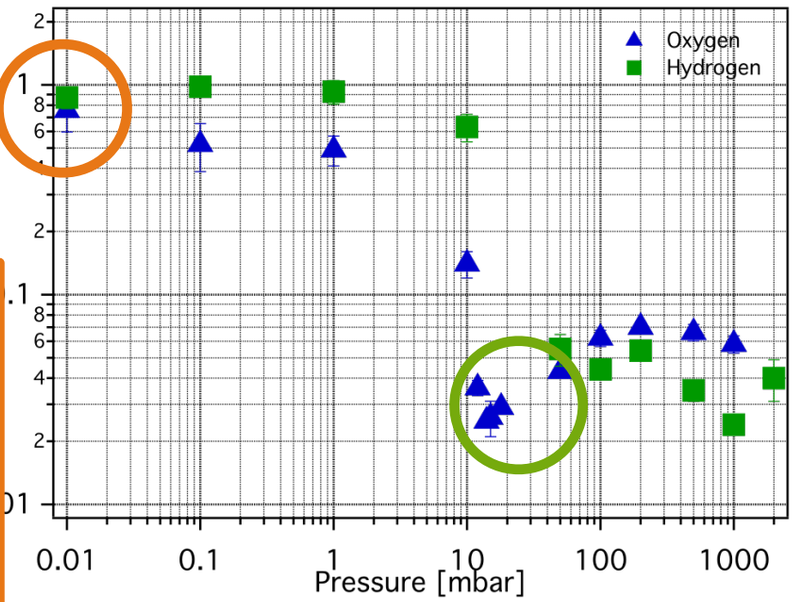
a-C:H:Si:O flat

Steel pin

HV and low pressure

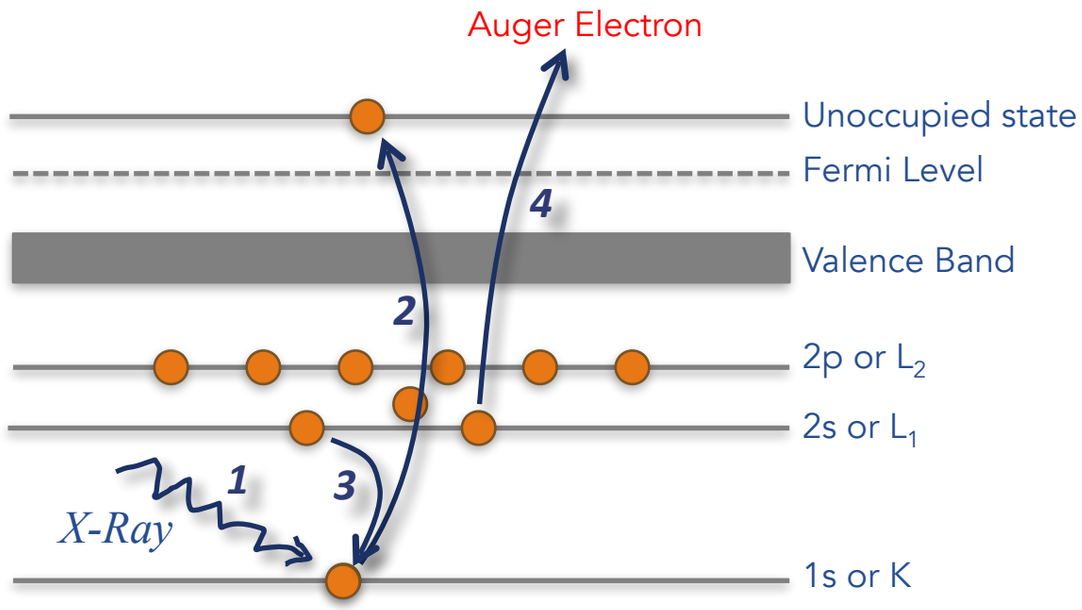
High pressure

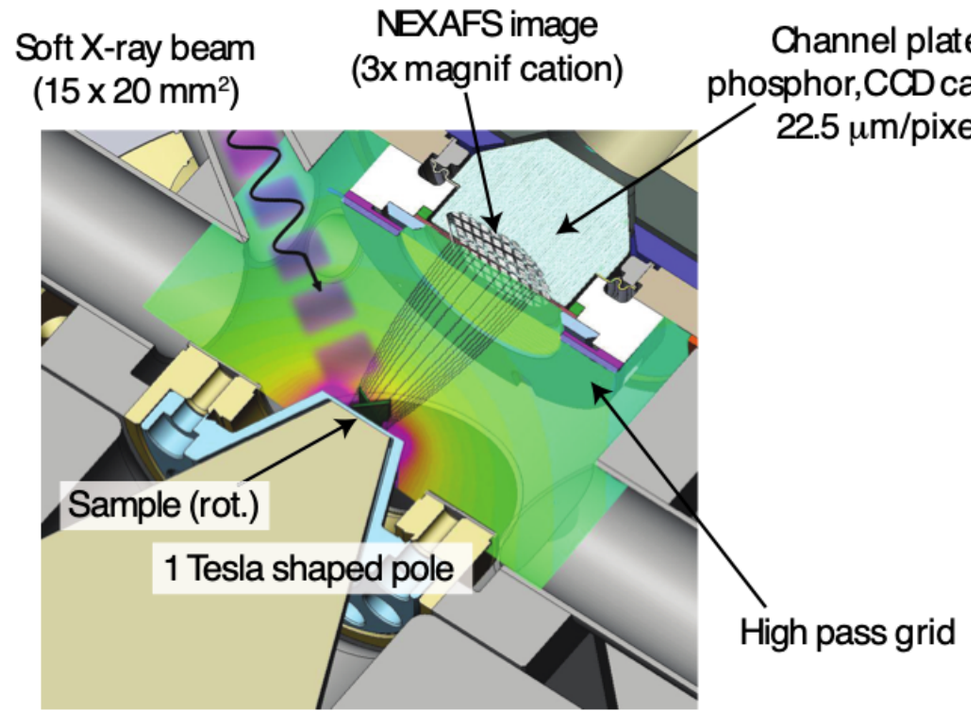




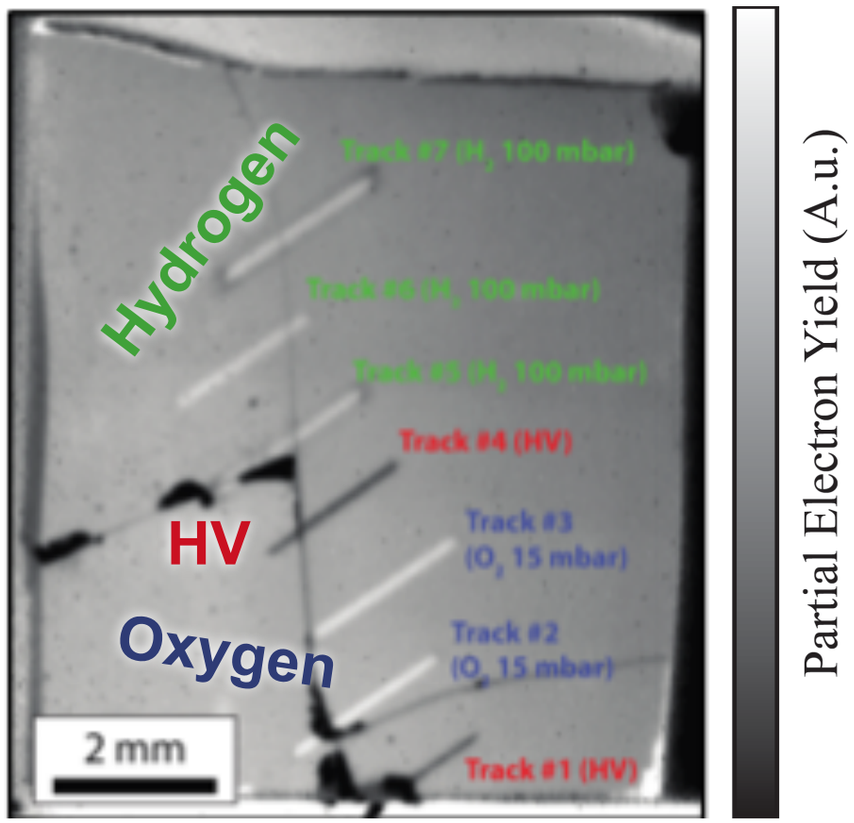
Breakage of adhesive junctions not only controlled by mechanical properties!

Near-edge X-ray absorption fine structure (NEXAFS)

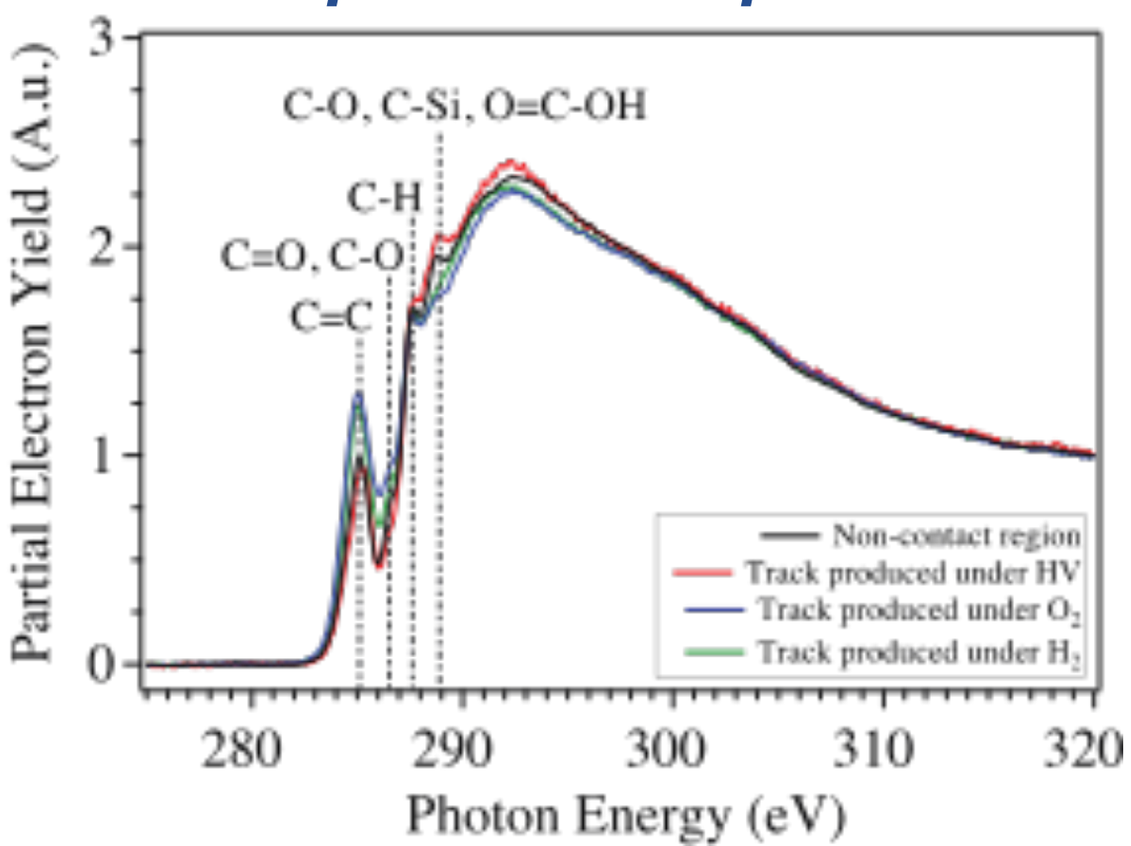




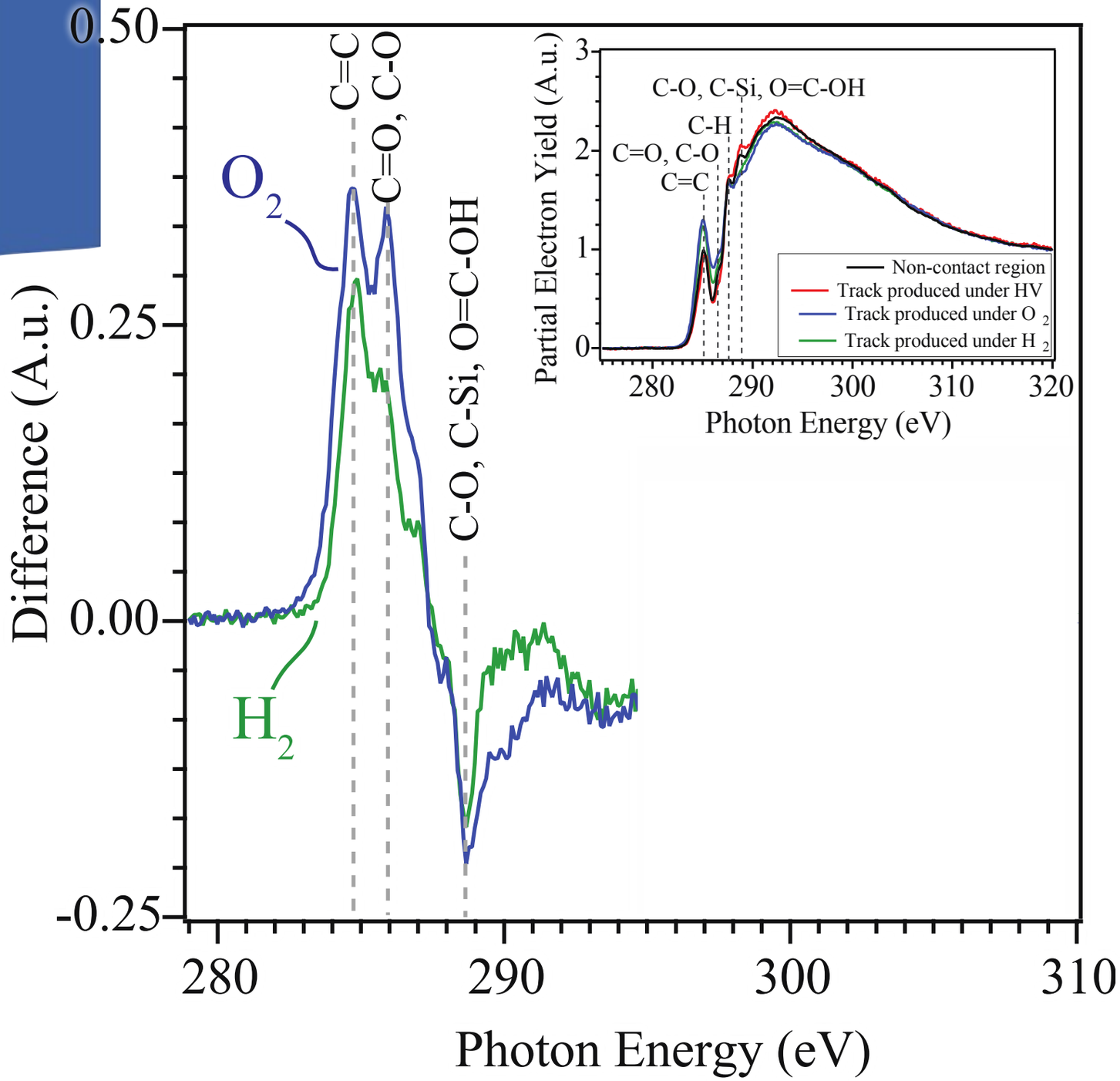
Acquisition of images…



Acquisition of spectra…

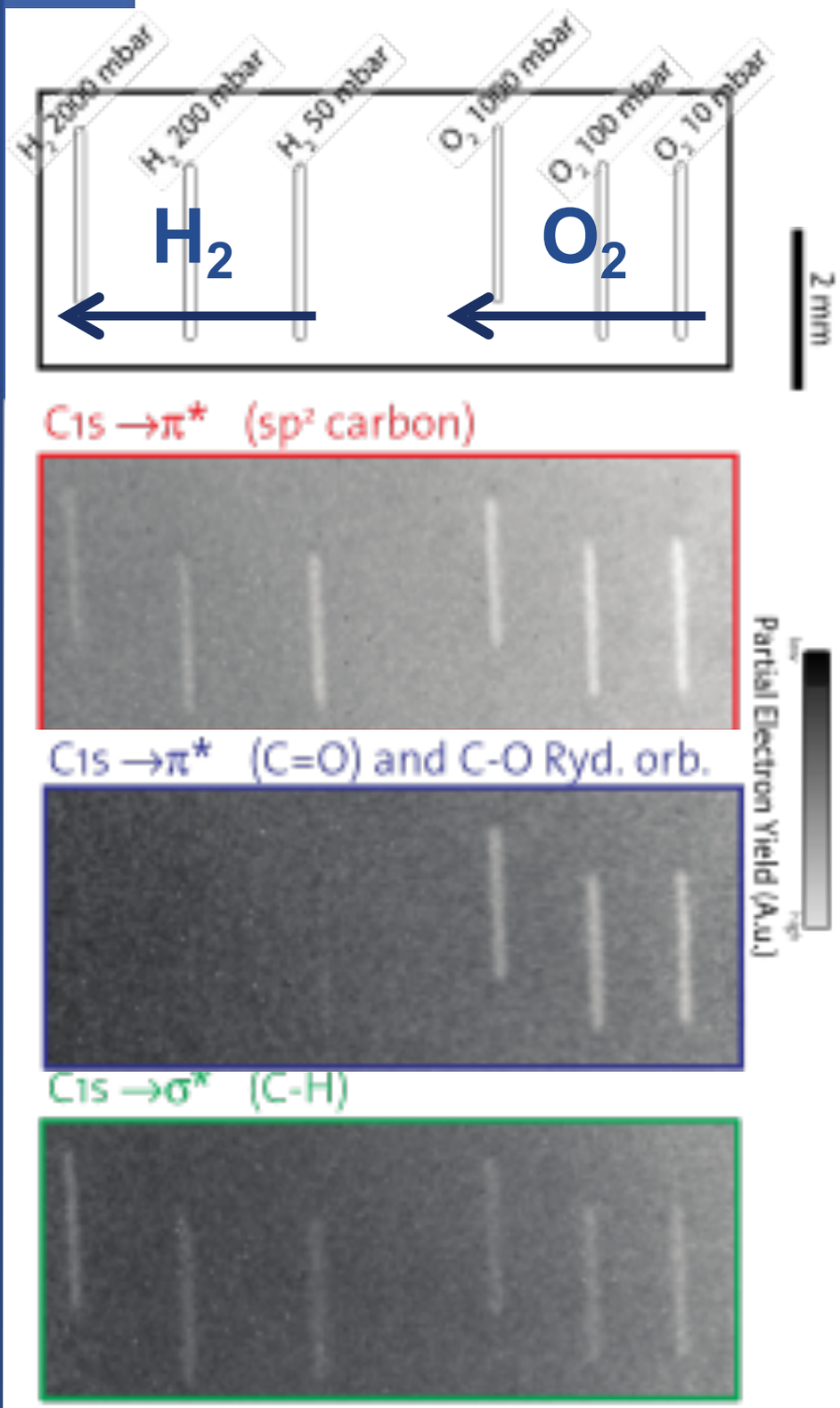


NEXAFS spectra on wear tracks

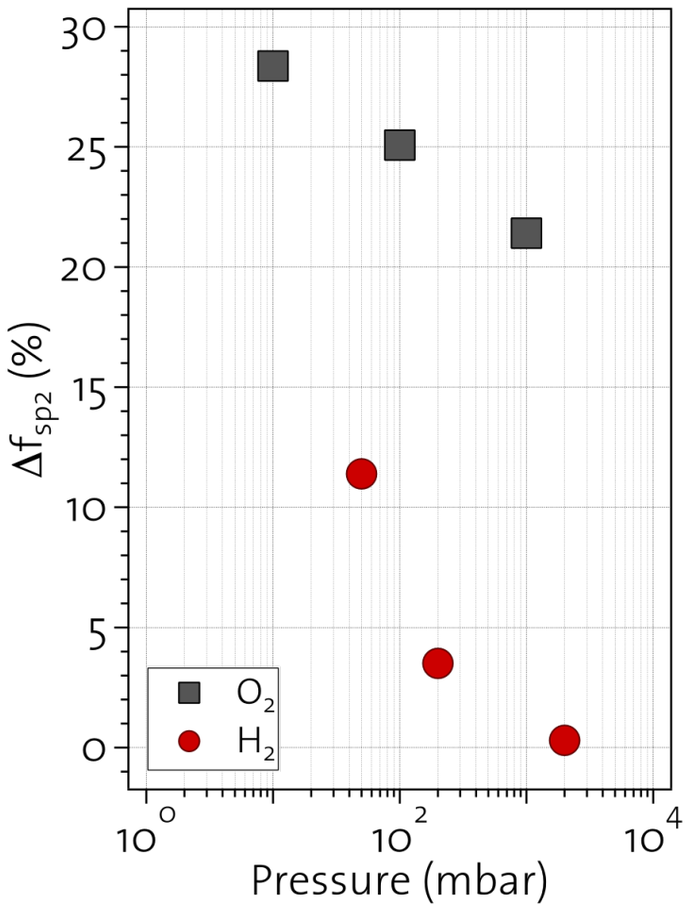


- Differential spectra by subtracting non-contact region spectrum (remove contribution of adventitious carbon)
- At 285 eV: strong sp^2 C increase
- Rehybridization due to C–C bond breaking?

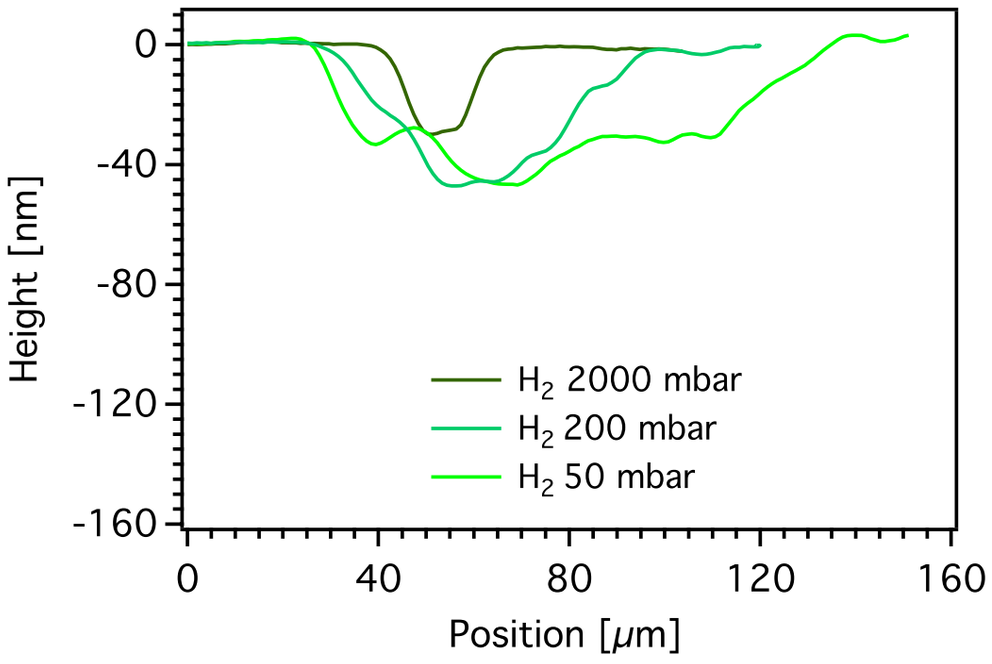
NEXAFS images of wear tracks

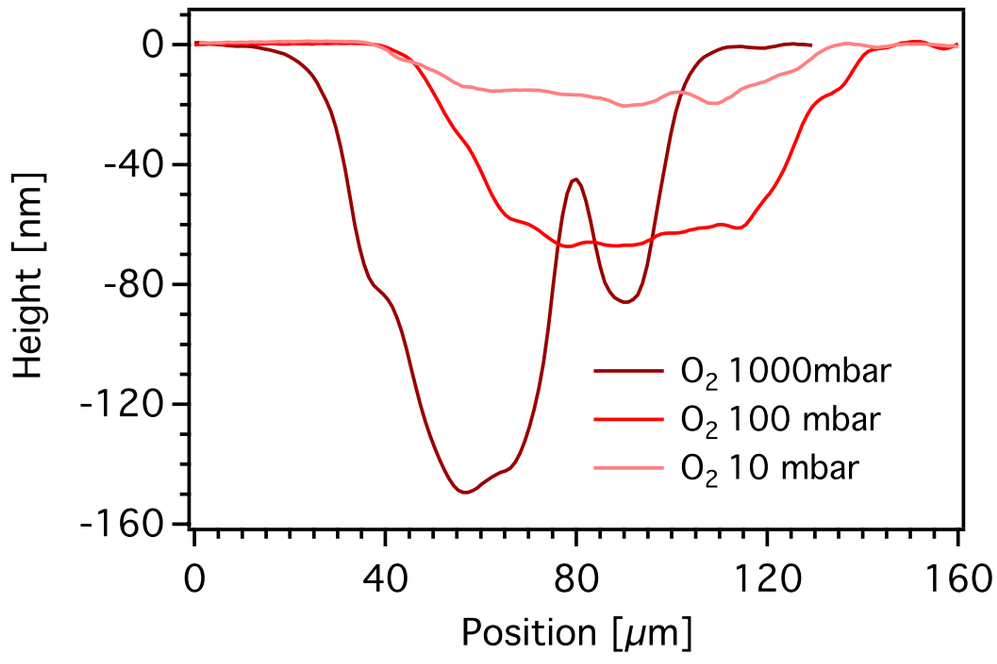


- Decreasing sp^2 fraction with increasing gas pressure for both H_2 and O_2
  ⇒ rehybridization decreases
- Increasing C–H bonds in H_2, but slightly decreasing C–O & C=O bonds in O_2
  ⇒ surface passivation or not?



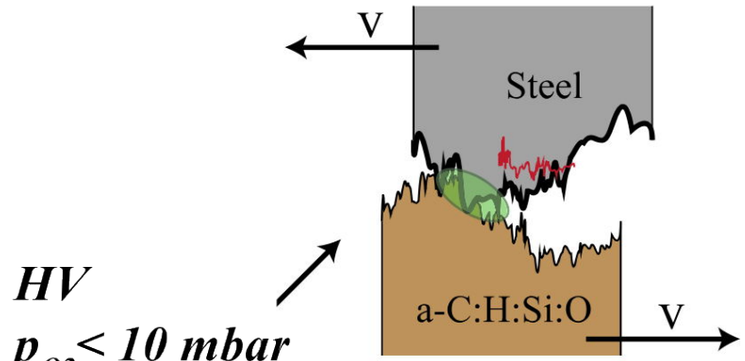
A look at environment effect on wear



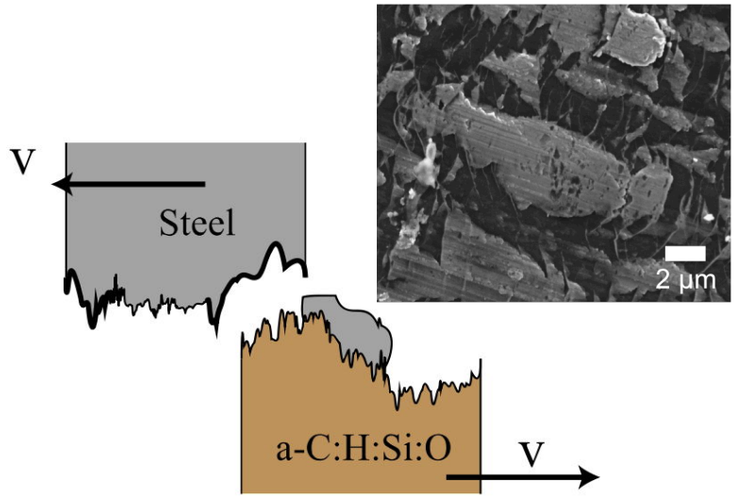


- Just above the threshold, **higher wear in H_2 than in O_2**
- When increasing gas pressure:
  - **Wear decreases in H_2**
    worn area becomes narrower than contact width!
  - **Wear increases in O2**
- Consistent with less C–C bond breaking in H_2, indeed!
- For O_2, are volatile species formed (CO, CO_2…)?
  Is there a gradient in sp^2 C near the surface?

A tentative tribological model for a-C:H:Si:O

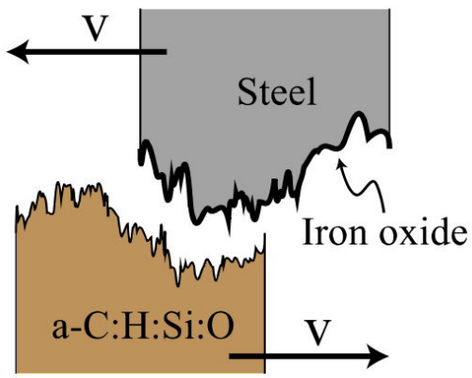


Stage 3.
Breakage adhesive junctions on steel side

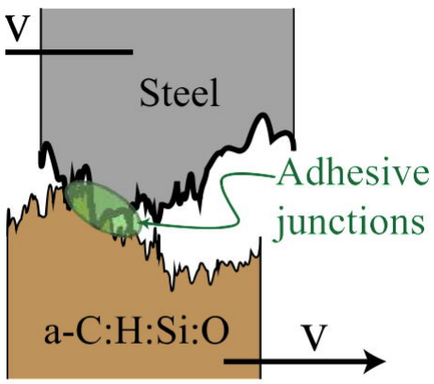


Stage 4.
Transfer from steel pin to a-C:H:Si:O

HV
$p_{O2} < 10$ *mbar*
$p_{H2} < 50$ *mbar*

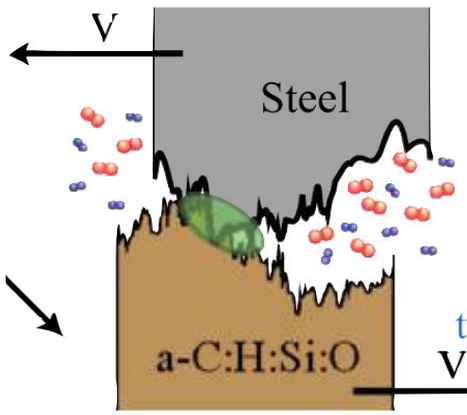


Stage 1.
Initial state

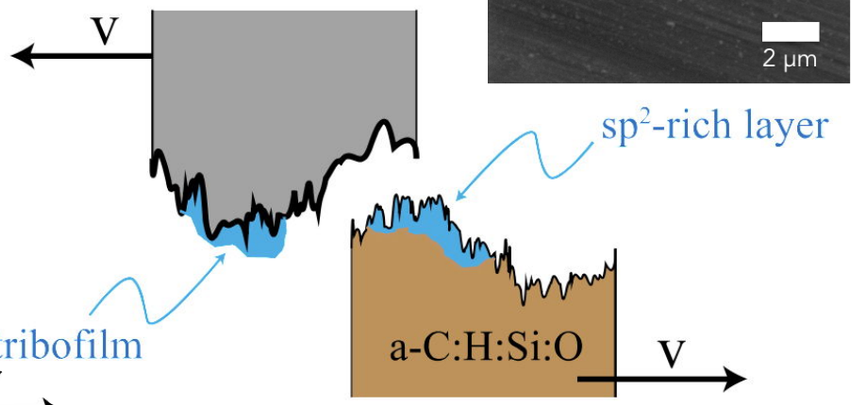


Stage 2.
Contact

$p_{O2} > 10$ *mbar*
$p_{H2} > 50$ *mbar*



Stage 3'.
Breakage adhesive junctions on a-C:H:Si:O side



Stage 4'.
Transfer from a-C:H:Si:O to steel pin

Koshigan et al., Carbon 2015

Solid lubrication processes of Diamond-Like Carbon

- Introduction to DLC coatings
- Role of surface chemistry
- Role of surface topography
- Interactions with environment
- **Discussion & summary**

Tribology of DLC: multi-physical aspects

Solid lubrication processes of DLC coatings seems to be controlled by:

- **Physical interactions**
  - Van der Waals forces (H-terminated surface)
  - Hydrogen bonding (with water vapor)
  - Overlap of π-orbitals (for low H coverage) or even metallic bonding?
  - Physisorption of environmental gases?
  - Contribution of electrostatic interactions?

- **Chemical reactions**
  - Covalent bonding between sliding surfaces
  - “Passivation” of dangling bonds by environmental gases
  - Controls the nature of sliding surfaces…

- **Surface mechanical behavior**
  - Controls the real area of contact
  - Controls the release of adhesive junctions
  - ***Not only hardness*** to be considered: viscoplasticity, fracture toughness…
  - Role of time-dependance of mechanical properties?
  - Importance of ductile/brittle transition?

Tribology of DLC: multi-scale aspects

Solid lubrication processes of DLC coatings take place at different scales:

- **At the scale of molecules…**
  - Adhesive phenomena are controlled by physical interactions & chemical reactions

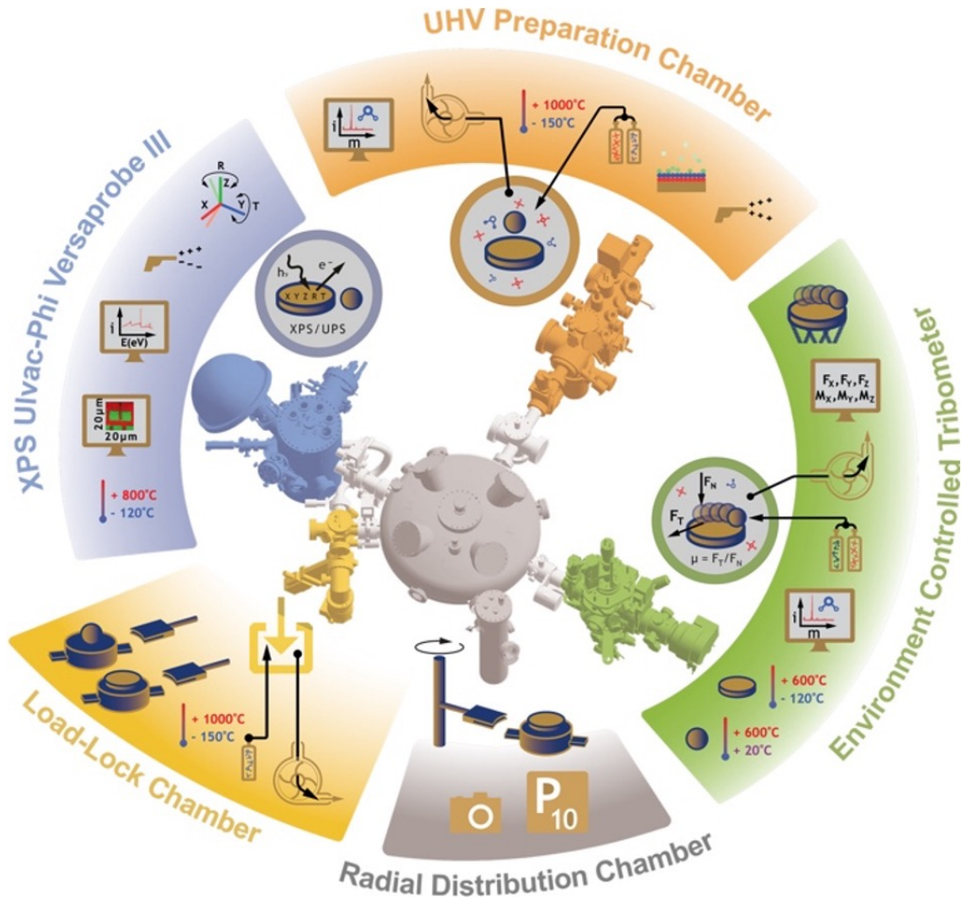
- **At the scale of asperities…**
  - Nanoscale surface topography controls the size of adhesive junctions
  - Mechanical behavior of asperities controls friction & wear

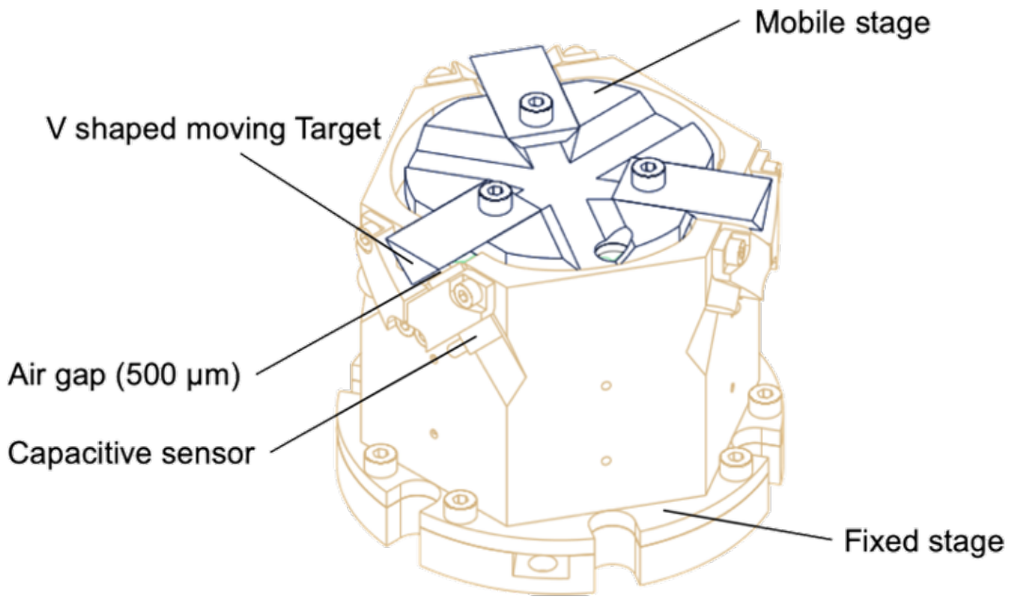
- **At the scale of the coating…**
  - Mechanical properties control the real area of contact
  - When large adhesive junctions are formed, they also control future evolution of the contact: where are these junctions released?

Few open questions on tribology of DLC…

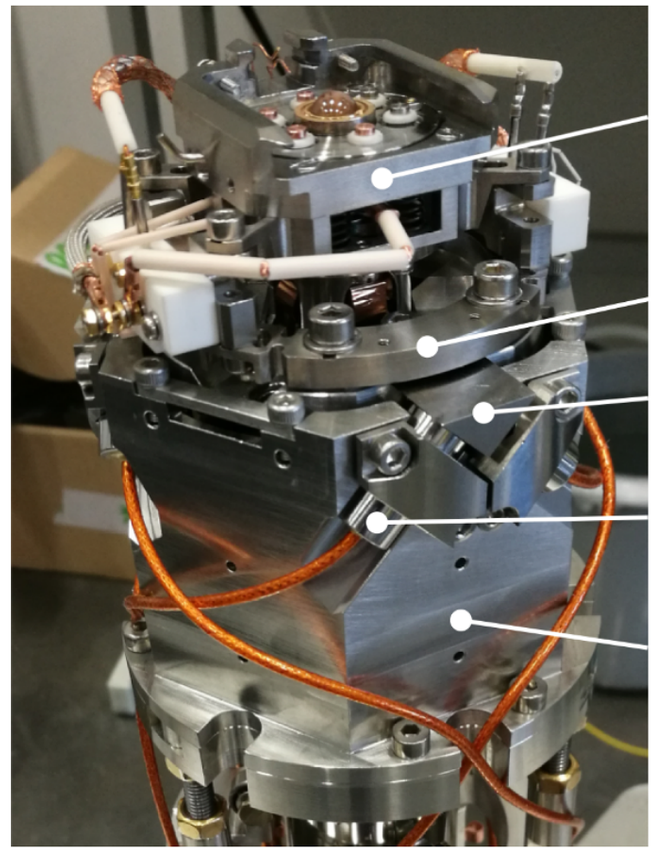
- ***How are nanoscale adhesive junctions released?***
  - Asperities on harder **AC8** are worn much quicker than on softer **AC5**!
  - Difference in “toughness” of the asperities?
  - “Healing phenomena” thanks to time-dependant mechanical properties?
- ***What is the frequency of contact for an asperity, and its average contact time/length?***
  - This might control passivation of dangling bonds as well as “viscous” recovery of asperities…
- ***What is the critical size of adhesive junctions to have surface damage and friction increase?***
  - Is there a size effect on some kind of “ductile/brittle” transition?
  - Small junction would have plastic behavior, while large ones would lead to cracking?
- ***What is the effect of environment on mechanical behavior of asperities?***
  - If asperities are sheared, bonds should break and may react with environmental gases…

One step further in friction studies

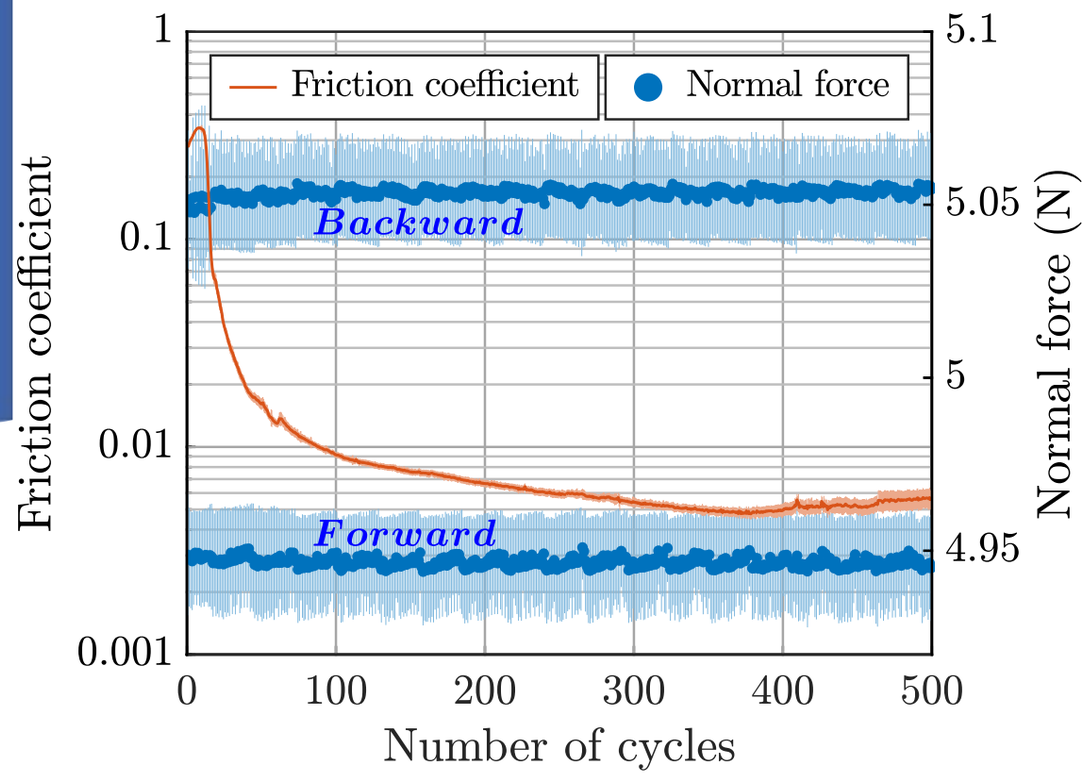


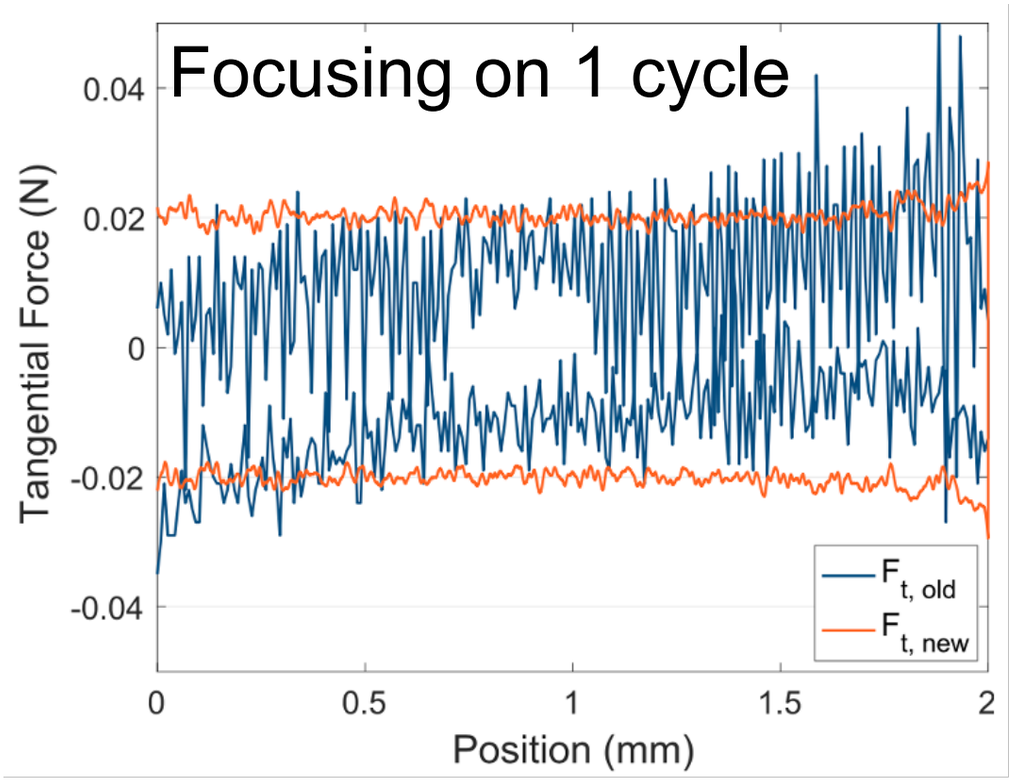


- **A new environment-controlled tribometer**
  - Based on a custom 6 axes sensor *(Forces: 1 mN up to 15 N)*
  - 4 motion axes: X, Y, Z, R_z
  - Environment: from 10^{-9} mBar to 1 atm
  - Temperature: -120 to 600°C



One step further in friction studies

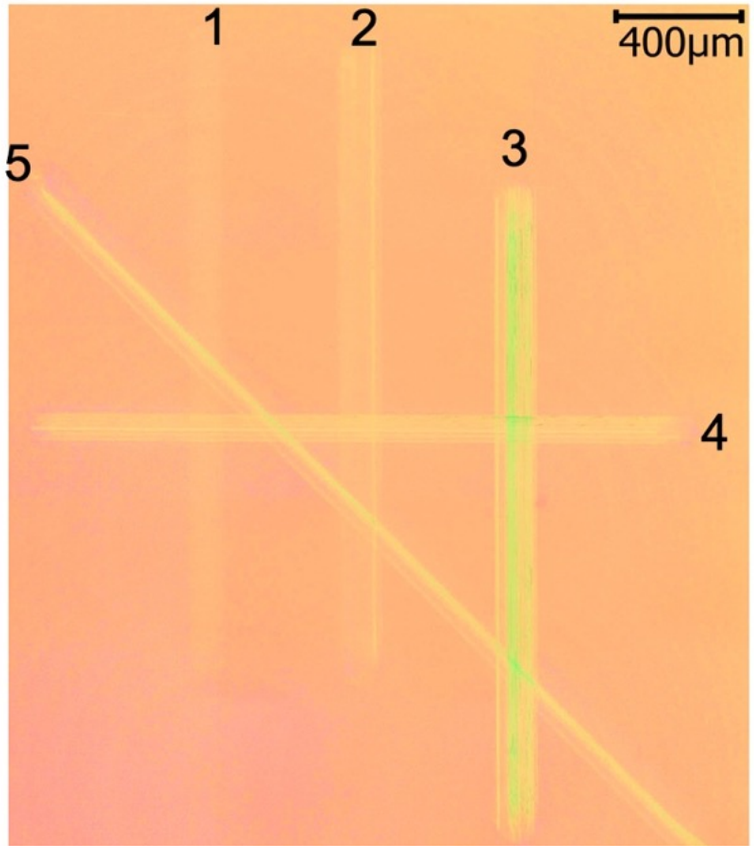




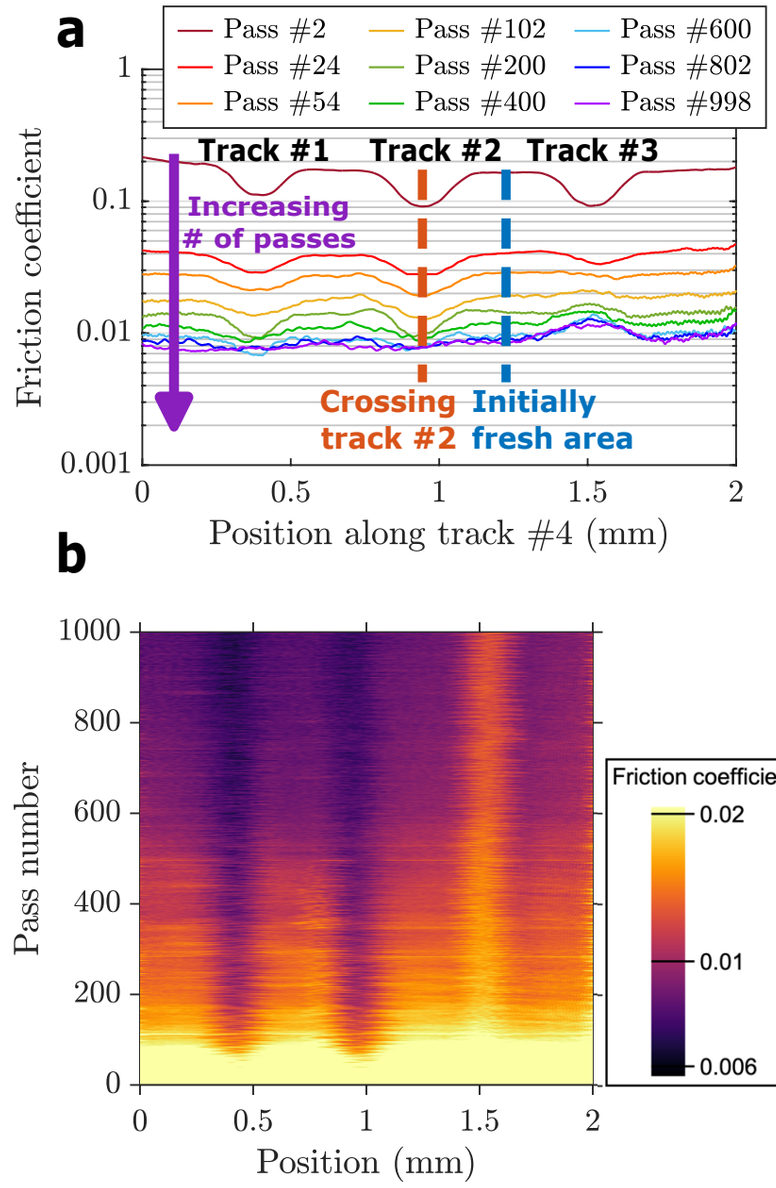
- Linear reciprocating ball-on-flat experiment
- Similar conditions as previous studies (5 N, 2 mm @ 1 mm/s…)
- Sample AC5 as in previous studies: similar results…
- **Drastic improvements in the signal/noise ratio!**

Rev. Sci. Instrum. 92, 085002 (2021)

One step further in friction studies



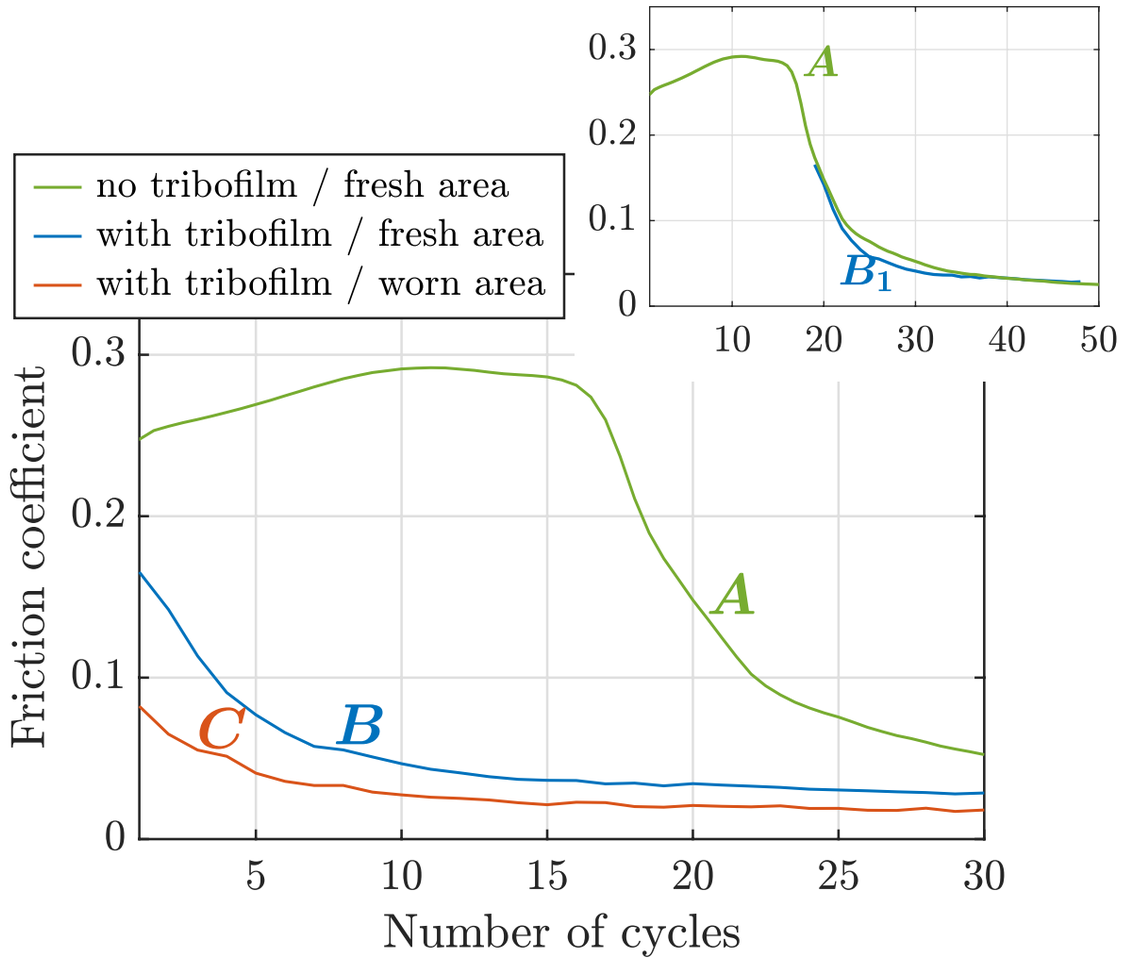
#	*Initial tribofilm*	*Load*	*Length*	*Cycles*	*Orientation*
1	No	3 N	2 mm	500	0°
2	Yes	5 N	2 mm	500	0°
3	Yes	5 N	2 mm	1000	0°
4	Yes	5 N	2 mm	500	90°
5	yes	5 N	3 mm	500	45°



- Crossing previous sliding tracks to probe surface modifications
- Significant friction decrease when crossing previous tracks
- It confirms that changes on the flat are necessary, friction decrease is not only due to tribofilm build-up

A. Normant & al., Tribology Online (2023) accepted

One step further in friction studies



A : Friction on fresh area without previous tribofilm

B : Friction on fresh area with pre-existing tribofilm

C : Crossing of previous tracks with pre-existing tribofilm

- Pre-existing tribofilm: *initial friction reduced by 32%*
- Previous wear on the flat: *initial friction further reduced by 36%*
- Drastic shortening of the transient regime leading to low friction

A. Normant & al., Tribology Online (2023) accepted

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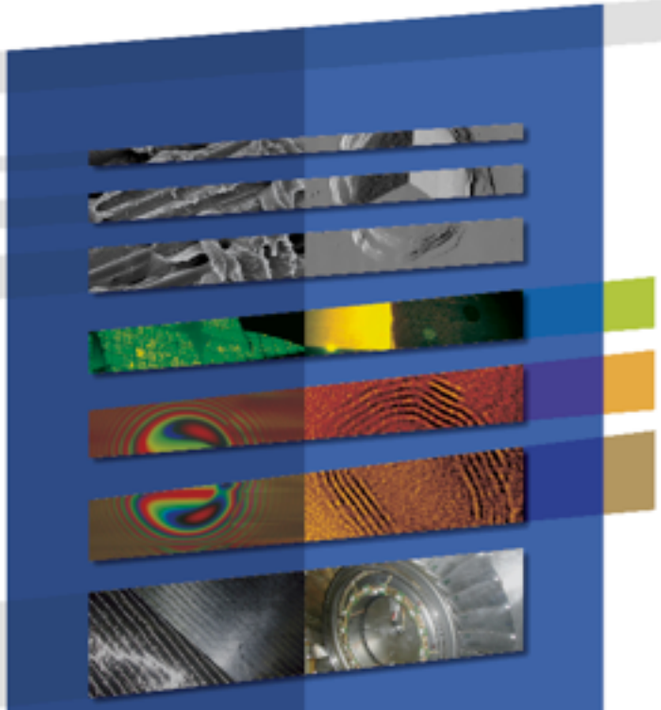

Thank you for your attention!

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