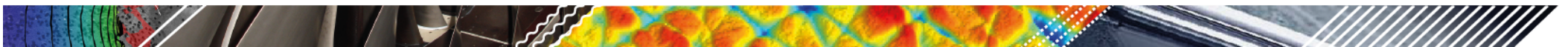


# ***Surfaces & Friction***

***Julien Fontaine***

*CNRS Research Scientist  
LTDS, Ecole Centrale de Lyon, France*



## ▶ **Tribology:**

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

*The key of most ancient techniques of mankind  
(stone tools, fire, wheel...)*

*Yet a very recent science: « Tribology » invented in 1966...*

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

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

## ▶ 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?

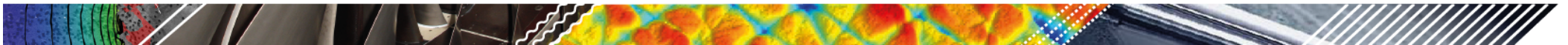
## ▶ Case-study

- ▶ Solid lubrication processes of Diamond-Like Carbon

# *Surfaces & Friction*

## *Dealing with surfaces...*

### *Part 1*



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

*(Gott schuf das Volumen, der Teufel die Oberfläche)*

*Wolfgang Pauli*

***Surface = Interface between two phases  
(or between a phase and vacuum)***

- ▶ Surface = discontinuity of matter!
  
- ▶ We need to describe 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)

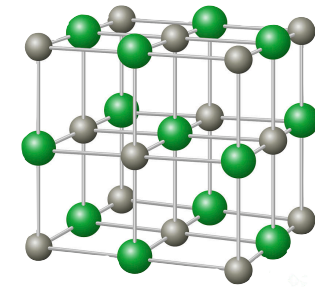
## ***Cohesion of solid: interactions between atoms or molecules***

*“Strong” interactions inside molecules or solids,  
“Weak” interactions between molecules or solids*

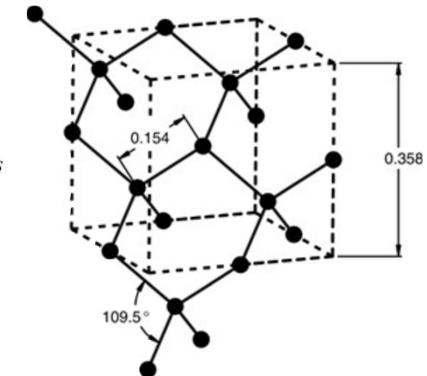
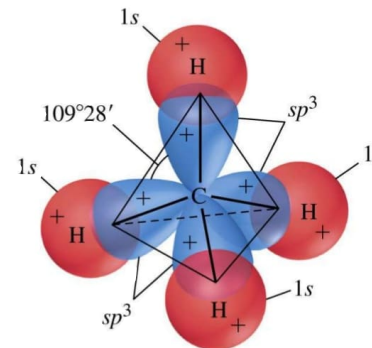
- ▶ **Chemical bonds:** electron charge distributions of the atoms (atomic orbitals) is completely changed
- ▶ **Physical “bonds”:** atoms/molecules remain distinct entities
- ▶ Yet physical binding may be quite strong as well...

- ▶ **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!)*



- ▶ **Covalent bond:** sharing of electrons between two atoms  
*Example: Methane CH<sub>4</sub> or Diamond*

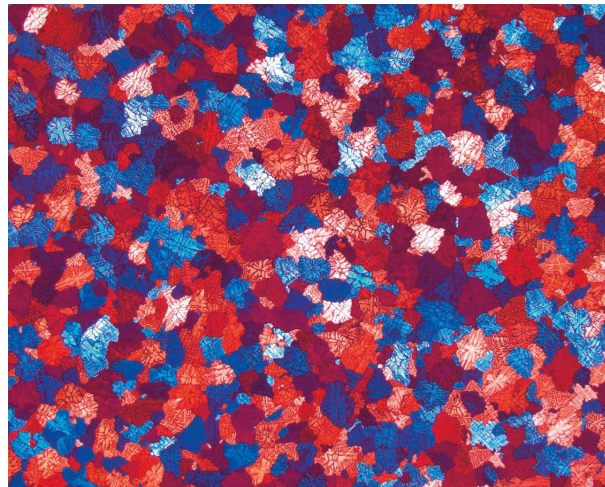


- ▶ **Metallic bonding:** bonding electrons are delocalised over a lattice of atoms, creating a « gas of electrons »  
The behaviour of this gas and its interactions with the lattice controls the metal properties

- ▶ **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...

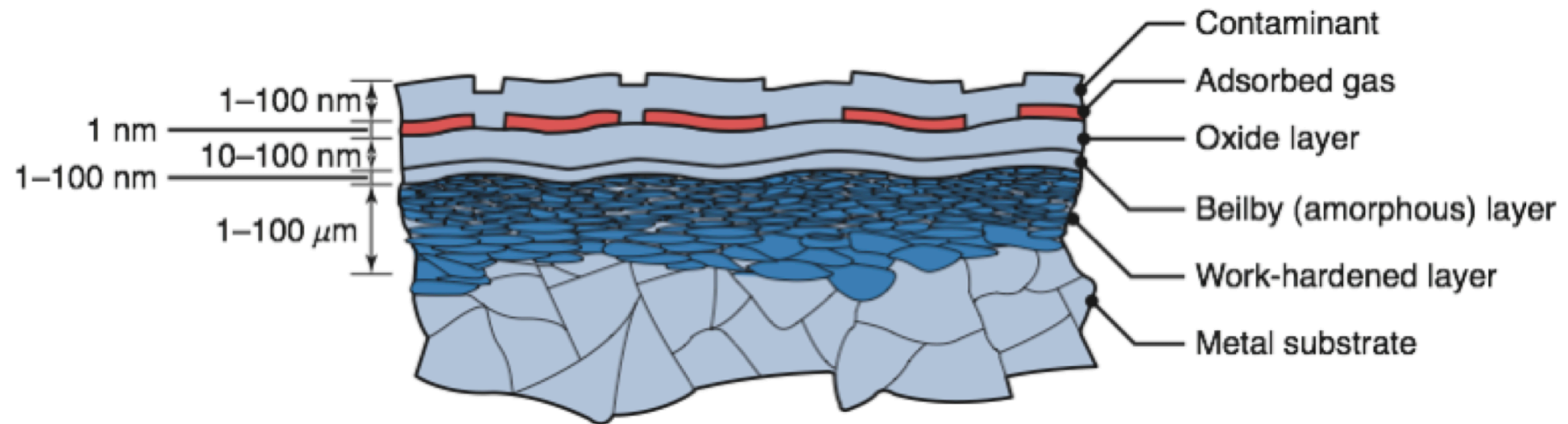
- ▶ Solids are the result of a fabrication process - **they can't be perfect!**
  
- ▶ Several types of defects can be found in crystalline materials:
  - ▶ *Point defects (0D)*: vacancies or impurities (solid solutions)
  - ▶ *Line defects (1D)*: dislocations
  - ▶ *Planar defects (2D)*: grain boundaries
  - ▶ *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)

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

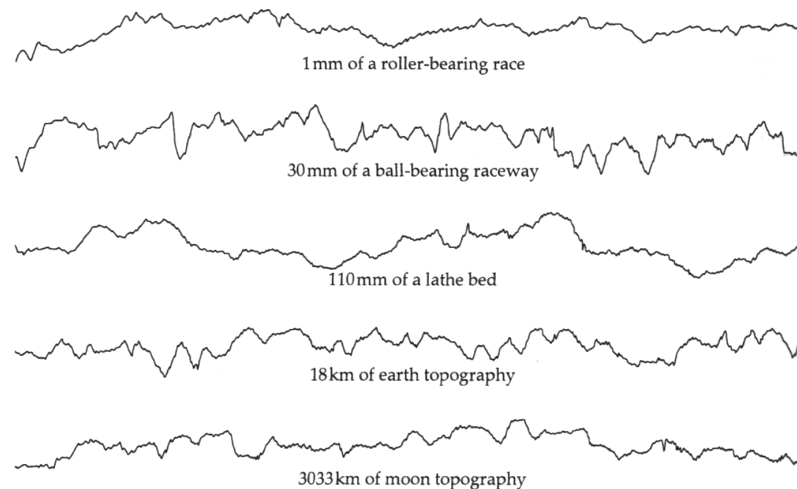
- ▶ Machining process or fabrication process lead to gradients in the microstructure: e.g. change in grain size close to the surface...
- ▶ Since the surface is an interface with the environment, chemical reactions may occur at the surface: oxide layers, adventitious carbon...



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

→ *there is always some roughness!*

- ▶ 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)

## ▶ Parameters describing the surface:

### ▶ Height characteristics

#### ▶ Arithmetical mean height

$$R_a = \frac{1}{L} \int_0^L |z| dx$$

#### ▶ Root mean square roughness

$$R_q = \sqrt{\frac{1}{L} \int_0^L z^2 dx}$$

#### ▶ Maximum peak to valley, skewness (asymmetry), kurtosis...

### ▶ Spatial characteristics (lateral)

#### ▶ Autocorrelation function, Power spectral density function...

### ▶ Multiscale characterisation

#### ▶ Fourier transformation, wavelet transformation...

- ▶ 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 Spectroscopy (SIMS), static (ToF-SIMS) or dynamic
  - ▶ X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES)
  - ▶ Electron Energy Loss Spectroscopy (EELS) in transmission or reflection
  - ▶ ...

- ▶ Surface energy corresponds to the **disruption of interatomic or intermolecular bonds** due to the surface creation
- ▶ Equivalence between **surface energy** (J/m<sup>2</sup>) and **surface tension** (N/m):  
*Increasing the size of a surface corresponds to the work of a force*

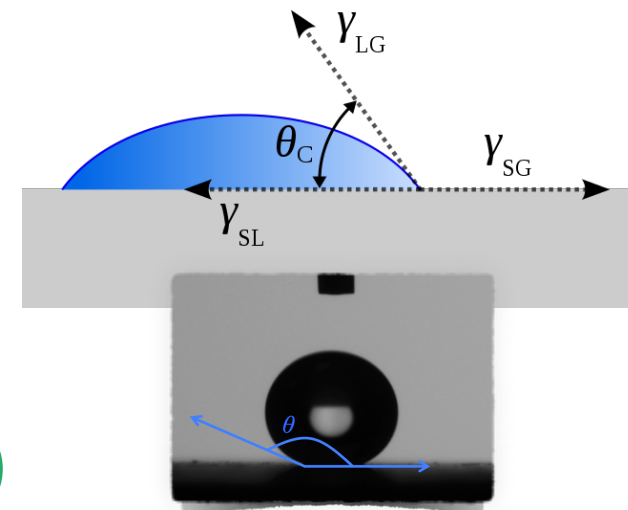
## ▶ **Measuring surface energy:**

### ▶ **Contact angle measurements**

- ▶ Liquid droplet on a surface

- ▶ Young's equation:  $\cos \theta_c = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$

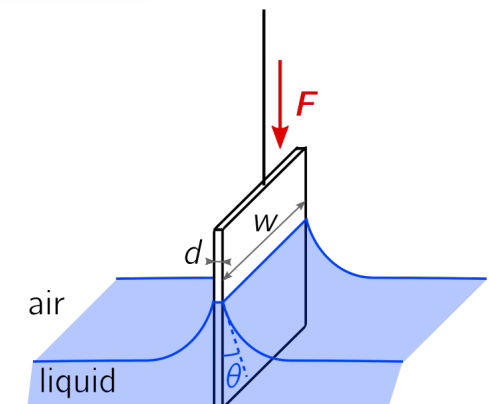
- ▶ Work of adhesion:  $W_{adh} = \gamma_{LG} (1 + \cos \theta_c)$



### ▶ **Surface tension measurements (Wilhelmy plate tensiometer)**

- ▶ Immersion of a plate with measurement of undergone force

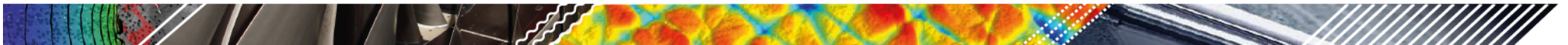
- ▶  $\gamma = \frac{F}{l \cos \theta}$ , where  $l$  is the perimeter



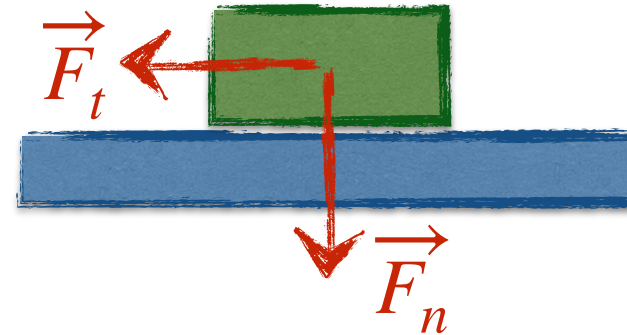
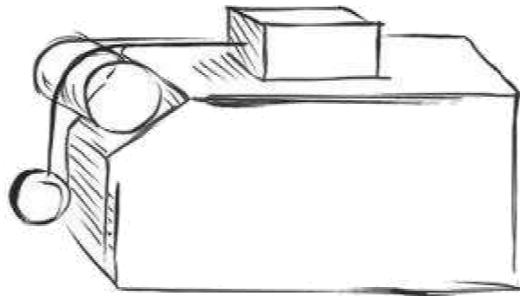
# *Surfaces & Friction*

## *Influence of surfaces on friction*

### *Part 2*



**Friction: the force resisting to relative motion between solids**



▶ **Early laws of dry friction** - Da Vinci, Amonton, Coulomb

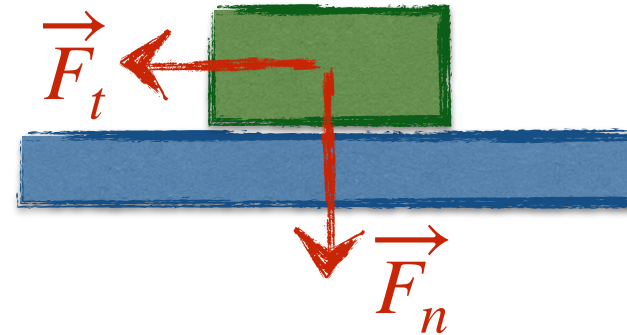
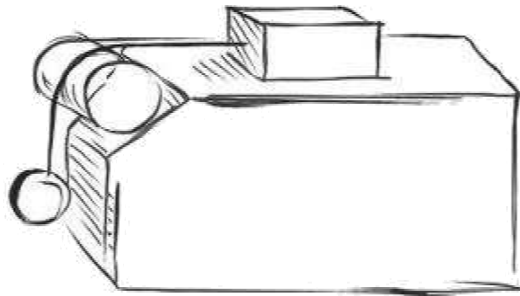
- ▶ *Friction force is proportional to load*
- ▶ *Friction force is independent of contact area*
- ▶ *Friction force is independent of sliding velocity*

▶ Definition of the **coefficient of friction**  $\mu$

*Ratio of the tangential force to the normal force:*

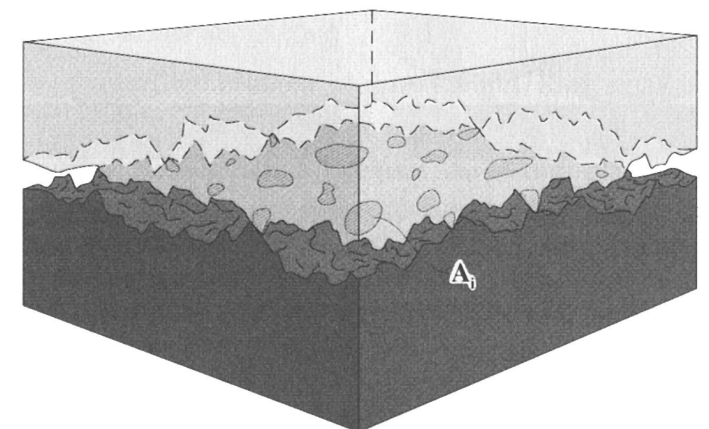
$$\mu = \frac{F_t}{F_n}$$

**Friction: the force resisting to relative motion between solids**

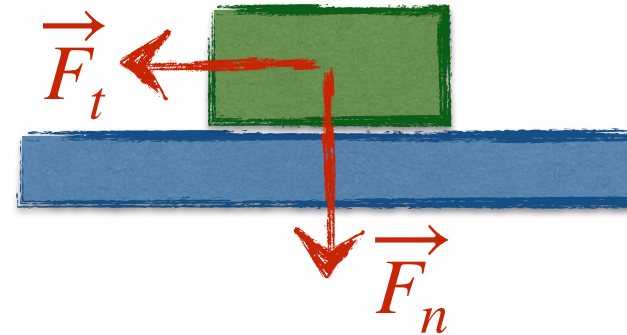
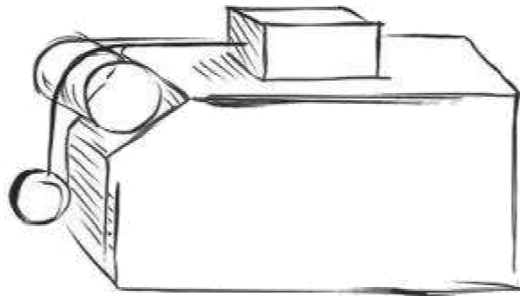


- ▶ **Early laws of dry friction** - Da Vinci, Amonton, Coulomb
  - ▶ *Friction force is proportional to load*
  - ▶ *Friction force is independent of contact area*
  - ▶ *Friction force is independent of sliding velocity*
  
- ▶ No effect of **apparent contact area!**  
*Due to roughness, only asperities are touching...*  
*Real vs. apparent contact area*

$$A_r \neq A_{app}$$



**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*  $\geq$  *Sliding friction* (or “kinetic” or “dynamic”)
  - Static friction: maximum friction force before sliding occurs*

*How to accommodate the difference  
in velocities of the contacting surfaces?*

*Where is shear occurring?*

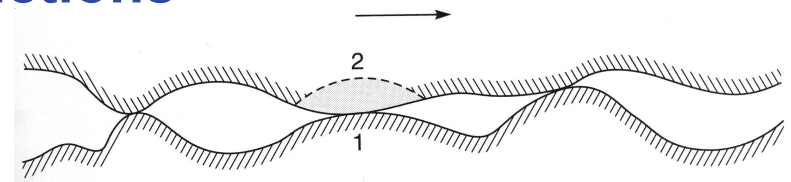
- ▶ **Lubrication with oils or liquids:** a fluid film separates the solids, allowing an easy shear of the sliding interface
  - ▶ **Hydrodynamic lubrication:** thickness of the fluid film is large compared to the surface roughness
  - ▶ **Elasto-hydrodynamic lubrication (EHD or EHL):** elastic deformation of solid surfaces due to high pressure, creating a load-bearing quasi-solid film
  - ▶ **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

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

- ▶ In case of seizure, breaking of **adhesive junctions**

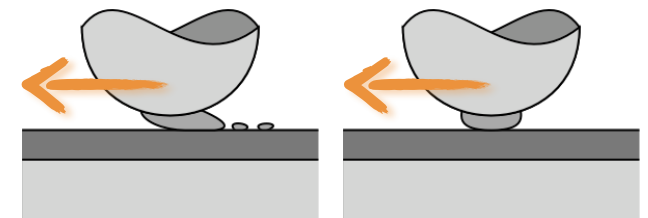
- ▶ at initial interface (1)

- ▶ inside the weakest material (2)  
(depending on hardness and brittleness)



- ▶ With solid lubricants, shearing of **interfacial films**:

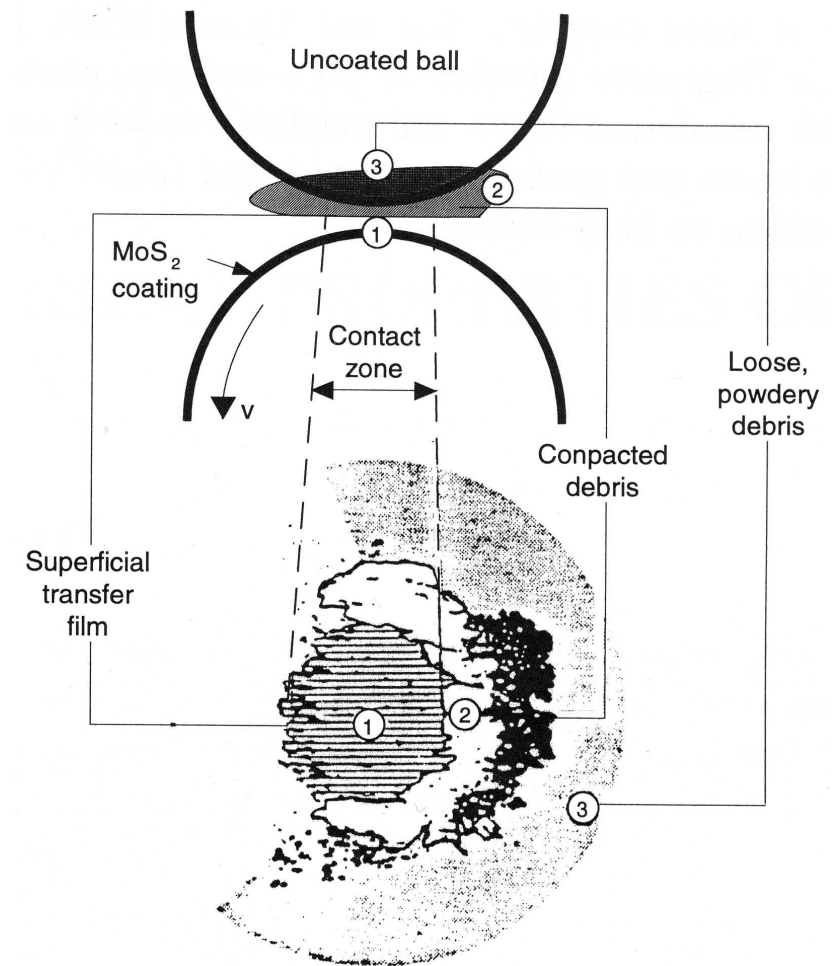
- ▶ “Intrafilm flow” or “interfilm sliding”



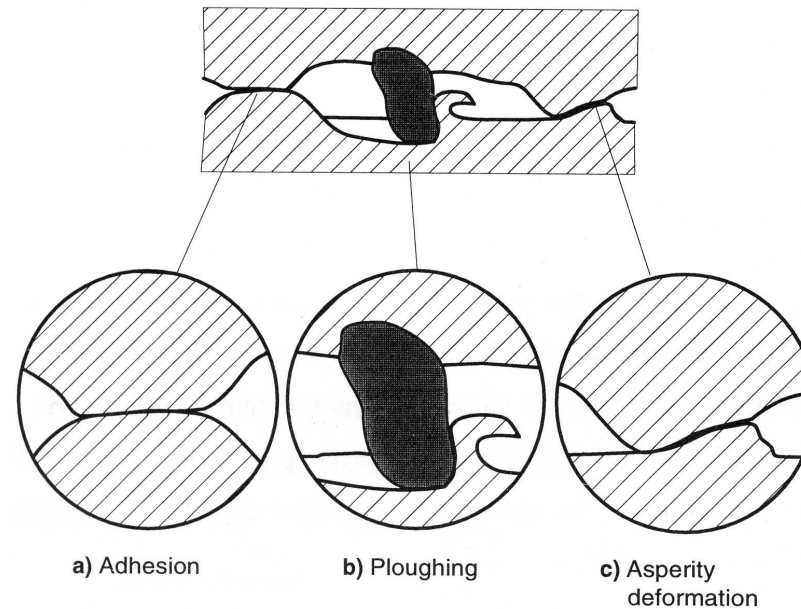
- ▶ General case: shearing of debris or trapped particles  
→ **Third body concept**

# What may be found in a “dry” contact?

- ▶ Flow from one solid to the other
- ▶ Compaction of wear debris: “third body”
- ▶ Build-up of “tribofilms” or “transfer layer”
- ▶ Chemical reactions between contacting bodies or with the environment



## Contributions to the friction force (*Bowden & Tabor*)



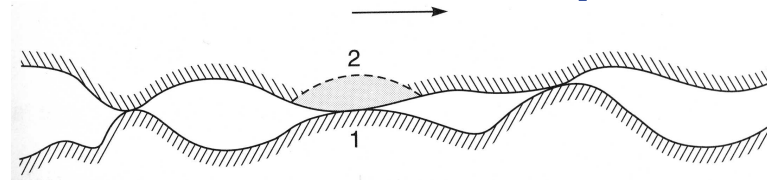
- ▶ **Adhesion:** shearing of adhesive junctions (where they were formed)

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

- ▶ **Plastic deformations:**

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

## Adhesive phenomena between asperities (*Rabinowicz*)



### ▶ Release of adhesive junctions:

- ▶ Controlled by surface energy → **strength of interface**
- ▶ Controlled by hardness → **strength of asperities**

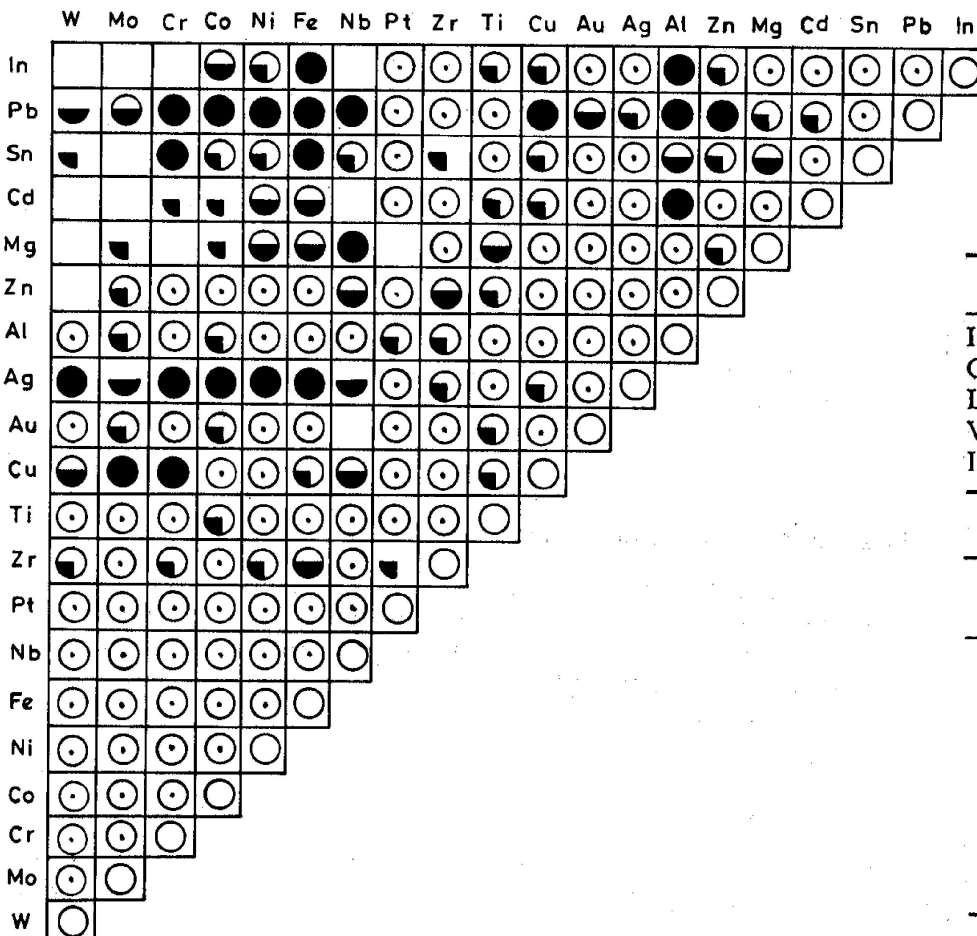
### ▶ Empirical formula based on experimental results:

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

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

$W_{12}$ : work of adhesion –  $\gamma_1, \gamma_2$ : surface energies  
 $C_1$ : geometrical constant –  $C_2$ : miscibility constant  
 $H$ : hardness of softer body

## Adhesive phenomena between asperities (*Rabinowicz*)



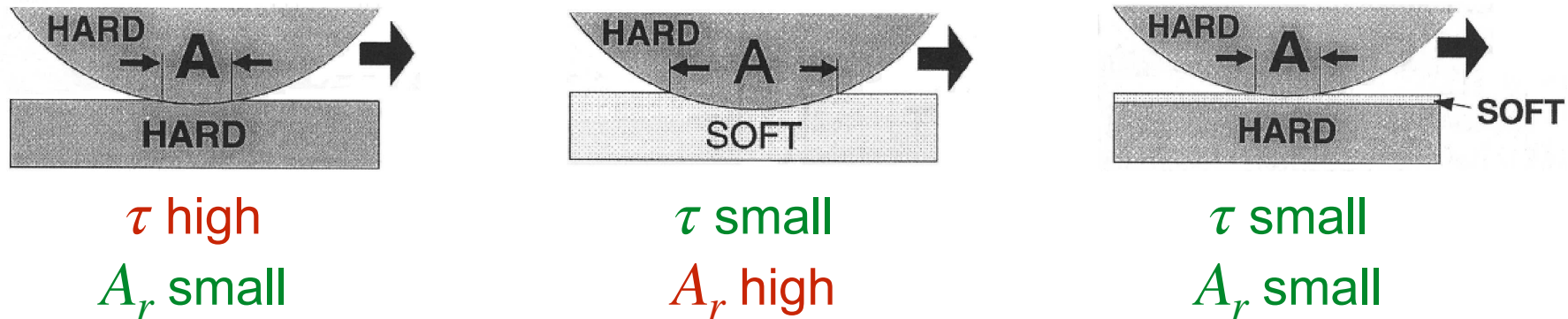
$$\mu \approx 0.3 + C_1 C_2 \frac{\gamma_1 + \gamma_2}{H}$$

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

▶ How to reduce dry friction of metals? (*Bowden & Tabor*)

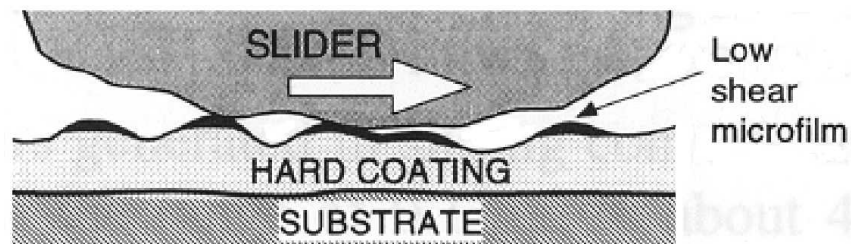
▶ Soft metal film – Playing with  $A_r$  &  $\tau$  in  $F_t = A_r \cdot \tau$



▶ General case with solid lubricants (*Holmberg & Matthews*)

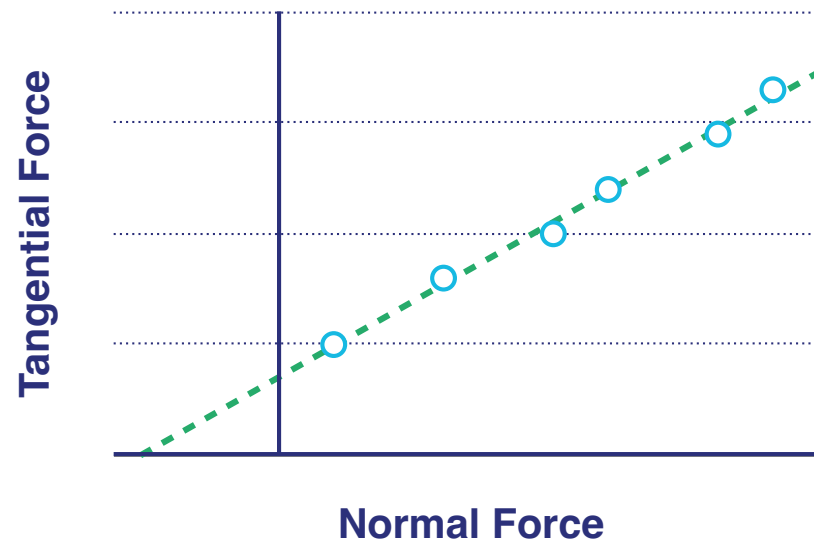
▶ Soft thin coating providing easy shear

▶ Hard and stiff substrates (or underlayers)



- 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?

- $F_t = \mu (F_n + F_{n_0})$ : Adhesive forces added to normal force?

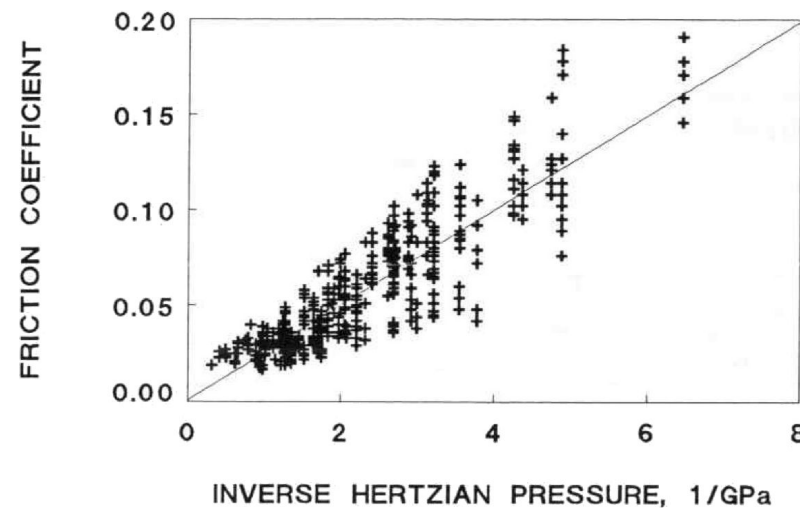
- Both tangential & normal force are proportional to contact area

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

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

- If  $\mu$  is changing with normal load, or contact pressure  $P$ , then it means that  $\tau$  depends on contact pressure  $P$

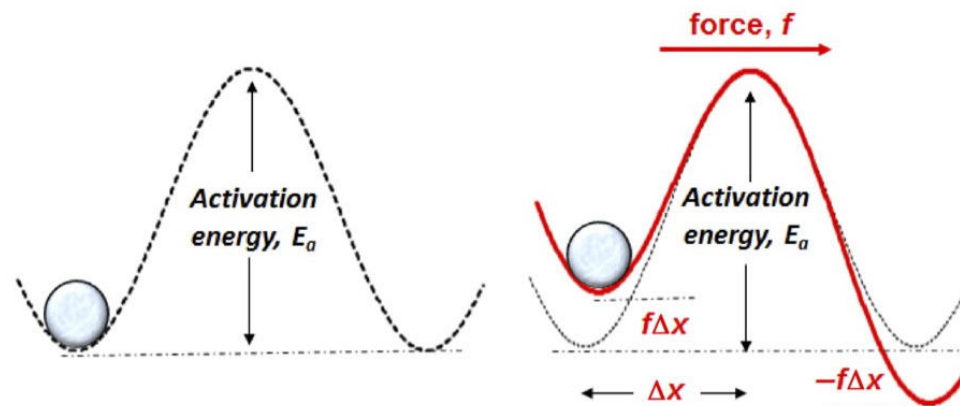
*Example with MoS<sub>2</sub>  
solid lubricant coatings*



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

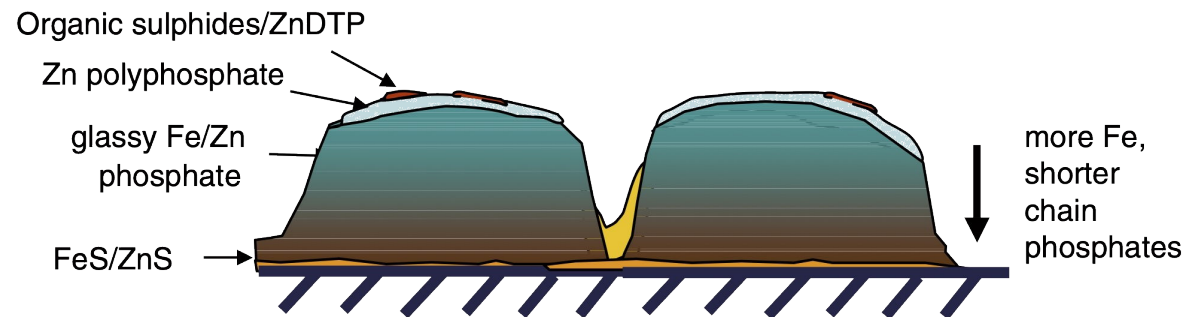
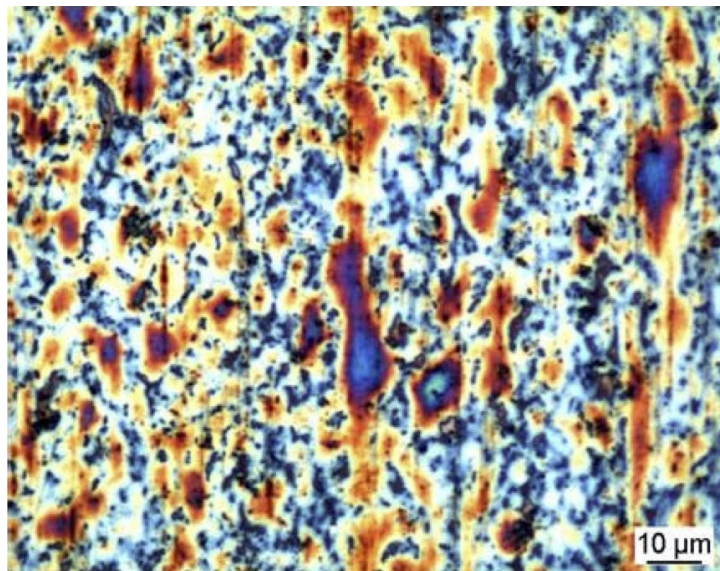
- ▶ Critical parameters controlling dry friction:
  - ▶ **Shear strength of interface:  $\tau$**   
*Depends on the nature of interfacial material*
  - ▶ **Load carrying capacity of the substrates:  $P$**   
*Elastic deformation as well as roughness affect the contact pressure*
- ▶ The nature, composition and properties of the interfacial material are thus critical for understanding friction and its evolution!

- ▶ 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**



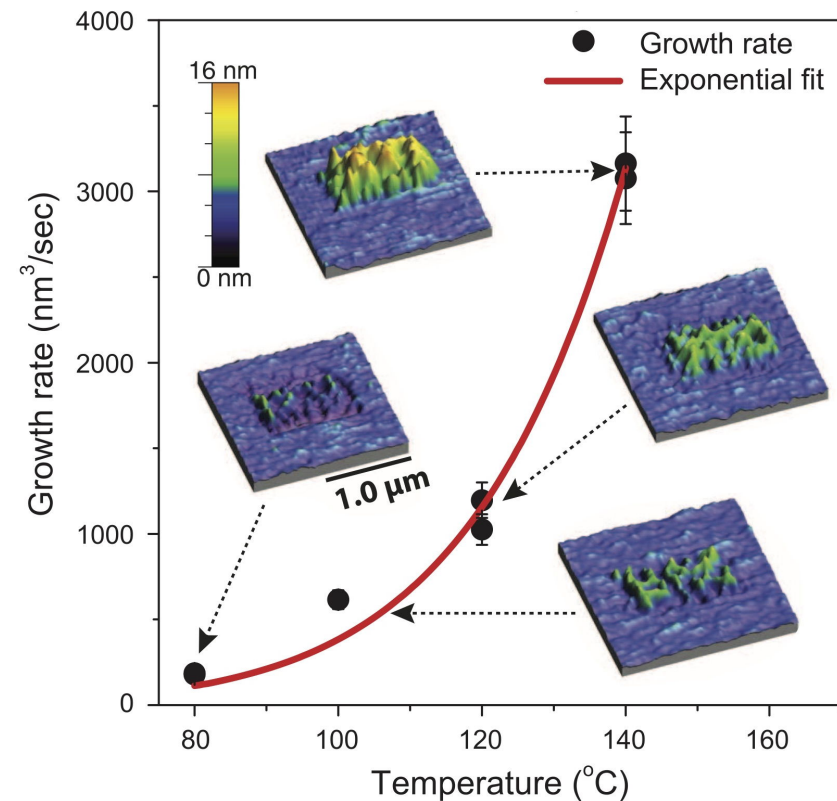
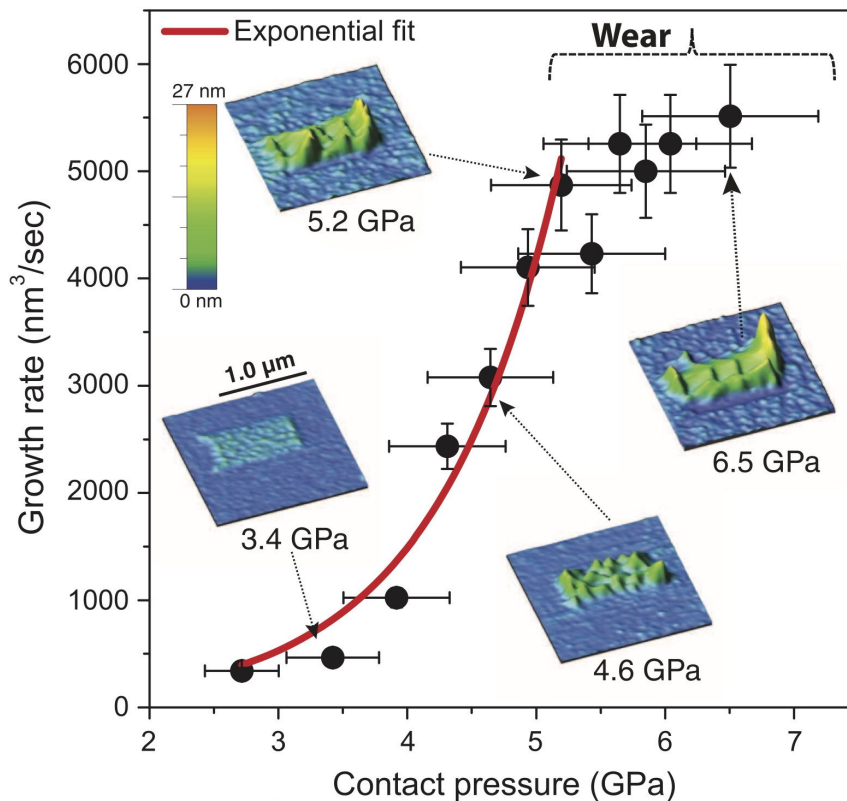
- ▶ *Contacts are « chemical reactors » where reactions may take place between the counterfaces and/or with the environment*

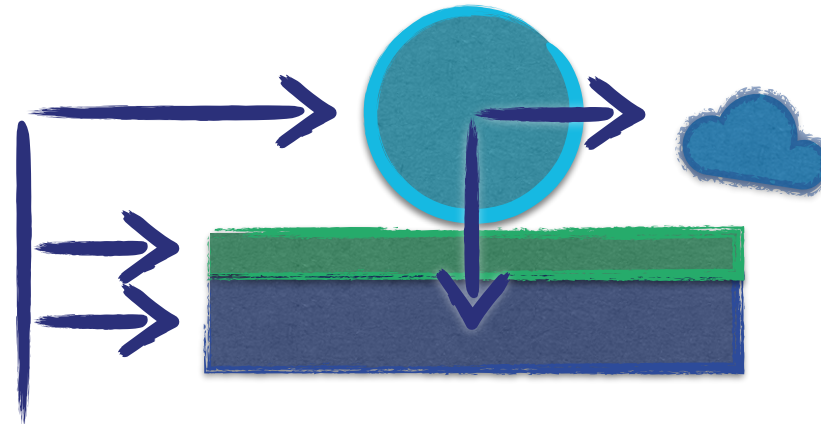
- ▶ Tribochemistry: some specificities though!
    - ▶ Reacting species must be “close enough”
    - ▶ Stress distribution in a real contact is highly heterogeneous
    - ▶ Nature of reaction products will affect tribological response
- ⇒ **Complex structure of “tribofilms” with lateral & vertical gradients**



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

- ▶ 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





## *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

## ▶ 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

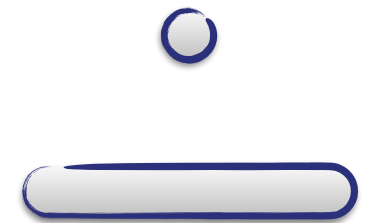
## ▶ Environment

- ▶ Nature & reactivity of the environment
- ▶ Imposed temperature

- ▶ 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!

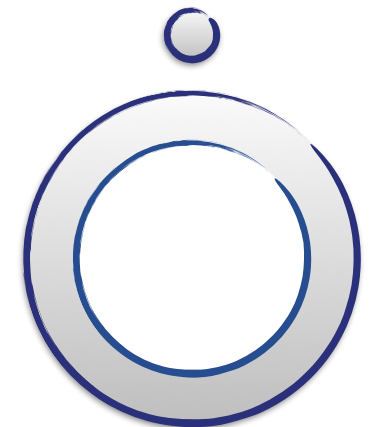
### ▶ **Linear ball-on-flat case**

- ▶ 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**

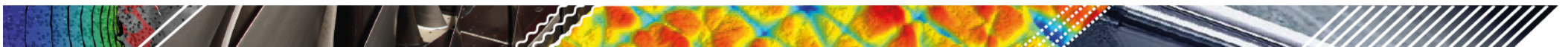
- ▶ Distance traveled by a point on the ball:  $L_{ball} = 2\pi R \cdot N$
- ▶ Distance traveled by a point on the flat:  $L_{flat} = 2a \cdot N$
- ▶ With  $2a = 100 \mu m$  &  $R = 15 mm$ , ratio:  $\frac{L_{ball}}{L_{flat}} = \frac{2\pi R}{2a} \simeq 1000$



*Surfaces & Friction*

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

***Part 3***

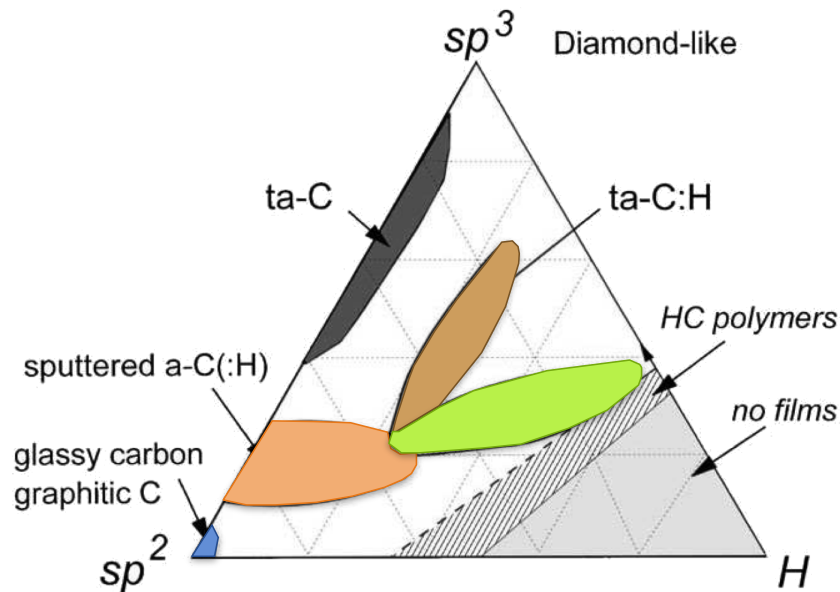


- ▶ **Introduction to DLC coatings**
- ▶ **Role of surface chemistry**
- ▶ **Role of surface topography**
- ▶ **Discussion & summary**

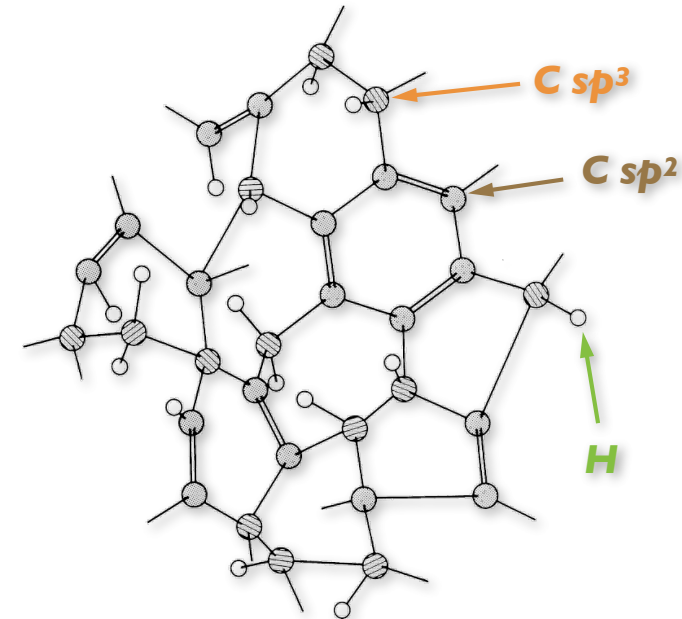


- ▶ DLC: a family of hard amorphous carbon films
- ▶ Provide low friction and wear:  
good performances as solid lubricants
- ▶ Many industrial applications...

# Diamond-Like Carbon: ... An amorphous carbon structure...



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

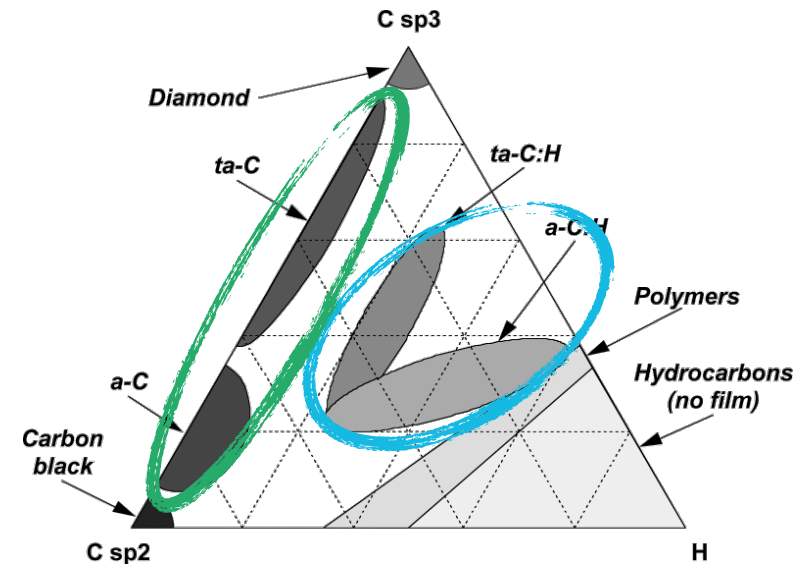


Random covalent network model of hydrogenated amorphous carbon films  
*Angus et al. (1992)*

## ▶ 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

- ▶ **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

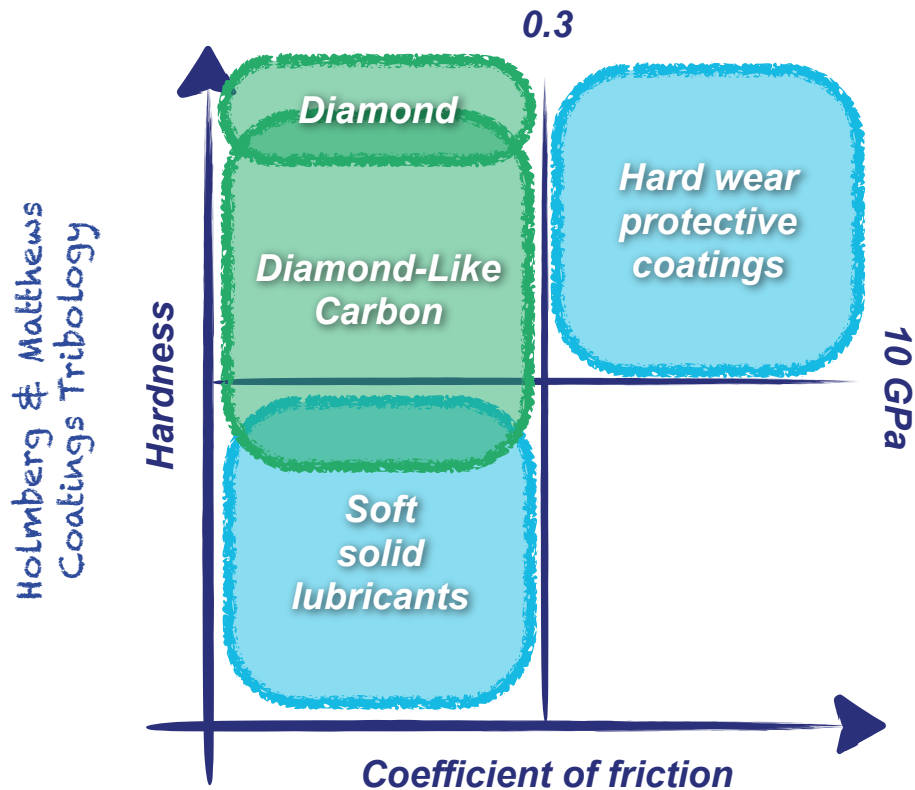


Hydrogen content	< 1 to > 50 at.%
Percentage of sp <sup>3</sup>	20 to 90%
Optical gap	0.4 to 4 eV
Compressive stress	up to few GPa
Surface energy	< 20 to > 60 mN.m <sup>-1</sup>
Thermal stability	up to ~300°C

	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<sup>3</sup> content ta-C)
- ▶ Higher H/E ratio (~ strain to failure)

# Diamond-Like Carbon: ... But a tribological paradox!



## ▶ Archard's law

The harder the more wear-resistant  
Nitrides, carbides, ceramic coatings

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

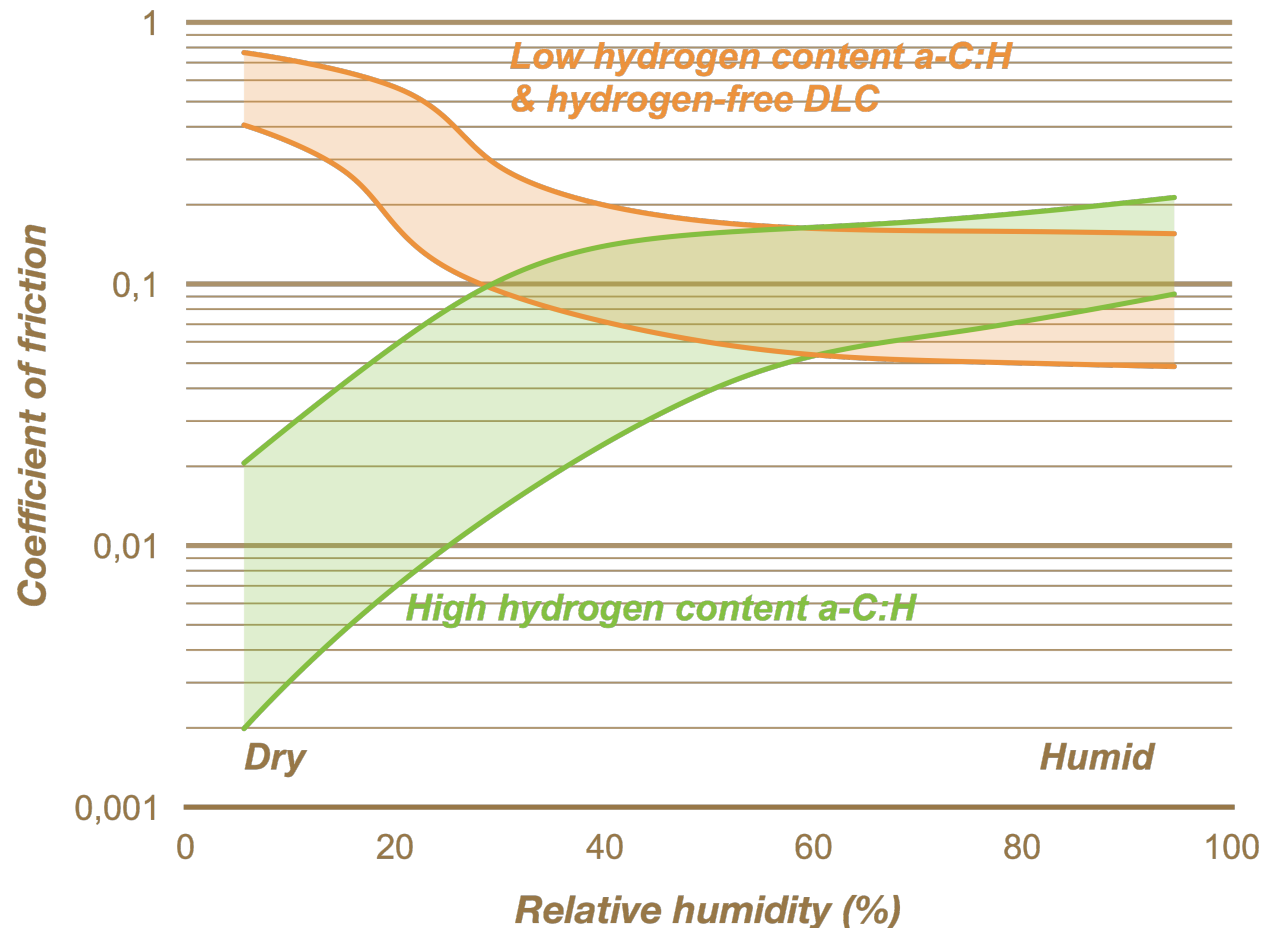
## ▶ Bowden & Tabor

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?*

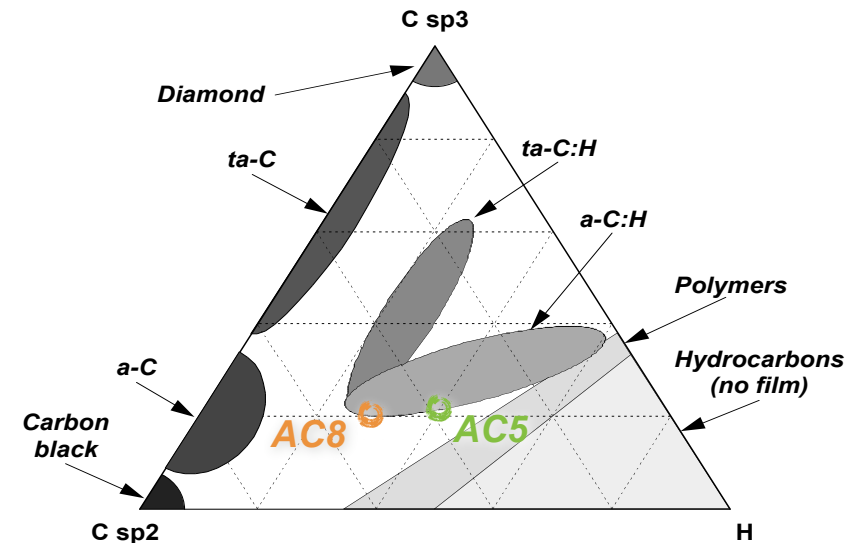
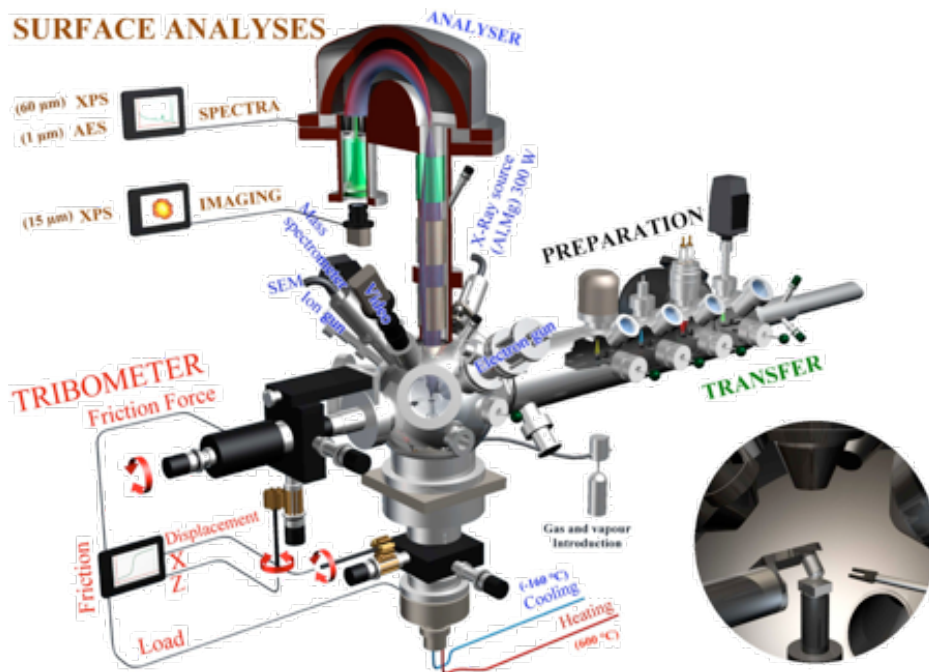
- ▶ Strong sensitivity to environment and coating composition!
- ▶ Versatility of the tribological performance...  
...dependence on deposition process parameters



- ▶ Introduction to DLC coatings
- ▶ **Role of surface chemistry**
- ▶ Role of surface topography
- ▶ Discussion & summary

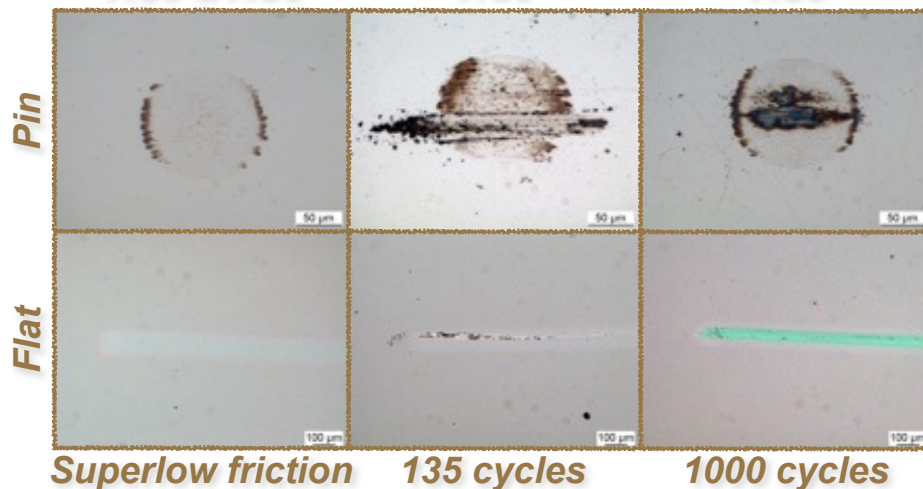
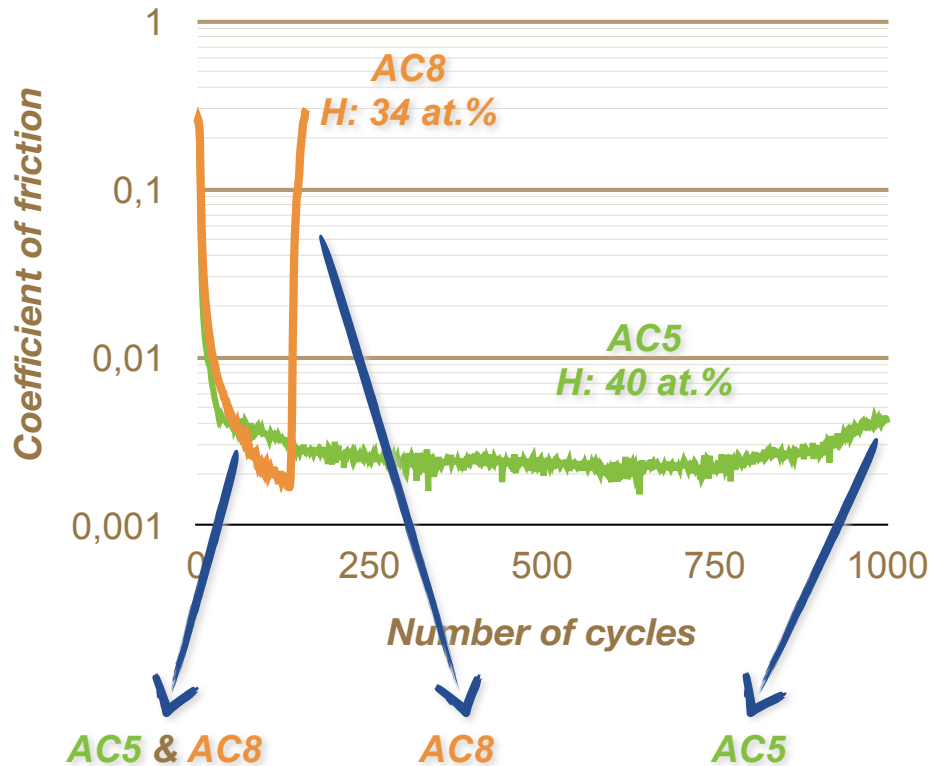
## Analytical UHV tribometer

- Linear reciprocating motion
- DLC (1  $\mu\text{m}$ ) 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:  $\sim 550$  MPa
- Contact width  $\sim 100$   $\mu\text{m}$
- Macroscopic contact**



	<b>dc-PECVD</b>	<b>AC8</b>	<b>AC5</b>
Precursor		C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>
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 <sup>3</sup>		30%	35%
C sp <sup>2</sup>		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



## Comparison of these 2 a-C:H films

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

**Superlow friction** is achieved  
( $\mu < 0.01$ )

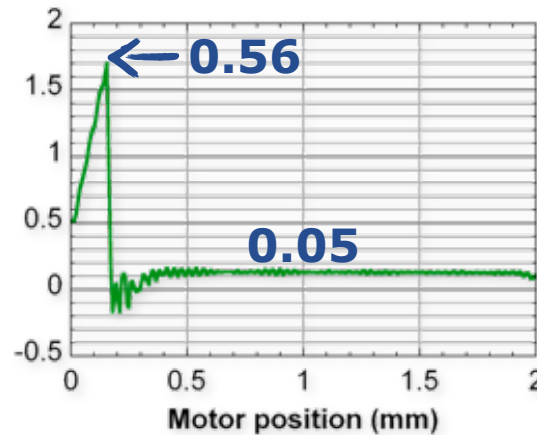
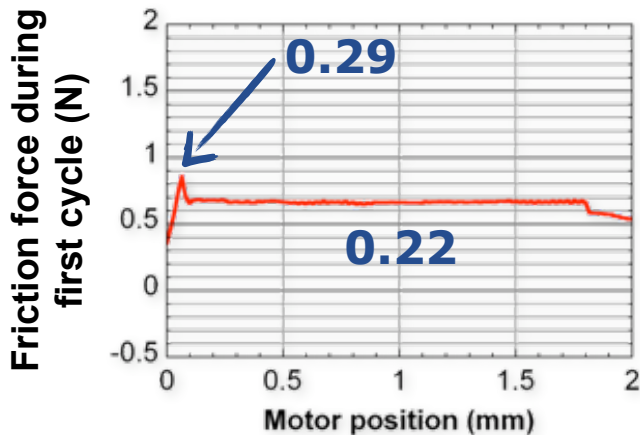
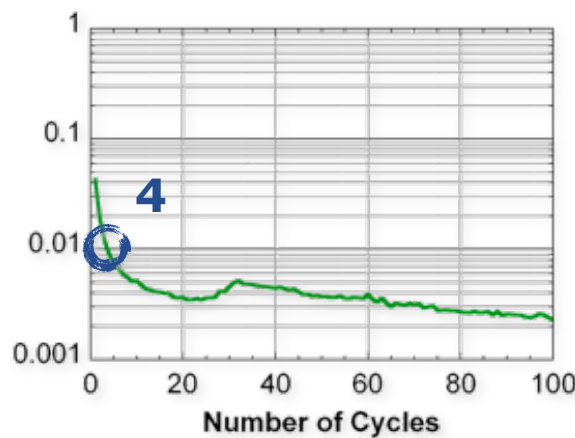
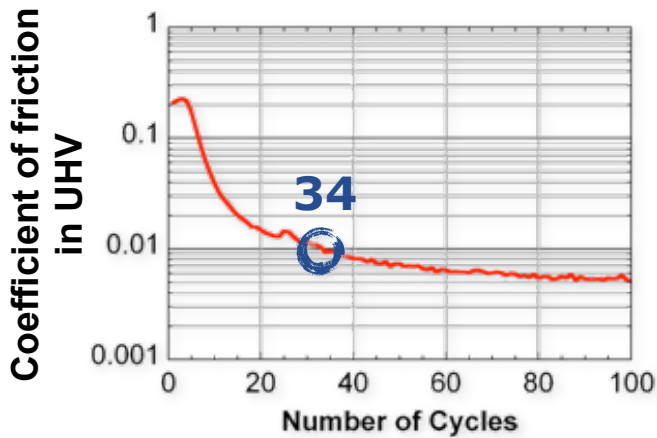
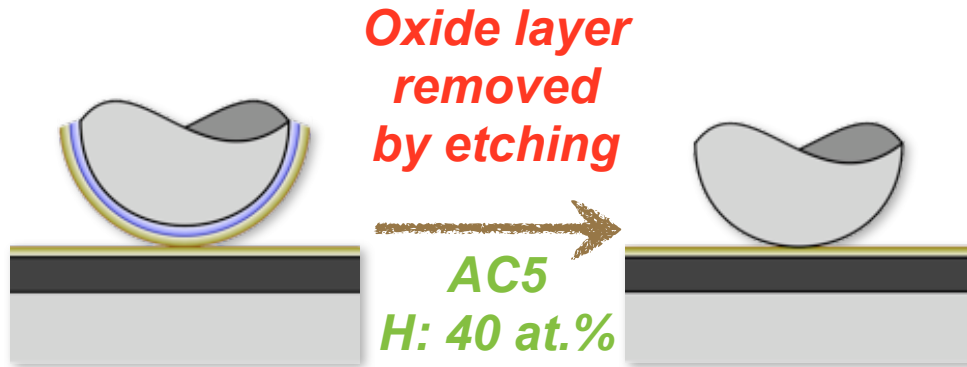
For **AC8**, **drastic friction increase** occurs  
after few tens of cycles  
( $> \times 100$ )

For **AC5**, **small friction increase** occurs  
after few hundreds of cycles  
( $< \times 10$ )

**Tribofilm** is formed during running-in

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

**Key-role of hydrogen content?**



**“Tribofilm”**  
Interfacial material on counterface could be different from initial a-C:H  
**≠ “Transfer film”**

**Removal of iron oxide**

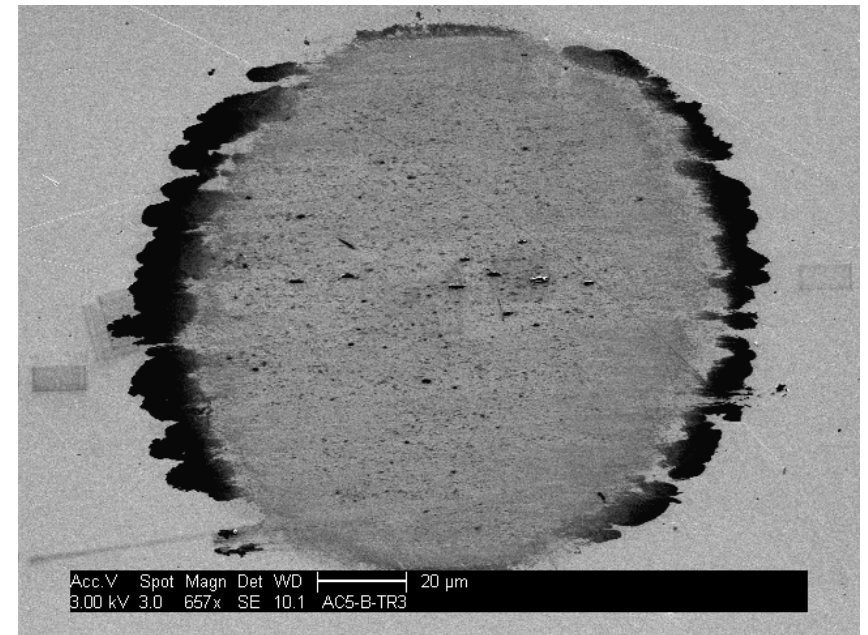
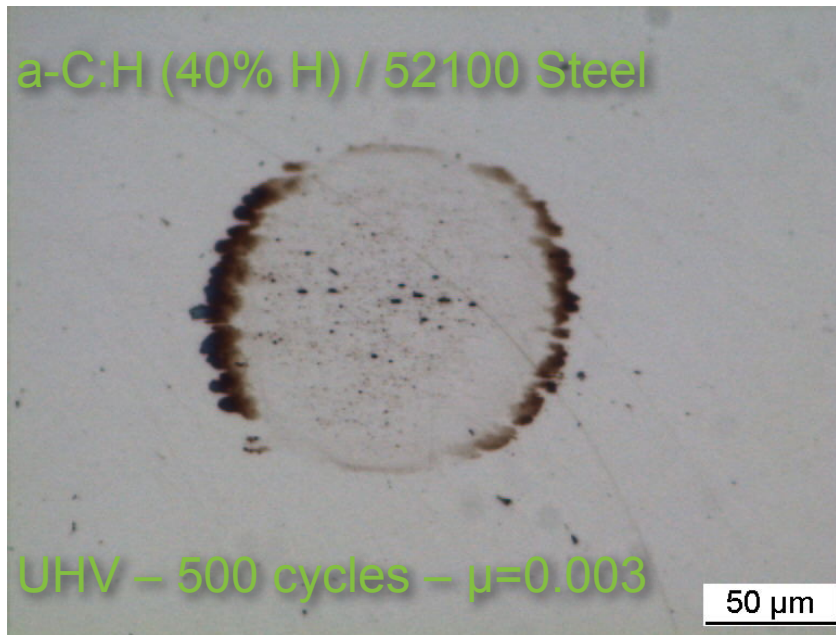
**Strong adhesion**

**Faster tribofilm build-up**

**Faster friction decrease**

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

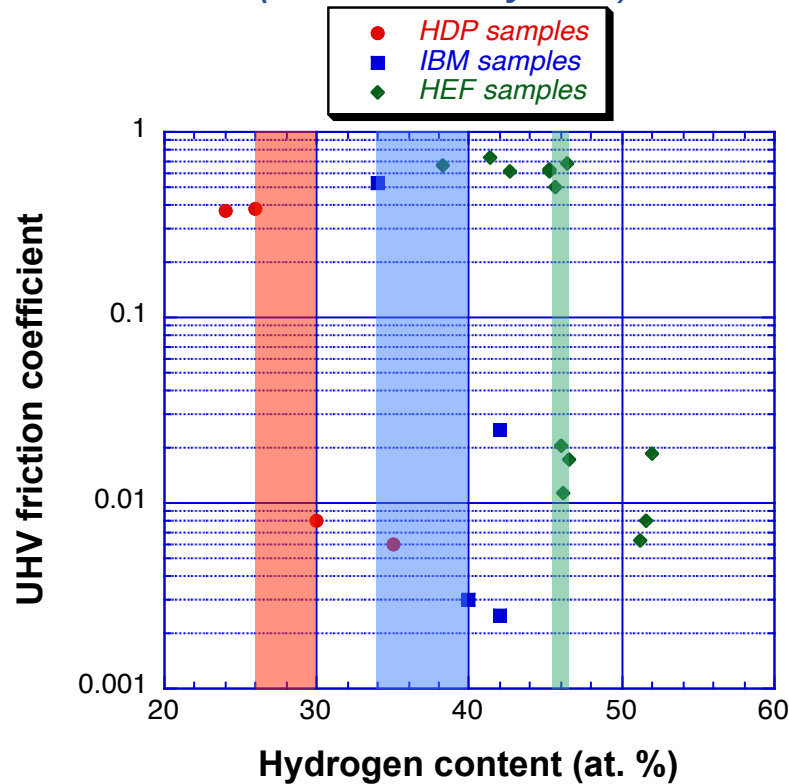
## ▶ Tribofilm grown on metallic counterface



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

▶ **Surface coverage by Hydrogen** would explain superlow friction of a-C:H under UHV?

“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. %



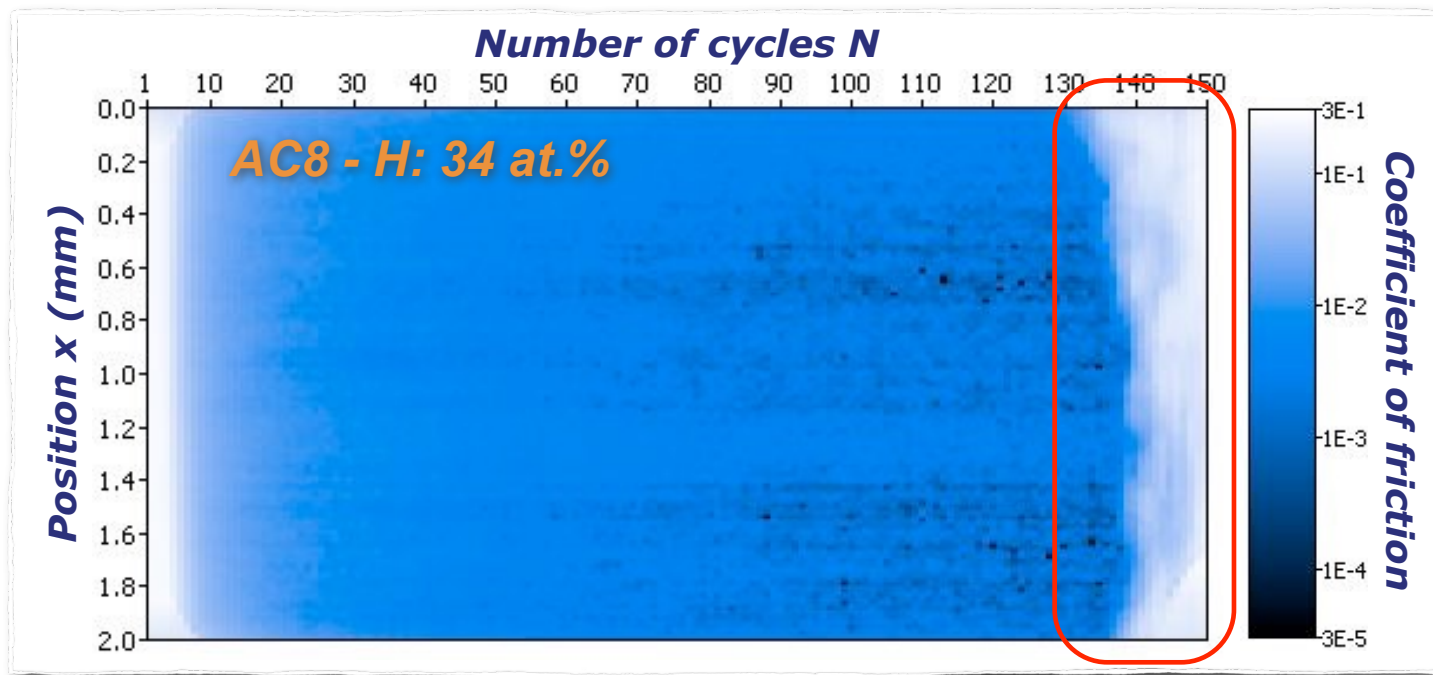
Threshold in hydrogen content  
depends on deposition process

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

- ▶ How to better understand the loss of the superlow friction regime?

## Triboscopy: “friction maps”

Friction as a function of position and number of cycles



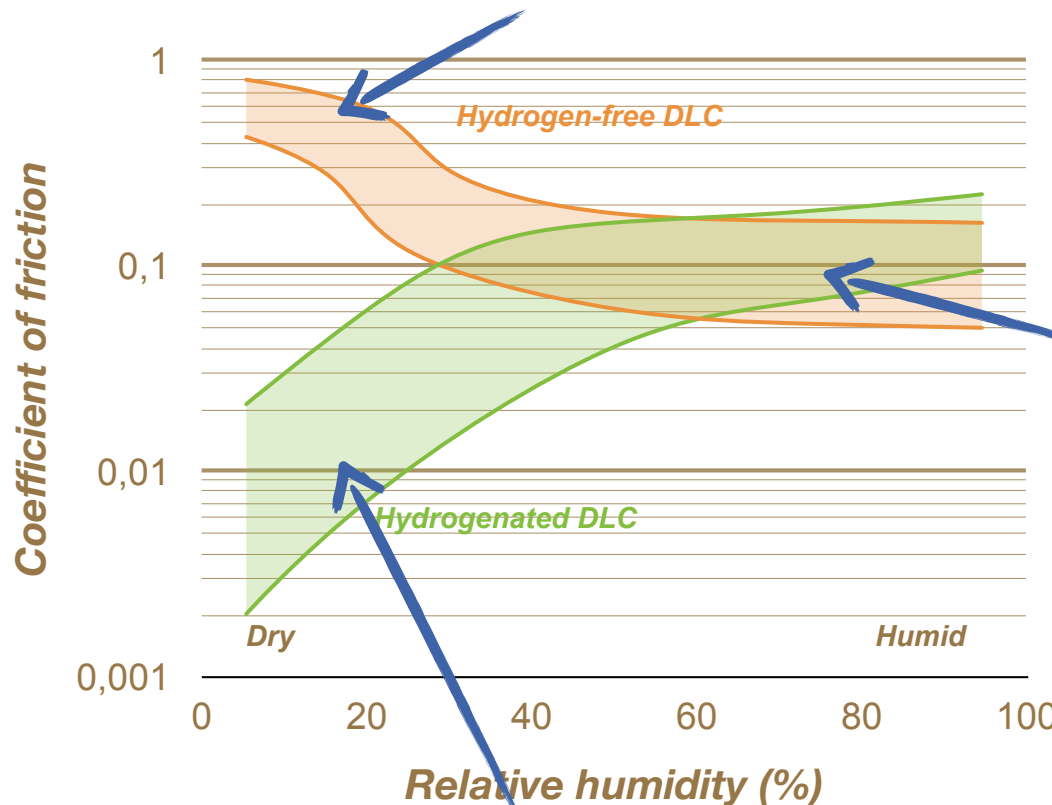
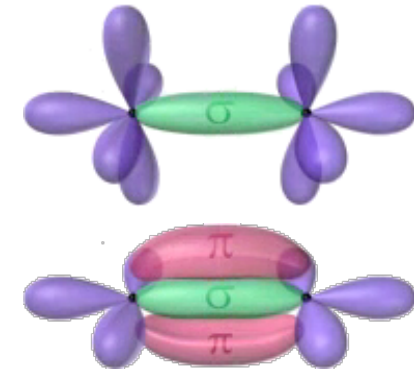
### Loss of “superlow” friction:

- ▶ Start at localized points of the wear track
- ▶ Quickly extends to an entire cycle  
⇒ **due to adhesive phenomena**

- ▶ **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?

## Strong adhesion

- ▶ “Dangling”  $\sigma$  bonds
- ▶  $\pi$  orbitals interactions? Metallic bonding?



## Intermediate adhesion

Critical role of water vapor

- ▶ Hydrogen bonding?
- ▶ Capillarity?

## Weak adhesion

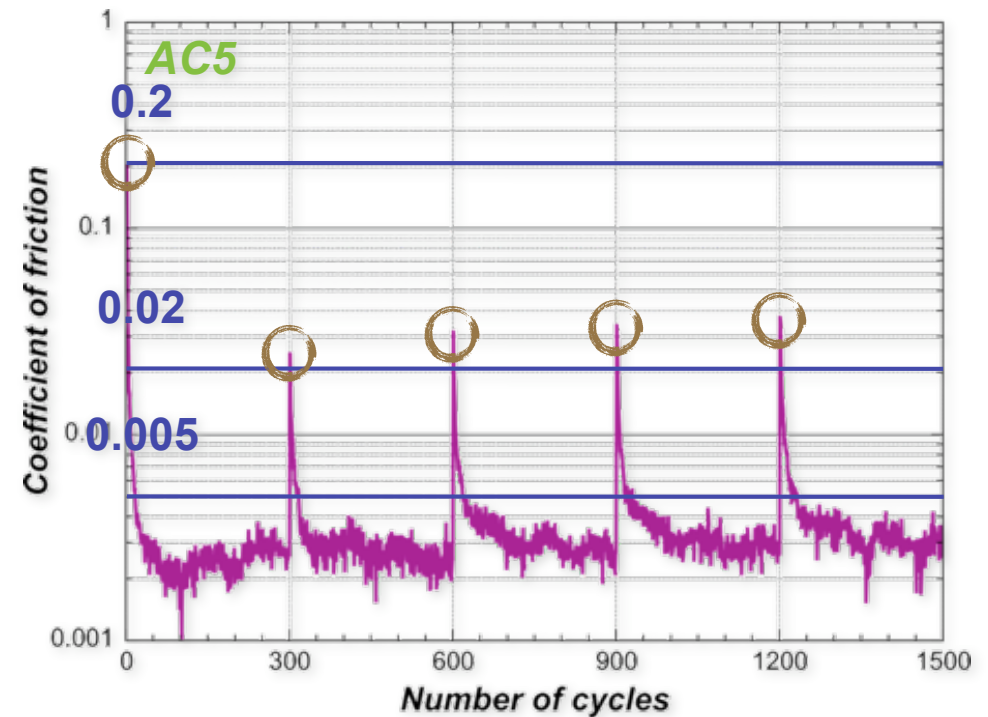
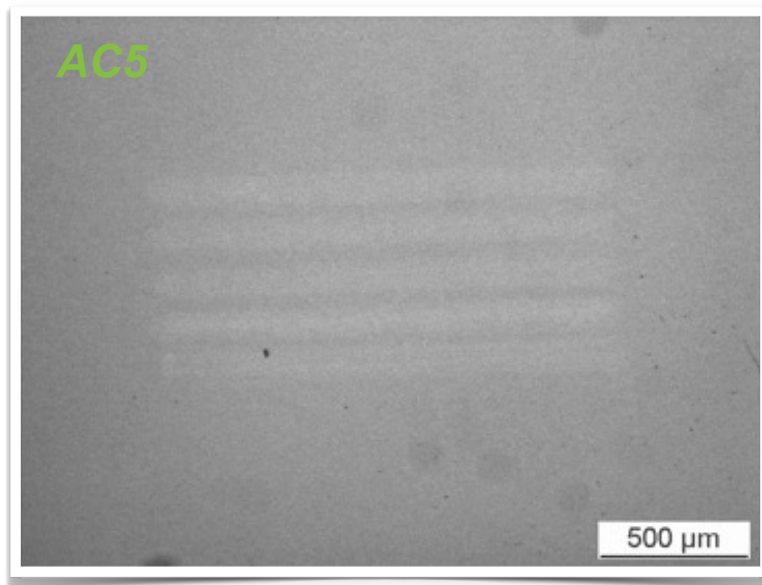
- ▶ Hydrogen-terminated surfaces
- ▶ Van der Waals interactions

- ▶ Introduction to DLC coatings
- ▶ Role of surface chemistry
- ▶ **Role of surface topography**
- ▶ Discussion & summary

## 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

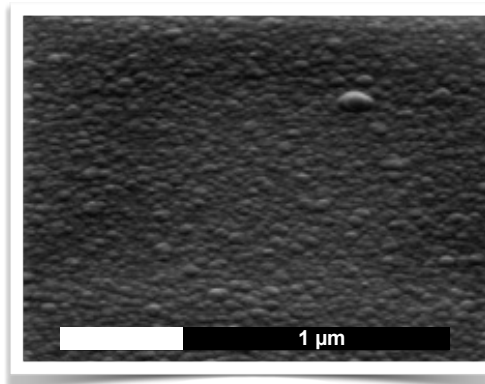


**Systematic running-in from  $> 0.02$  during  $> 15$  cycles...**  
**Something has to change on DLC surface!**

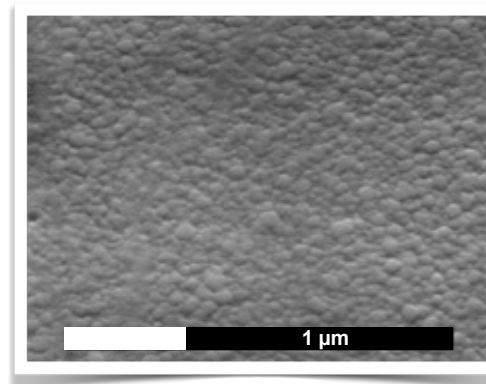
**AC5**  
**0 cycles**

$R_a = 2.7 \text{ nm}$   
 $R_q = 3.4 \text{ nm}$

$\mu \approx 0.25$



*Before friction*



*Superlow friction*

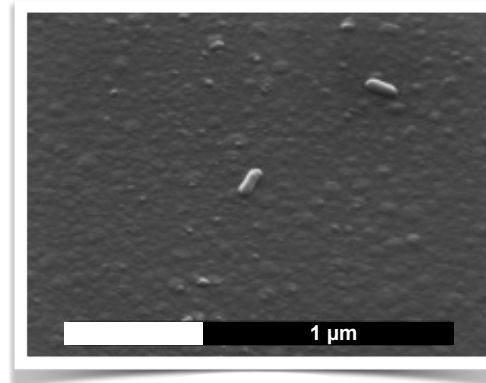
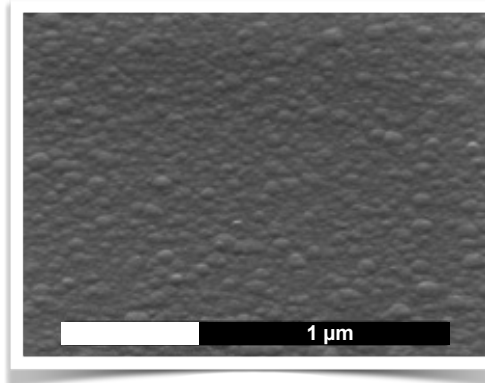
**AC5**  
**500 cycles**

$R_a = 1.4 \text{ nm}$   
 $R_q = 1.9 \text{ nm}$

$\mu \approx 0.003$

**AC8**  
**0 cycles**

$R_a = 1.8 \text{ nm}$   
 $R_q = 2.4 \text{ nm}$

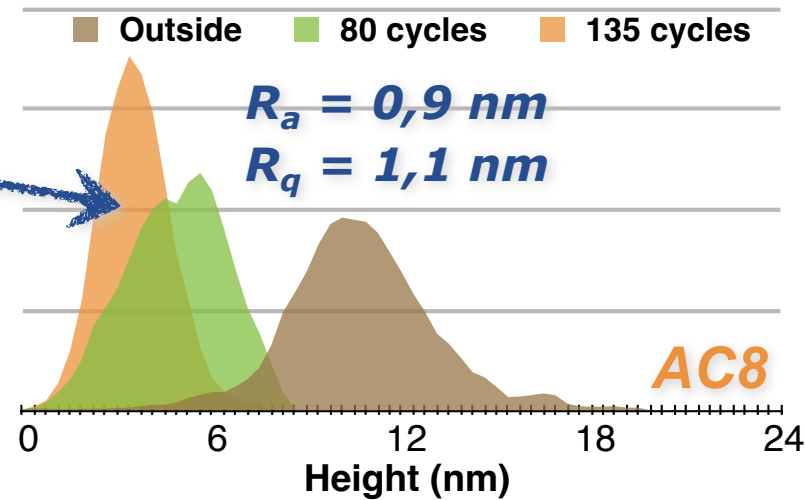
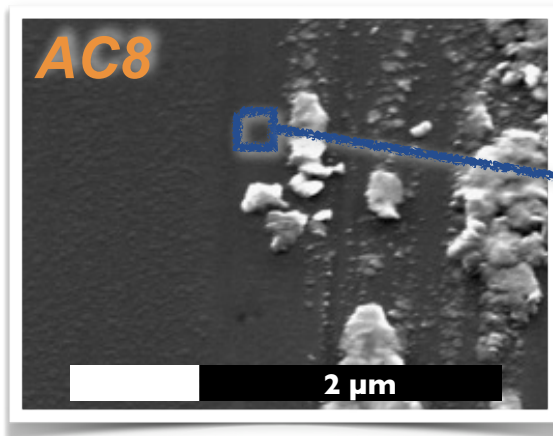
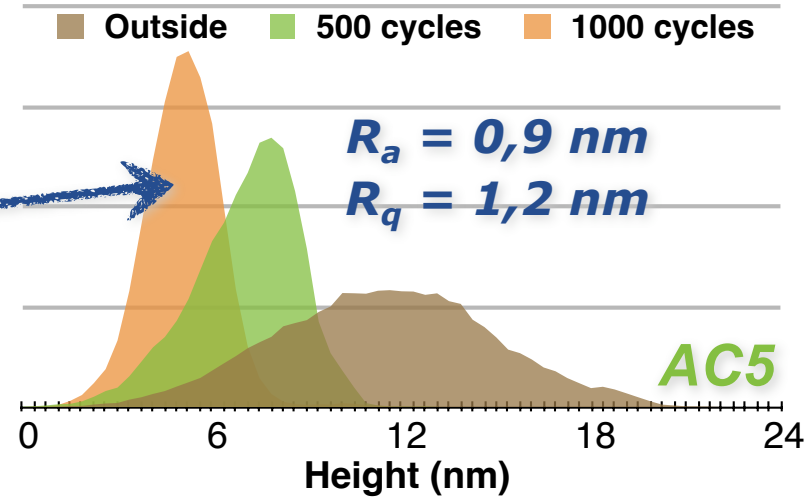
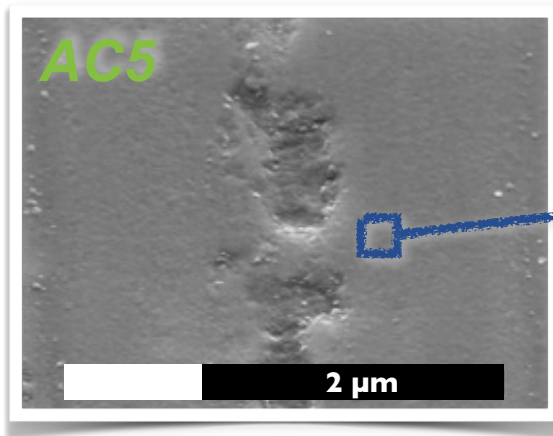


**AC8**  
**80 cycles**

$R_a = 1.3 \text{ nm}$   
 $R_q = 1.6 \text{ nm}$

- ▶ 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**

## What happens near the high friction areas?

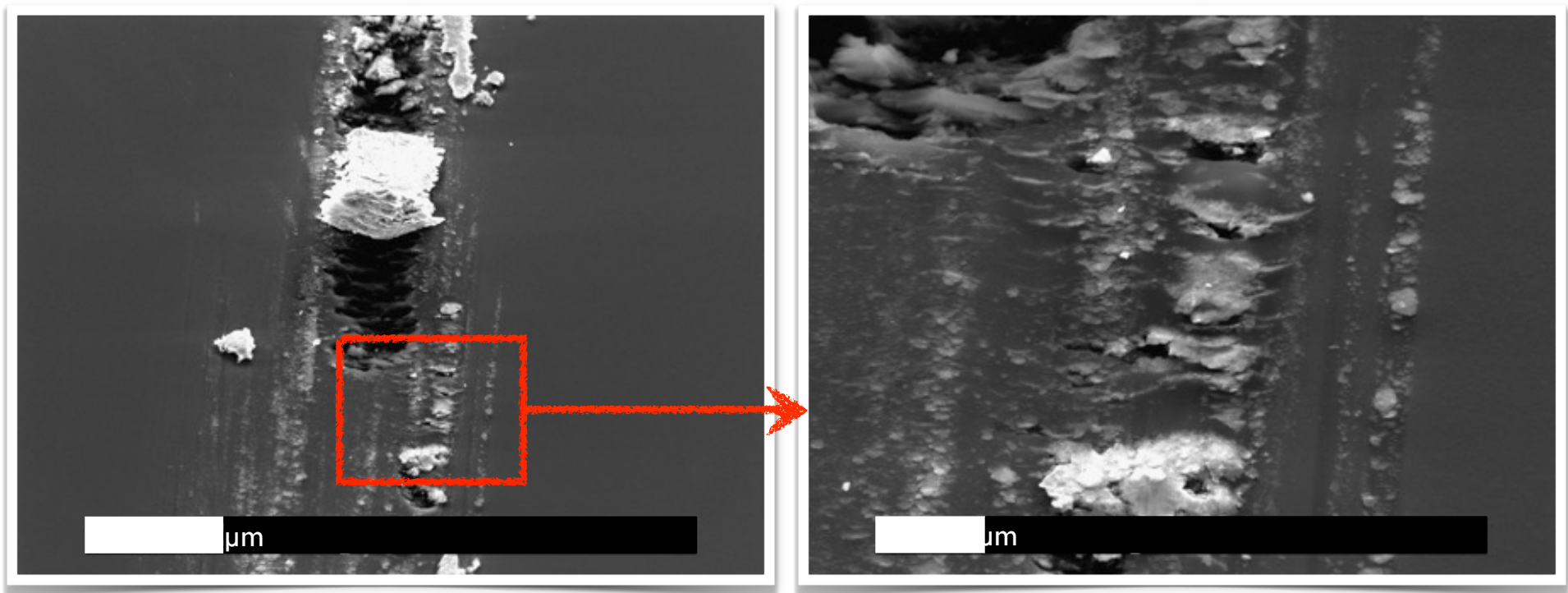


Smoothing of nanoscale roughness leads to **large adhesive phenomena**

**Why such different friction evolution between these two coatings?**

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

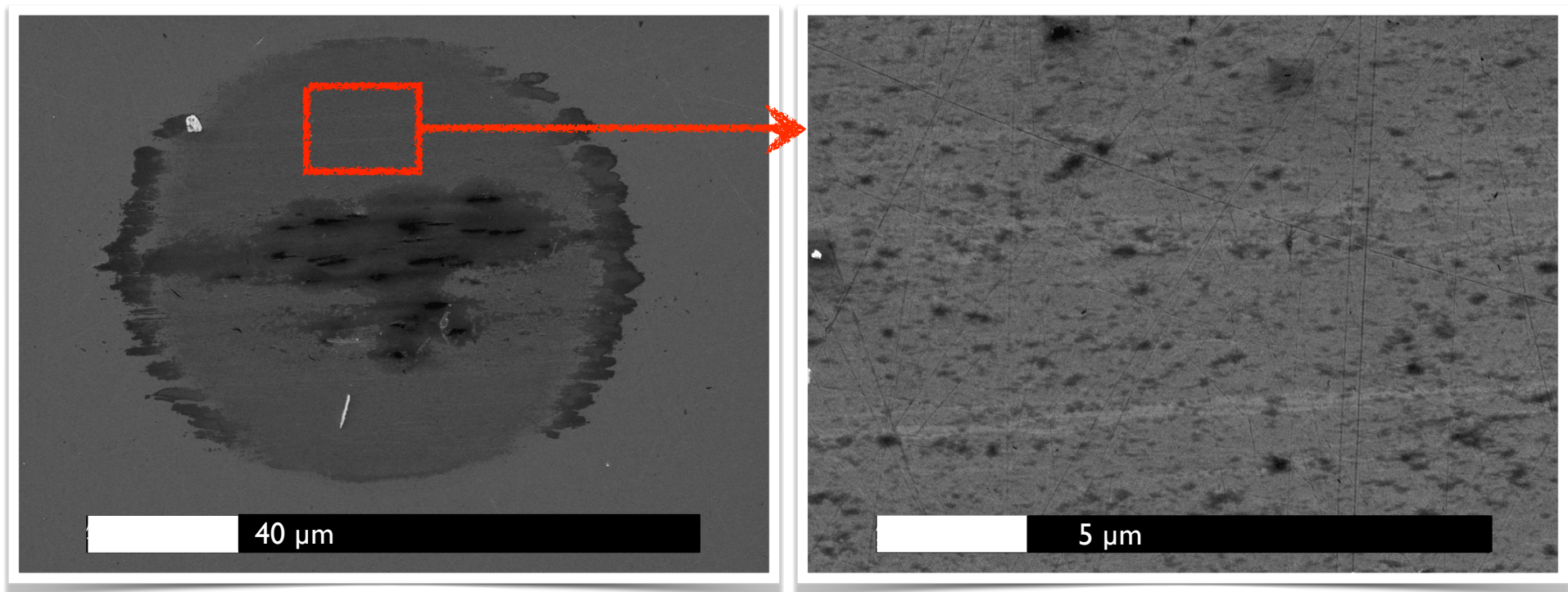
- ▶ *Iron is transferred to the DLC surface (in high friction zones)*
- ▶ *Some cracks can be found in the DLC around transferred iron particles*
- ▶ *Deep grooves are then formed from these “adhesive junctions”*
- ▶ *Adhesion is clearly controlling the loss of superlow friction for AC8*



**AC8 - 34 at.% H**

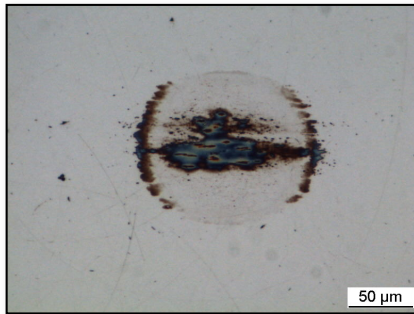
## SEM / EDX observations of tribofilm on counterface of AC5:

- ▶ 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

**Mechanical properties of DLC control how adhesive junctions will break :**

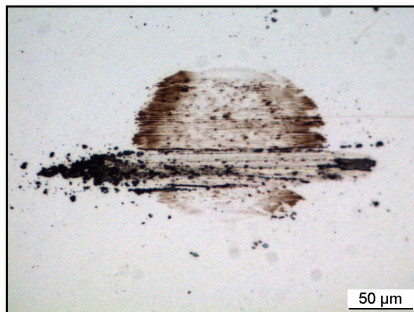
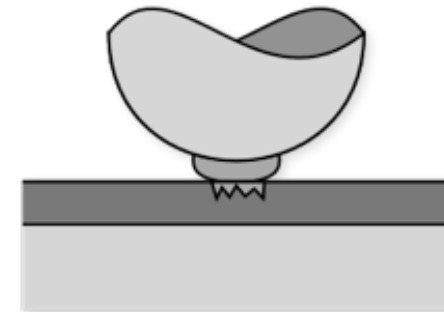


**SOFTER AC5 :**  
 $H = 7.5 \text{ GPa}$   
 Viscoplasticity:  $6.8 \cdot 10^{-2}$

**Adhesion**

↓  
 Transfer of DLC to steel pin  
**thicker tribofilm**

↓  
 Preserving **low friction**

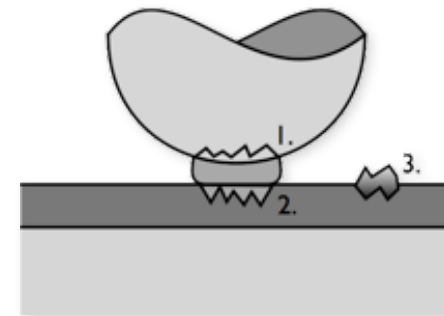


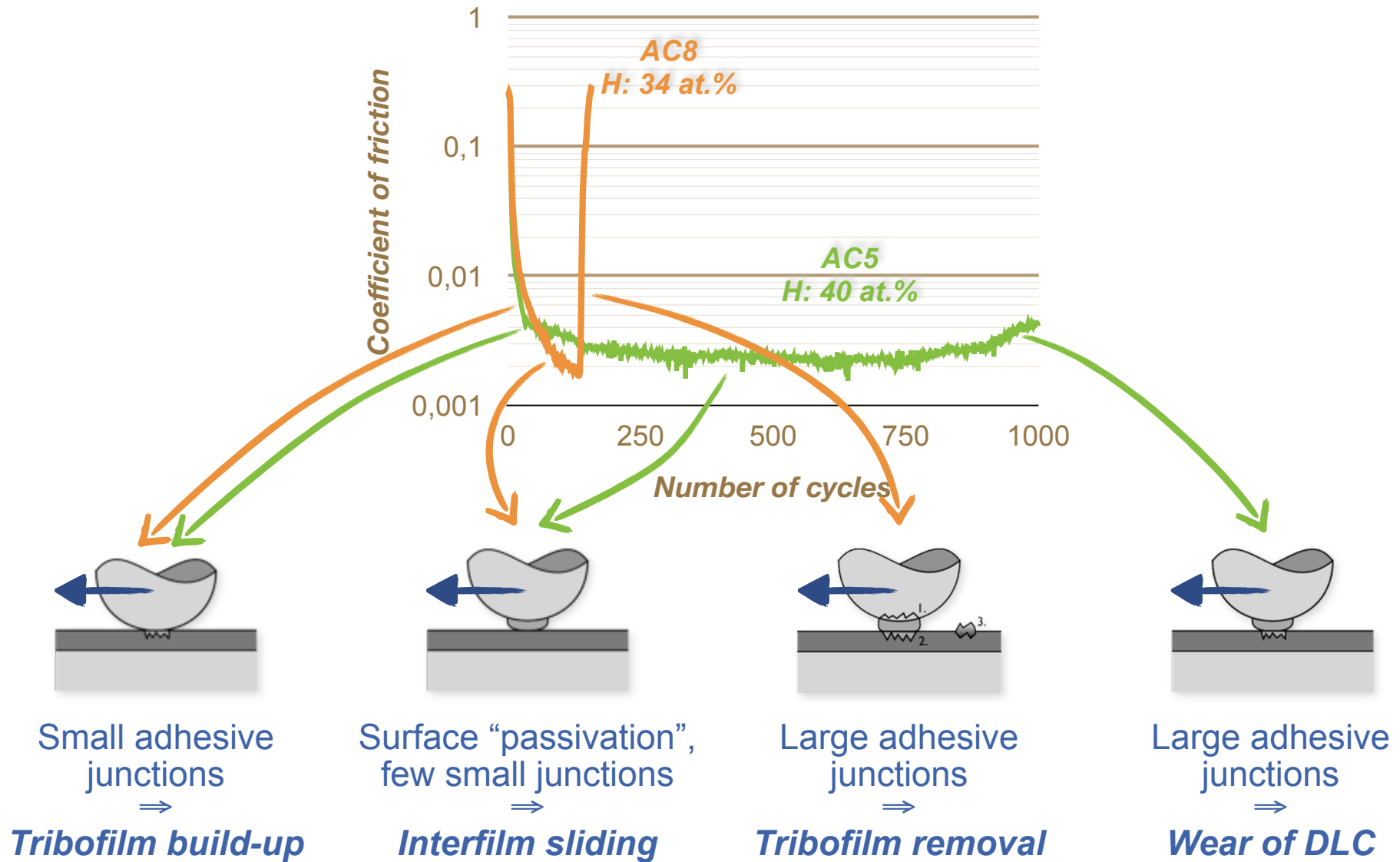
**HARDER AC8 :**  
 $H = 10.5 \text{ GPa}$   
 Viscoplasticity:  $1.4 \cdot 10^{-2}$

**Adhesion**

↓  
 Transfer of steel to DLC flat  
**Tribofilm removal**

↓  
 Leading to **high friction**





- ▶ Introduction to DLC coatings
- ▶ Role of surface chemistry
- ▶ Role of surface topography
- ▶ Discussion & summary

**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  $\pi$ -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?

## ***Solid lubrication processes of DLC coatings involve 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 behaviour 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?