PHS 6317 Nanoengineering of thin films

Course schedule – Winter 2024

12 January	Introduction – Scientific and technological challenges
19	Fabrication methods – Vacuum physics and vapor-phase techniques
26*	Fabrication methods – Plasma processes and process optimization
2 February	Fabrication methods - Plasma-surface interactions and diagnostics
9**	Fabrication methods – Thermal/Plasma spray technologies
16*	Optics of thin films 1, optical characterization, *Miniquiz1 (5%)*
23*	Optics of thin films 2, design of optical filters
1*** March	*Presentations – Emerging fabrication techniques (30%)*
March 4-8 - Winter/Spring break	
15**	Tribo-mechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion *(filter-20%)*
5 April	Passive functional films and coatings, *Miniquiz 2 (5%)*
12	Active functional films and coatings
16	Life cycle analysis and environmental impact, **visits**
18* **	*Presentations – Emerging applications of nanostructured films (40%)*

Deadlines:

Project #1 – Fabrication technique:

Choice of the subject: **26 January**

Abstract and references: **9 February**

Report and presentation: **1st March**

Projet #2 – Design of an optical filter:

Choice of the subject: **23 February**

Report: **22 March**

Projet #3 – Application of nanostructured thin films:

Choice of the subject: **16 February**

Abstract and references: **15 March**

Presentation: **18 April p.m.**

Report: **22 April at 23:59**

Projet #3 – Applications des couches minces

Thomas Sicotte and Alexandre Gamache - Cellules photovoltaïques à pérovskite

Alexandre Lussier - Fenêtres intelligentes thermochromiques

Mohamed Ammari - Thermal barrier coatings for aerospace gas turbine engine

Luc Montpetit - Passivation of CdZnTe for x-ray detectors

Veronika Cervenkova - Solar-thermal energy conversion - Transition metal nitrides as potential candidates

Émilien Martel - Electrochromic, photochromic and gasochromic coatings for consumer optics

Étienne Tremblay et Nathan Sasseville - Couches minces pour l'électronique organique - OLEDs

Thomas Lapointe - Photodétecteurs et leur conception/optimisation à l'aide des couches minces

Alexandre Carrière et Youssef Ben Mami - Électrodes transparentes pour les cellules solaires

Arghavan Yazdanpanah Ardakani - Nanoengineering of thin films to produce hydrophobic coatings for aircraft surfaces

Mathieu Bruzzese - Atomic oxygen barrier coating for aerospace/space exploration

Bastien Izacard - Revêtements pour la protection des composantes aérospatiales contre la corrosion

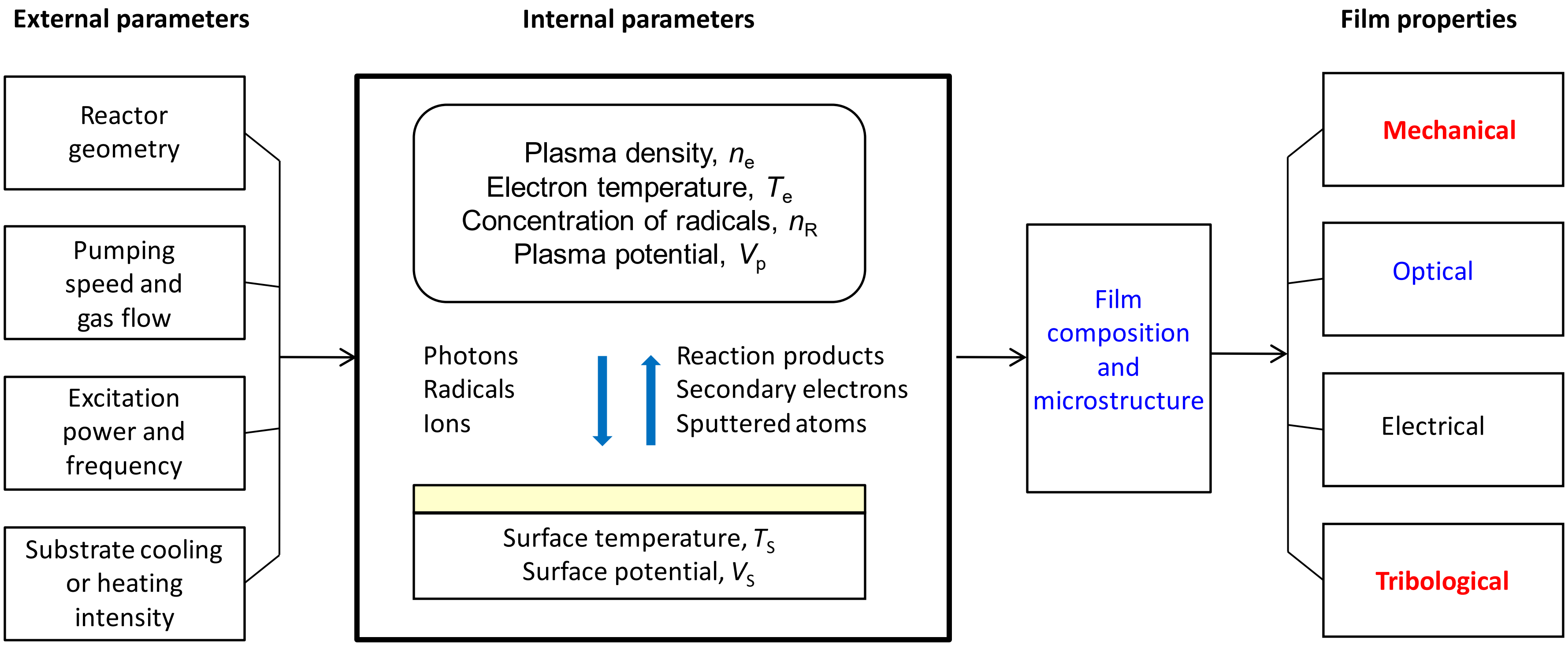
Alexandre Fall - Carbon nanotubes for sodium-ion batteries (or coated cathodes of other batteries)

Alexandre Pinel - Couches minces d'hydroxyapatites pour les implants en biomédical

Gabriel Juteau - Dynamic infrared radiators for satellites

Christelle Abou Zeidan – à venir

Plasma system and process control



External parameters

Reactor geometry

Pumping speed and gas flow

Excitation power and frequency

Substrate cooling or heating intensity

Internal parameters

Plasma density, n_e
Electron temperature, T_e
Concentration of radicals, n_R
Plasma potential, V_p

Photons
Radicals
Ions

Reaction products
Secondary electrons
Sputtered atoms

Surface temperature, T_S
Surface potential, V_S

Film composition and microstructure

Film properties

Mechanical

Optical

Electrical

Tribological

Today:

Mechanical and tribological properties

PHS6317:
Nanoengineering of
Thin Films - W2024

L. Martinu et al., Chapter 9 in "*Handbook of Thin Film Process Technology*", P.M. Martin, ed., Elsevier, 2010.

General references

1. **Milton Ohring, 1992.** ***The materials science of thin films.*** **San Diego: Academic Press, (2nd edition 2002) – Part 1: Chapters 2, 3, 4, 5; Part 2: 9, 11, 12**

2. Bharat Bhushan, 1999. *Principles and applications of tribology.* New York: John Wiley & Sons, Inc. 1020p.

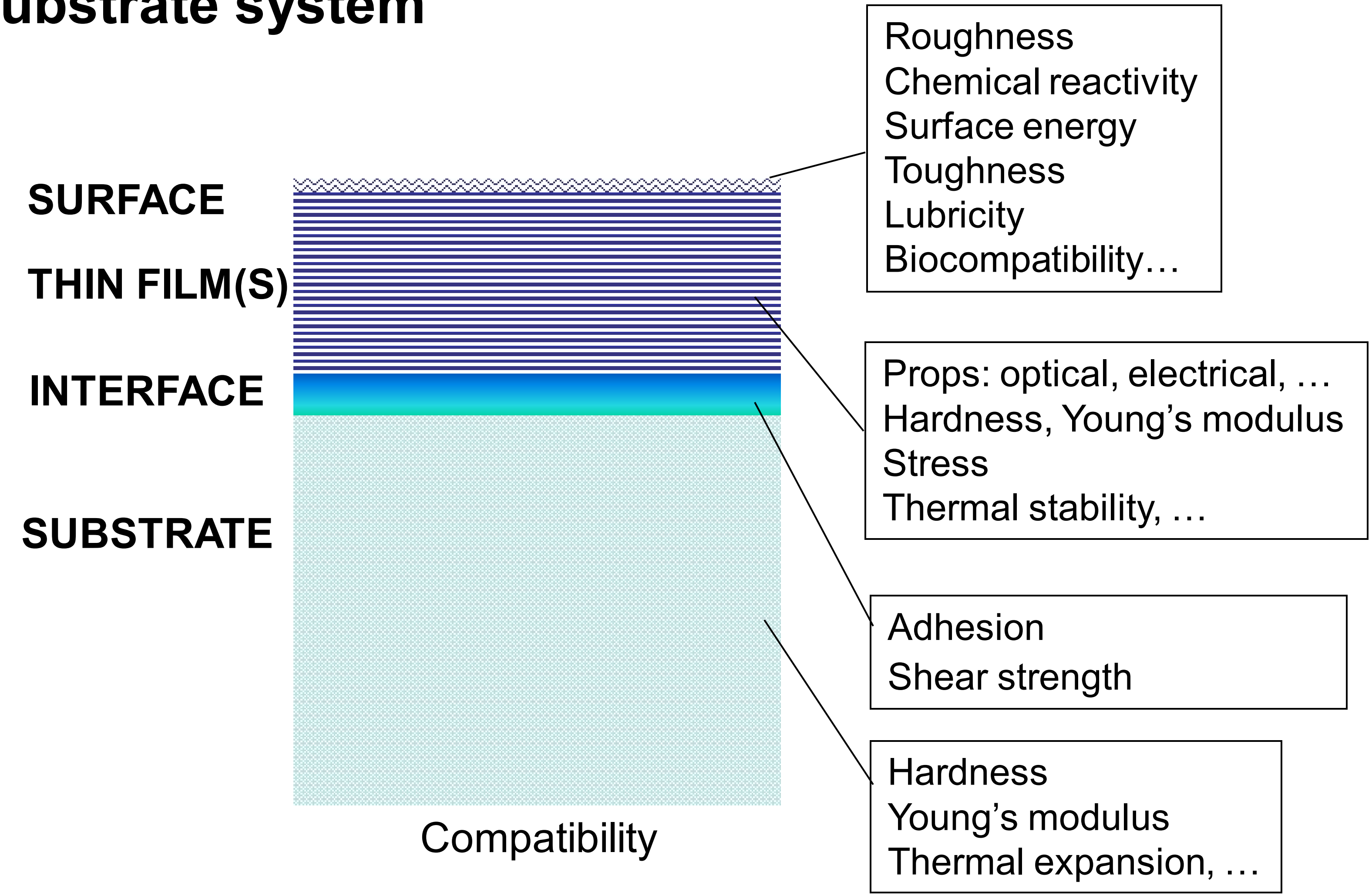
3. A.C. Fischer-Cripps, 2002. *Nanoindentation. New York*: Springer. 197p.

4. Kenneth Holmberg and Allan Matthews: Coatings Tribology: Properties, Technique and Applications in Surface Engineering, Elsevier, 2009.

5. D. Dowson, *History of tribology*. London : Professional Eng. Publishing. 1998, 768p.

6. Pawel Jedrzejowski, 2003. *Mechanical and optical properties of plasma deposited superhard nanocomposite coatings.* 179p. Thèse de doctorat en génie physique, École Polytechnique de Montréal.

Control of the properties through the microstructure: Film-substrate system



SURFACE

THIN FILM(S)

INTERFACE

SUBSTRATE

Compatibility

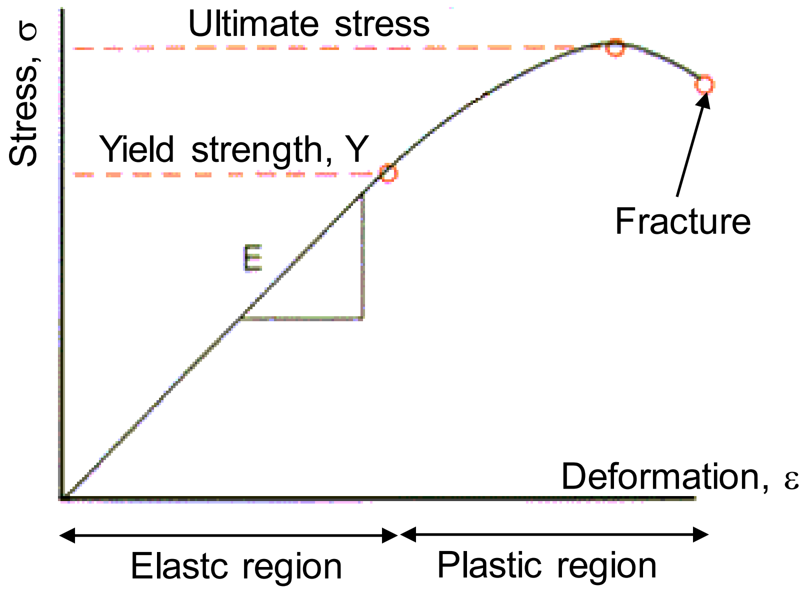
Roughness
Chemical reactivity
Surface energy
Toughness
Lubricity
Biocompatibility…

Props: optical, electrical, …
Hardness, Young's modulus
Stress
Thermal stability, …

Adhesion
Shear strength

Hardness
Young's modulus
Thermal expansion, …

Elasto-plastic regime



Plastic region
When σ > Y
irreversible

Elastic regime
reversible
Linear according to the Hook's law

Young's (elastic) modulus $$E = \frac{\sigma_x}{\varepsilon_x}$$

where

$$\sigma_x = \frac{F}{A} \quad \text{and} \quad \varepsilon_x = \frac{\Delta l}{l_0}$$

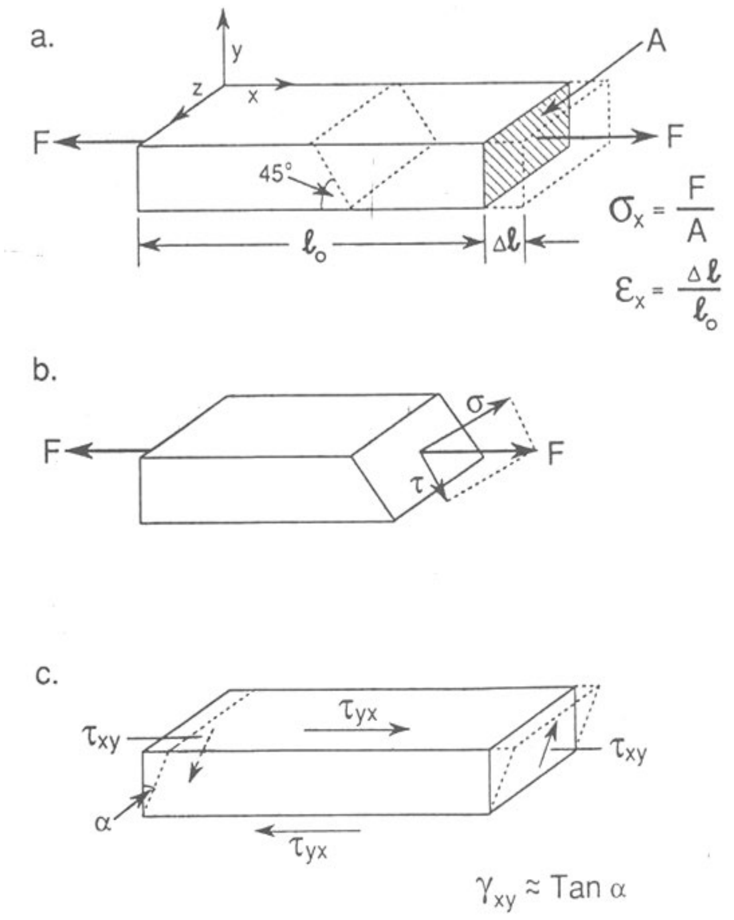
In shear

Shear modulus $$\mu = \frac{\tau}{\gamma}$$

N.B. $$\mu = \frac{E}{2(1+\nu)}$$

Mechanical behavior of thin films

Elasto-plastic range



In shear

Shear modulus

$$\mu = \frac{\tau}{\gamma}$$

N.B. Shear stress τ is largely responsible for plastic deformation in cristalline materials; γ – surface area

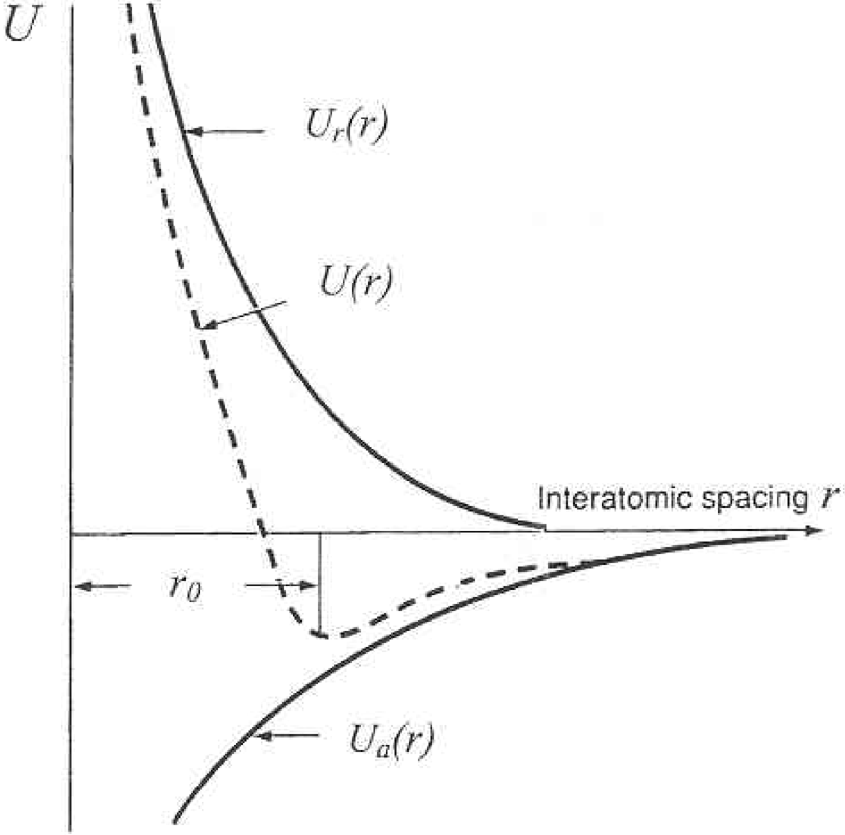
For a materials that can freely deform along y and z;
ν – Poisson's ratio

$$\varepsilon_y = \varepsilon_z = -\nu\varepsilon_x$$

N.B. $$\mu = \frac{E}{2(1+\nu)}$$

Electrostatic model of the mechanical properties

Macroscopic deformation of the material changes the interatomic distances and hence the potential energy U(r) between the atoms.



Morse function: $U(r) = U_a(r) + U_r(r)$

where

attraction potential $U_a(r) = \frac{-A_{el}}{r}$

and

repulsion potential $U_r(r) = \frac{B_{el}}{r^m}$

A_{el}, B_{el} and m are constants

Minimum energy at r = r_o

according to $F = \frac{dU(r)}{dr} = 0$

Electrostatic model of the mechanical properties

$\sigma_y^{max} \sim E/10$ E. Orowan, Rep. Prog. Phys. 12 (1949) 185.

In reality:

$$\frac{E}{100} \leq \sigma_y^{\max} \leq \frac{E}{1000}$$

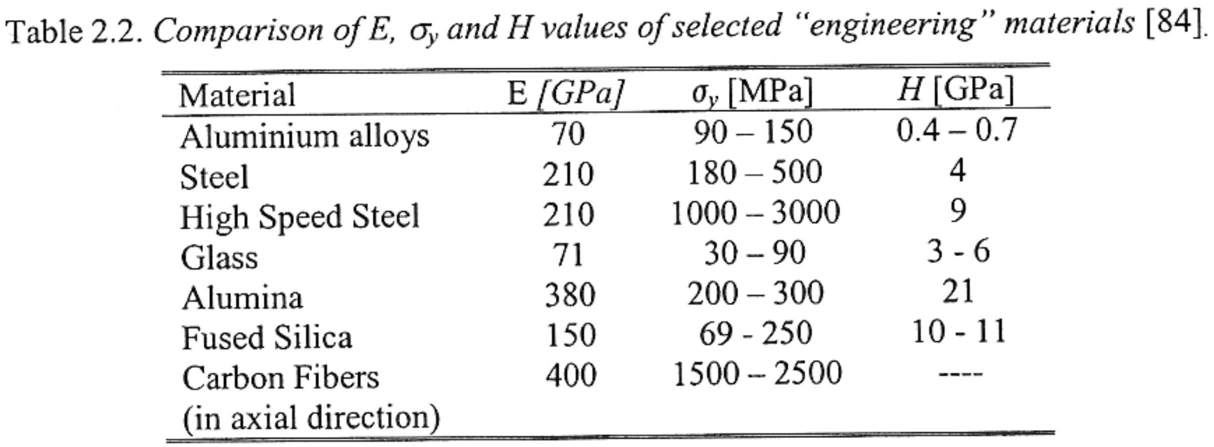


Table 2.2. *Comparison of E, σ_y and H values of selected "engineering" materials* [84].

Material	E *[GPa]*	σ_y [MPa]	*H* [GPa]
Aluminium alloys	70	90 – 150	0.4 – 0.7
Steel	210	180 – 500	4
High Speed Steel	210	1000 – 3000	9
Glass	71	30 – 90	3 - 6
Alumina	380	200 – 300	21
Fused Silica	150	69 - 250	10 - 11
Carbon Fibers (in axial direction)	400	1500 – 2500	----

Ductile fracture

In ductile materials, the mouvement of dislocations is not hampered. The material fracture occurs due to plastic deformation **caused by dislocation sliding.**

Energy that needs to be supplied to make the dislocations move depends on the shear modulus, on the type of the interatomic bonding and on the crystalline structure.

Mechanical resistance of a ductile material can be improved by the **increase in the density of dislocations by**:

- Plastic deformation (dislocation hardening/ « **Strain Hardening** »)
- Introduction of **inner interfaces** (inclusions or different phases)
- Reduction of the grain size (**Hall-Petch effect**.)

$$\sigma_y = \sigma_o + K d^{-1/2}$$

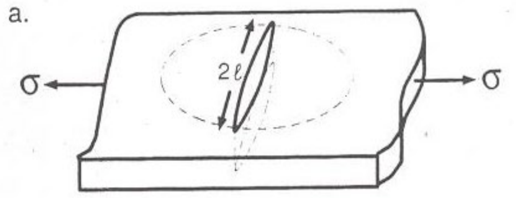
σ_o is the intrinsic residual stress of the films, K is a constant, and d is the grain size.

Hall, E.O., Proc. Roy. Soc. London B64 (1951) 474,
Petch N.J., Jour. Iron Steel Inst.174 (1953) 25.

Fragile fracture

Fracture theory of Griffith

Propagation of a fracture of a length of 2l and depth of d.



Tensile stress opens the crack and elastic energy is liberated from the film. This energy is opposed by the interatomic bonds; we obtain: $E_e = \frac{\sigma^2}{2E}$

$$E_{Tot} = -\frac{\sigma^2}{2E}\pi d l^2 + 4\gamma l d$$

where πdl² is the elastic energy interaction volume

To express fast crack propagation:

$$\frac{dE_{Tot}}{dl} = 0 \qquad \Rightarrow \sigma_c = \sqrt{\frac{4\gamma E}{\pi l}}$$

Fragile fracture

N.B. The metals are generally more tough since the plastic deformation slows down the crack propagation.

Toughness

Generally, $\sqrt{4\gamma E}$ represents the **fracture toughness, K_c**.

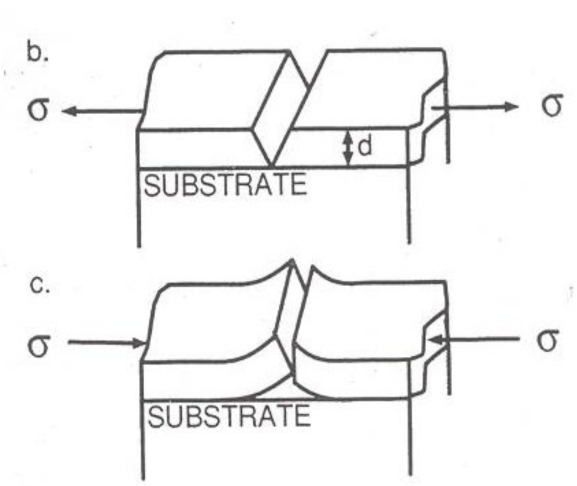
Hence, for a fast crack propagation, we obtain:

$$\sigma\sqrt{\pi l} \geq K_c \quad \textbf{(MPa}\sqrt{\textbf{m}}\textbf{)}$$

Crack propagation across a film with thickness d:

$$\sigma d^{\frac{1}{2}} \geq K_c(c) \big/ \sqrt{\pi}$$

where $K_c(c)$ is the toughness of the film



Delamination

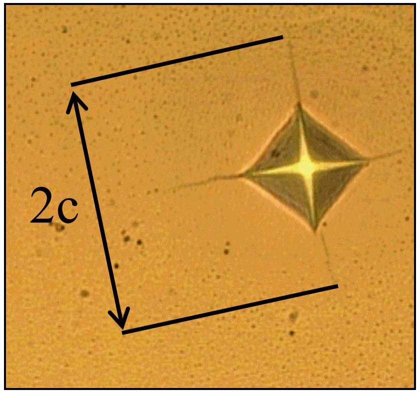
$$\sigma d^{\frac{1}{2}} \geq K_c(i) \big/ \sqrt{\pi}$$

where $K_c(i) = \sqrt{4\gamma E}$ where γ is the delamination interfacial energy.

Fragile cracking

Measurement technique

By indentation



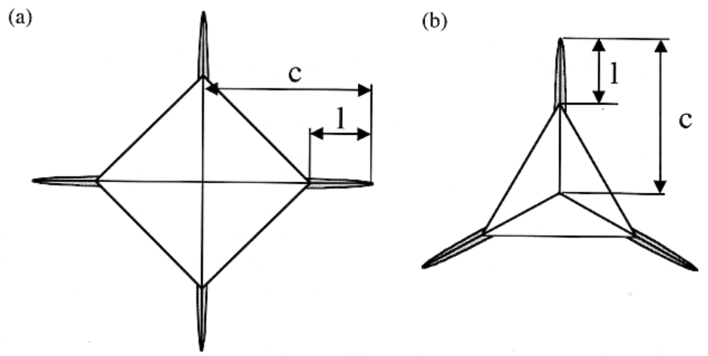


Fig. 7.12 Crack parameters for Vickers and Berkovich indenters. Crack length c is measured from the center of contact to end of crack at the specimen surface (After reference 47).

Vickers

$$K_C = X_v \left(\frac{a}{l}\right)^{1/2} \left(\frac{E}{H}\right)^{2/3} \left(\frac{L}{c^{3/2}}\right)$$

where
K = toughness of the film
X_v = constant
E = Young's modulus
H = hardness
L = load
and
c = l + a

Berkovich

$$K_C = 1.073 X_v \left(\frac{a}{l}\right)^{1/2} \left(\frac{E}{H}\right)^{2/3} \left(\frac{L}{c^{3/2}}\right)$$

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2. **Mechanical stability of thin films**
    - 2.1 Elasto-plastic regime, electro-static model
    - 2.2 Ductile and fragile fracture

3. **Adhesion**

4. **Mechanical stress**

5. **Hardness**
    - 5.1 Hardness measurement techniques
    - 5.2 Static and depth-sensing indentation

6. **Nanocomposite materials – case study**
    - 6.1 Superhard and ultrahard materials
    - 6.2 Nanostructured systems
    - 6.3 Hardness in nanocomposites

Adhesion

Definition

ASTM D907-70 defines adhesion as:

« State in which two surfaces are held together by the interface forces that may the valence forces or the interface interlocking or both »

In practice, the main difficulty is to separate two surfaces by which the two objects are held together.

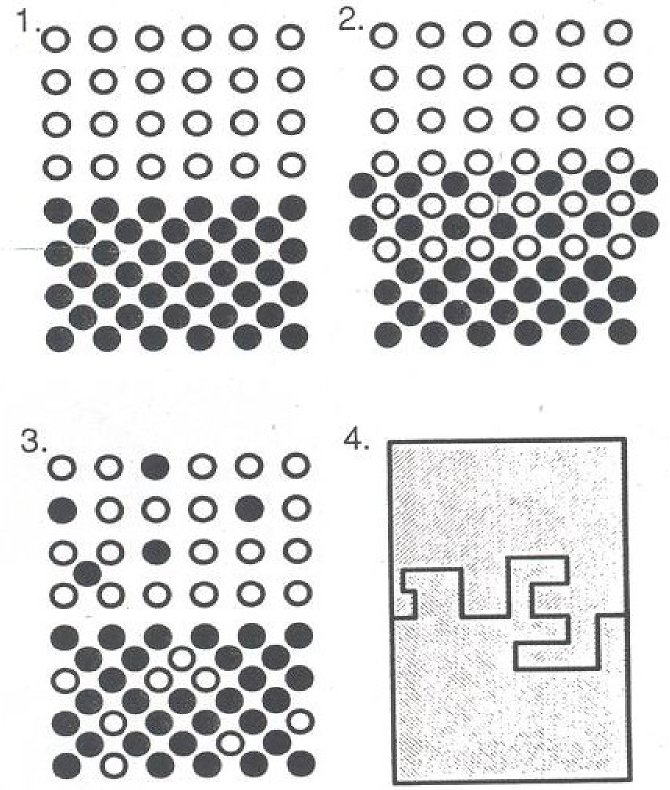
Microscopic approach: Nature of the interatomic bonds
Pragmatique approach: Mechanical testing

Adhesion models

a) Mechanical interlocking
   ⇒ Penetration of the film in the irregularities across the interface (cavities, pores, asperities etc.)

b) Electrostatic
   ⇒ Coulombic attraction between two surfaces (generally applies to metals)

c) Diffusion
   ⇒ Diffusion of the atoms or molecules of the film toward the substrate and vice-versa (depends on the material and the temperature)



Adhesion models (cont'd)

d) Thermodynamic

$\Rightarrow$ The most accepted model;

$\Rightarrow$ Interatomic or intermolecular interactions (ionic, covalent, metallic, hydrogen and Van der Waals forces)

$\Rightarrow$ these interactions are represented by the surface energy

Work necessary to separate two surfaces

$$W_A = \gamma_f + \gamma_s - \gamma_{fs}$$

where γ_f, γ_s and γ_{fs} are surface energies of the film, of the substrate and of the interface

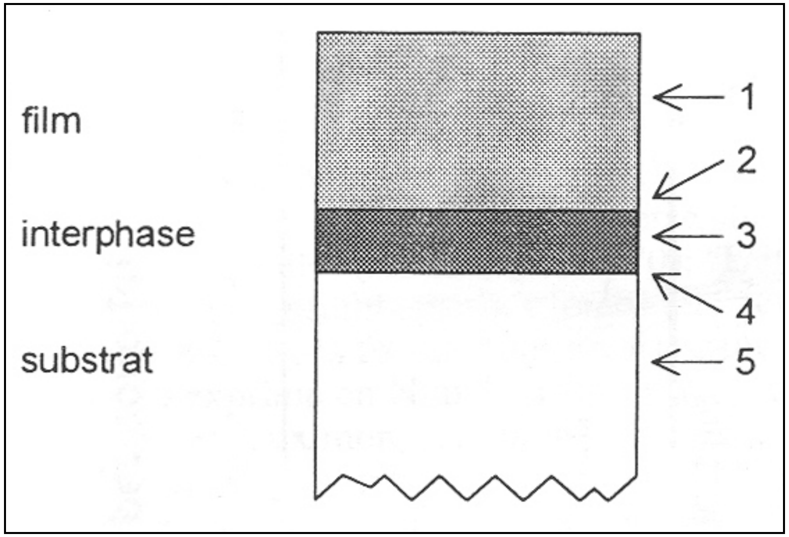
For $W_A > 0$ we have attraction (or adhesion) and for $W_A < 0$ we have repulsion.

Measurement approaches

In the majority of cases, we do not directly measure the adhesion forces: Comparative measurements

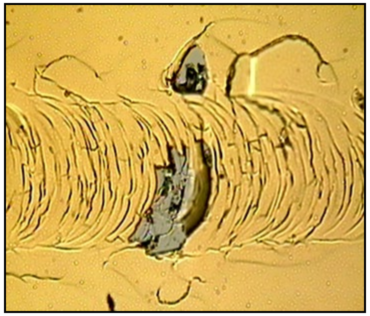
Five modes of rupture are possible:

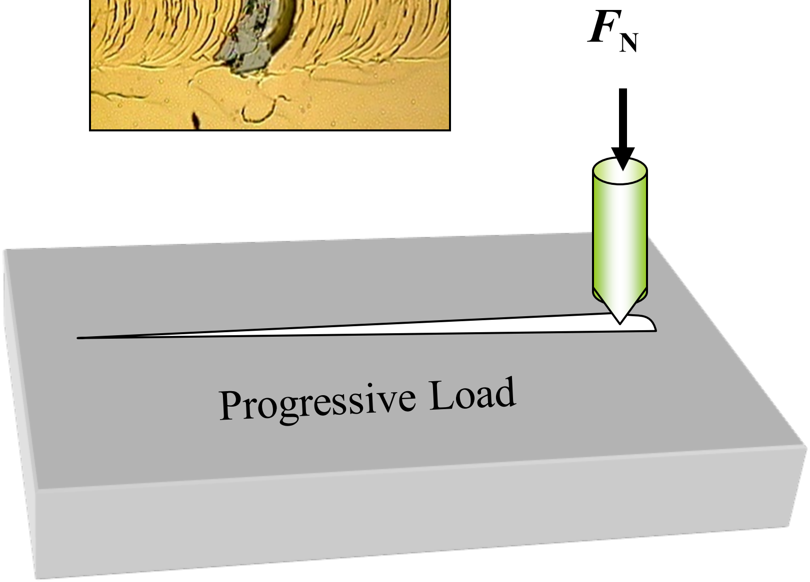
1. Within the film (cohesive)
2. Within the film-interphase (adhesive)
3. Interphase (adhesive)
4. Interphase-substrate (adhesive)
5. Within the substrate (cohesive)

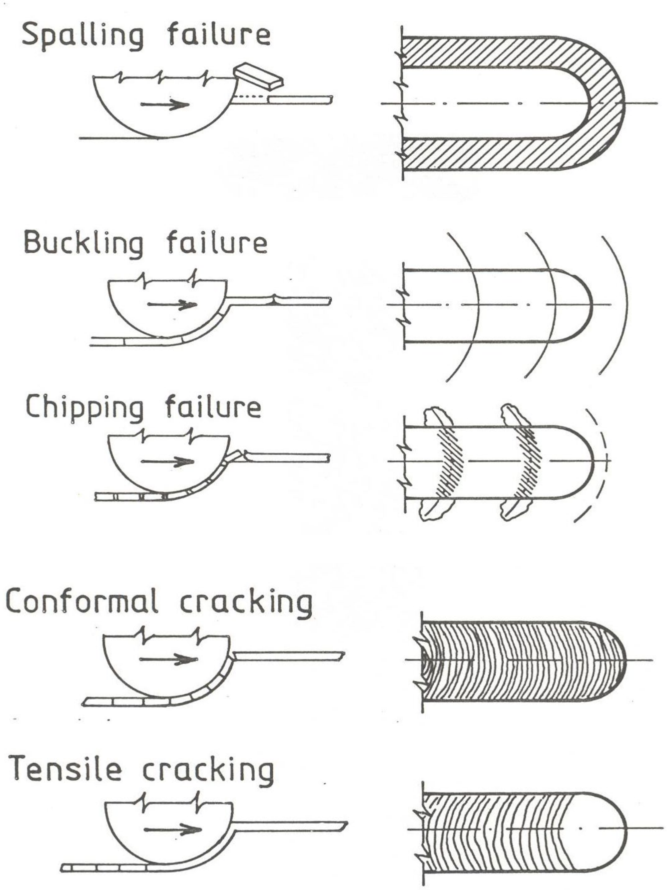


Measurement technique - scratching

Determination of a critical load L_c during scratching of the film using a Rockwell C type diamond tip.







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Why is it important to study the stress of thin films ?

⇒ Negative effects

- Decrease of adhesion
- Substrate deformation
- Generation of crystal defects
- etc.

⇒ Positive effects

- Increase of hardness
- Improvement of the wear-, abrasion-, and erosion resistance
- Functional properties
- etc.

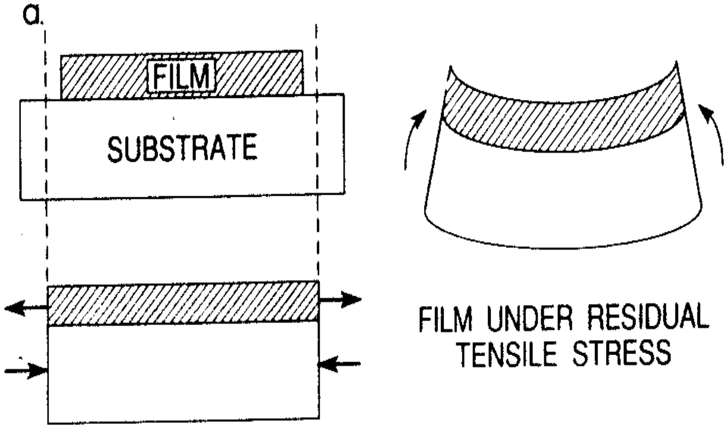
Stress is always present in films and coatings even when there is no external load (solicitation).

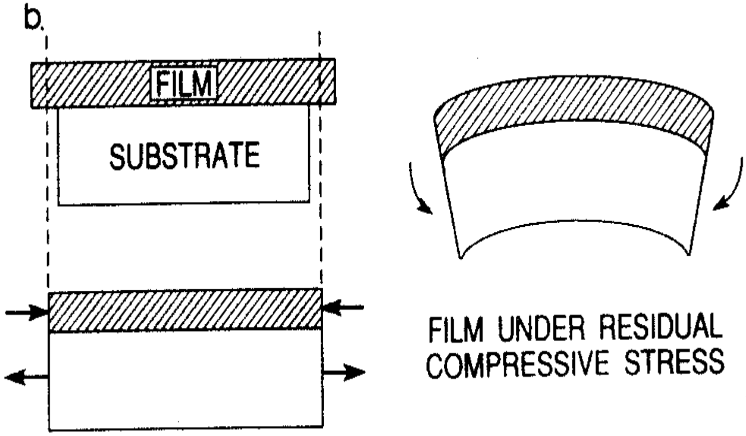
⇒ Optimization of the film systems

Residual stress in thin films

Definition: Forces present in the film without other external forces

Behavior in tension and in compression





Film < substrate

To maintain the system in equilibrium:

- Film must be in *tension*
- *Substrate needs to be in compression*
- *Curvature established to equilibrate the moments*

Film > substrate

To maintain the system in equilibrium:

- Film needs to be in *compression*
- *Substrate needs to be in tension*
- *Curvature established to equilibrate the moments*

Residual mechanical stress

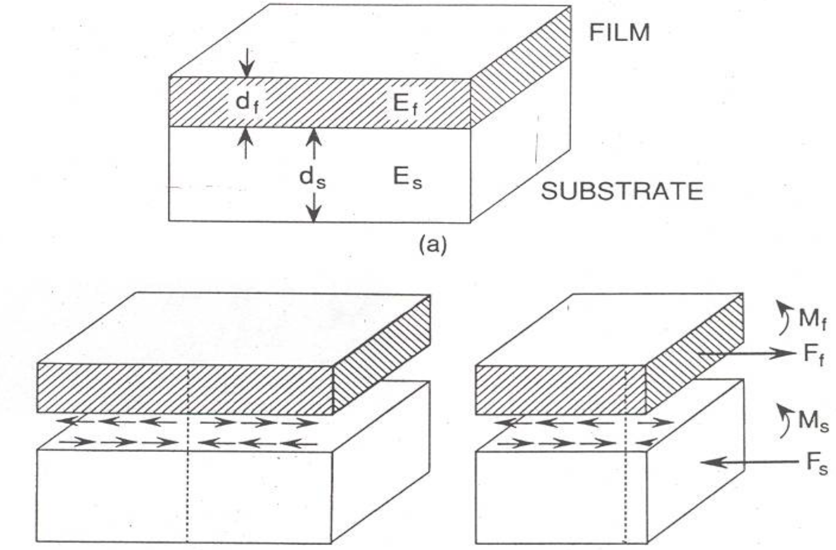
Phenomena controlling intrinsic stress

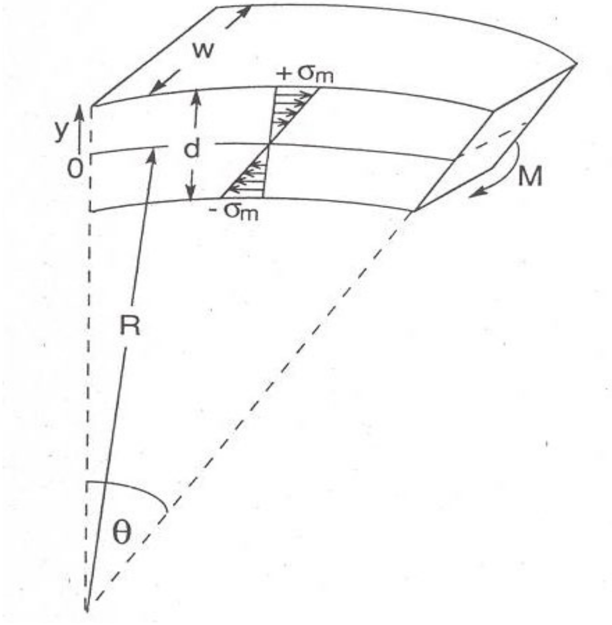
1. Difference of the thermal expansion coefficients
2. Atoms incorporation
3. Chemical reactions
4. Difference between the crystal structures
5. Variation of the interatomic distances due to different crystal size
6. Recrystallization (metals)
7. Microscopic porosity, dislocations
8. Phase transformation

$$\sigma_{tot} = \sigma_{int} + \sigma_{therm} + \sigma_{env}$$

Useful reference:
G. Abadias, E. Chason, J. Keckes, M. Sebastiani, G.B. Thompson, E. Barthel, G.L. Doll, C.E. Murray, C.H. Stoessel, L. Martinu, **"Review Article: Stress in thin films and coatings: Current status, challenges, and prospects",** J.Vac.Sci.Technol.A, **36**(2) (2018) 020801.

Derivation of the Stoney equation





Hooke's law

$$\sigma_m = E\left\{\frac{(R \pm d/2)\theta - R\theta}{R\theta}\right\} = \pm\frac{Ed}{2R}$$

In equilibrium: $M_{tot} = 0$

$$\left(\frac{d_f + d_s}{2}\right)F_f = M_f + M_s$$

Intrinsic stress

Stoney equation (total stress)

$$\boxed{\sigma_f = \frac{F_f}{d_f w} = \frac{1}{6R}\frac{E_s d_s^{\,2}}{(1-\nu_s)d_f}}$$

Thermal stress

$$\sigma_f(T) = \frac{F_f}{d_f w} = (\alpha_s - \alpha_f)\Delta T \frac{E_f}{(1-\nu_f)}$$

Se: Milton Ohring, *The materials science of thin films,* Academic Press, San Diego, 1992, 2nd edition 2002.

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Hardness

Definition

Capability of material to resist plastic (permanent) deformation when an external force is applied.

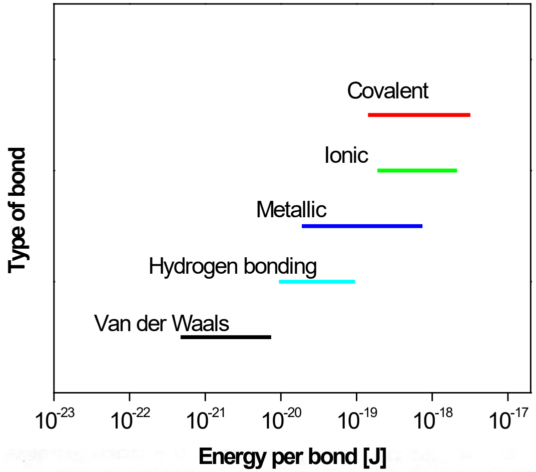
The hardness is related to σ_y in compression, and it depends on : Type of interatomic bonds

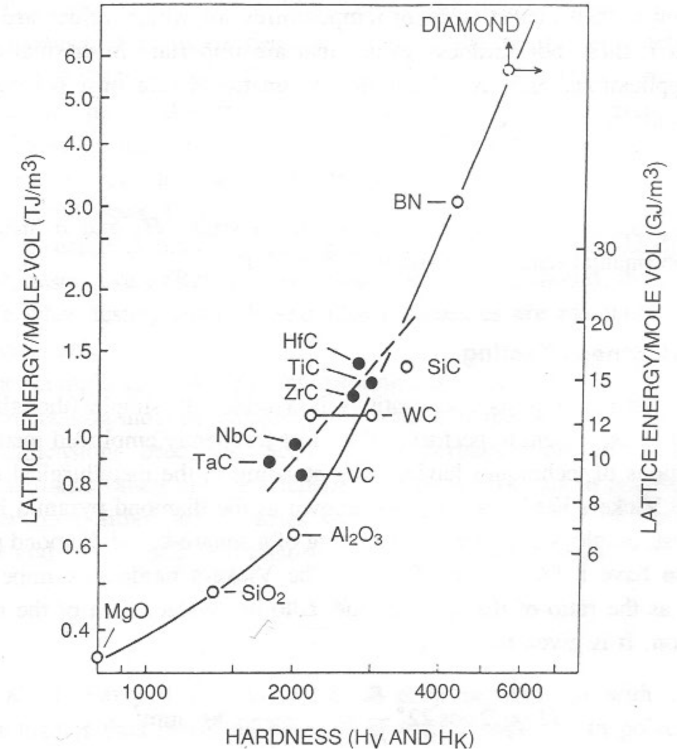
$\Rightarrow$ The hardness increases with the cohesive energy and is inversely proportional to the bond length.

- Microstructure
  - $\Rightarrow$ Phases
  - $\Rightarrow$ Impurities
  - $\Rightarrow$ Density of dislocations
  - $\Rightarrow$ Grain size (Hall-Petch effect)

$$H = H_i + K_H d^{-1/2}$$

where H_i is the intrinsic hardness of a monocrystal, K_H is a constant and d is the grain size.





Measurement of the hardness:

Generally, the hardness represents an average pressure under the indentation tip.

$$H = \frac{L}{A_{in}}$$

where L is the applied load and A is the contact area between the load and the sample.

Three principal methods to measure hardness:

1. Scratching according the Mohs scale (Diamond = 10 and talc = 0). (used in geology)
2. Static indentation where one measures the trace and calculates the hardness from the known geometry
3. Depth-sensing indentation

Static indentation

ASTM documents:

E10-01e1 Standard Test Method for Brinell Hardness of Metallic Materials

E18-05e1 Standard Test Methods for Rockwell Hardness and Rockwell Superficial Hardness of Metallic Materials

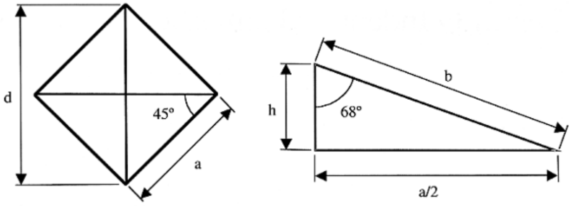
E92-82(2003)e2 Standard Test Method for Vickers Hardness of Metallic Materials

E384-05a Standard Test Method for Microindentation Hardness of Materials

C1326-03 Standard Test Method for Knoop Indentation Hardness of Advanced Ceramics

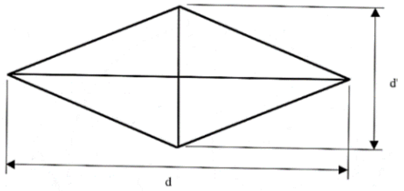
C1327-03 Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics

Static indentation



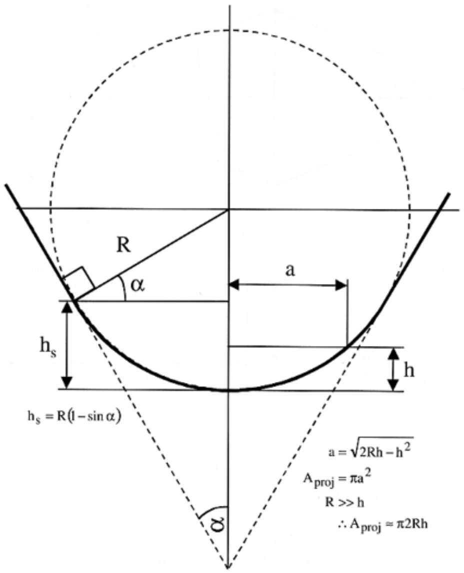
Vickers indenter $$H_v = 2\cos 22^o \frac{L}{(d)^2} \quad \left(\frac{Kg}{mm^2}\right)$$

L – load in kg, d – length of the diagonal



Knoop indenter $$H_k = 14.23\frac{L}{(d)^2} \quad \left(\frac{Kg}{mm^2}\right)$$

Spherical indenter



Brinell hardness (contact area)

$$H_B = \frac{2L}{\pi D\left(D - \sqrt{D^2 - d^2}\right)} \quad \left(\frac{Kg}{mm^2}\right)$$

Meyer hardness (projected area)

$$H_M = \frac{4L}{\pi d^2} \quad \left(\frac{Kg}{mm^2}\right)$$

Fischer-Cripps, A.C. 2002. *Nanoindentation. New York*: Springer. 197p.

Static indentation

« Indentation size effect », ISE

In static indentation, we suppose that the indentation trace equal to the final (residual) trace.

For shallow indentations, the final trace can be significantly reduced by the elastic rebound of the materials – overestimating the value of H.

To account for the ISE, one can express H as:

$$H = qs^{M-2}$$

Here, q is a constant, s is the diagonal, and M is the ISE index (Meyer).

Burnett, P.J., Rickerby D.S., Thin Solid Films 148 (1987) 41-65.

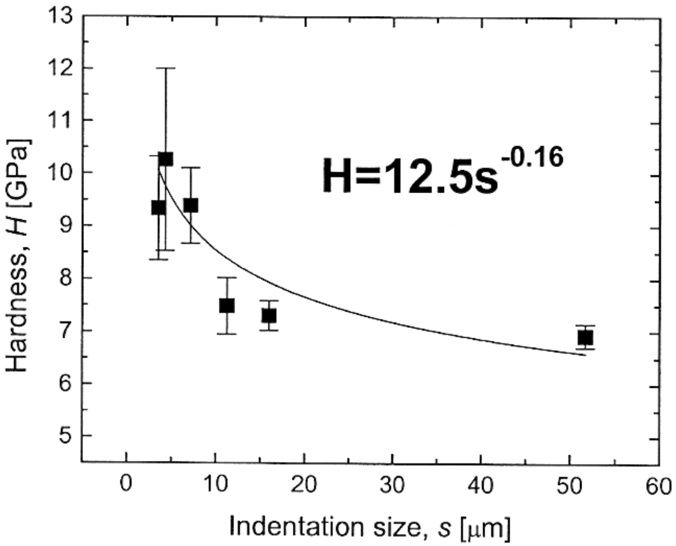


Figure 4.1. *Indentation Size Effect (ISE) for a c-Si substrate.*

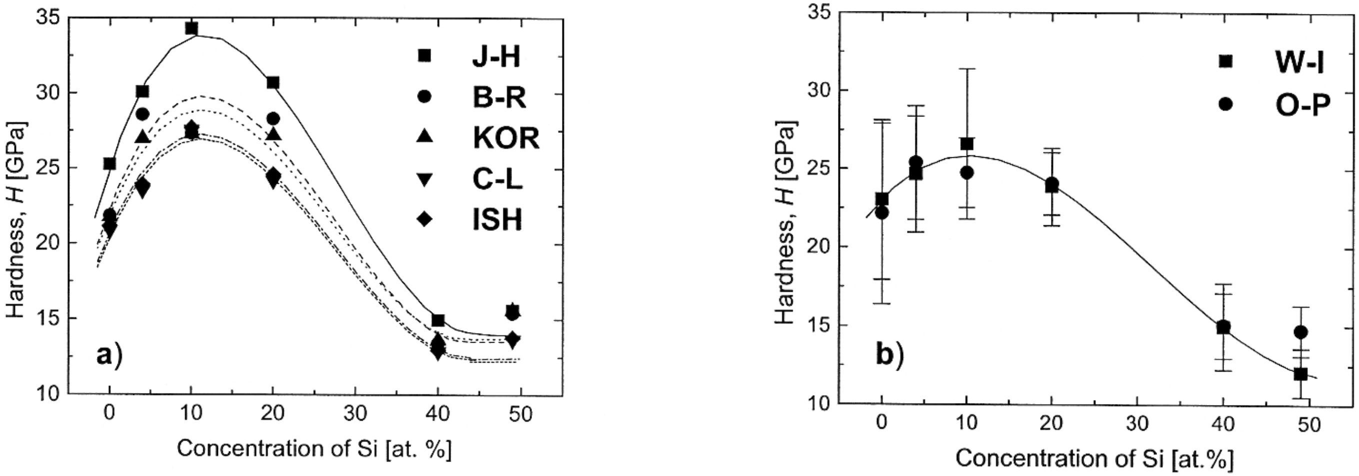
Static indentation models

Substrate effect

Need to separate the hardness of the film (H_f) from the hardness of the substrate (H_s) - the measured hardness is « composite » (H_c).

$$H_c = H_s + a_h (H_f - H_s)$$

There are different models to evaluate $\mathbf{a_h}$.



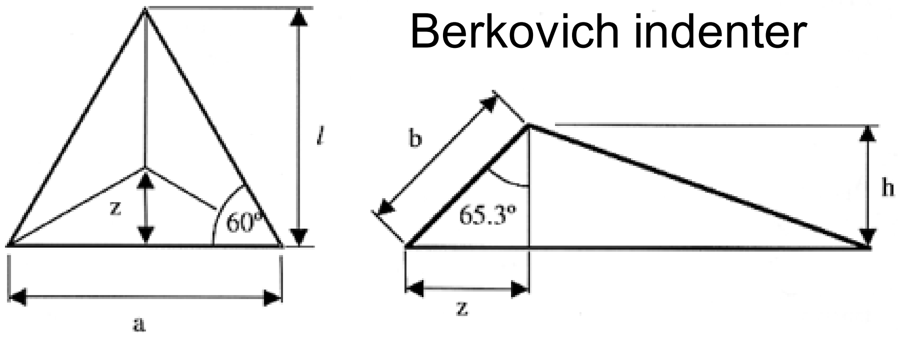
P. Jedrzejowski *et al.*, TSF, 2004

Depth-sensing indentation

Static methods are mainly used for bulk materials and for relatively thick layers (d> 5 microns).

To limit the influence of the substrate in the measurements, the zone of plastic deformation under the indenter must not reach the substrate. For this reason, the maximum depth of indentation should generally be less than 10% of the thickness of the film.

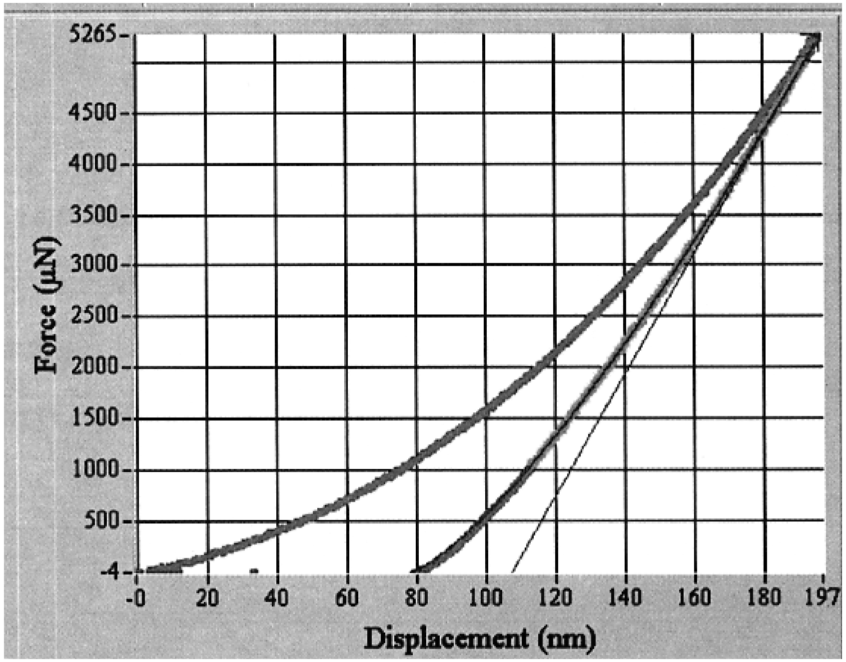
- It is a dynamic indentation measurement technique that measures the position of a point during the loading and unloading of a specimen.
- Bypasses the problems of static indentation by not using the final trace of the indenter but rather the behavior of the material during the indentation.



Berkovich indenter

Used mainly for the indentation resolved in depth.

Fischer-Cripps, A.C. 2002. *Nanoindentation. New York*: Springer. 197p.



Depth-sensing indentation

Theory

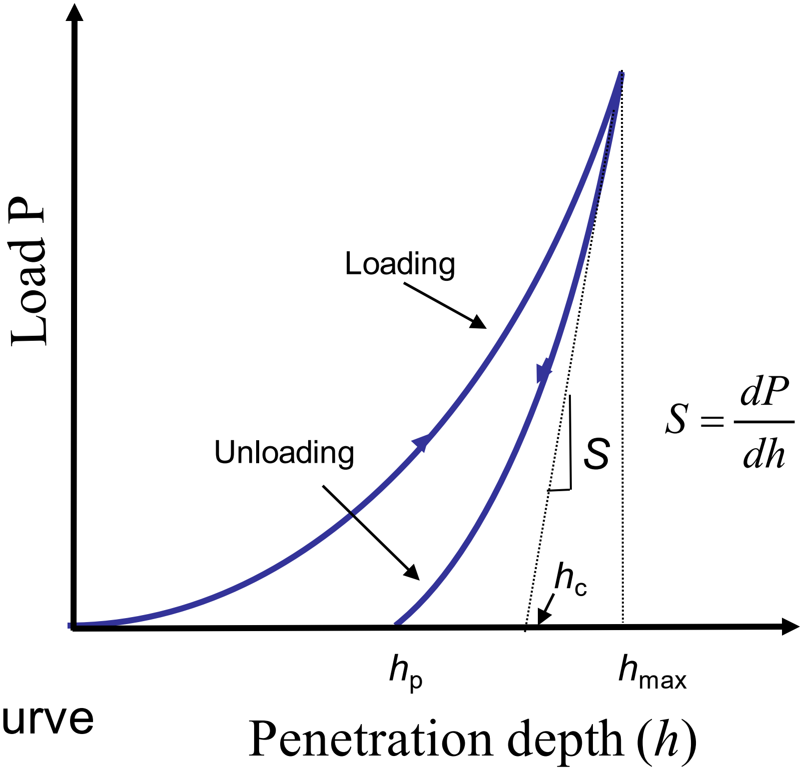
Using the theory of elastic contact, Bulychev et al. proposed:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

where, accroding to Sneddon:

$$\frac{1}{E_r} = \frac{1-\upsilon^2}{E} + \frac{1-\upsilon_i^2}{E_i}$$

(index i stands for the indenter)



Hence, by modeling the load displacement curve and knowing the contact area during the indentation, one can calculate the reduced modulus E_r of the indented material.

Sneddon I.N., Int. J. Mater. Res. 7:3 (1965) 47.

Bulychev S.I., Alekhin V.P., Shorshorov M.K.H. 8 (1976) 1084-1097.

Depth-sensing indentation

Theory

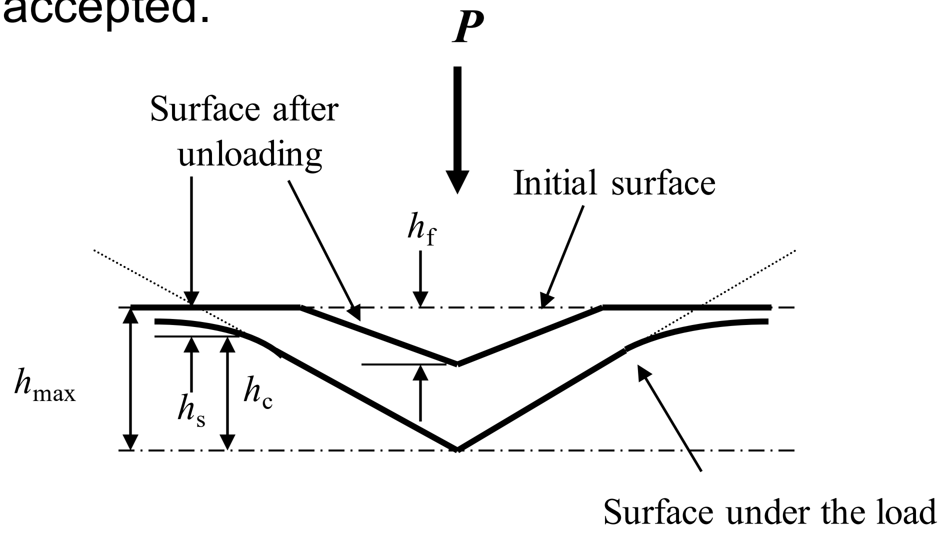
Sneddon, Oliver *et al* and Doerner and Nix have all proposed models to evaluate P and A as a function of indentation depth. These works led to the method proposed by **Oliver et Pharr** that is now generally accepted.

Area function:

$A = f(h_c)$ where h_c is the depth corresponding to the situation when the indenter and the material are in contact.

Perfect Berkovich tip

$A = 24.5\ h_c^2$



But how to evaluate h_c?

$$h_{max} = h_c + h_s$$

where h_s is the dislacement of the material's surface during indentation.

Doerner M.F., Nix W.D., J. Mater. Res. 1 (1986) 601-609.

Depth-sensing indentation

Methodology

1. Chose the loading function
2. Data acquisition
3. Model the unloading curve as: $P = D(h_{\max} - h_k)^m$
4. Calculate the stiffness S : $S = \dfrac{dP}{dh}$
5. Evaluate h_c : $h_c = h_{\max} - \eta \dfrac{P_{\max}}{S}$
6. Calculate the contact area:

$$A = f(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{\frac{1}{2}} + C_3 h_c^{\frac{1}{4}} + \ldots$$

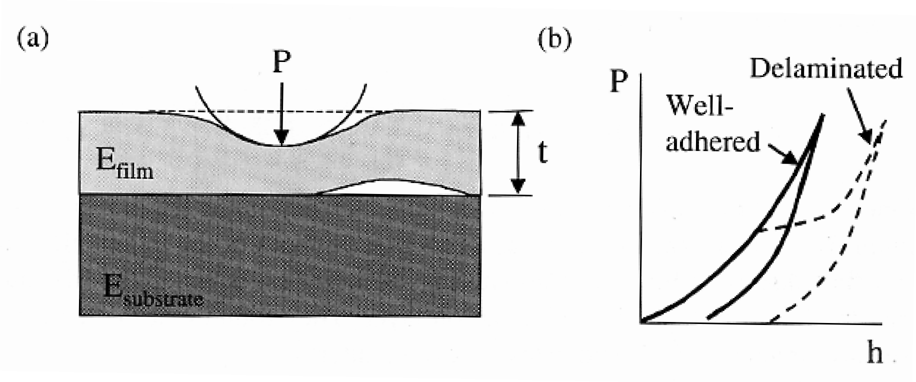
7. Calculate H and E_r

$$H = \frac{P_{\max}}{A} \qquad E_r = S\frac{\sqrt{\pi}}{2\sqrt{A}}$$

Oliver W.C., Pharr G.M., J. Mater. Res. 7, 1564-1583 (1992)

Depth-sensing indentation

Analysis of the curves



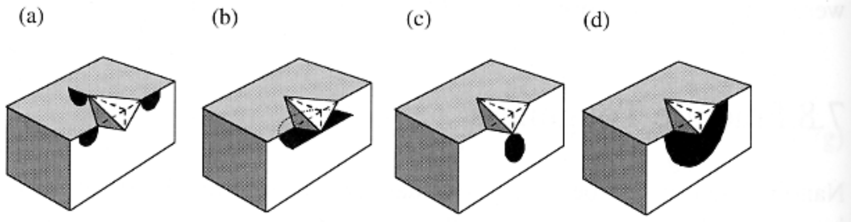
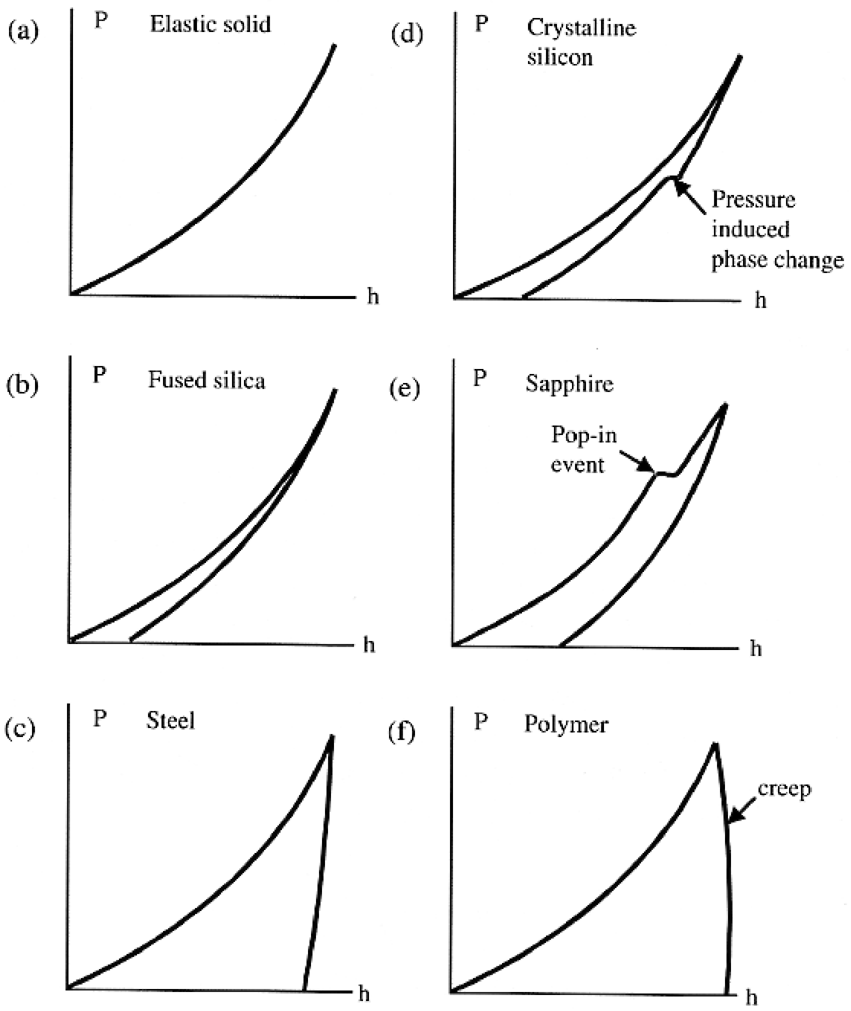


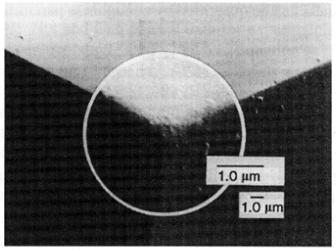
Fig. 7.11 Crack systems for Vickers indenter: (a) radial cracks, (b) lateral cracks, (c) median cracks, (d) half-penny cracks (after reference 47).

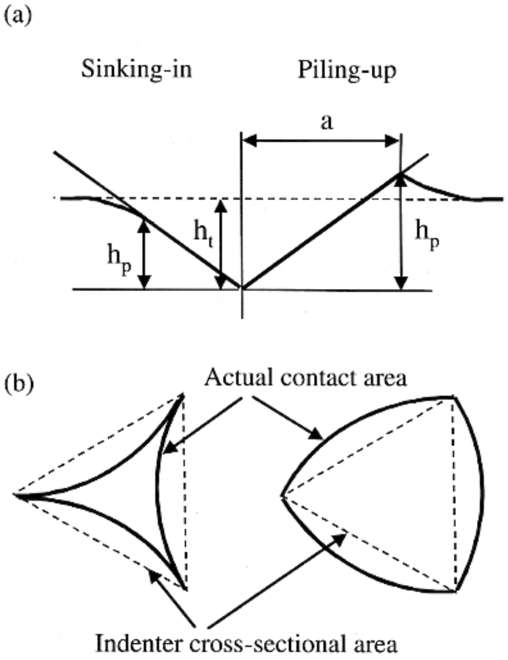


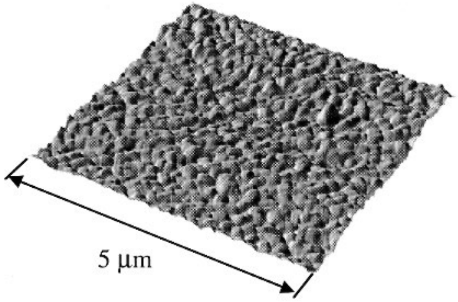
Depth-sensing indentation

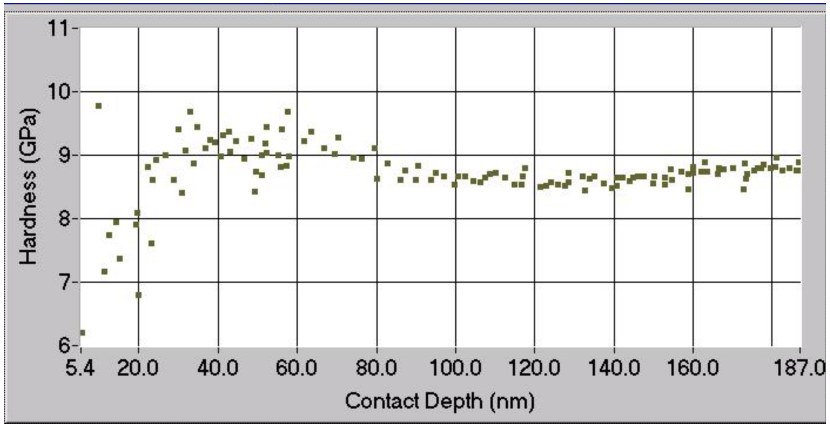
Sources of artefacts

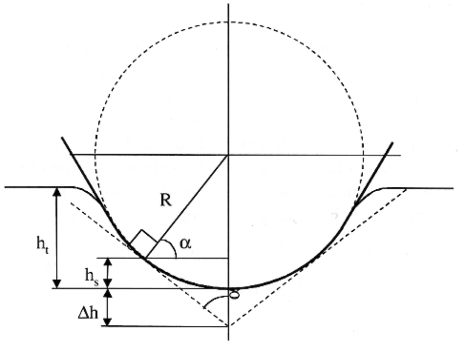
1. Thermal drift
2. Initial depth of penetration
3. Equipment compliance
4. Indenter geometry
5. Indentation size
6. Sample (surface finish, homogeneity, substrate, contamination etc.)







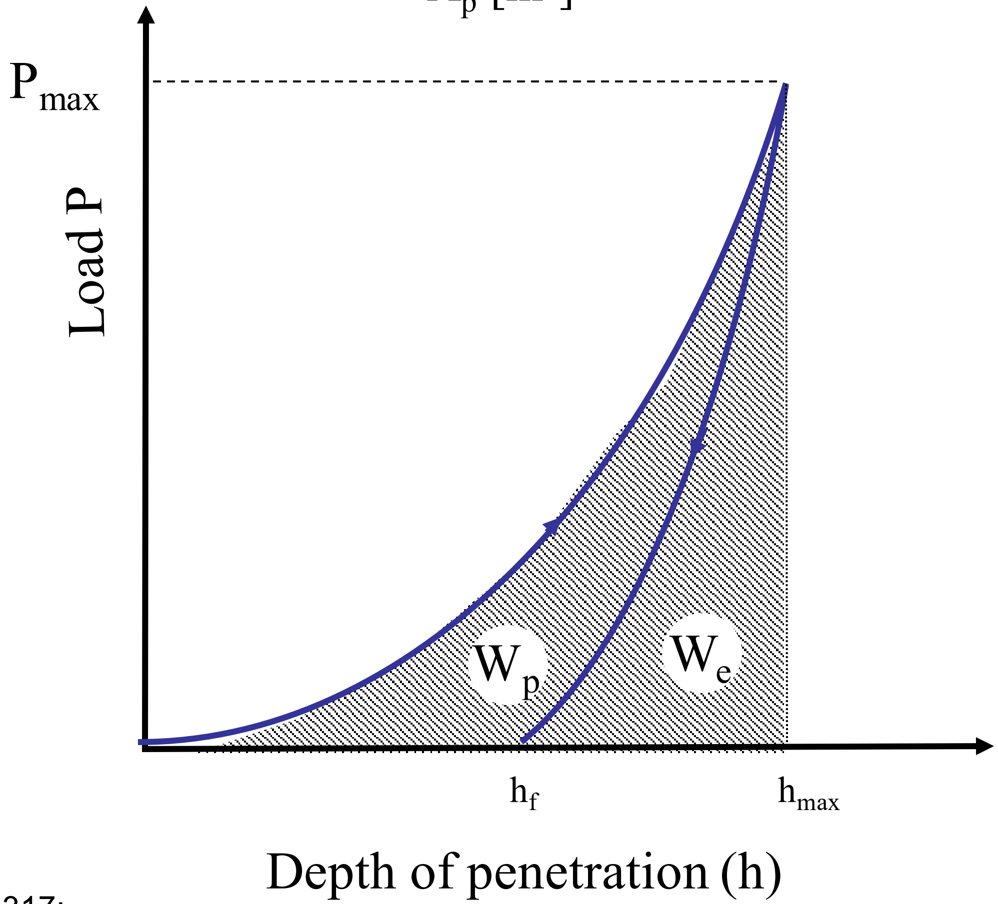




Depth-sensing indentation

Data analysis using the Work of indentation

$$\text{Hardness} = \frac{\text{Load } P\ [\text{N}]}{A_p\ [\text{m}^2]} = \frac{\text{Plastic work } W_p\ [\text{J}]}{\text{Plastic volume } V_p\ [\text{m}^3]}$$



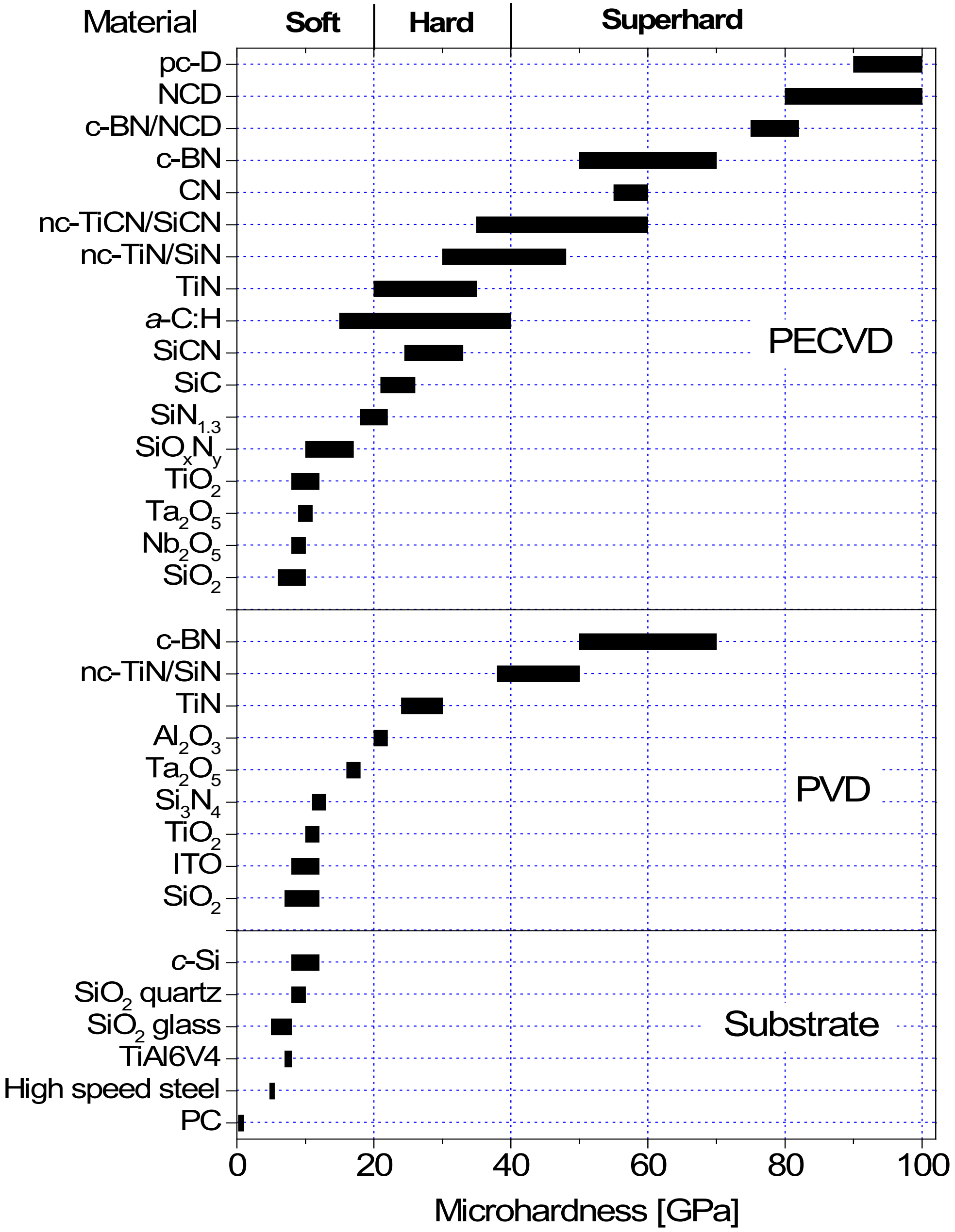
Hardness = Energy dissipated per unit of volume during indentation

$$W_{Tot} = W_p + W_e$$

$$H_p = \frac{kP^3}{9W_p}$$

k – geometrical constant of the indenter

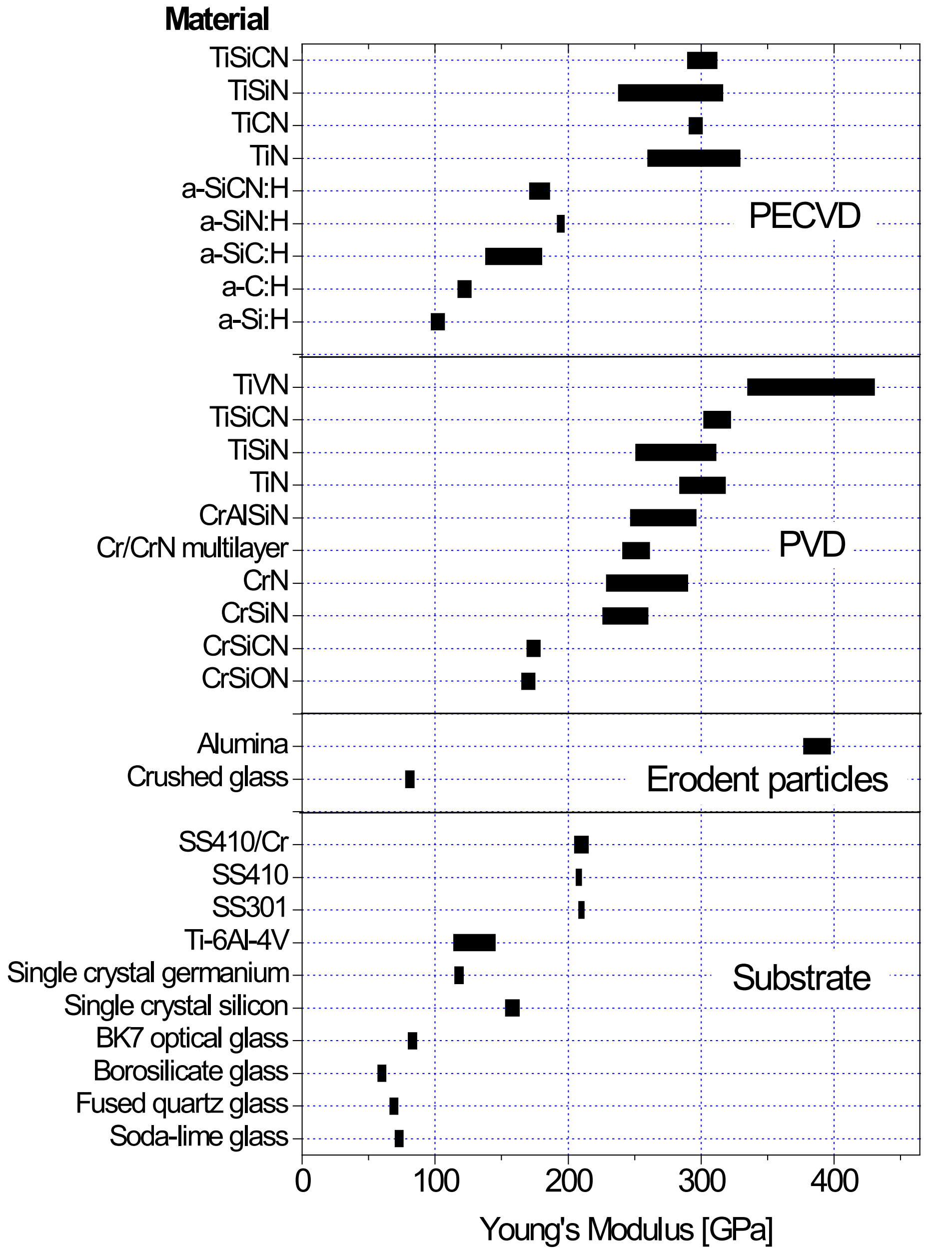
H - Microhardness of PVD and PECVD coatings



From:

L. Martinu, O. Zabieda, J.E. Klemberg-Sapieha: "*Plasma-Enhanced Chemical Vapor Deposition of Functional Coatings", in the "*Handbook on Thin Film Deposition Technologies", P.M. Martin, ed., Elsevier, Amsterdam, 2010, pp. 394-467

E - Elastic modulus of PVD and PECVD functional coatings



L. Martinu et al, in the "Handbook on Thin Film Deposition Technologies", P.M. Martin, ed., Elsevier, Amsterdam, 2010, pp. 394-467

Case studies on hard nanocomposite films

Superhard and ultrahard

Materials can be qualified as **superhard** when their *H* is higher than 40 GPa.

Such materials can be divided into two categories:
Materials with **intrinsic and extrinsic hardness**.

Intrinsic hardness depends on:
- Nature of interatomic bonds
- Bond length
- Coordination level

Example of diamond:
- Hardness between 70 and 100 GPa
- Four covalent bonds
- Small atoms

Other examples:
- Boron nitride
- B-C-N system

Extrinsic – microstructurally controlled - hardness:

⇒ Different phases
⇒ Introduction of inpurities
⇒ Increase of the density of dislocations
⇒ Decrease of the grain size
⇒ (Hall-Petch effect)

Structural design of CVD and PVD coatings

Nanostructured coatings

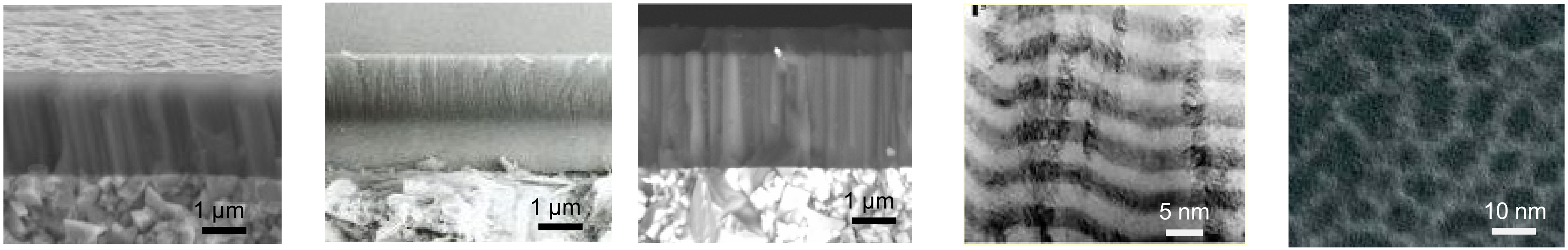
single layer coating

gradient coating

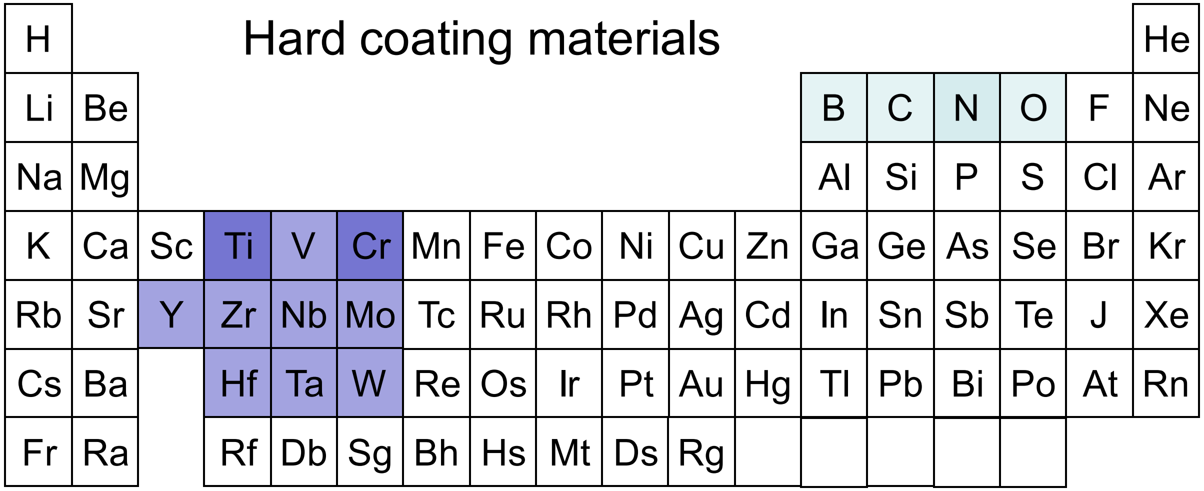
bilayer coating

nanolayered coating

nanocomposite coating



Hard coating materials



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

nitrides	TiN
carbides	TiC
borides	TiB_2
oxides	TiO_2
carbonitrides	Ti(C,N)
ternaries	(Ti,Al)N

diamond-like carbon DLC
composites nc-TiN/a-SiN

Nanocomposites

Nanostructured systems

Increase of hardness through the control of the microstructure on nanometer scale

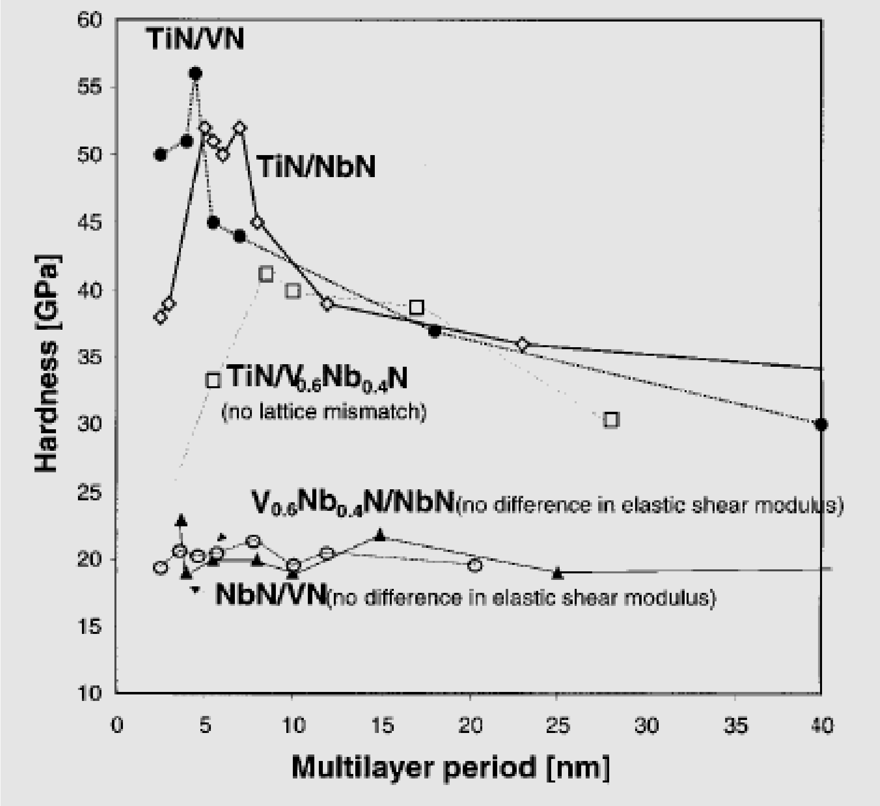
The hardness exceeds that of a mixture law according to which the hardness should be :

$$H_{ab} = \frac{V_a H_a + V_b H_b}{V_a + V_b}$$

where V_a et V_b are the volume fractions of phases a and b and H_a and H_b are the hardness values of the individual phases.

Nanolaminate structures

Multilayer systems with very thin layers with a periodicity **Λ** typically between 5 and 50 nm. Such small size restricts the movement of dislocations.

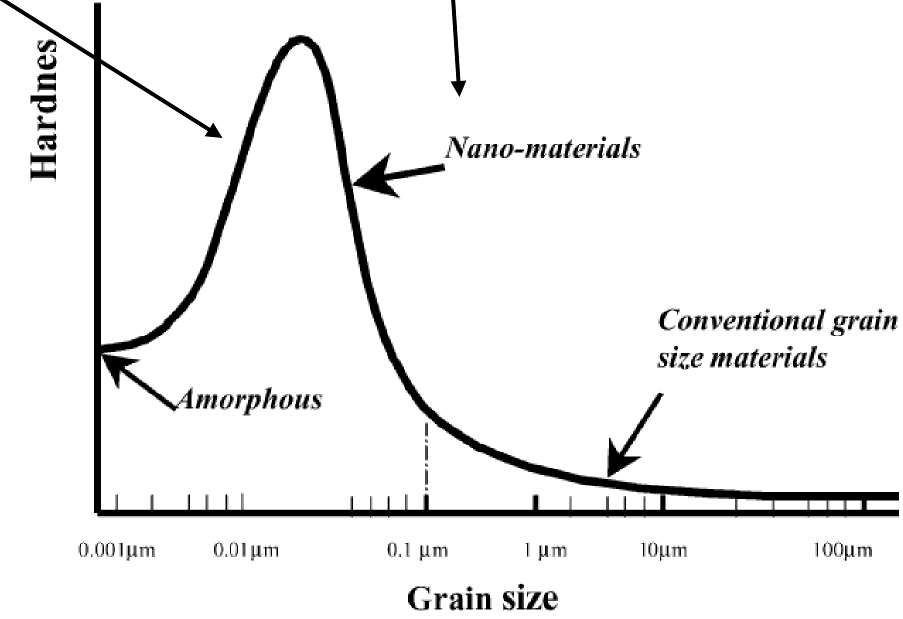


Nanocomposites

Hardness is maximized by restricting the movement of dislocations and propagation of defects by reducing the grain size:
inverse Hall-Petch effect and (more traditional) Hall-Petch effect

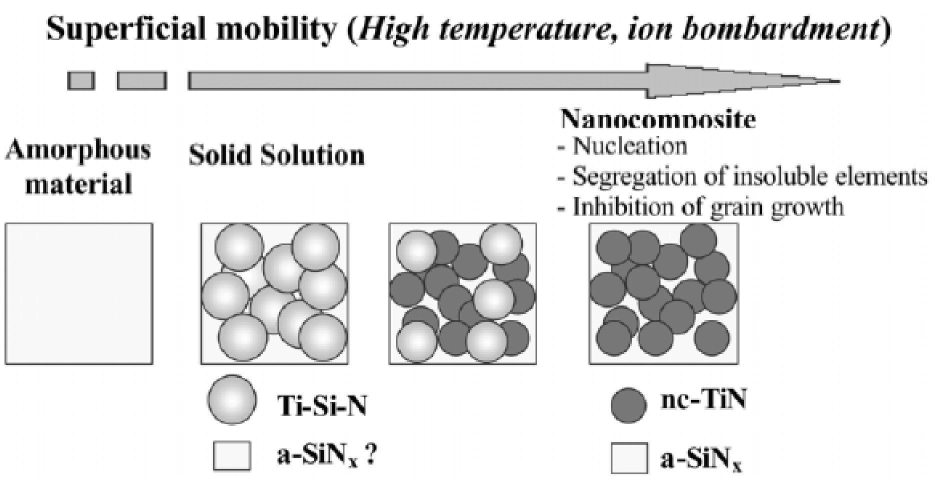
Significant effect for very small grains below the critical size: inverse effect:

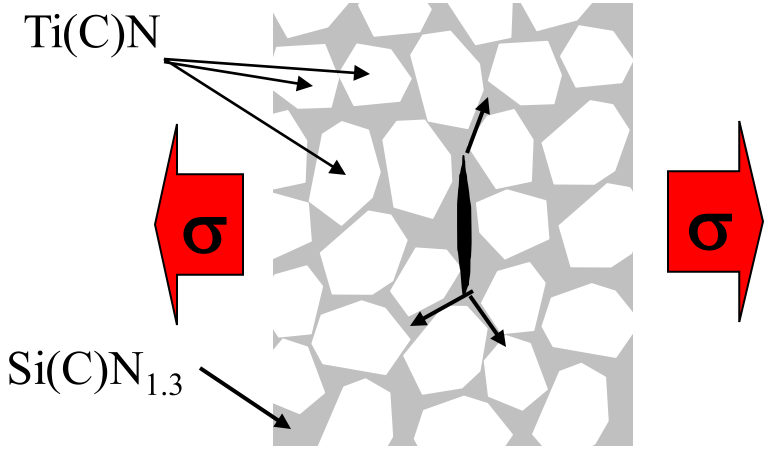
- Movement of dislocations is stopped;
- Grain boundary sliding is hampered by strong interfaces;
- The grains are too small to develop defects.



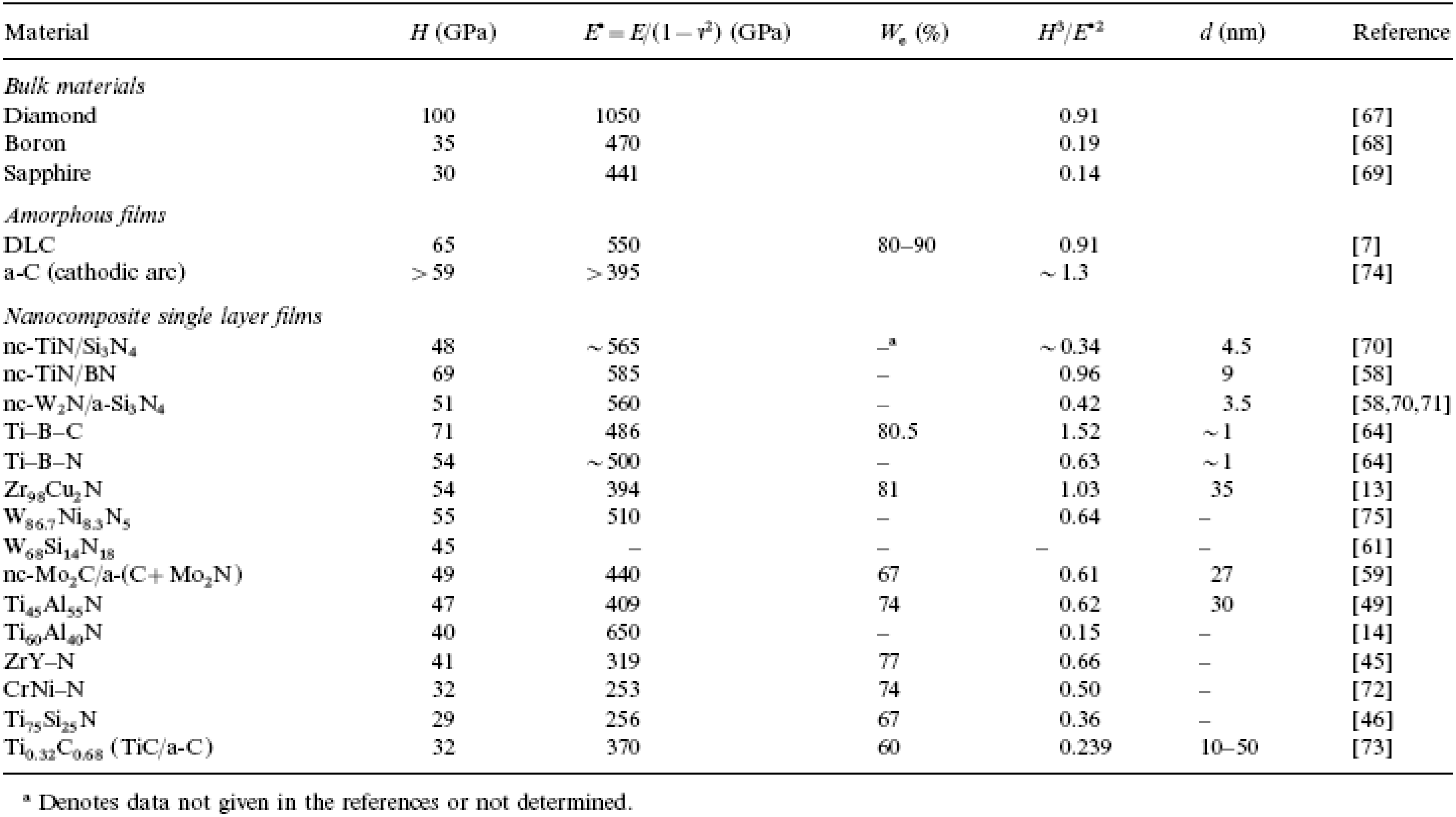
Nanocomposites

- Heterogeneous structures
- High hardness due to the presence of nanocrystalline particles in an amorphous or a polycrystalline matrix
- High cohesive forces at the grain boundaries
- The two phases need to be immiscible
- Large variety of combinations





Hard and superhard materials, nanocomposites



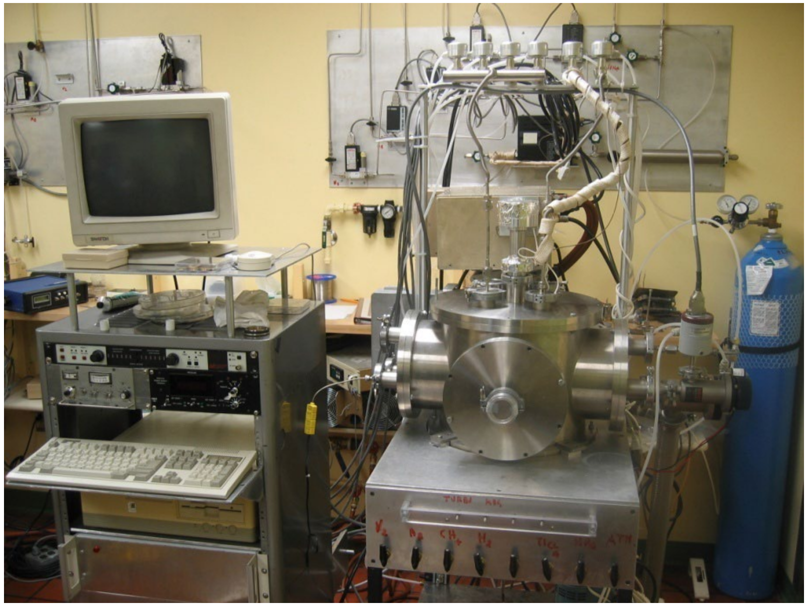
Material	H (GPa)	$E^* = E/(1-\nu^2)$ (GPa)	W_e (%)	H^3/E^{*2}	d (nm)	Reference
Bulk materials						
Diamond	100	1050		0.91		[67]
Boron	35	470		0.19		[68]
Sapphire	30	441		0.14		[69]
Amorphous films						
DLC	65	550	80–90	0.91		[7]
a-C (cathodic arc)	> 59	> 395		~ 1.3		[74]
Nanocomposite single layer films						
nc-TiN/Si_3N_4	48	~ 565	–[a]	~ 0.34	4.5	[70]
nc-TiN/BN	69	585	–	0.96	9	[58]
nc-W_2N/a-Si_3N_4	51	560	–	0.42	3.5	[58,70,71]
Ti–B–C	71	486	80.5	1.52	~ 1	[64]
Ti–B–N	54	~ 500	–	0.63	~ 1	[64]
$Zr_{98}Cu_2N$	54	394	81	1.03	35	[13]
$W_{86.7}Ni_{8.3}N_5$	55	510	–	0.64	–	[75]
$W_{68}Si_{14}N_{18}$	45	–	–	–	–	[61]
nc-Mo_2C/a-(C+ Mo_2N)	49	440	67	0.61	27	[59]
$Ti_{45}Al_{55}N$	47	409	74	0.62	30	[49]
$Ti_{60}Al_{40}N$	40	650	–	0.15	–	[14]
ZrY–N	41	319	77	0.66	–	[45]
CrNi–N	32	253	74	0.50	–	[72]
$Ti_{75}Si_{25}N$	29	256	67	0.36	–	[46]
$Ti_{0.32}C_{0.68}$ (TiC/a-C)	32	370	60	0.239	10–50	[73]

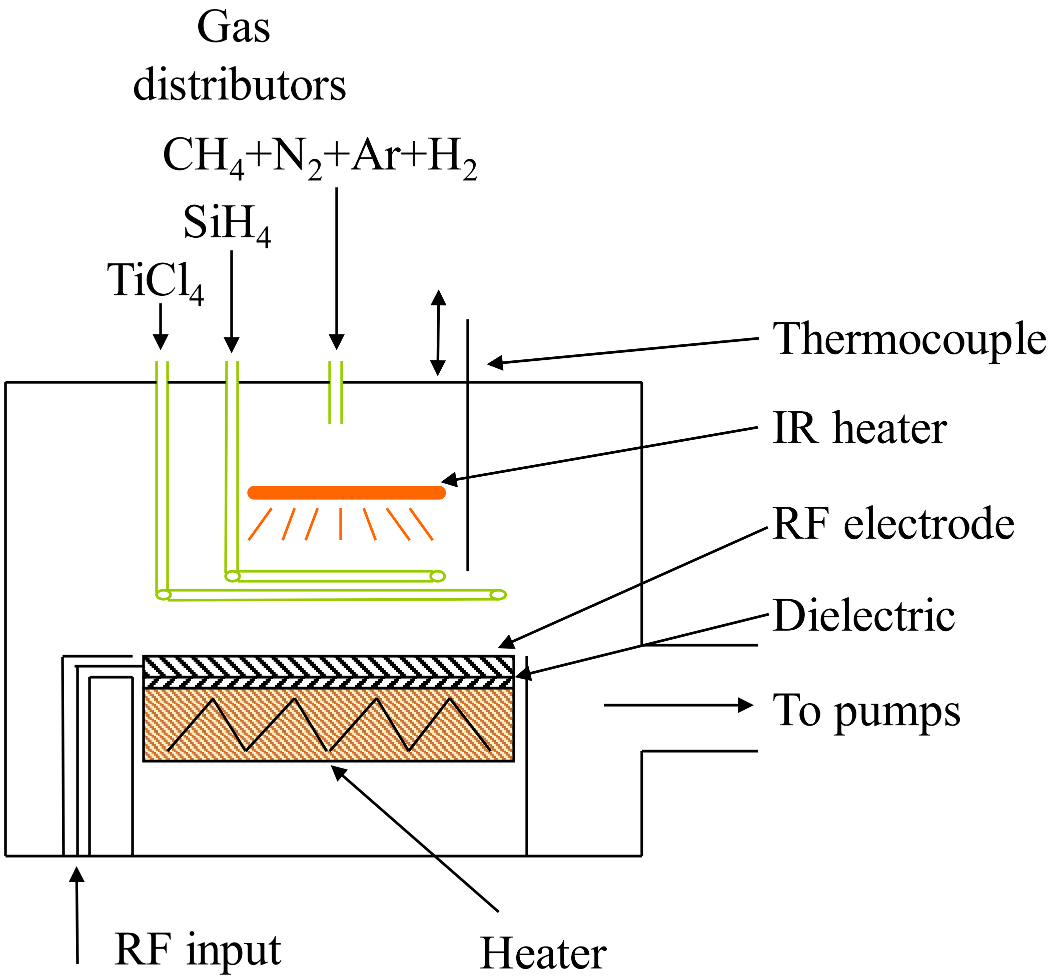
[a] Denotes data not given in the references or not determined.

PECVD deposition system for superhard coatings

Deposition

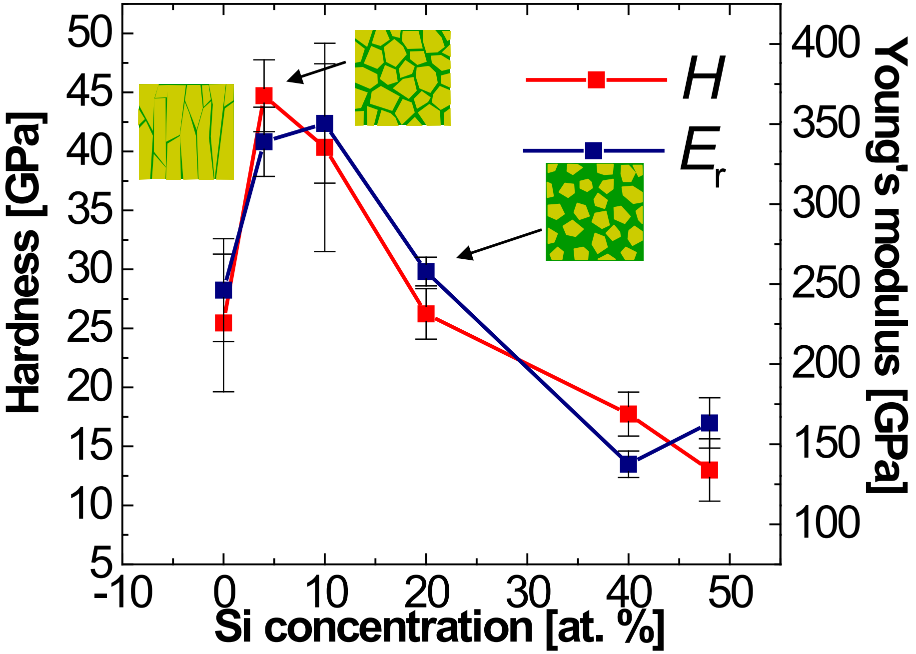
$TiCl_4$, SiH_4, CH_4, Ar, N_2, H_2
P = 100 - 200 mTorr
V_B = -600 V
T_S = 300-500 °C



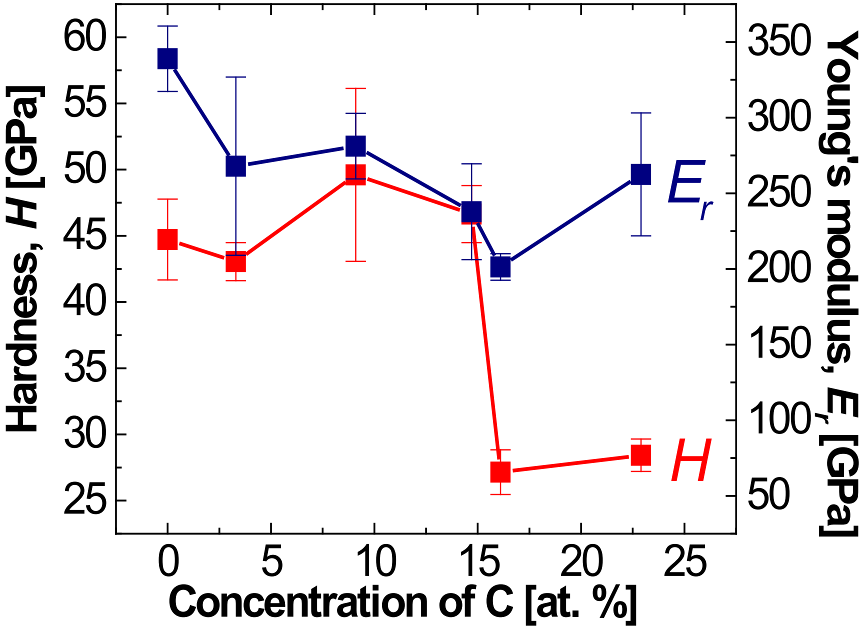


Mechanical properties of nanocomposites

nc-TiN/a-Si_3N_4

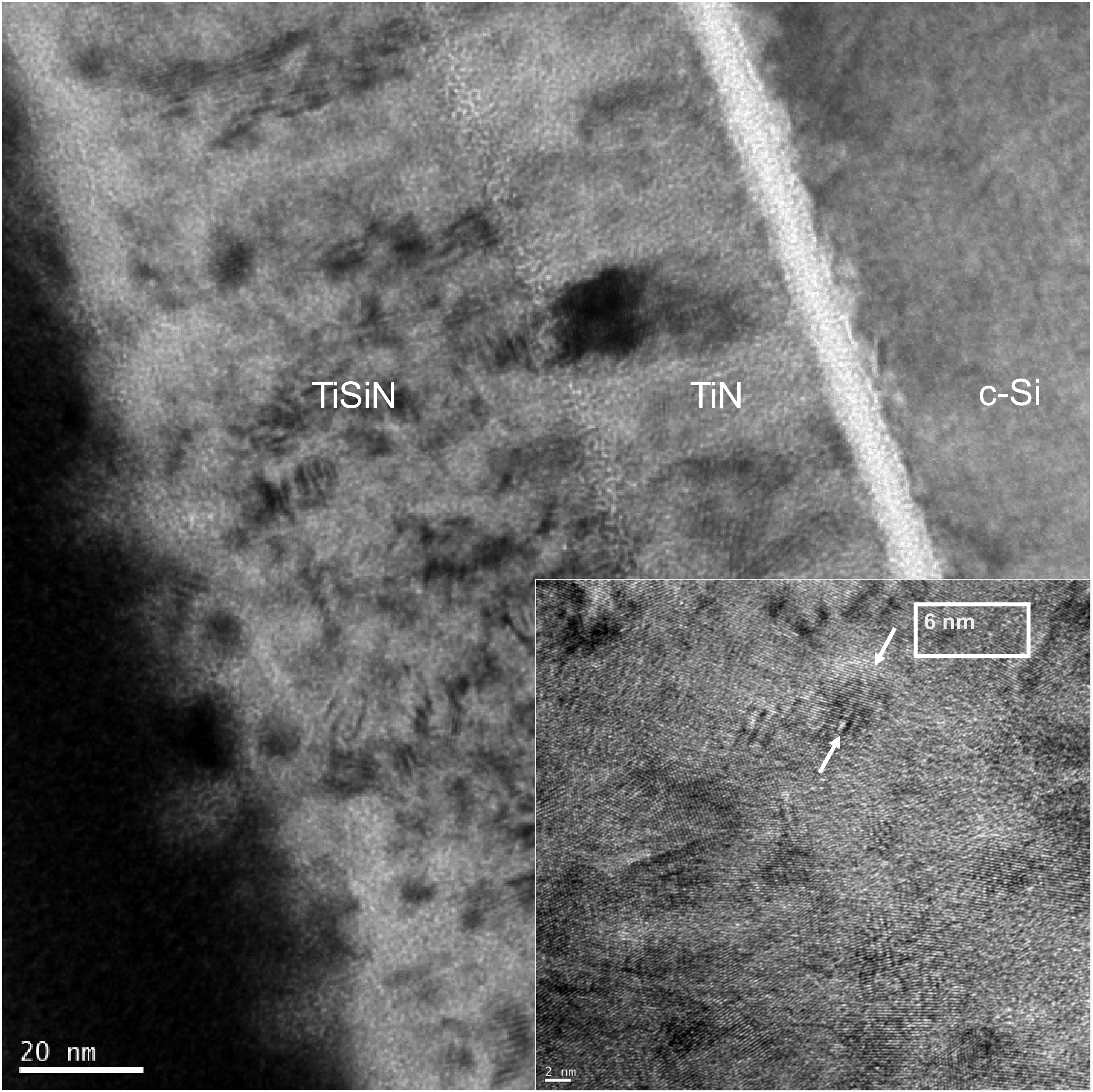


nc-TiCN/a-SiCN



- **Highest hardness at 5 at.% Si**
- **Highest hardness at 9 at.% C**

P. Jedrzejowski, J.E. Klemberg-Sapieha, L. Martinu, Thin Solid Films 466 (2004) 189-196

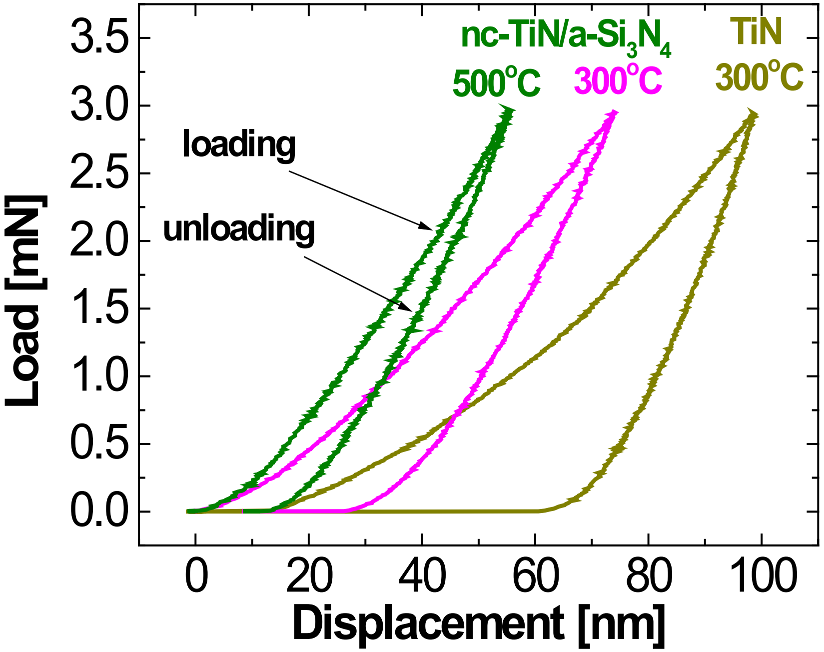


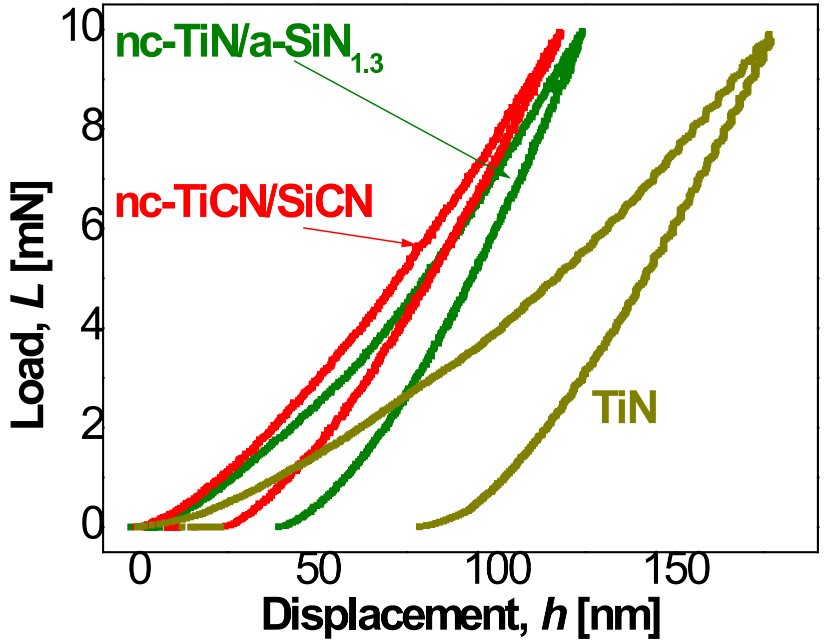
Substrate:
c-Si(001)
Native oxide < 2 nm

RF Pretreatment:
Ar
V_B = -600V
P = 50 mtorr
15 minutes

Deposit TiSiN/TiN:
$TiCl_4 + N_2 + Ar (+ SiH_4)$
V_B = -600 V
P = 200 mtorr
T_s = 500^{o}C

Load-displacement curves for nanocomposites





TiN	**nc-TiN/a-SiN$_{1.3}$**	**nc-TiCN/SiCN**
H = 22 GPa; E_r = 190 GPa	H = 43 GPa (27 GPa @ 300°C) E_r = 350 GPa (250 GPa @ 300°C)	H = 57 GPa E_r = 306 GPa

P. Jedrzejowski, J.E. Klemberg-Sapieha, L. Martinu, Thin Solid Films 466 (2004) 189

Tribological properties

1. Introduction and a little bit of history

2. Nature of the surfaces

3. Surface texture
3.1 Definitions
3.2 Roughness – main parameters

4. Contact between surfaces

5. Friction and friction mechanisms

6. Wear and wear mechanisms

Special acknowledgement to Étienne Bousser for the preparation of parts of this section

Introduction

Definition of tribology

According to the « UK Department of Education and Science » (1986)
Tribology is « the science and technology of interacting surfaces in relative motion and the practices related thereto. »

Originates from Greek « tribos » = friction

In general, tribology relates to the study of friction, wear, lubrication and lubricants, etc. Includes different types of environments, working conditions and materials

Why?

This field has often been neglected in the education and training of engineers. This is dispite the fact that malfunction of equipement is very frequently related to the interaction between surfaces.

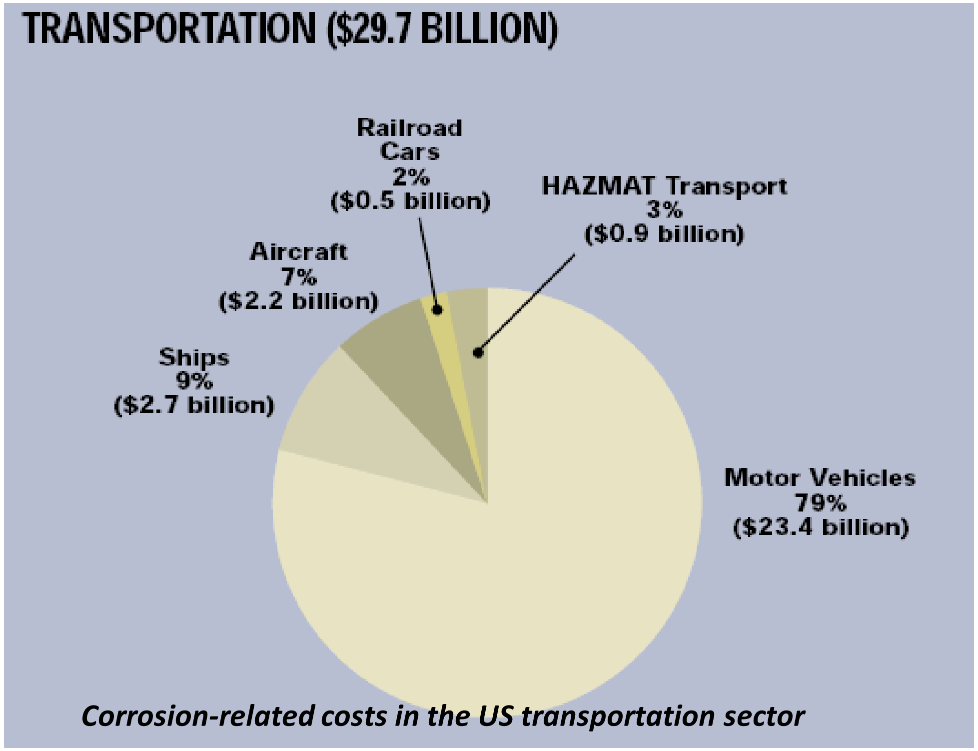
⇒ The economic loss in the US (for ex.) caused by friction and wear is estimated at 100 G$ per year (WebSite of the Oak Ridge National Laboratory)

Tribology is multidisciplinary: chemistry, physics, materials, mech. eng. etc.

Wear and corrosion

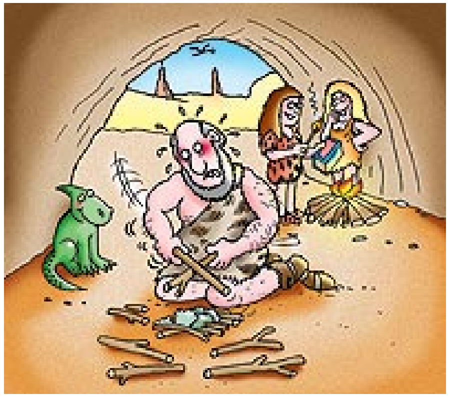
- **Wear and corrosion** are the most important failure mechanisms in industry. Repair and replacement of components lead to a significant decrease in performance, efficiency and safety, and substantially increase production cost.
- According to NACE (National Association of Corrosion Engineers), the cost of **corrosion, wear and other materials deterioration** in USA in 2013 exceeded **$1 trillion US$** (6.1% of the GDP).

- Similar studies show that **Wear** imposes a cost level of **100 billion US$** (0.7 % of the GDP).
- This cost can be enormously reduced through better **understanding of failure mechanisms** and **Surface Engineering.**



Corrosion-related costs in the US transportation sector

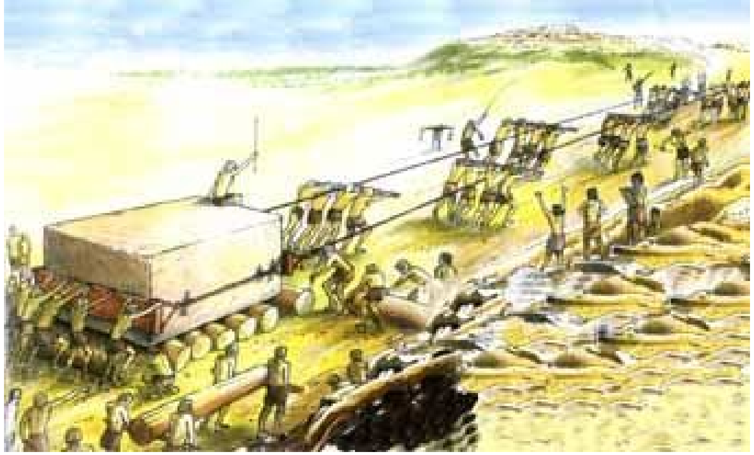
A bit of history



Prehistory

- Fire (200 000 years)
- Tools (10 000 years)
- Agriculture (3000 to 5000 years)
- Crafts (3000 to 5000 years)

First civilisations (Mesopotamia, Egypt, Grece, Rome and China)

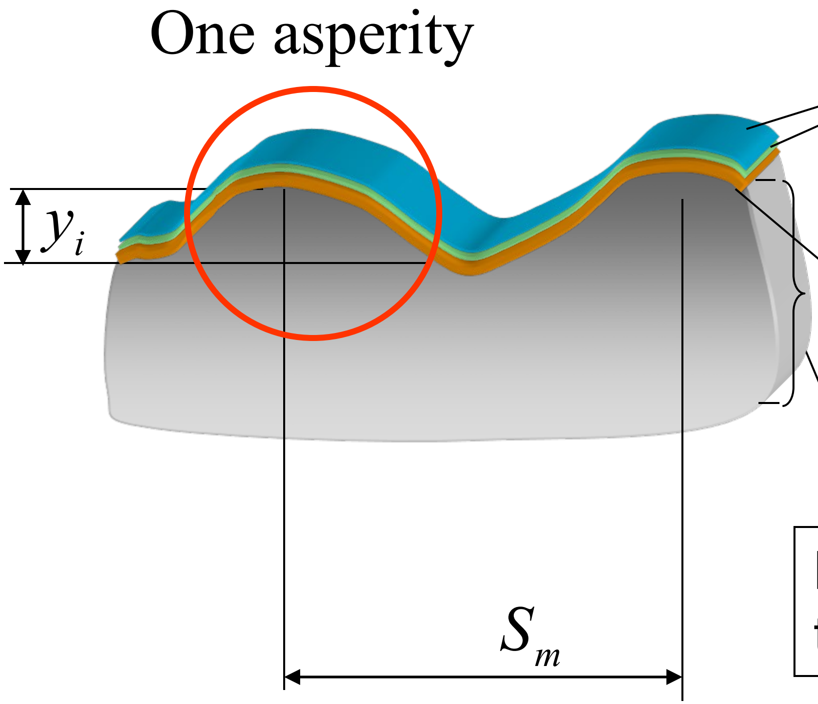


- Drills
- Lubricants (vegetable and animal oils)
- Transport of the construction material (lubricants, rolls)
- Reduction of the wear of wheels (metal pieces around the perimeter)
- Metallic and wooden bearings, …

The science of tribology was born during the renaissance period with the works of Leonardo da Vinci, and it has largely expanded during the industrial revolution (printing, wind and water mills, heavy industry, transport, … machining etc.)

The nature of surfaces

Surface and near-surface zones have generally different characteristics compared to the bulk material.



Molecules of grease, water, and adsorbed gas (1 to 1000 nm)

Oxide layer (more saturated toward the surface; $FeO \rightarrow Fe_2O_3 \rightarrow Fe_3O_4$ (≈3 to 15 nm)

Base metal increasingly hardened toward the surface

Nature of the surface

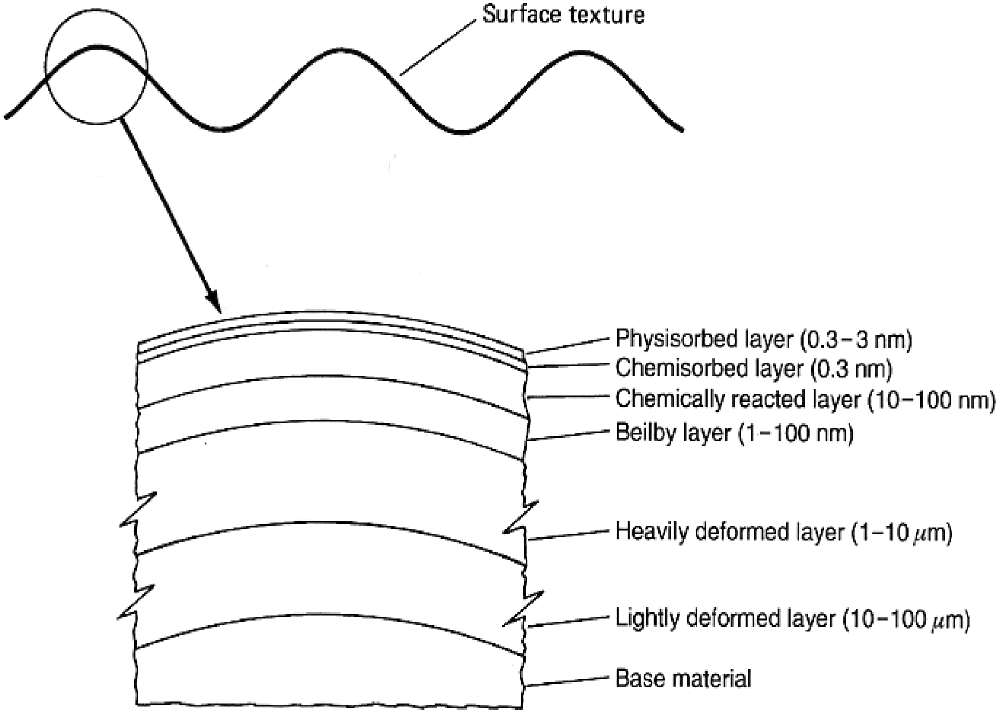


Fig. 3.1.1 Solid surface details: surface texture (vertical axis magnified) and typical surface layers.

- Films that are little or strongly deformed
- Film called « Beilby »
- Native reacted layer (oxides, nitrides, sulfides, chlorides etc.)
- Chemisorbed or physisorbed layers

The solid surface layers have an important effect on wear and friction

Deformed layers

- Result of the fabrication process (ex: extrusion, machining)
- The amount of the deformed material and the degree of deformation depend on the energy supplied by the process and on the nature of the material;
- There are two types of deformed layers: strongly deformed (1 to 10 microns) and weakly deformed (10 à 100 microns);
- The physicochemical and mecanical properties of the surface layers can be completely different from the bulk material.

Beilby layer

- Amorphous or microcrystalline layer produced by fusion, flow and redeposition during machining
  Molecular layer (1 to 100 nm)

Native reactive layer

Present on almost all materials (except some noble metals)

Generally not very thick but it depends on the environment (temperature, reagents etc.)

Physisorbed layer

Typically monomolecular or polymolecular

Liquid or gaseous layer on the solid surface

Adsorption by weak bonds of Van der Waals forces

Chemisorbed layer

Layer formed by creating chemical bonds (el. sharing or el. exchange)

Link type depends on the materials (ionic or covalent)

Bond much stronger and therefore it is much more difficult to remove chemisorbed species than those physisorbed

Contrary to the chemical reaction, the chemisorbed species retain their individual properties

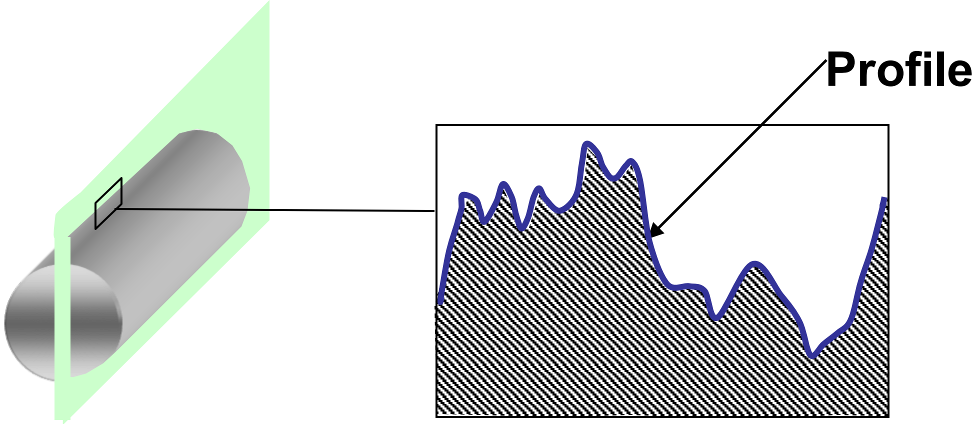
Thickness limited to a mono-layer

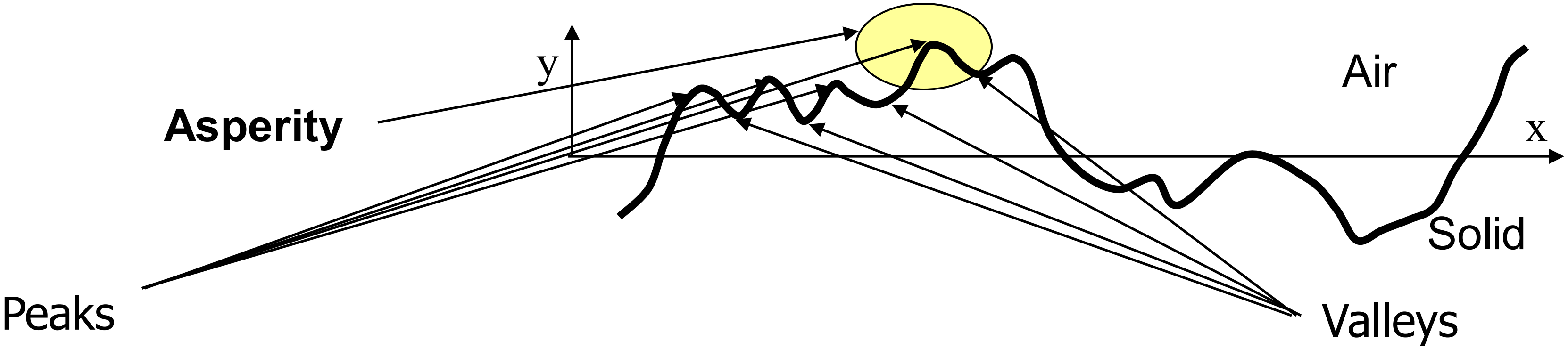
Geometrical surface:

Ideal surface specified by the manufacturing design

Surface profile:

Intersection line of a geometric surface and cross section. The enlarged profile of the surface shows defects.





Surface texture

Definitions

The surface texture can be defined as the variation in surface relative to a nominal reference regularly or not, thus forming a three-dimensional topography of the surface

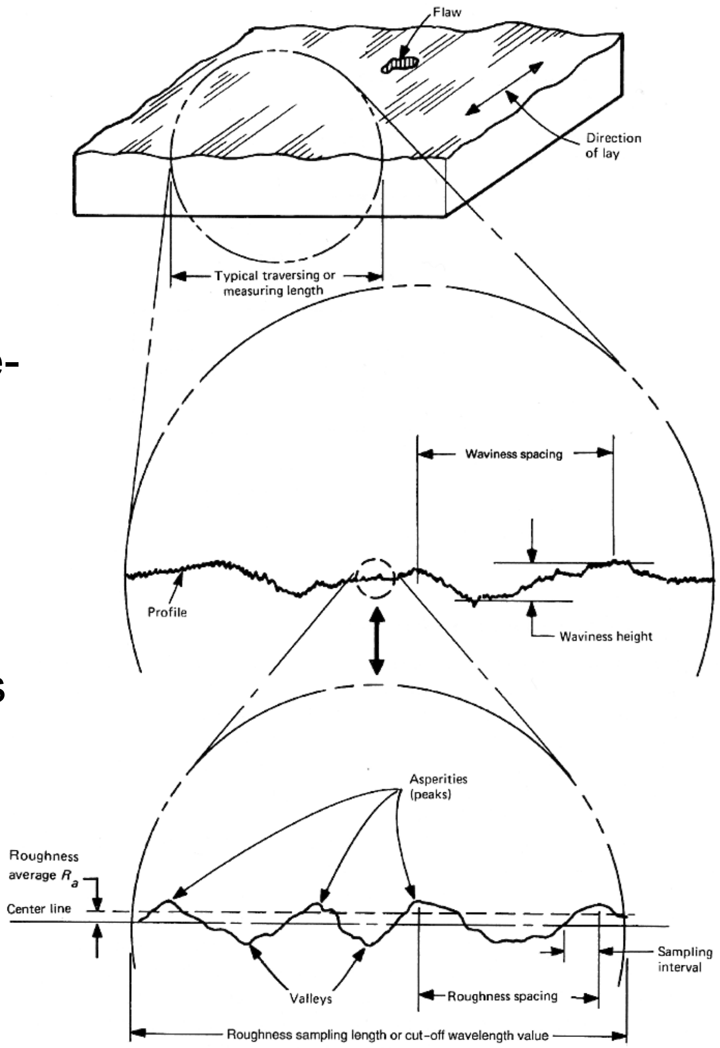


Fig. 3.3.1 Pictorial display of surface texture (Anonymous, 1985).

Forms:

Roughness: Asperities and valleys varying in amplitude and frequency

Ripple: Surface variations of larger dimensions caused by machining

Machining streaks: the trace of machining direction according to the production method

Faults: random and unexpected interruptions of the surface texture

Form errors: Changes in dimensions but on a very large scale

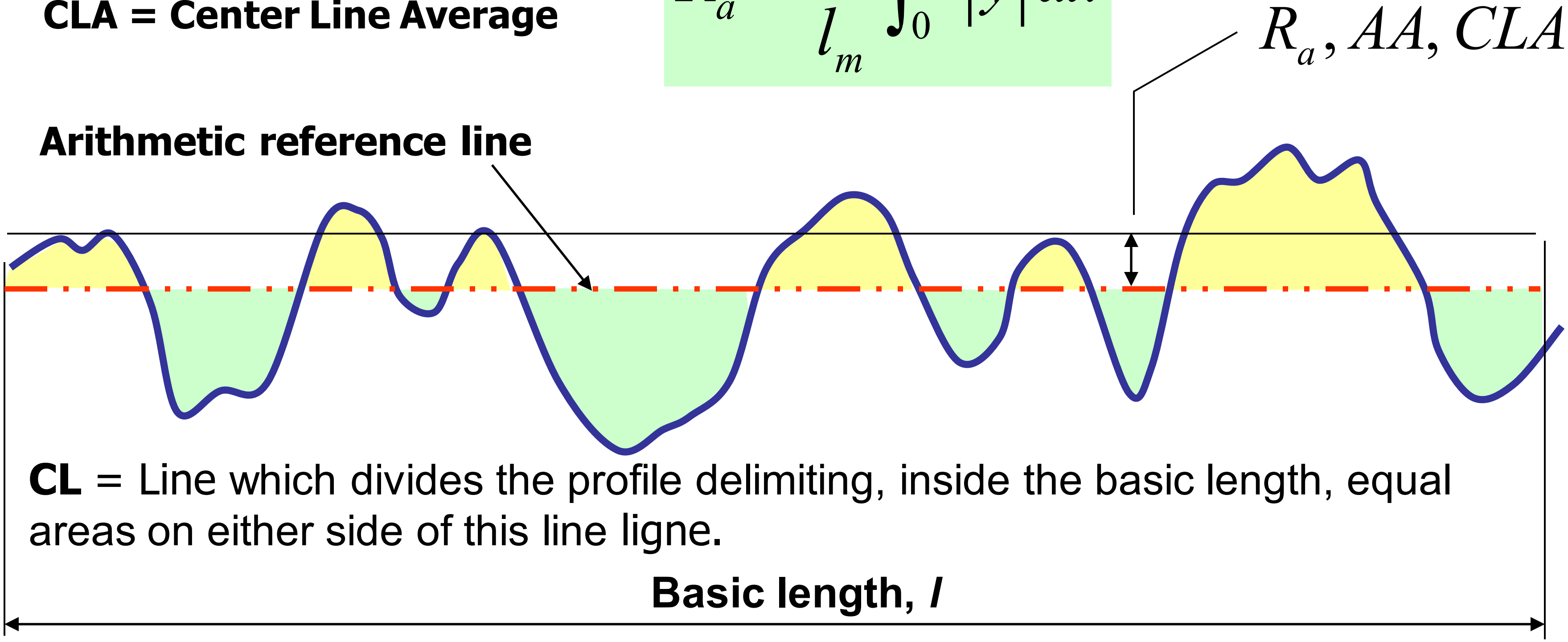
Surface roughness - quantification

Arithmetic mean deviation, R_a, AA or CLA :

Arithmetic average of the absolute values of the deviations of the profile with respect to the arithmetic reference line within the sampling length.

AA = Arithmetic Average
CLA = Center Line Average

$$R_a = \frac{1}{l_m}\int_0^{l_m} |y|\,dx$$



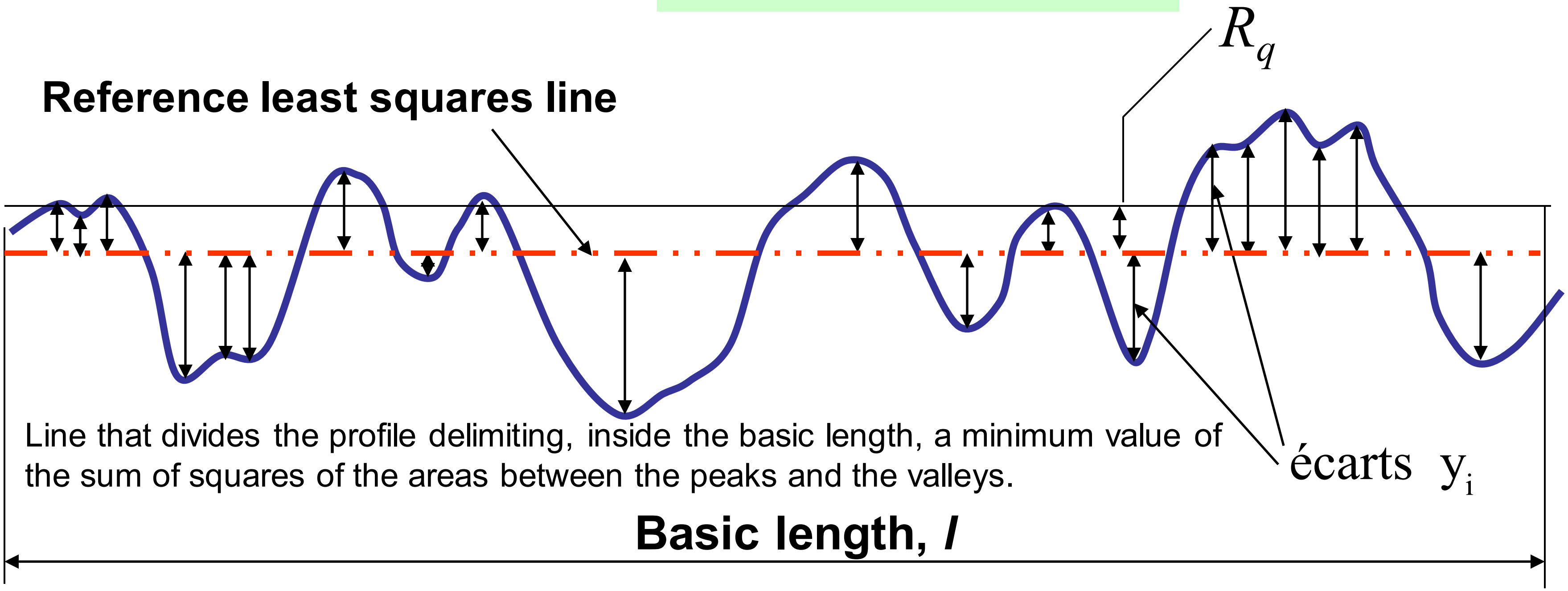
CL = Line which divides the profile delimiting, inside the basic length, equal areas on either side of this line ligne.

Standard (quadratic) deviation, *R_q* or RMS :

Root mean square value of the differences of the profile with respect to the reference line of least squares within the basic length.

RMS = Root Mean Square

$$R_q = \sqrt{\frac{1}{l_m}\int_0^{l_m} y^2(x)dx}$$



R_q

Reference least squares line

Line that divides the profile delimiting, inside the basic length, a minimum value of the sum of squares of the areas between the peaks and the valleys.

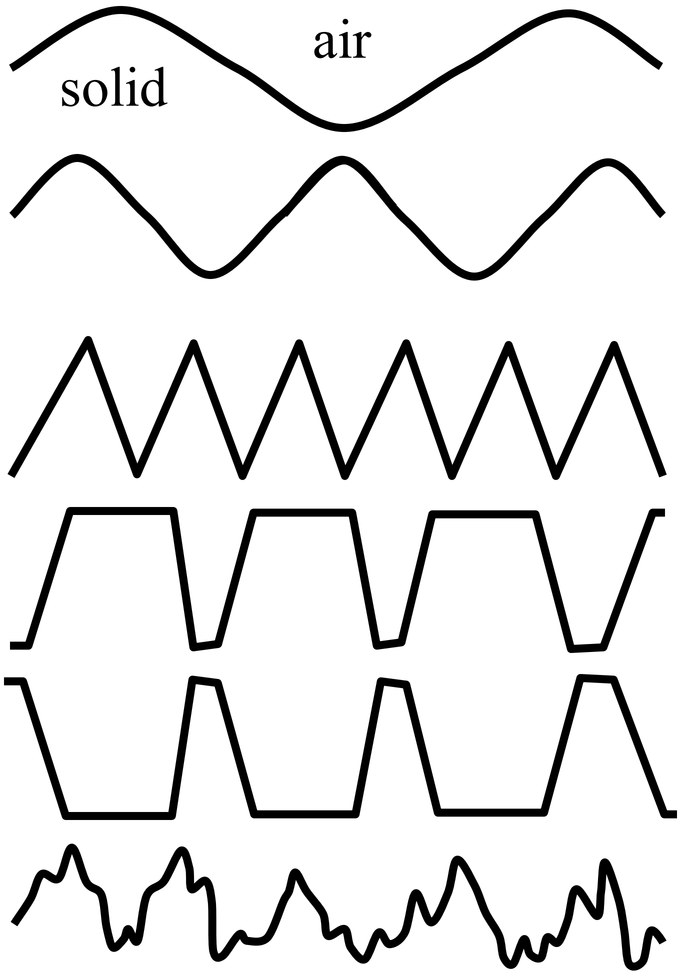
écarts y_i

Basic length, *l*

R_a and R_q roughness values obtained with various manufacturing processes

Finishing process	**Surface roughness R_a, R_q [μm]**
Solidified glass floating on a molten metal	0.001
Finely polished metal and glass	0.0015 to 0.0020
Polishing (commercial quality) and molded from these surfaces	0.01 to 0.10
Commercial grinding	0.025 to 0.25
Good quality machining	0.25 to 2.50
Laminated surfaces	1.0 to 10
Sand blasted surfaces	2.5 to 25

All these profiles have the same values of R_a and R_q



R_a or R_q characterize the height of the irregularities but not their form.

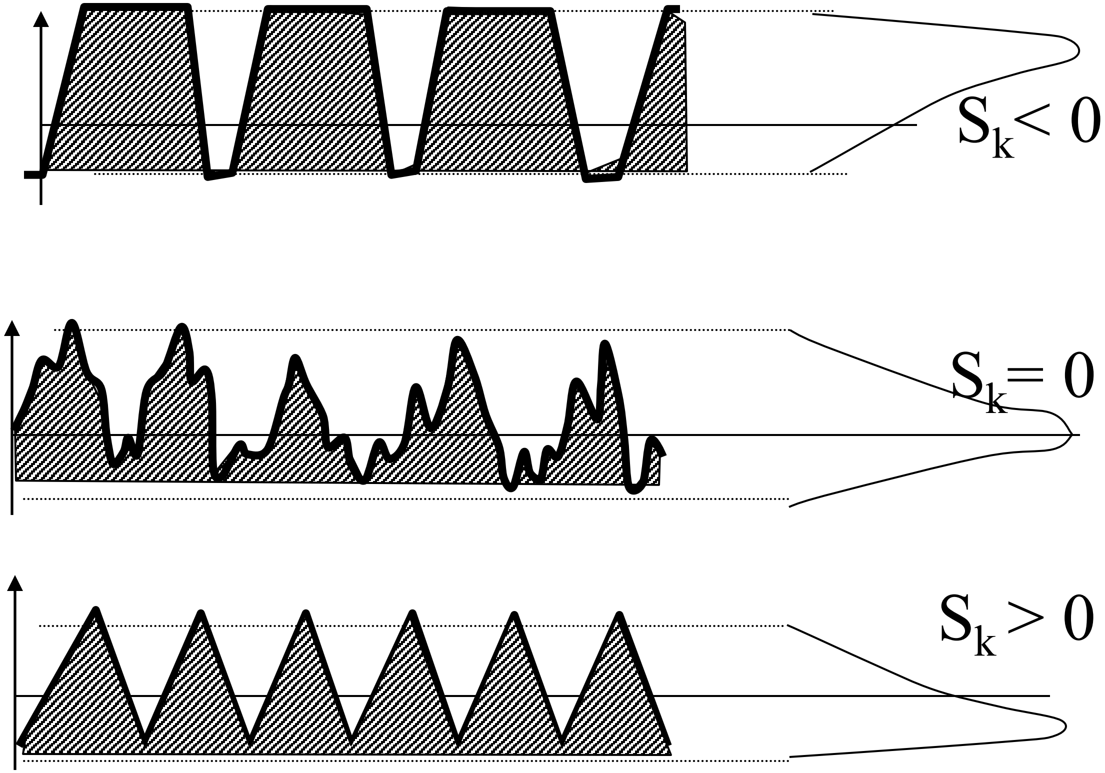
⇓

R_a and R_q are insufficient to characterize well the surfaces from the tribological stand point.

Measurements: profilometry, AFM, STM, light scattering, …

S_k **«skewness » :**

Corresponds to the symmetry of the profile compared to the reference line; shows the load bearing capacity or porosity of the surface profile



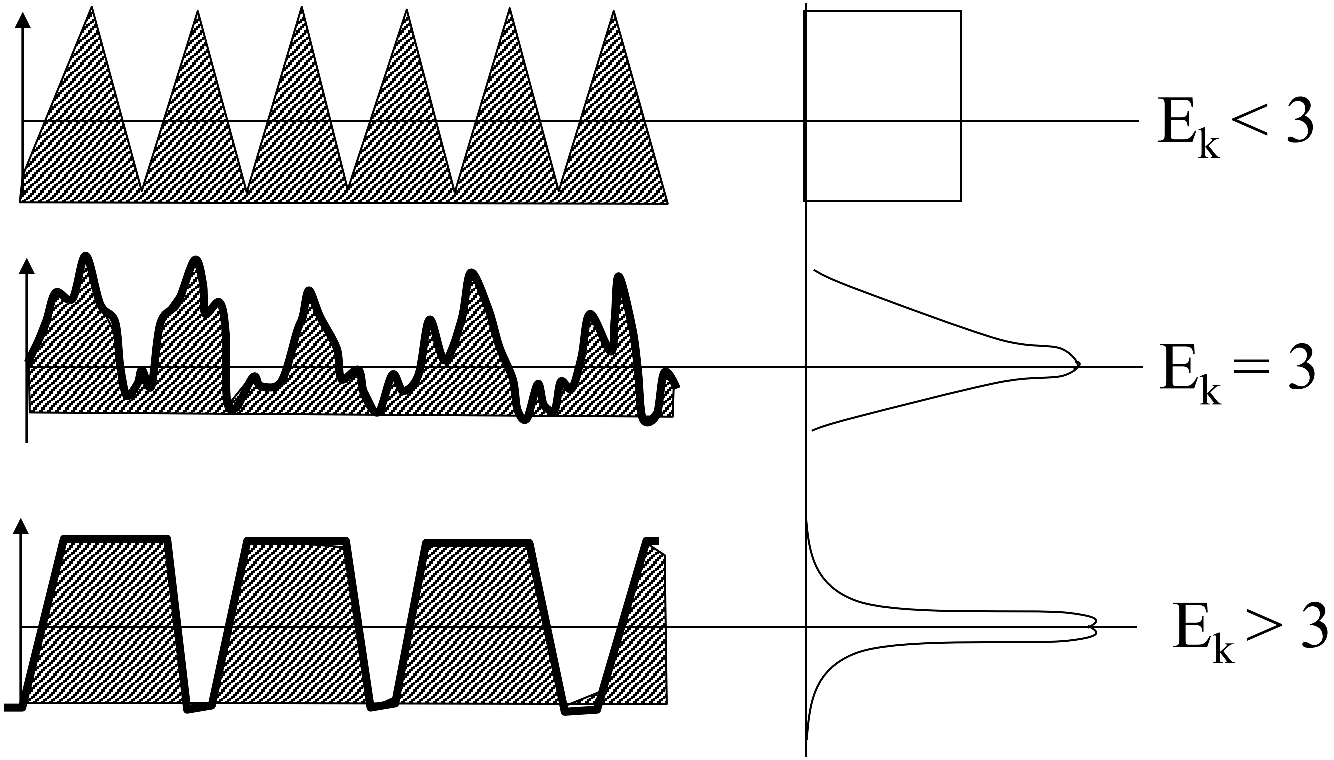
$$S_k = \frac{1}{R_q^3}\frac{1}{n}\sum_{i=1}^{n}(y_i - \bar{y})^3$$

Corresponding S_k values are very different.

***E_k* « kurtosis » :**

Measure of the sharpness of the deviations and their distribution

$$E_k = \frac{1}{R_q^4}\frac{1}{n}\sum_{i=1}^{n}(y_i - \bar{y})^4$$



These profiles had originally the same R_a or R_q values,

they have now very different kurtosis values.

Tribological properties

1. Introduction and a little bit of history

2. Nature of the surfaces

3. Surface texture
3.1 Definitions
3.2 Roughness – main parameters

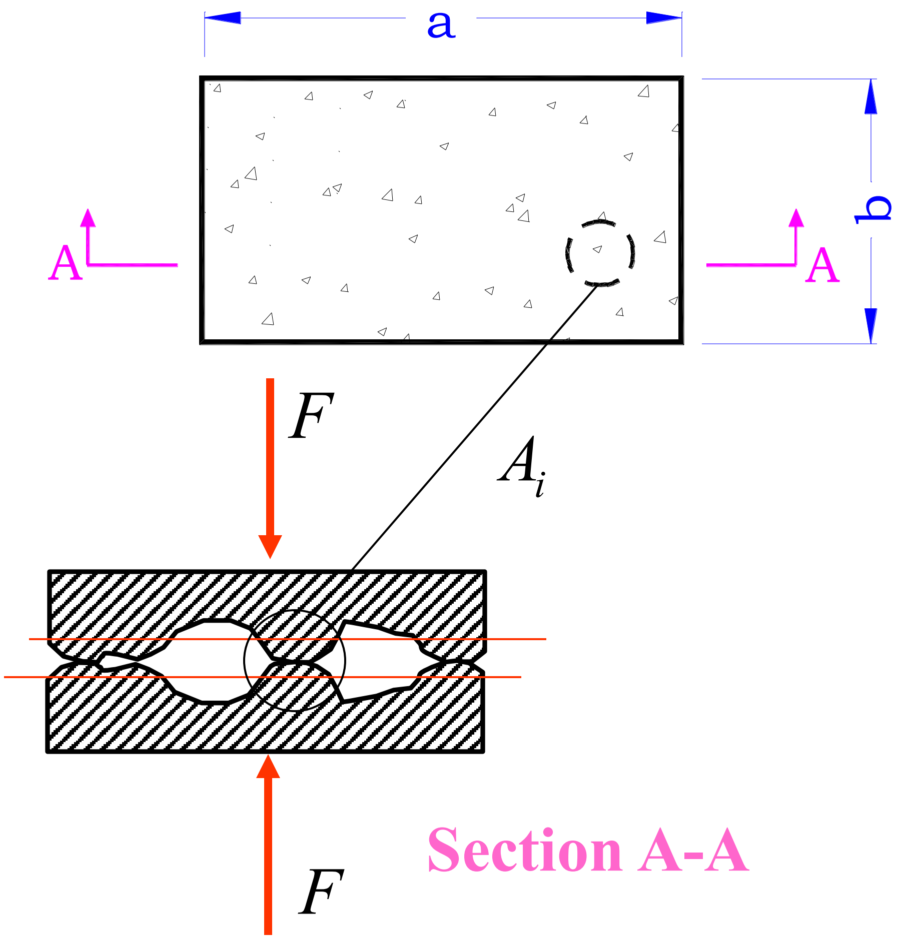
4. Contact between surfaces

5. Friction and friction mechanisms

6. Wear and wear mechanisms

7. Case study – Nanocomposite optical films

Contact area



Apparent contact area

A = a x b

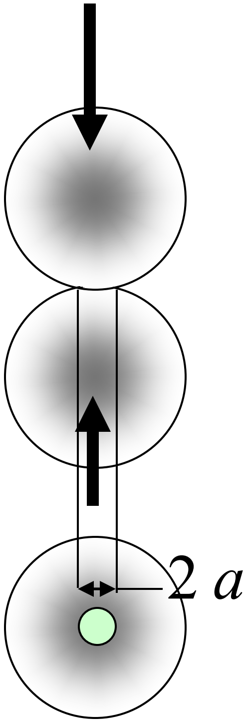
In equilibrium, at a load *F*, the real contact area (A_r) is the sum of the individual contact areas A_i at the asperity level. All asperities in contact are generally plastically deformed.

Tribology = science and technology of solid surfaces in contact

Contact mechanics – contact deformation and generated stress and stress distribution

→ Static contact (Hertzien): static or pure rolling

→ Dynamic contact: rolling and sliding



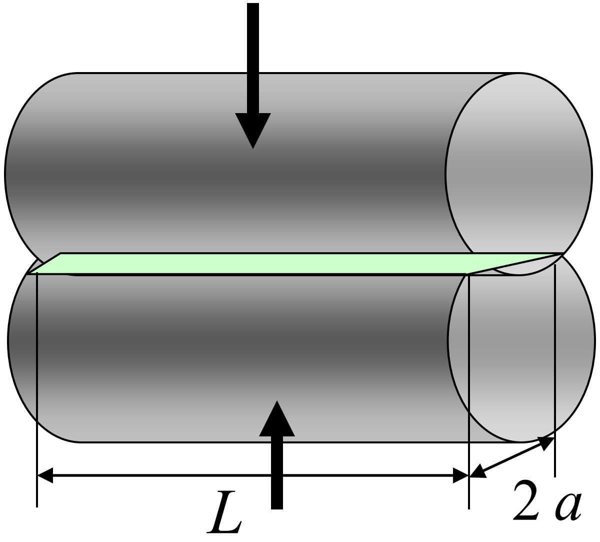
Contact area :

$$A_i = \pi a^2$$

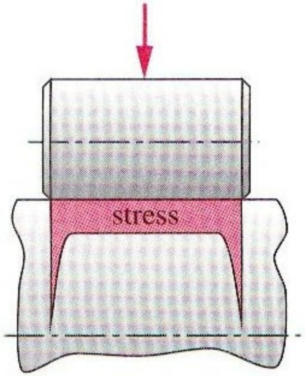
Spherical contact

$$A_i = 2aL$$

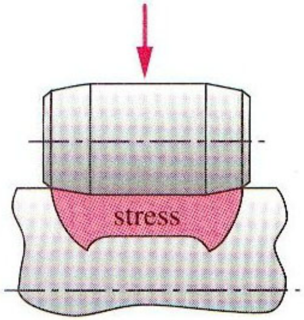
Cylindrical contact



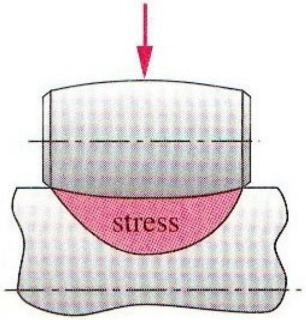
Effect of geometry (concentration of stress)



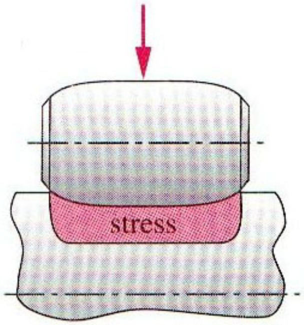
(a) Straight roller



(c) Part-crown roller



(b) Crowned roller



(d) Logarithmic roller

Friction

Definition: Resistance to movement during sliding and rolling

⇒ The friction force acts always in a direction opposed to the movement
⇒ Dry friction – Coulomb-like
⇒ Viscous friction (lubrication)
⇒ Aerodynamic friction

Friction is not an intrinsic property of a material;
it is rather a response of the system: it is therefore function of the interacting materials, of the surface texture, surface contamination, environnement, lubrication etc.

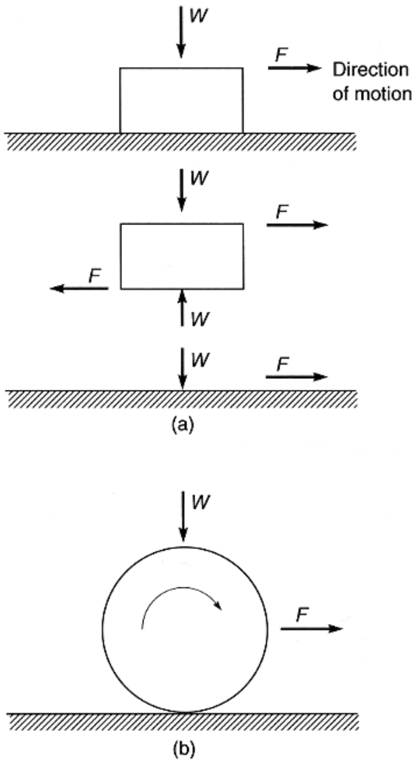


Fig. 6.1.1 Schematic illustrations of (a) a body sliding on a surface with a free body diagram, and (b) a body rolling on a horizontal surface; W is the normal load (force) and F is the friction force.

The laws of friction

XV^e century (Leonardo da Vinci) :

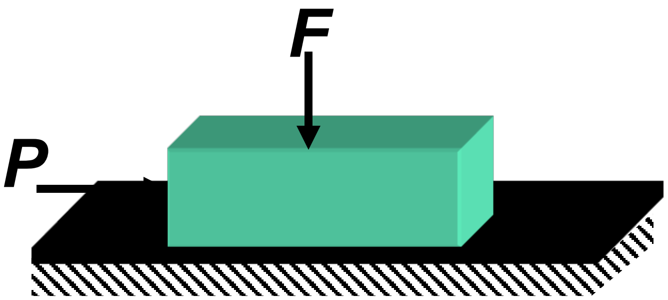
1. F_f independent of the apparent contact surface → $A_r \neq f(A)$
2. $F_f = \mu * F$, μ = friction coefficient

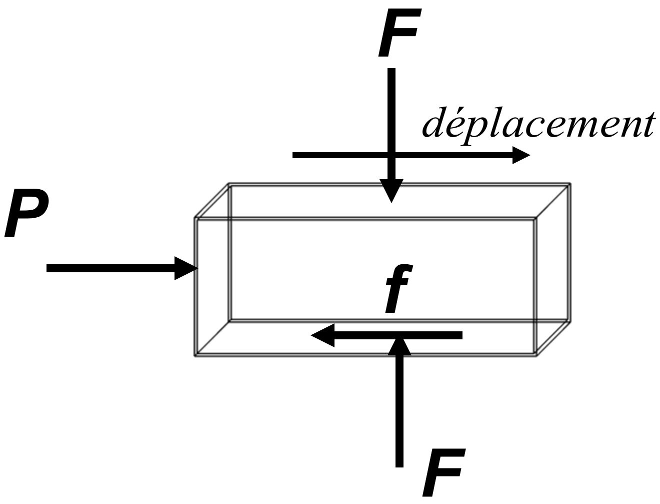
   F = normal force

Amontons (XVII) - Coulomb (XVIII) :

3. F_f depends on the nature of the surfaces in contact
4. F_f is independent of the relative speed between the two surfaces

Classical definition of (dry) sliding



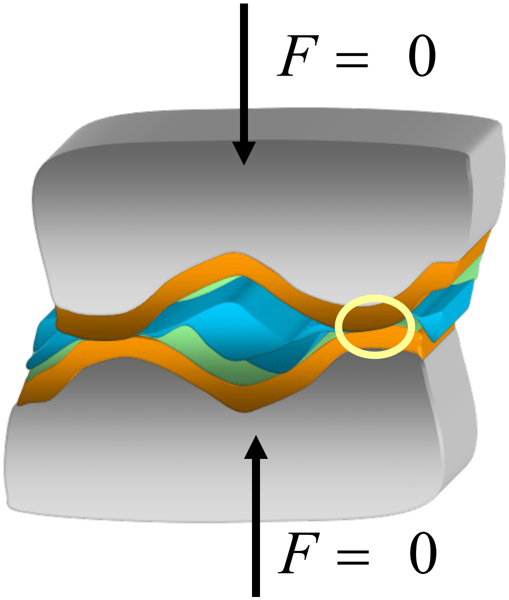


Before the start of movement: $P < f$

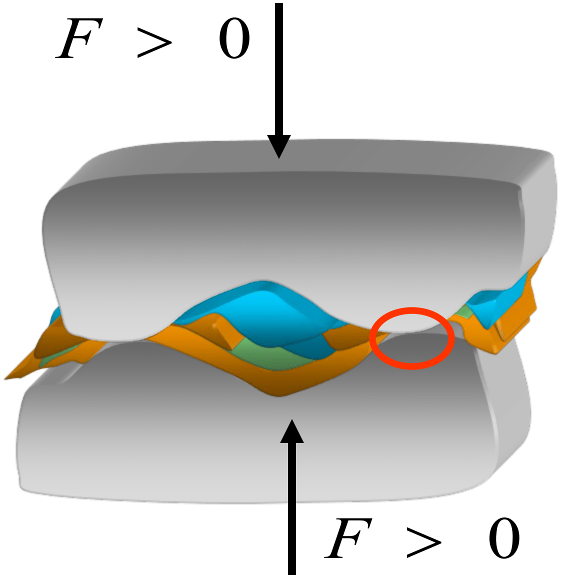
When moving: $P = f$

Friction coefficient of sliding (μ):

$$\boxed{\mu = \frac{f}{F}}$$

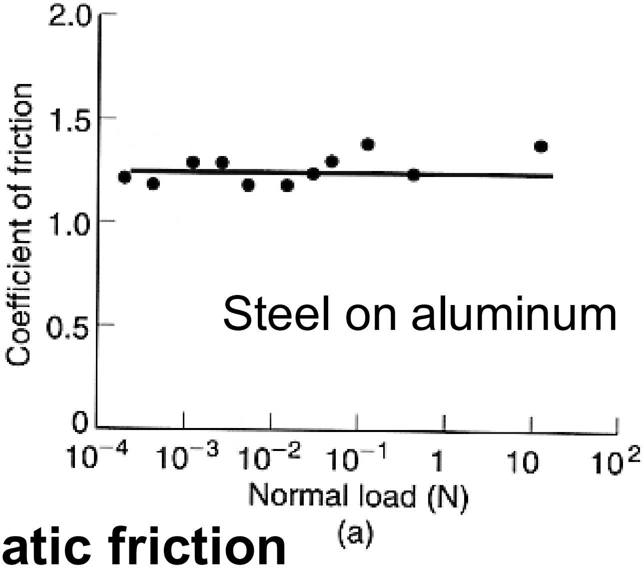


First contact ($F = 0$) : the solids touch each other through a layer of gas, water and oxide.

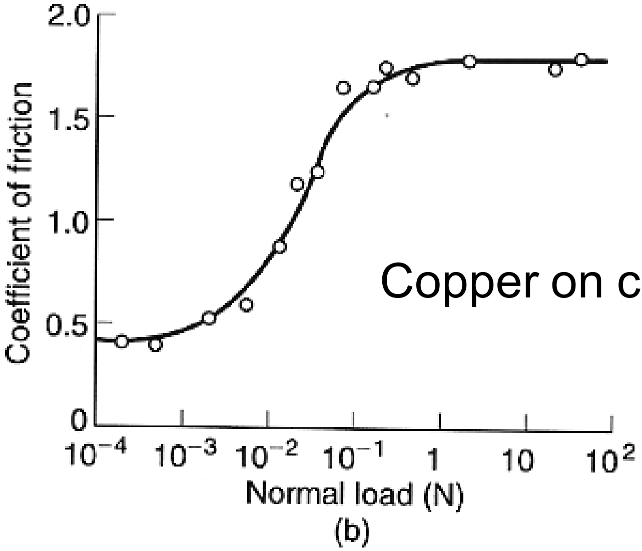


At a certain load, the asperities get plastically deformed and the gas, water and oxide layers are broken. More reactive materials enter into contact. Interatomic forces are activated: covalent, ionic, *Van der Waals* …
This leads to interface adhesion.

Friction mechanisms – solid/solid contact



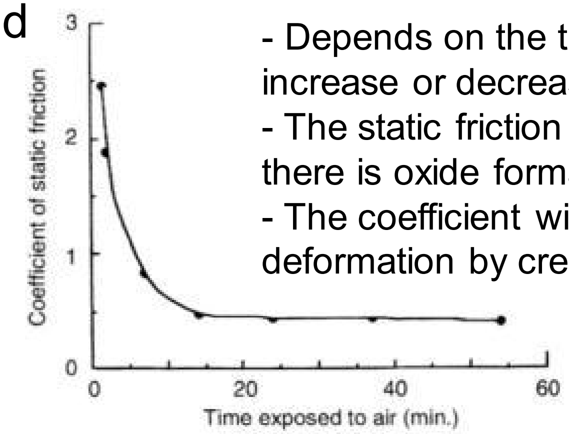
Steel on aluminum



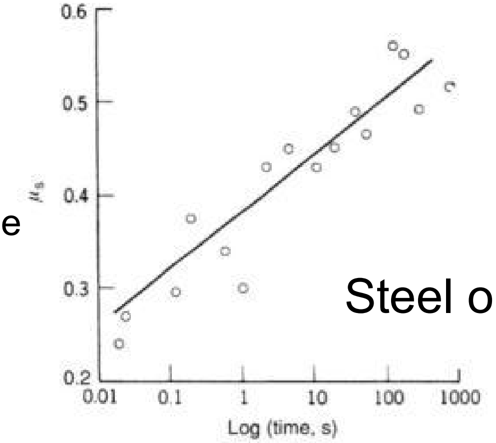
Copper on copper

Static friction

Cleaved salt in air



- Depends on the time of immobilisation; can increase or decrease
- The static friction coefficient will decrease if there is oxide formation;
- The coefficient will increase if there is surface deformation by creep.



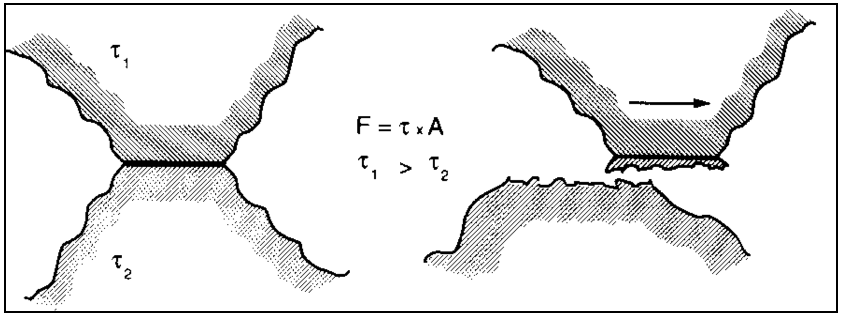
Steel on steel

Fig. 5.2.20 Coefficient of static friction as a function of time of exposure to air for cleaved salt surface (Kragelskii, 1965).

Fig. 5.2.21 Coefficient of static friction as a function of rest time for steel on steel in air. (From Dokos, 1946. Reproduced by permission of ASME.)

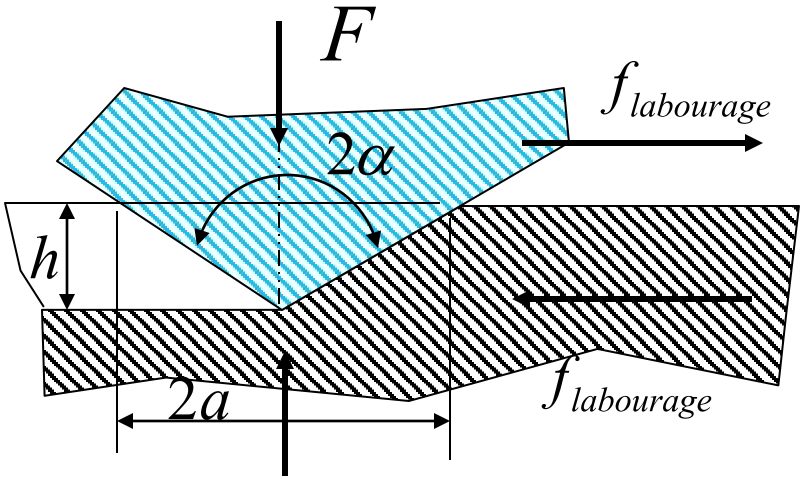
Friction mechanism by adhesion

The frictional force is partially composed of a force required to break the adhesive bond in shear at the interface.
This component of the frictional force (F) is proportional to the actual contact area and the ultimate shear stress of the weakest material.



Friction mechanism by ploughing

Asperities of the harder material may sink into the softer material and are plowing it.



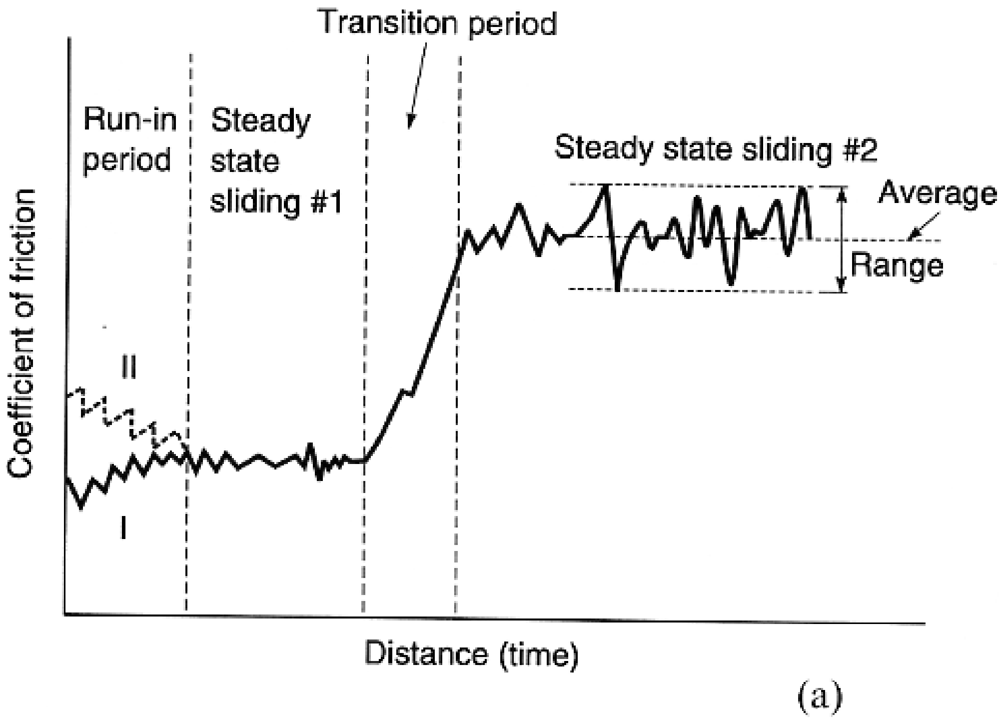
NB: the frictional force induced by plowing is generally much smaller than that induced by the mechanism of adhesion.

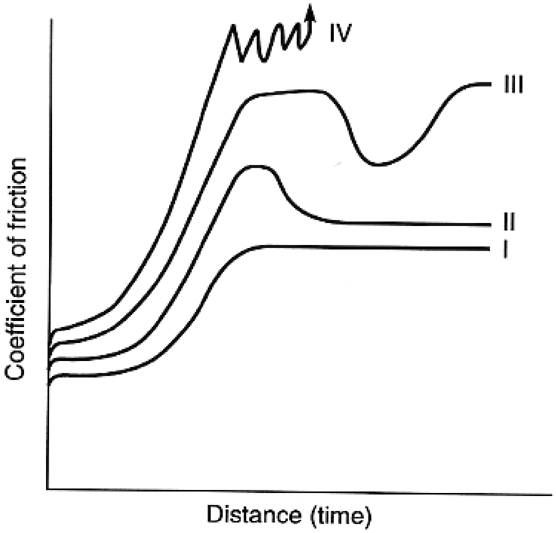
Minimizing friction

- Use incompatible materials
- Promote the formation of low shear surface films such as lubricating films, oxides, adsorbed organic materials or low-strength materials (graphite, PTFE, MoS_2)
- Promote the formation of oxide films on the surface
- Hard surfaces prevent penetration of asperities (surface treatments or hardening)
- Very smooth surfaces increase the contact area A_r and therefore friction. Very rough surfaces promote the entrenchment and also increase friction. Therefore, there is an optimum roughness to minimize sliding friction.

Transitions during sliding

There is first a break-in period where the asperities break, oxide layers can wear, structural changes can take place. During that time the coefficient may increase or decrease. There may also be other transitions (increased roughness, abrasive particles, etc.)



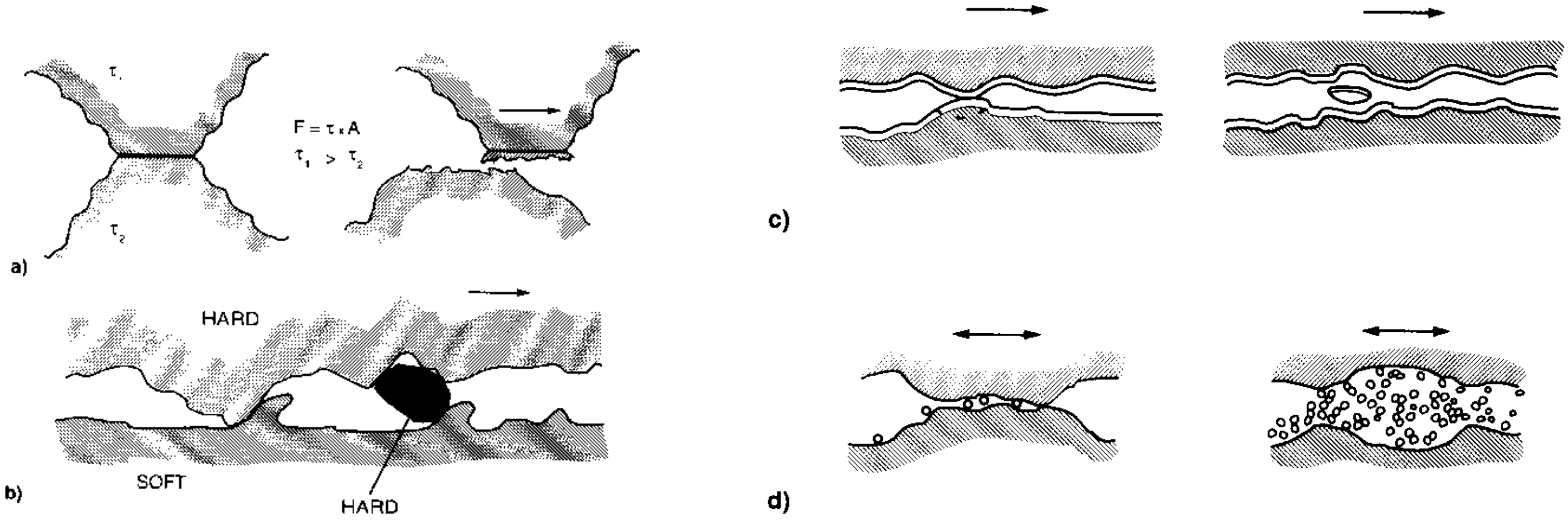


I) Identical materials
II) Adhesion dominates
III) Plastic contacts
IV) Multiple contributions

Wear

Definition: surface damage or material removal of one or two surfaces which are in relative movement with respect to one another

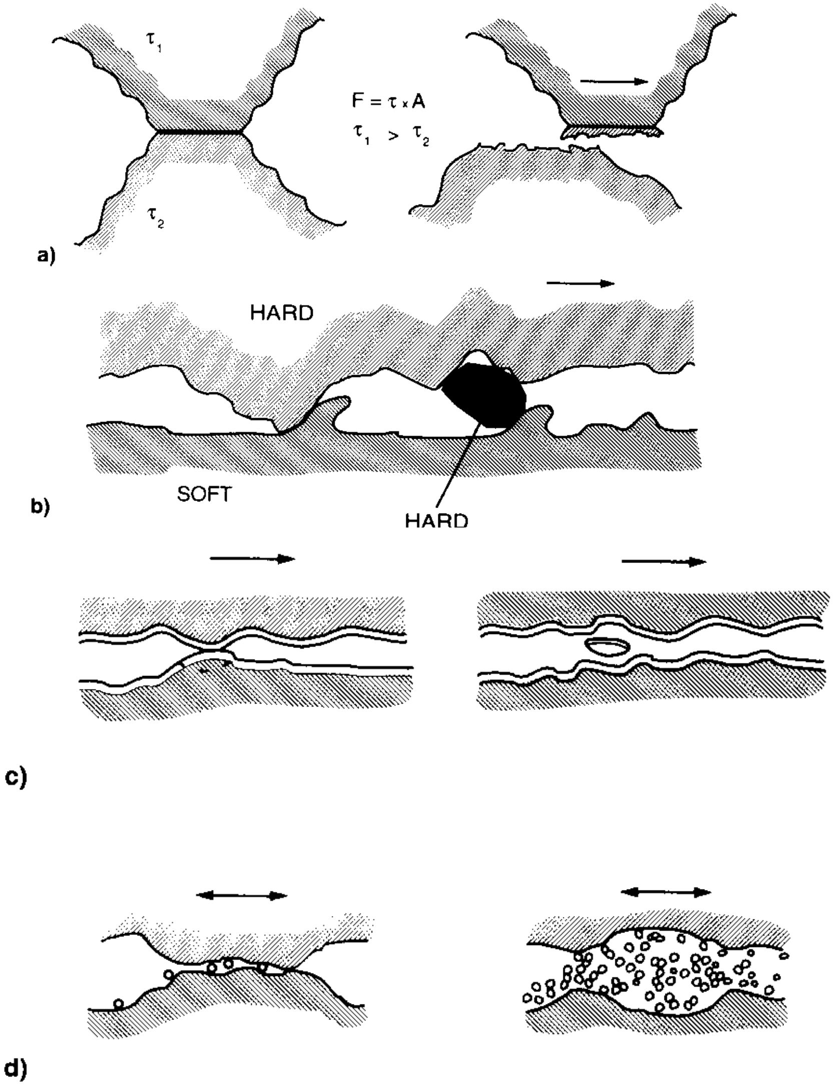
⇒ The wear usually occurs through the interaction of asperities



Wear can be positive (eg., machining) or negative (eg., brakes)
⇒ Whatever the case, we must successfully control wear so that it is constant and predictable.

Wear mechanisms

- adhesion (a)
- abrasion (b)
- erosion
- corrosion (d)
- surface fatigue (c)
- fatigue + corrosion
- « *fretting* » + corrosion :
  abrasion + adhesion + corrosion + fatigue



Abrasion wear

The abrasion mechanism naturally follows that of adhesive one as soon as there is formation of wear debris.

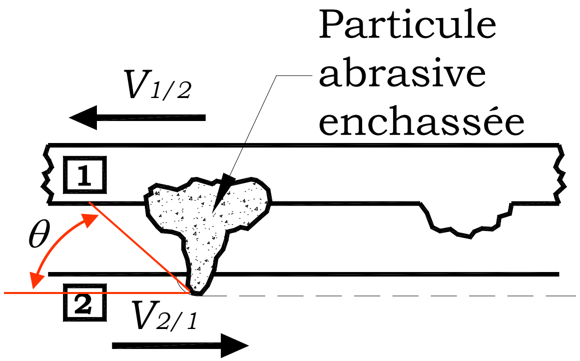
This is the wear mechanism prevalent in all machines, the more severe and the one that causes the most losses of material.

Abrasion can be divided in:

1) Two-body abrasion wear, and

2) Three body abrasion wear

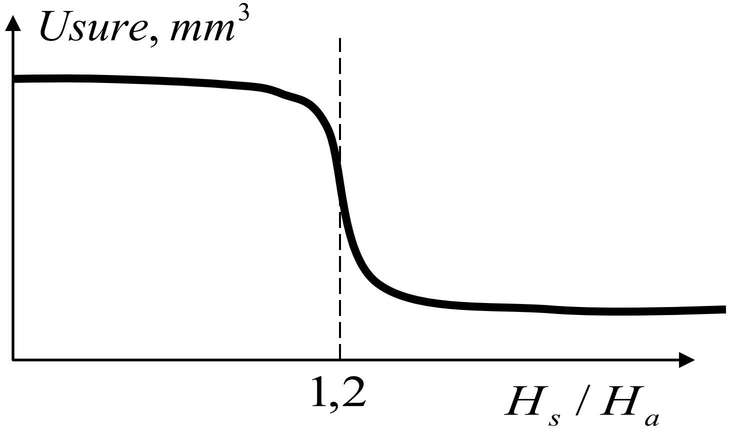
Two body wear



Three body wear

To minimize abrasive wear:

- Use surfaces with very low roughness
- Relative hardness of surfaces is paramount: it must $\mathbf{H_s / H_a \geq 1.2}$
  here, H_a is the hardness of the abrasive
  H_s is the hardness of the surface.



The use of hard coatings can significantly increase the abrasion resistance

One should also promote the elimination of wear debris (lubricant filtering, trapping the particles in a soft metal, providing micro-channels the surface by using surfaces with deep valleys ($S_k > 0$ or $E_k > 3$)).

Wear mechanisms – Abrasion

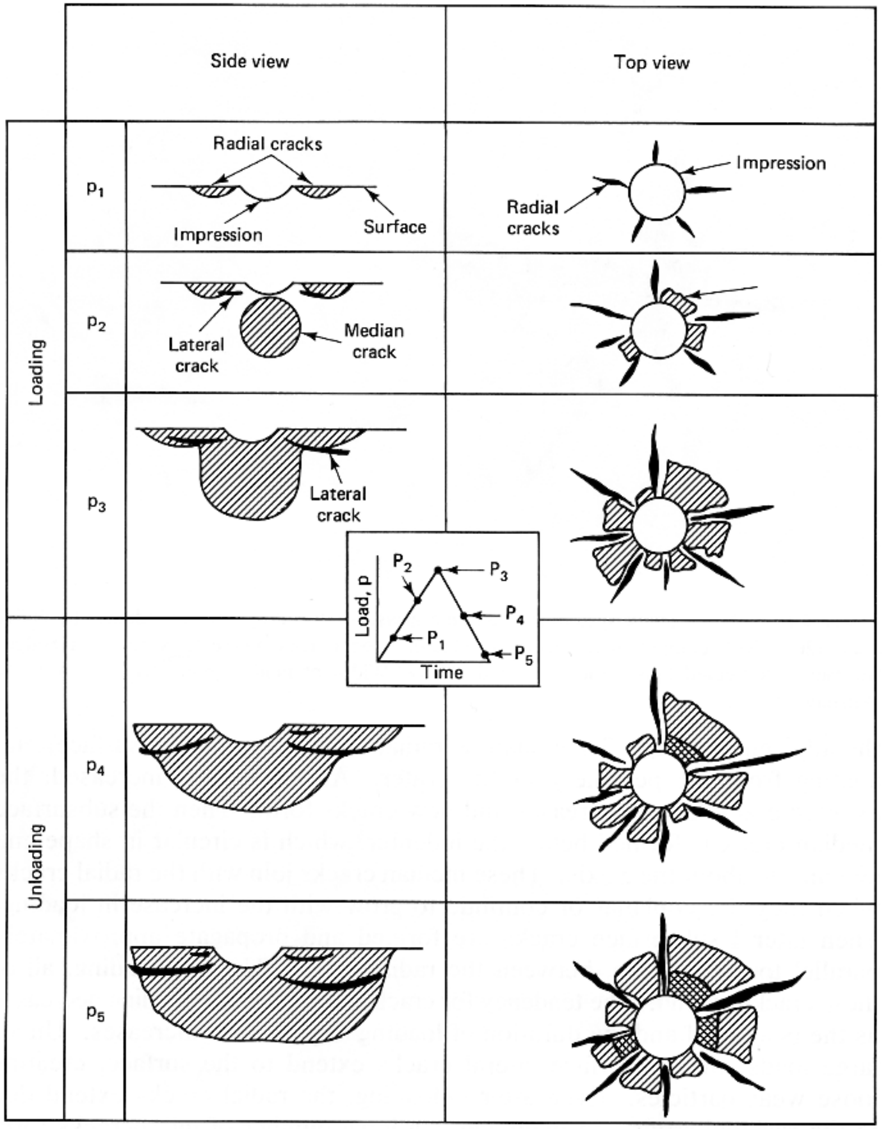


Figure 4.20 Schematic showing the sequence of crack formation and growth events during loading and unloading. (From Evans and Wilshaw, 1976.)

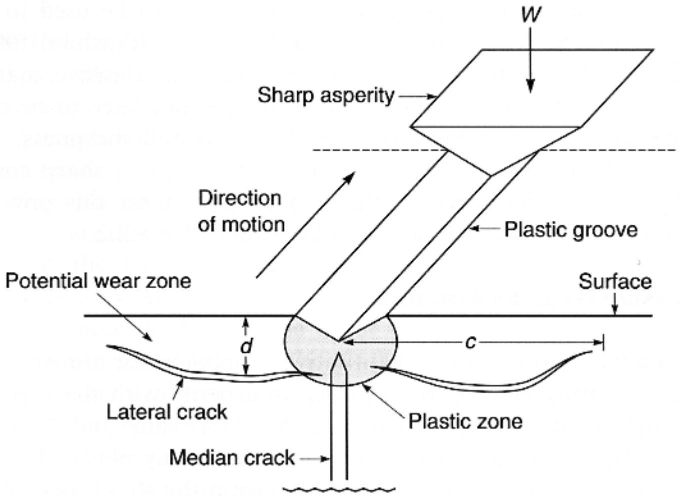
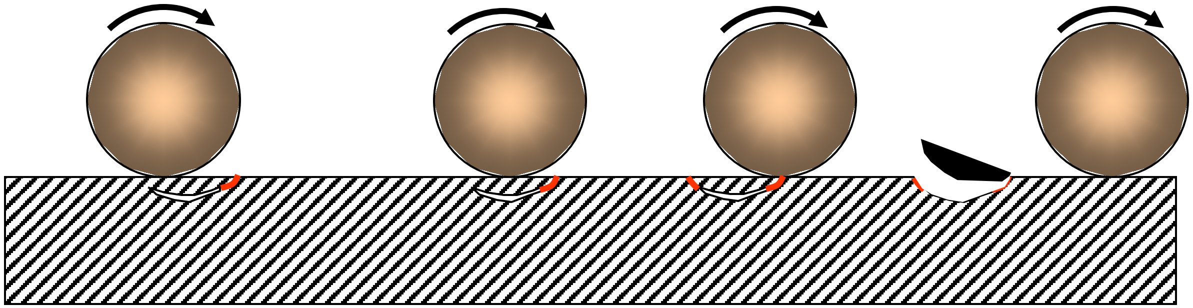


Fig. 8.2.27 Schematic of the mechanism of wear by a sharp asperity sliding on the flat surface of a brittle material by lateral fracture (Evans and Marshall, 1981).

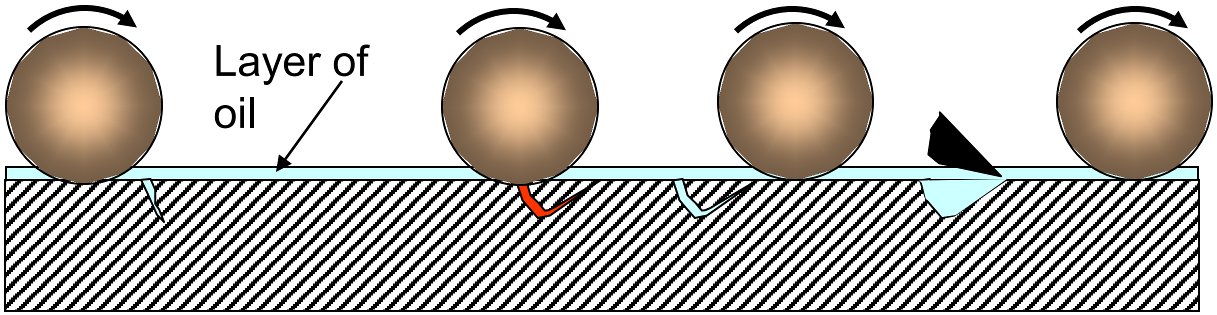
Wear mechanisms – Fatigue by rolling or sliding

Dry rolling/sliding



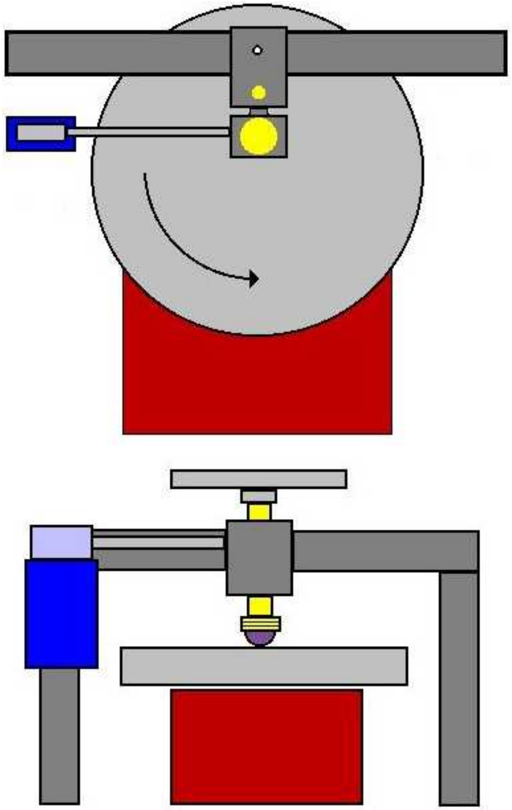
Cracks under the surface will spread and eventually detach a fragment of the surface, creating a wear debris and leaving a crater in the surface (pitting).

Rolling/sliding with lubricant



The surface cracks are filled with oil. When the rolling element passes over the crack, it closes and strongly compresses the trapped oil (several hundreds of MPa). The crack advances in the material, it bends, and later re-joins the further surface at another point. Thus it forms a wear fragment and leaves behind a crater (pitting).

Sliding wear measurement techniques – Pin-on-disk



sapphire - 18 GPa
$SiN_{1.3}$ - 17 GPa
Al_2O_3 - 15 GPa
HS steel - 0.9 GPa
$r \sim 3$ mm

Wear rate:

$$K = V / F_N * s \ [mm^3/Nm]$$

V – worn volume
F_N – normal force
s – travelled distance

monitoring parameters :
frictional force F_T
sliding speed u: 0.3 cm/s
load F_N = 0.3 - 10 N
RH = 50 %

Norm **ASTM G99-05** Standard Test Method for Wear Testing with a PIN-on-Disk Apparatus.

PHS6317 Nanoengineering of thin films

Course schedule – Winter 2024

12 January	Introduction – Scientific and technological challenges
19	Fabrication methods – Vacuum physics and vapor-phase techniques
26*	Fabrication methods – Plasma processes and process optimization
2 February	Fabrication methods - Plasma-surface interactions and diagnostics
9**	Fabrication methods – Thermal/Plasma spray technologies
16*	Optics of thin films 1, optical characterization, *Miniquiz1 (5%)*
23*	Optics of thin films 2, design of optical filters
1*** March	*Presentations – Emerging fabrication techniques (30%)*

March 4-8 - Winter/Spring break

15**	Tribo-mechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion*(filter-20%)*
5 April	Passive functional films and coatings, *Miniquiz 2 (5%)*
12	Active functional films and coatings
16	Life cycle analysis and environmental impact, **visits**
18***	*Presentations – Emerging applications of nanostructured films (40%)*

Deadlines:

Project #1 – Fabrication technique:

Choice of the subject: **26 January**

Abstract and references: **9 February**

Report and presentation: **1st March**

Projet #2 – Design of an optical filter:

Choice of the subject: **23 February**

Report: **22 March**

Projet #3 – Application of nanostructured thin films:

Choice of the subject: **16 February**

Abstract and references: **15 March**

Presentation: **18 April p.m.**

Report: **22 April at 23:59**

Projet #3 – Applications des couches minces

Thomas Sicotte and Alexandre Gamache - Cellules photovoltaïques à pérovskite

Alexandre Lussier - Fenêtres intelligentes thermochromiques

Mohamed Ammari - Thermal barrier coatings for aerospace gas turbine engine

Luc Montpetit - Passivation of CdZnTe for x-ray detectors

Veronika Cervenkova - Solar-thermal energy conversion - Transition metal nitrides as potential candidates

Émilien Martel - Electrochromic, photochromic and gasochromic coatings for consumer optics

Étienne Tremblay et Nathan Sasseville - Couches minces pour l'électronique organique - OLEDs

Thomas Lapointe - Photodétecteurs et leur conception/optimisation à l'aide des couches minces

Alexandre Carrière et Youssef Ben Mami - Électrodes transparentes pour les cellules solaires

Arghavan Yazdanpanah Ardakani - Nanoengineering of thin films to produce hydrophobic coatings for aircraft surfaces

Mathieu Bruzzese - Atomic oxygen barrier coating for aerospace/space exploration

Bastien Izacard - Revêtements pour la protection des composantes aérospatiales contre la corrosion

Alexandre Fall - Carbon nanotubes for sodium-ion batteries (or coated cathodes of other batteries)

Alexandre Pinel - Couches minces d'hydroxyapatites pour les implants en biomédical

Gabriel Juteau - Dynamic infrared radiators for satellites

Christelle Abou Zeidan – à venir