### Tribology Summer School, Visp 2023

## Tribology of Materials

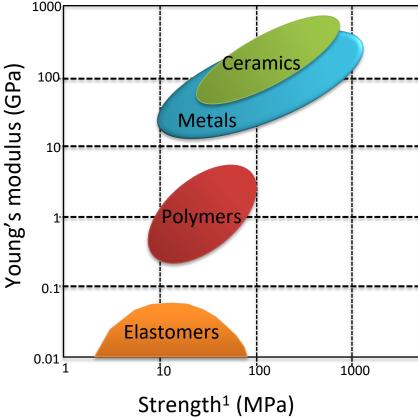
S. Mischler

### Content

- Material classes and their tribological relevant properties
- Metals
- Ceramics
- Polymers

## Mechanical properties of materials' classes

Ashby, Materials Selection in Mechanical design (Fourth Edition), 2011, 57–96



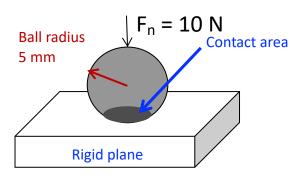
Strength+ (IVIPa) Metals: vield stress Ceramics: stre

<sup>1</sup>Metals: yield stress, Ceramics: stress at which brittle fracture occurs, Polymers/Elastomers: stress at which stress/strain curve becomes markedly non-linear

Metals and ceramics are mechanically much stronger than polymers.

They are also significantly less elastic.

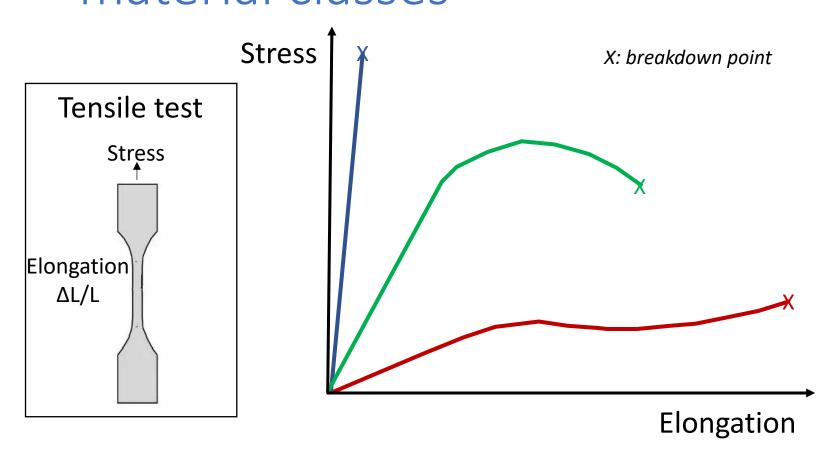
# Softer but more elastic materials can accommodate contact stresses without plastic deformation



Ball Material	Elastomer	Polymer	Metal	Ceramic	Unit
E Module	0.02	1	200	500	GPa
Poisson ratio	0.5	0.5	0.3	0.3	
Radius of contact area	1.121	0.304	0.057	0.043	mm
Hertz average pressure	3	34	995	1740	MPa
Yield Strength	10	20	350	350	MPa
Av. Pressure/YS	0.3	1.7	2.8	5.0	

Thanks to their low Young's modulus, materials such as polymers exhibit extended elastic deformation and thus provide lower contact pressures. Despite their usually lower mechanical resistance they can even better withstand contact loading.

# Typical stress-strain curves for different material classes



Ceramics: elastic deformation and breakdown without plastic flow. Brittle

Metals: initial elastic deformation followed by plastic deformation and breakdown. Elasto-plastic

**Polymers**: initial elastic followed by time dependent deformation before breakdown. **Viscoelastic** 

## Thermal properties

- Temperature in a contact depends on:
  - Frictional heat generation at interface : f(friction, velocity, contact area)
  - Heat transport away from interface: f(temperature gradient, thermal conductivity of materials)
- Thermal conductivity in W m<sup>-1</sup> K<sup>-1</sup>
  - Metals 20 390
  - Ceramics 2-126
  - Polymers < 0.5

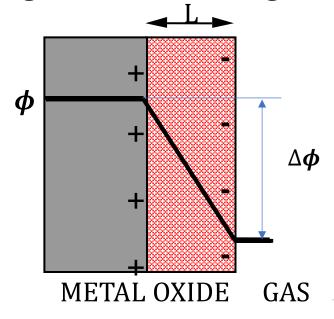
Due to their low thermal conductivity and low softening temperature polymers are very sensitive to frictional heating. Ceramics maintain mechanical properties up to their melting point and are therefore less sensitive to frictional heating.

## Chemical properties of materials' classes

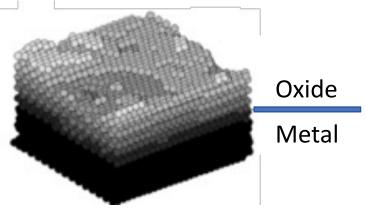
- Metals (except noble metals), once exposed to air, oxidize
  - Examples
    - Oxidation of Nickel:  $2 \text{ Ni} + \text{O}_2 \rightarrow 2 \text{ NiO}$
    - Oxidation of Chromium:  $4 \text{ Cr} + 6 \text{ O}_2 \rightarrow 2 \text{ Cr}_2 \text{O}_3$
- Non oxide ceramics can also oxidize as metals do
  - Example:
    - Oxidation of Silicon Carbide: SiC + 2O<sub>2</sub> -> SiO<sub>2</sub> + CO<sub>2</sub>
    - Oxidation of Silicon
       Si + O<sub>2</sub> -> SiO<sub>2</sub>
- Polymers are usually chemically inert except in organic solvents

## Oxide film growth at low temperature

• Growth by ion migration under high electric film (10<sup>7</sup> V/cm)

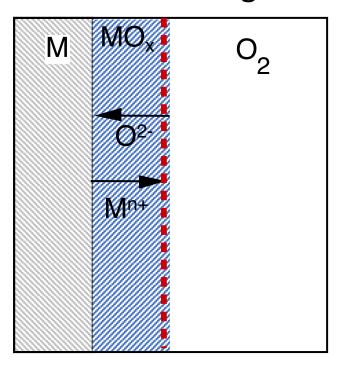


 Migration implies very thin film (a few nanometers)

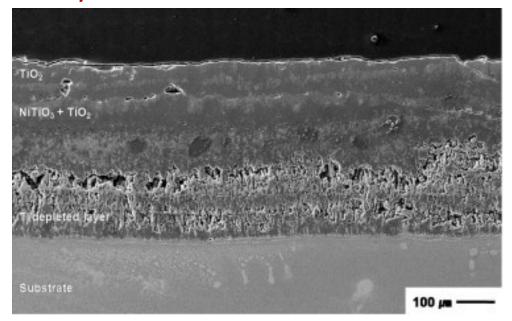


## Oxide film growth at high temperature

Growth by diffusion under concentration gradient



 Diffusion allows the growth of very thick oxide films

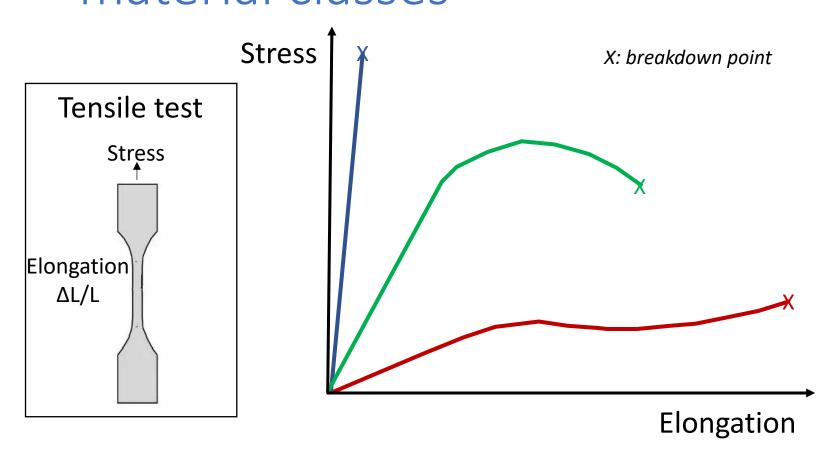


Example: oxidation of a NiTi alloy
Kyong MinKim, Thermochimica Acta 2014

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# Typical stress-strain curves for different material classes

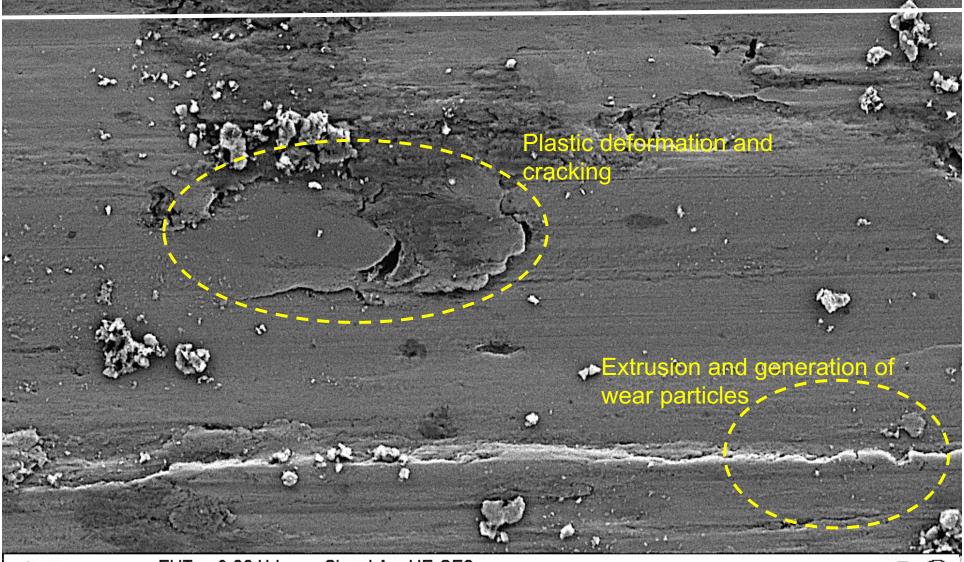


Ceramics: elastic deformation and breakdown without plastic flow. Brittle

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# Mechanical wear phenomena: SEM plane view of a HC CoCrMo worn surface



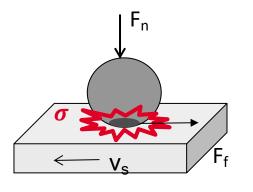
1 µm

EHT = 3.00 kV WD = 5.4 mm Mag = 25.00 K X Signal A = HE-SE2 I Probe = 300 pA Column Mode = Crossover

Date :8 Mar 2013 Sample ID = S21\_4



### Stress field $\sigma$ and wear of metals



 $\sigma$  < elastic limit

no plastic deformation

### Fatigue wear

Spalling off of metal particles after large number of loading cycles



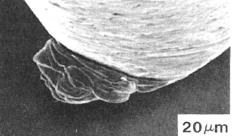
 $\sigma$  > elastic limit plastic deformation

(micro) Cutting



 $50 \mu m$ 

Metal cutting directly forms wear particles (abrasion)

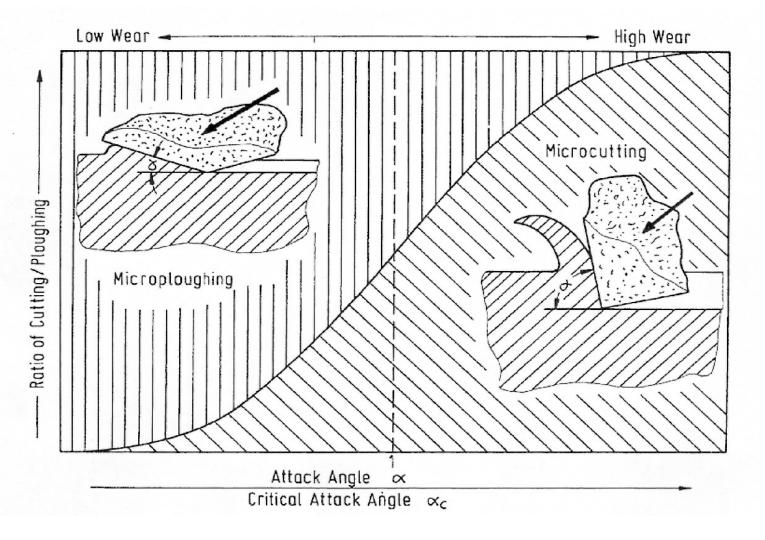


1st phase: Strain accumulation during repeated passes(no wear)

2<sup>nd</sup> phase: Break (wear particles) when accumulated strain> critical strain

(micro) Plowing

# The attack angle of the indenter determines the cutting ↔ ploughing transition

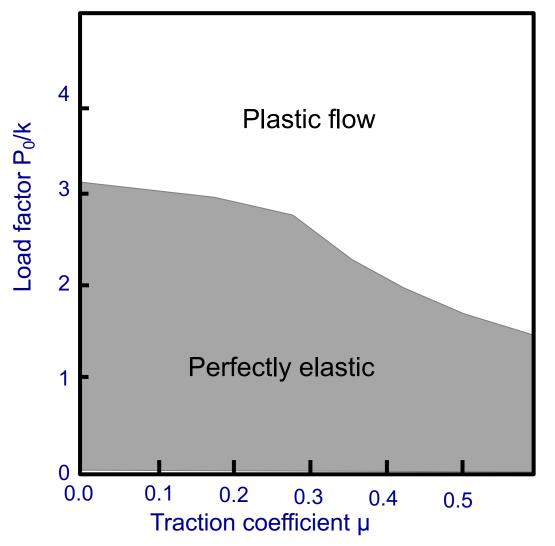


#### **Experimental values:**

Al  $\alpha_c = 85^{\circ}$ Cu  $\alpha_c = 45^{\circ}$ 

ZumGahr, Microstructure and Wear of Materials, Elsevier (1987)

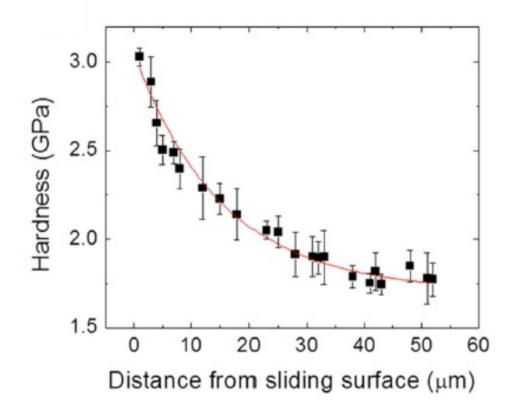
# Continuum mechanics approach: do not exceed elastic limit of the material.



- P<sub>0</sub>: maximal Hertz stress
- k: yield stress in shear (for uniaxial tension k = 0.5 yield strength)

## Deforming metals harden (work hardening)

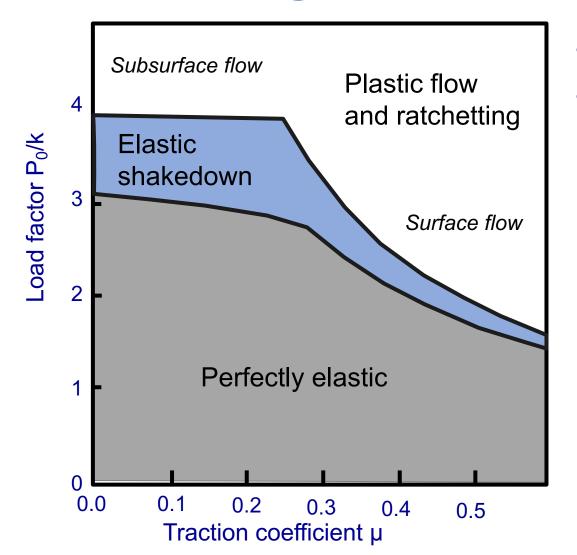
Plastic deformation generates dislocations (as well as other defects) in the metal. The increased concentration of dislocations limits their mobility and thus strengthen the deformed material.



Evolution of hardness below the wear track formed on a Ag-28.1 Cu alloy by rubbing against martensitic steel.

W. Cai, P. Bellon, Wear 303 (1) (2013)

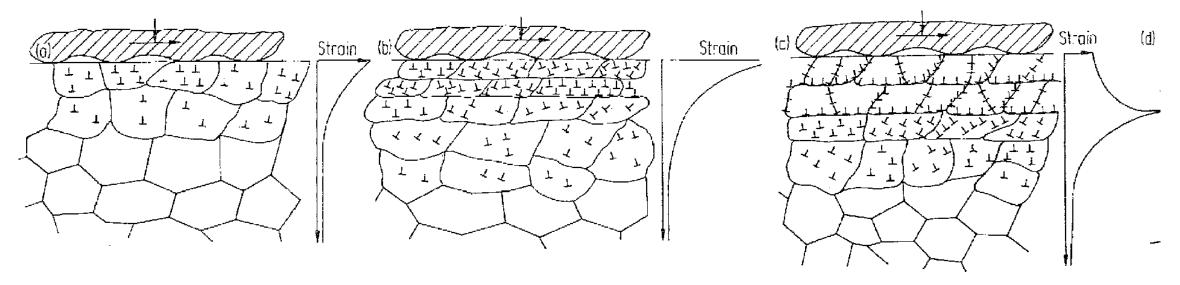
# Continuum mechanics approach including work hardening.



- P<sub>o</sub>: maximal Hertz stress
- k: yield stress in shear (for uniaxial tension k = 0.5 yield strength)

Adapted from A. Kapoor et al Wear 1996

### Friction induced dislocation structures

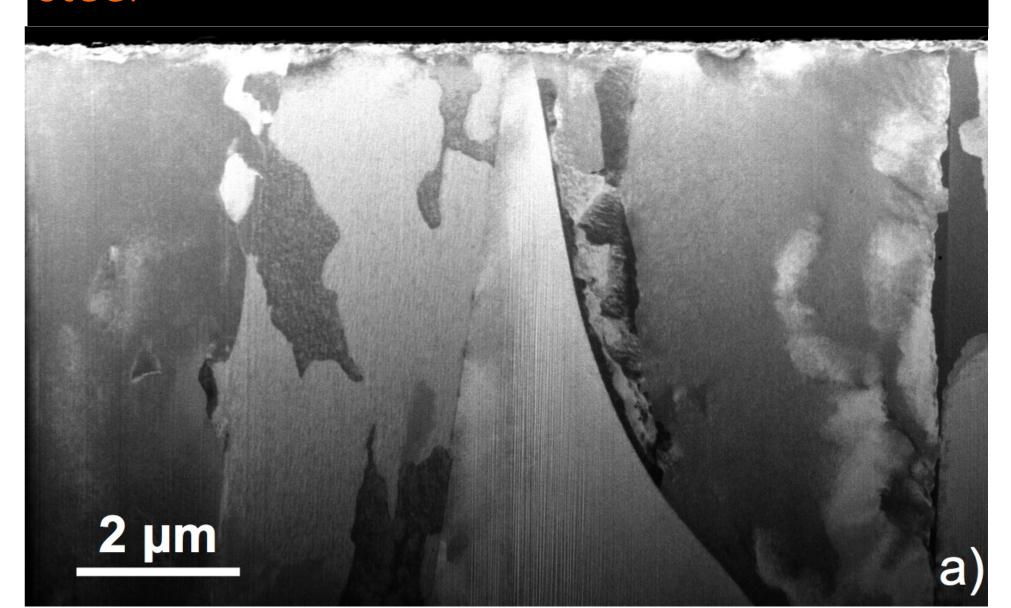


Under the frictional stress, dislocations are generated in the metal below the surface.

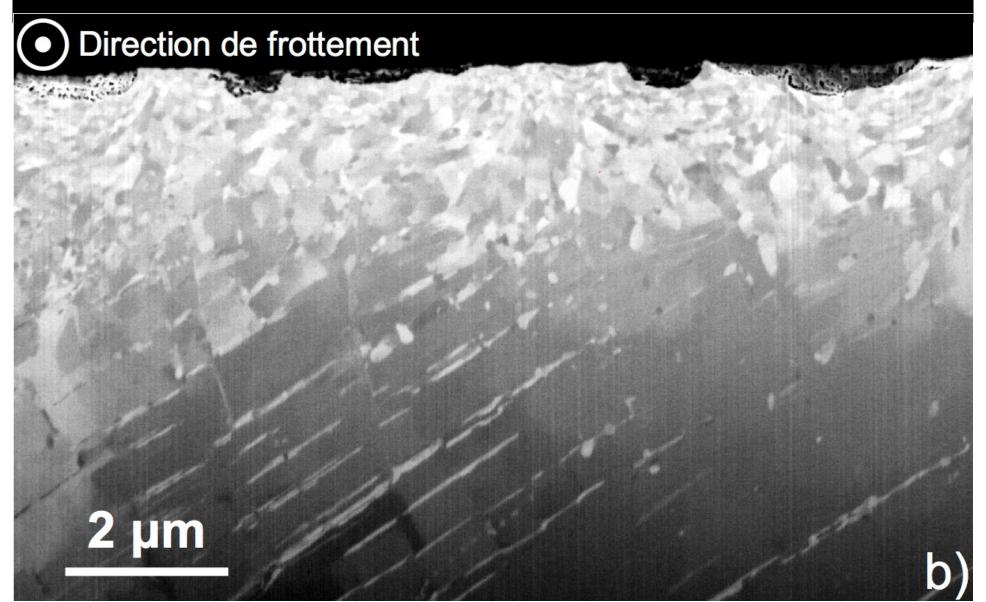
High concentration of dislocations are attained close to the surface where the stress field is larger.

The dislocations rearrange themselves in more energetic favourable configuration and lead to recrystallization in form of smaller grains.

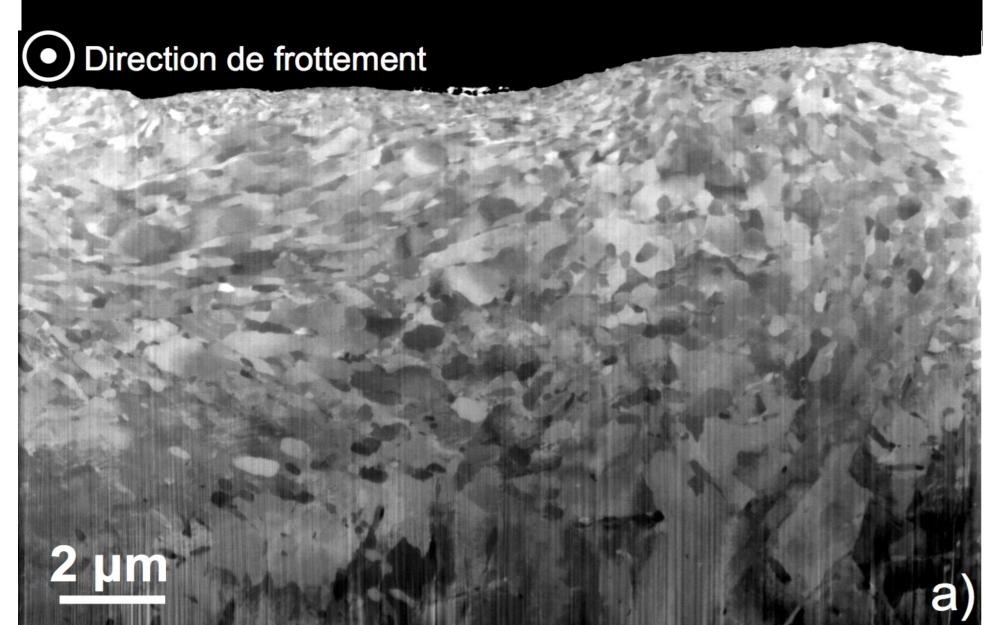
# FIB cross section of polished, unworn 304L steel



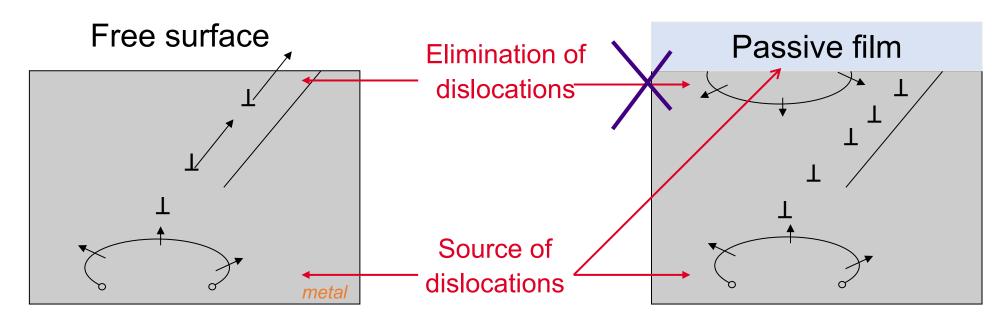
# FIB cross section of the wear scar formed in absence of surface film (cathodic polarized in acid)



FIB cross section of the wear scar formed in absence of surface film (anodic polarized in acid)



# Hypothesis: passive films block and/or generate dislocations



Equilibrium between generation and elimination of dislocations: limited strain accumulation

Passive film blocks the surface, act as source of dislocations and inhibits their elimination: strain accumulation

## Tribological Transformed Surface (TTS)

Strain Surface Nano-crystalline layer Strain hardened metal **Bulk metal** 

## Cracking and particle detachment mechanisms

Detachment of single nano-grains • < Surface Cracking within the nanocrystalline layer Cracking within the bulk metal

### Wear accelerated corrosion

Many tribological devices operate in aqueous, corrosive environments



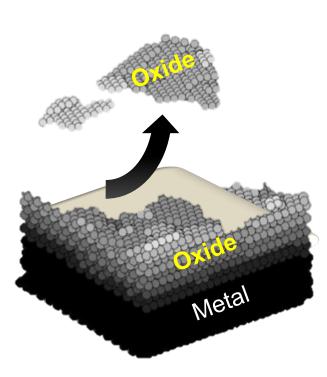






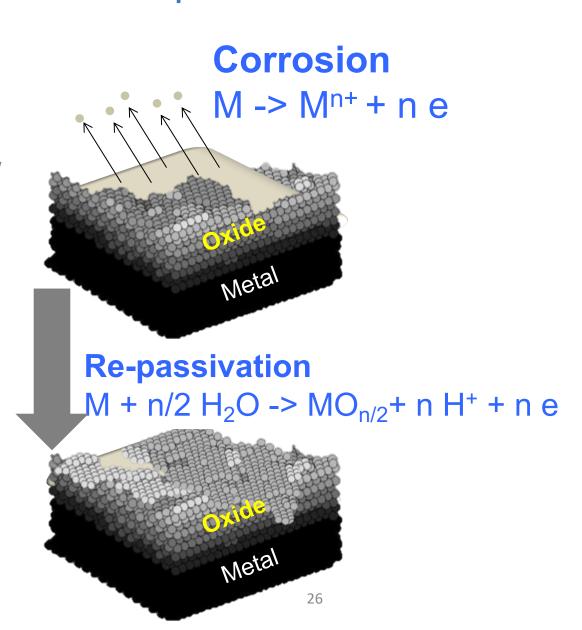
- For such applications, passive alloys (e.g. stainless steel, titanium, ...) alloys are used to prevent corrosion.
- However, when rubbing in aqueous solution passive materials undergo severe corrosion due to the periodic abrasion of the passive film

## Wear accelerated corrosion of passive metals

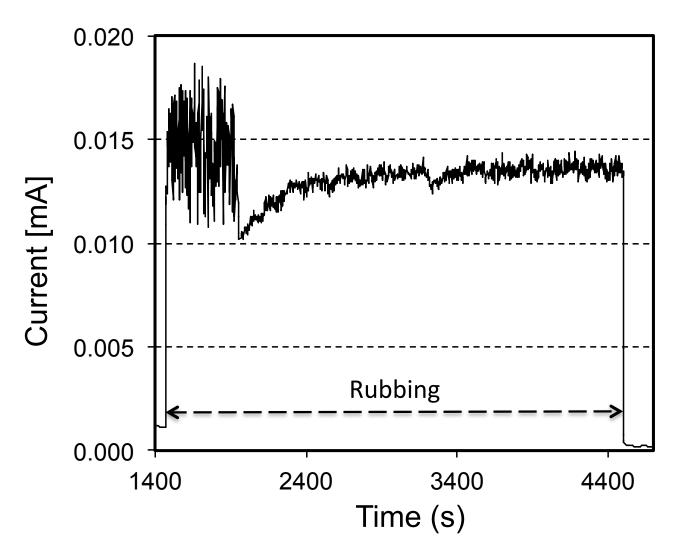


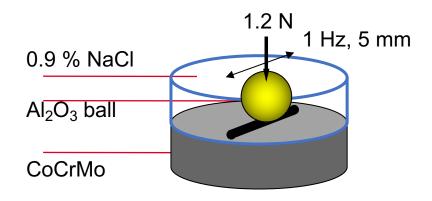
### **Depassivation** by:

- Plastic deformation
- Wear particle generation
- Cracking



# Enhancement of corrosion can be recorded using tribo-electrochemical experiments



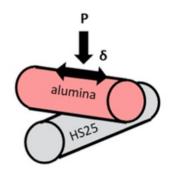


The corrosion rate of passive metals under rubbing can increase by several orders of magnitude

Igual Munoz et al, J. of Eng. in Medicine (2010)

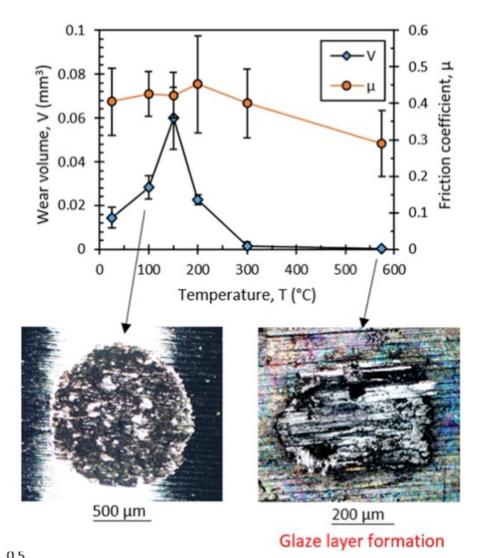
# High temperature wear: example of fretting wear of HS25 alloy (Co54Cr26Ni11W5Fe2Mn2)

#### Test configuration (air)



Dreano et al, Wear 440-441 (2019) 203101

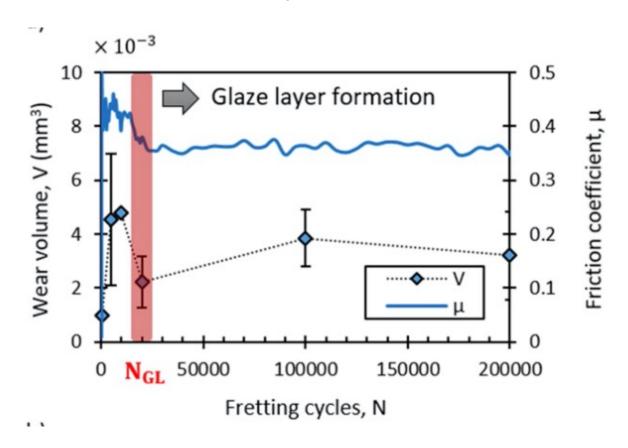
 $\times 10^{-3}$ 



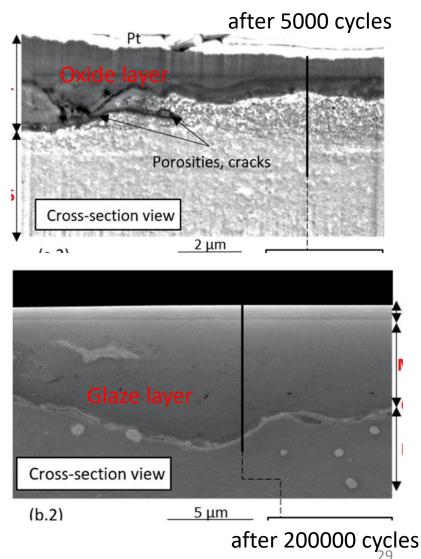
The wear rate increases up to 150°C because of oxidation is faster (tribochemical wear by oxide film particle removal).

At higher temperature, particles start compacting and forming a wear protective layer (glaze layer).

# High temperature wear: glaze layer forms after a certain time by accumulation of oxidized wear debris



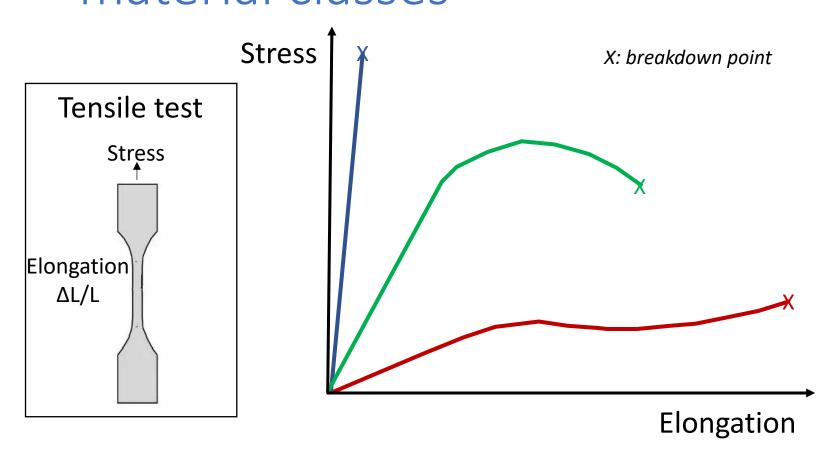
Build up of glaze layer (hard, smooth), after sufficient wear debris particles are compacted, reduces wear and friction



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# Typical stress-strain curves for different material classes



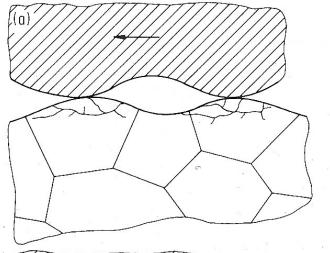
Ceramics: elastic deformation and breakdown without plastic flow. Brittle

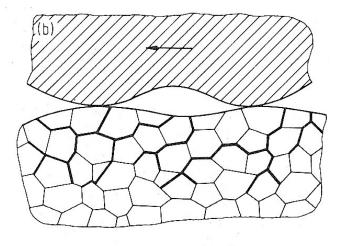
Metals: initial elastic deformation followed by plastic deformation and breakdown. Elasto-plastic

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## Typical degradation mechanisms of ceramics

a)
Transgranular
cracking at
asperities (low
load).

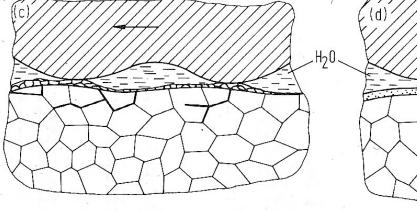


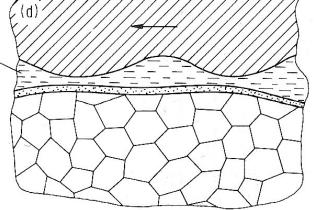


b)
Intergranular cracking
below the surface
(high load).

c)

A layer of compacted debris of ceramics and reaction products forms (low moisture).



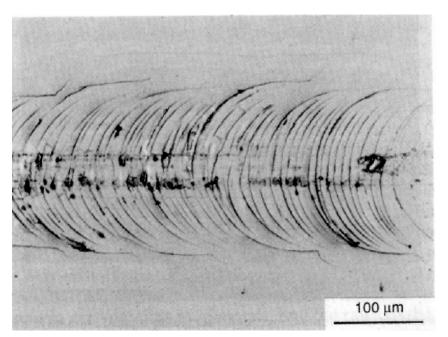


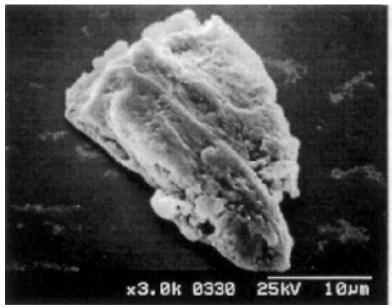
A compact layer of reaction products forms (high moisture).

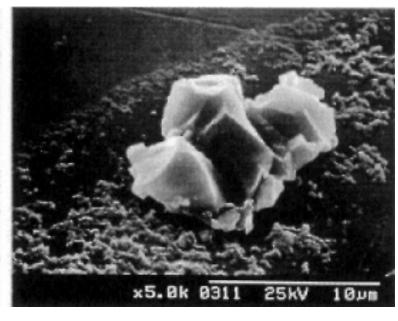
d)

K.H. Zum Gahr, Microstructure and wear of materials, Elsevier 1987.

## Tribological degradation features in ceramics







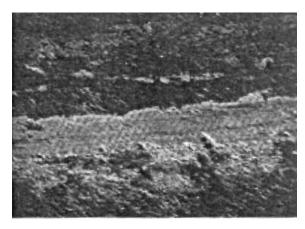
Glass surface after friction (left to right) with a tungsten carbide ball. Hutchings, Tribology, Arnold (1992)

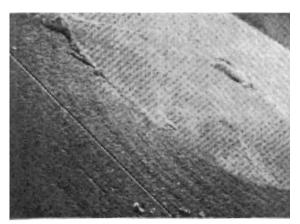
Wear particles formed by transgranular (left) or intergranular (right) fracture of silicon nitride.

## Tribological degradation features in ceramics

•Wear morphology after friction of silicon nitride against silicon nitride (1mm/s, 10N, T ambient, sliding distance 3 m). T.E. Fischer, H. Tomizawa, Wear 105 (1985) 29-45

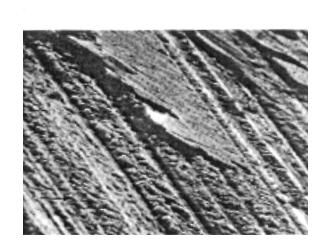
Air, 45% humidity

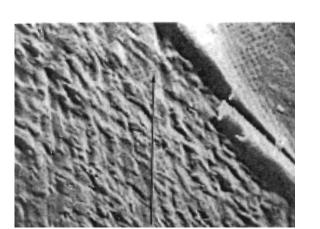




Argon, 98% humidity

Film composed by SiN and reaction products

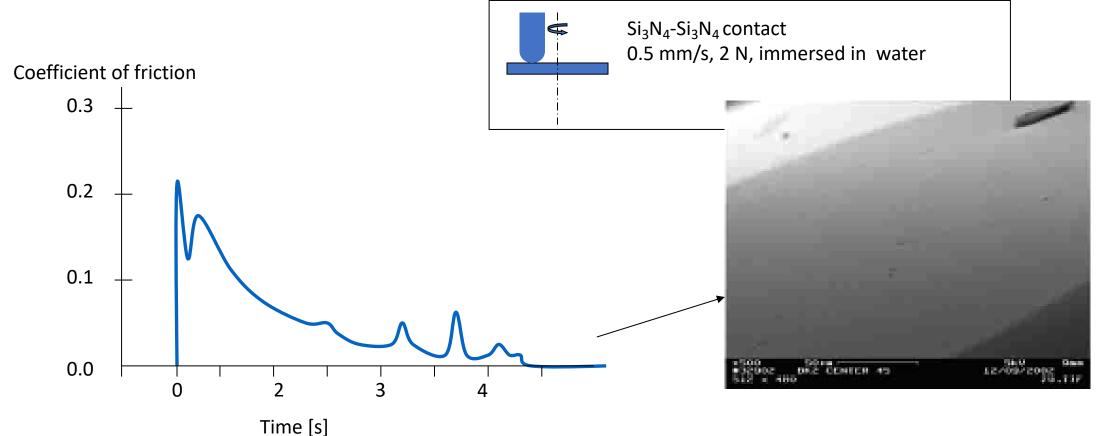




Reaction film comprising only Si and O, but no nitrogen.

# Establishment of an hydrodynamic regime by a tribochemical mecanism

Wear by tribochemical reaction in water can quickly transform a non conforming contact in a conforming one involving super-smooth surfaces. This allows for hydrodynamic lubrication to occur, due to a favorable  $\lambda = h / R_{\alpha}$  ratio.



## Phase transformation: the case of Zirconia ZrO<sub>2</sub>

The heat produced by friction can induce a transformation of the tetragonal and monoclinic structures of zirconium oxide into cubic structures.

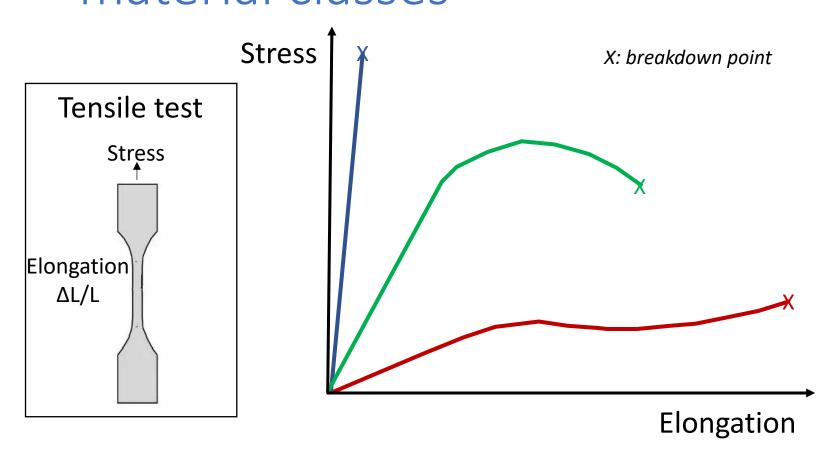
The molar volume of the cubic structure being lower, traction stresses appear in the material and the wear rate increases considerably.

The low thermal conductivity of ZrO<sub>2</sub> makes this phenomenon observable at relativly low temperatures (600°C), even at low speed.

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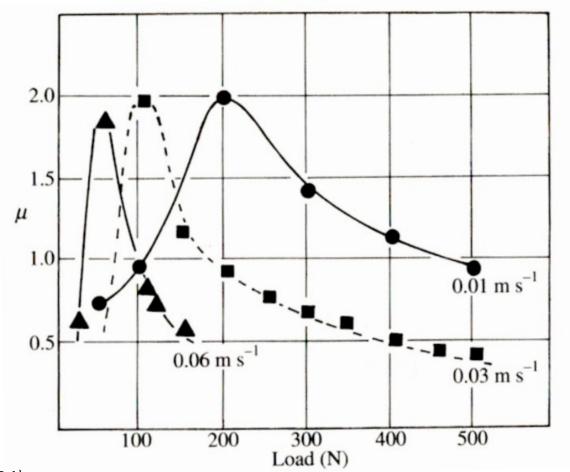
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# The visco-elastic nature of Polymers influences their frictional behaviour

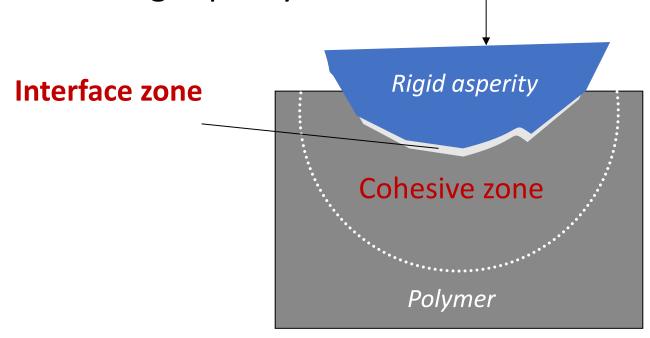
CoF versus normal load for three sliding speeds for nylon on steel: friction rules (  $\mu$  independent on load and velocity) are not respected.



Source: Williams "Engineering Tribology" (1994)

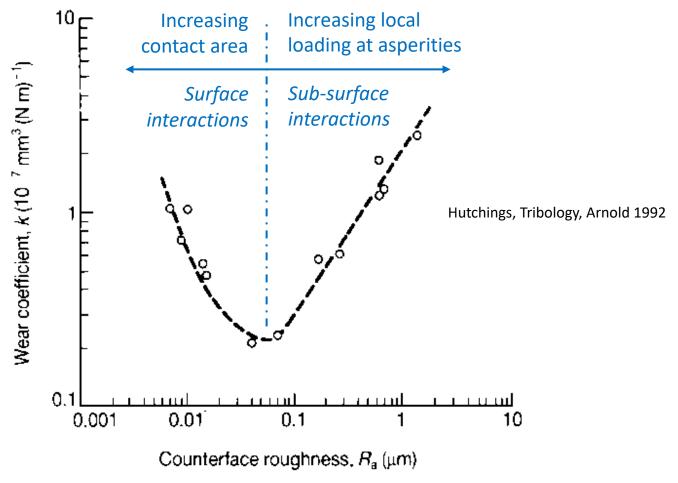
### Interfacial and cohesive zones

Two different zones can be identified in a contact between a polymer and a moving asperity.



Variable	Interface zone	Cohesive zone	
Temperature	High	Environment	
Pressure	High	Moderate	
Strain	High	Moderate	

# Transition between interfacial and cohesive wear



Wear rate of ultra-high molecular weight PE sliding against steel counter face as a function of steel roughness.

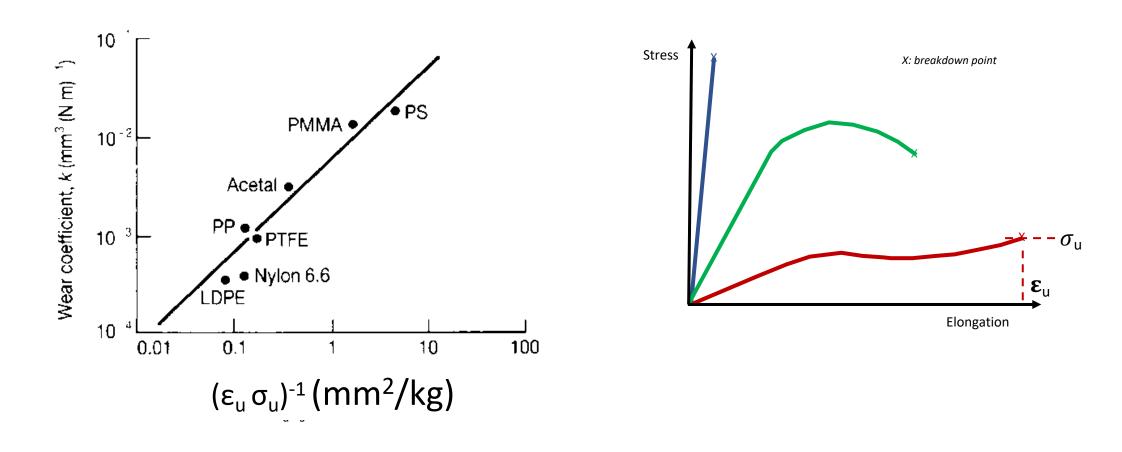
### Cohesive wear

### One can distinguish two different situations:

- Plastic deformation
  - abrasive wear
  - very rough surfaces, high modulus rigid polymers

- Elastic deformation
  - fatigue wear
  - mildly rough surface, high modulus flexible polymers

### The Ratner-Lancaster correlation for cohesive abrasive wear



Ratner-Lancaster correlation between wear coefficient of polymers under abrasive conditions and reciprocal of the product of the stress  $\sigma_u$  and strain  $\epsilon_u$  at rupture in tensile tests. Hutchings, Tribology, Arnold 1992

## Elastic deformation: fatigue

### 1. Crack initiation:

- Local stress concentration due to:
  - Counter part roughness
  - Structural defects in the polymer

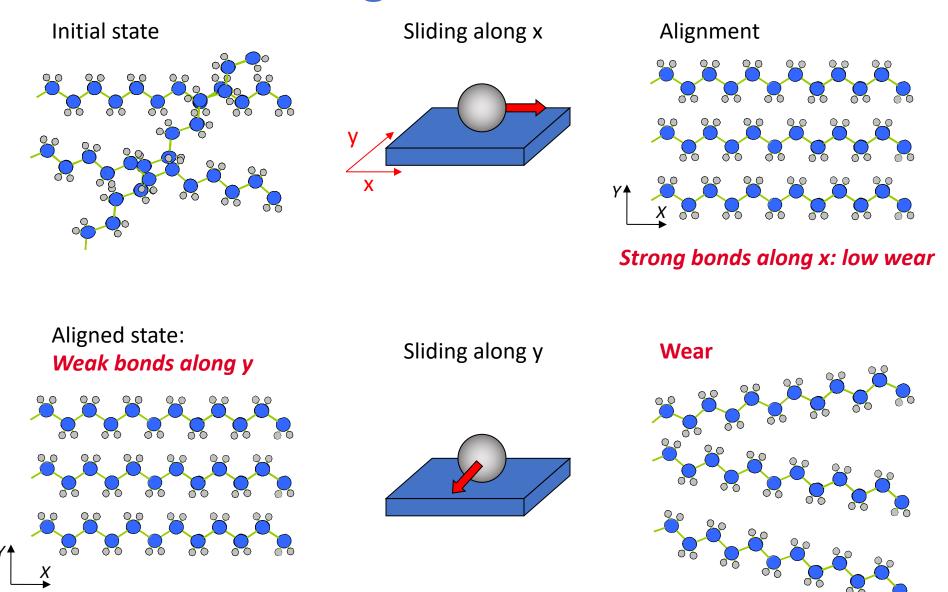
### 2. Crack propagation:

$$\frac{da}{dN} = k\Delta K_{I}^{m}$$

m, k: function of the environment

K<sub>I</sub>: function of local stress concentrations

## Interfacial wear: alignement of molecules



## Interfacial wear: melting due to frictional heating

Surface melting of a polymer under high speed friction results in high wear rate.

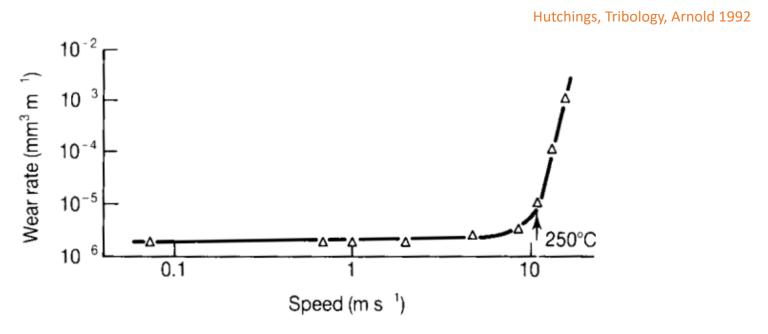


Fig. 5.39 The variation of steady-state wear rate with sliding speed for nylon 6.6 sliding against a smooth mild steel counterface ( $R_a = 0.15 \,\mu\text{m}$ ) under unlubricated conditions (from Evans D C and Lancaster J K, in Scott D (Ed.), Wear, Treatise on Materials Science and Technology, Academic Press, 13, 85–139, 1979)

### Conclusive remarks

Materials can respond in a variety of modes to tribological loading (structural changes, chemical reactions, deformation, cracking).

Although some general mechanisms can be deduced from the overall properties of the materials, the exact response can hardly be anticipated as it depends very much on the overall structure and properties of the tribological system.

Observation of the worn surfaces can yield information about the prevailing mechanisms and thus on the in-situ conditions experiences by the contacting materials.