Chapter 7
Material responses to tribological loading

MSE 485
Tribology

1 Material classes and their tribological relevant properties

2. Metals

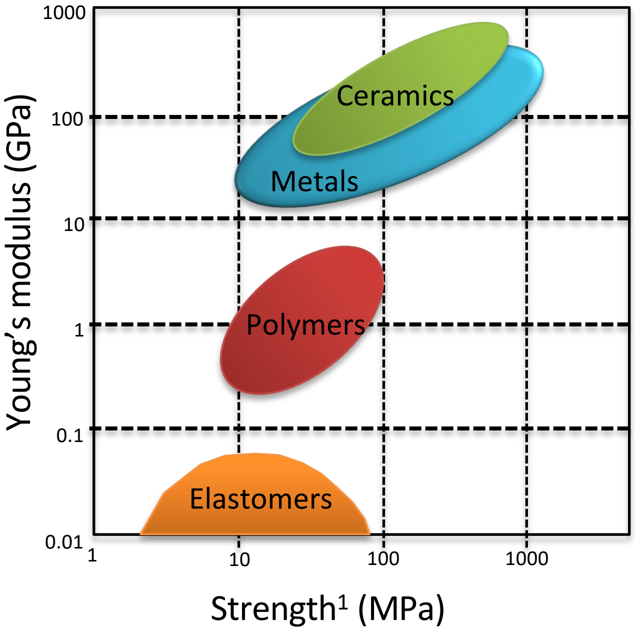
3. Ceramics

4. Polymers

5. Composite materials: the importance of the interface

Mechanical properties of materials' classes

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

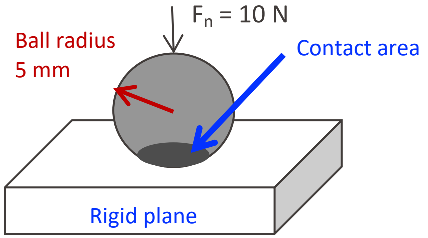


Metals and ceramics are mechanically much stronger than polymers.

They are also significantly less elastic.

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

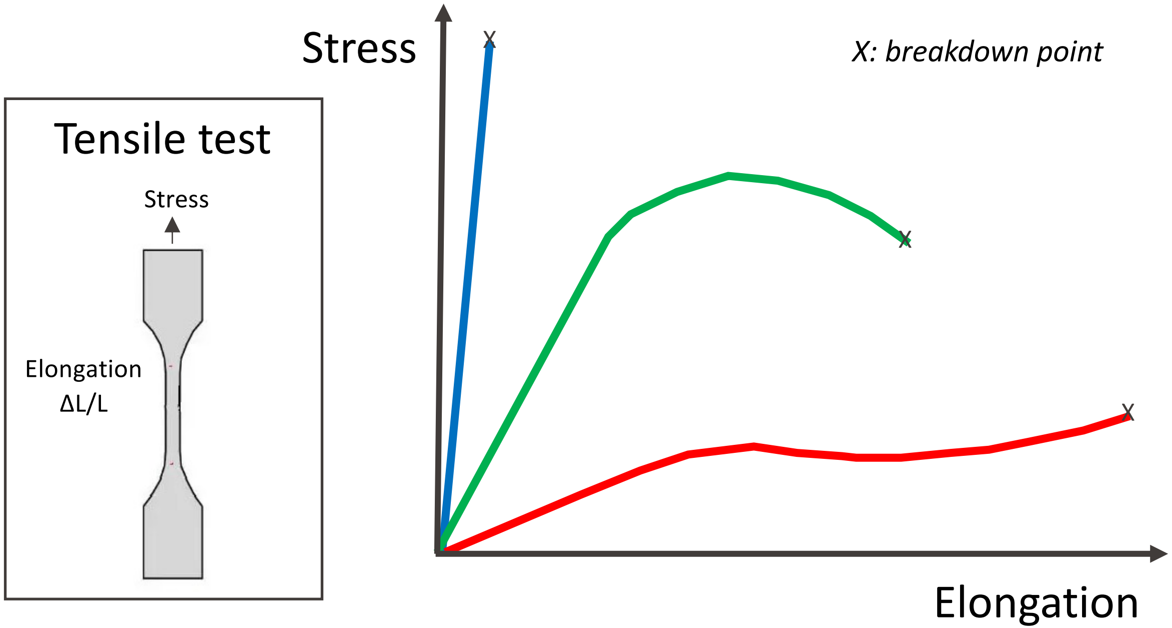
Softer but more elastic materials can accommodate contact stresses without plastic deformation



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^{-1} K^{-1}
  - Metals 20 – 390
  - Ceramics 2 – 126
  - Polymers < 0.5

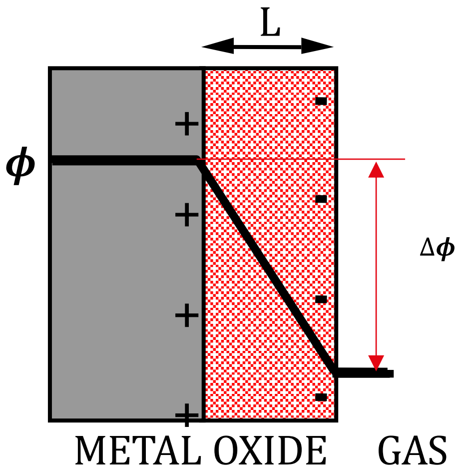
Due to their low thermal conductivity and low softening temperature polymers are very sensitive to frictional heating. Ceramics maintain mechanical properties up to their melting point and are therefore less sensitive to frictional heating.

Chemical properties of materials' classes

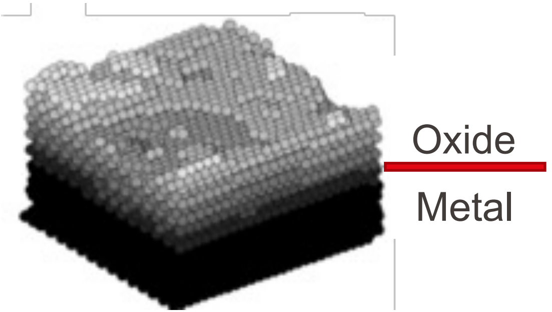
- Metals (except noble metals), once exposed to air, oxidize
  - Examples
    - Oxidation of Nickel: $2\,Ni + O_2 \rightarrow 2\,NiO$
    - Oxidation of Chromium: $4\,Cr + 6\,O_2 \rightarrow 2\,Cr_2O_3$
- Non oxide ceramics can also oxidize as metals do
  - Example:
    - Oxidation of Silicon Carbide: $SiC + 2O_2 \rightarrow SiO_2 + CO_2$
    - Oxidation of Silicon $Si + O_2 \rightarrow SiO_2$
- Polymers are usually chemically inert except in organic solvents

Oxide film growth at low temperature

- Growth by ion migration under high electric field (10^7 V/cm)

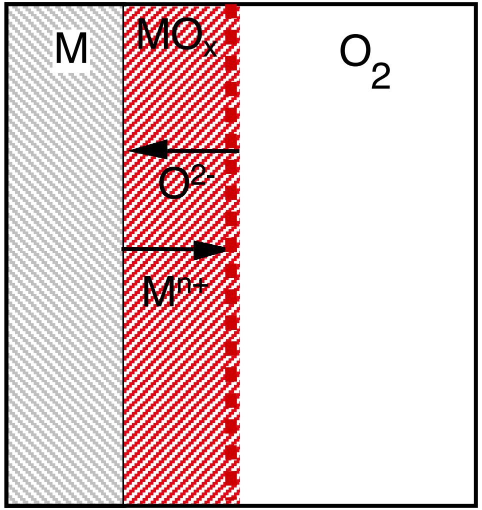


- Migration implies very thin film (a few nanometers)

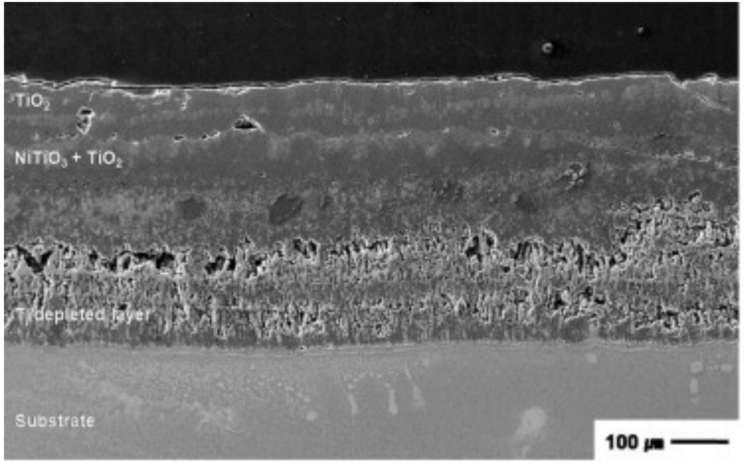


Oxide film growth at high temperature

- 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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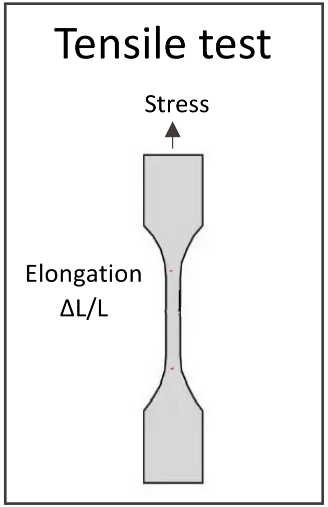

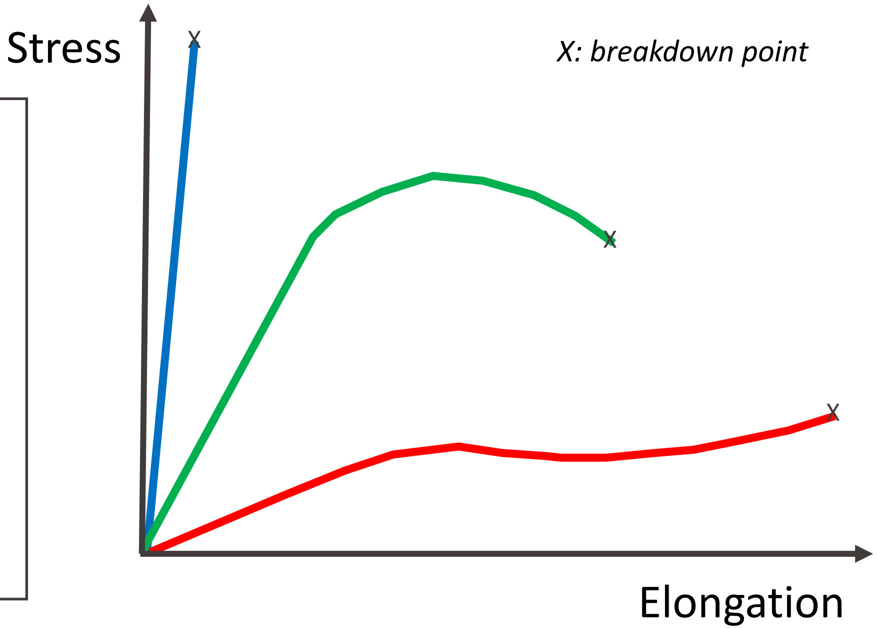

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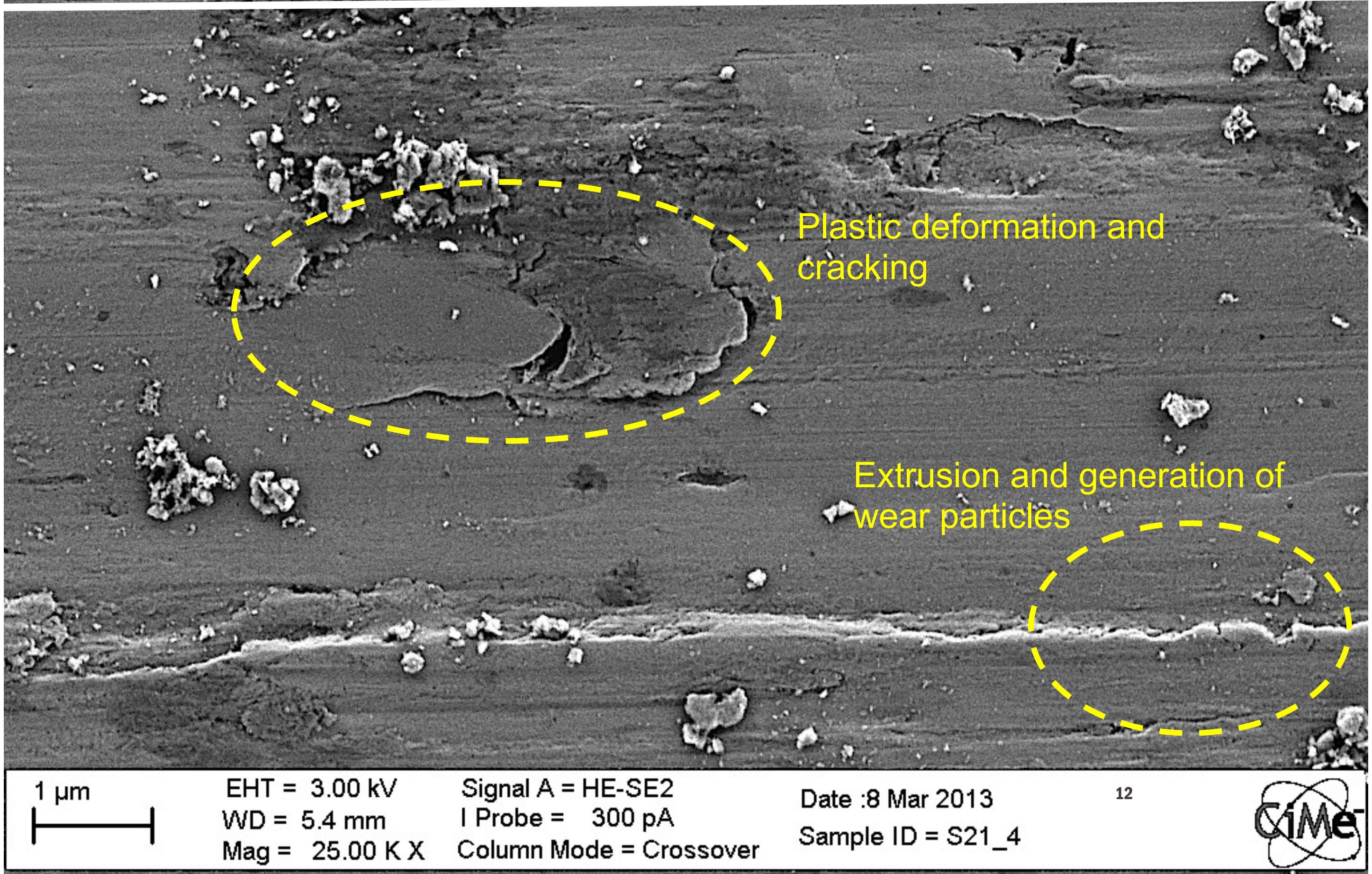
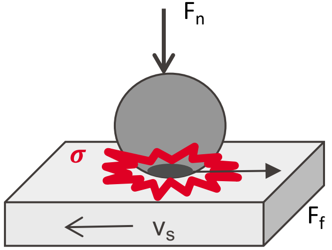
Mechanical wear phenomena: SEM plane view of a HC CoCrMo worn surface



Stress field σ and wear of metals

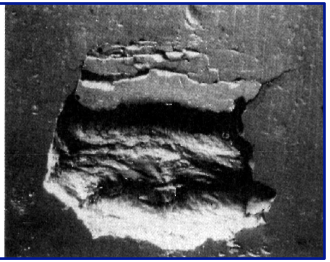


σ < elastic limit

no plastic deformation

Fatigue wear

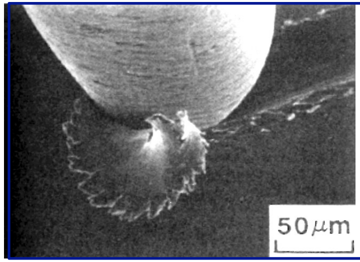
Spalling off of metal particles after large number of loading cycles



σ > elastic limit

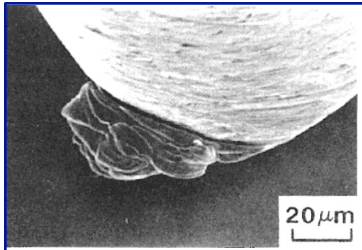
plastic deformation

(micro) Cutting



Metal cutting directly forms wear particles (abrasion)

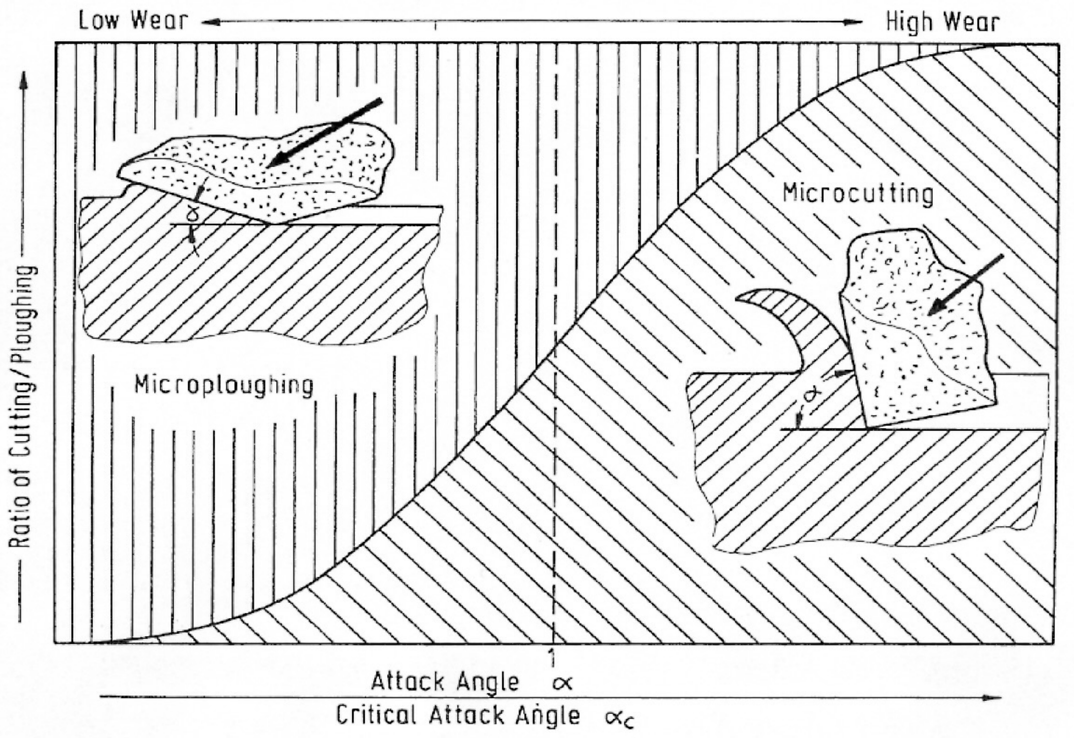
(micro) Plowing



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

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

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

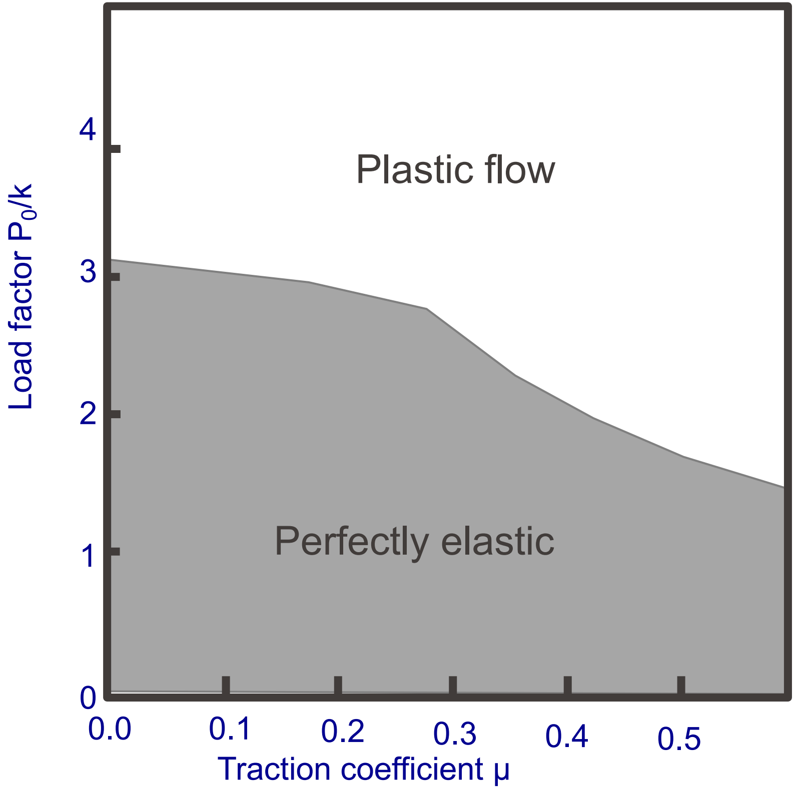


Experimental values :

Al α_c = 85°
Cu α_c = 45°

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

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

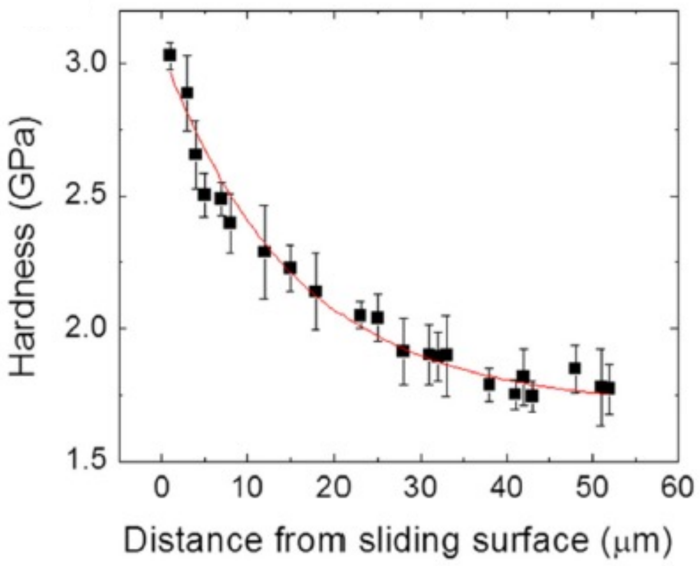


- P_0: maximal Hertz stress
- k: yield stress in shear (for uniaxial tension k = 0.5 yield strength)

Adapted from A. Kapoor et al Wear 1996

Deforming metals harden (work hardening)

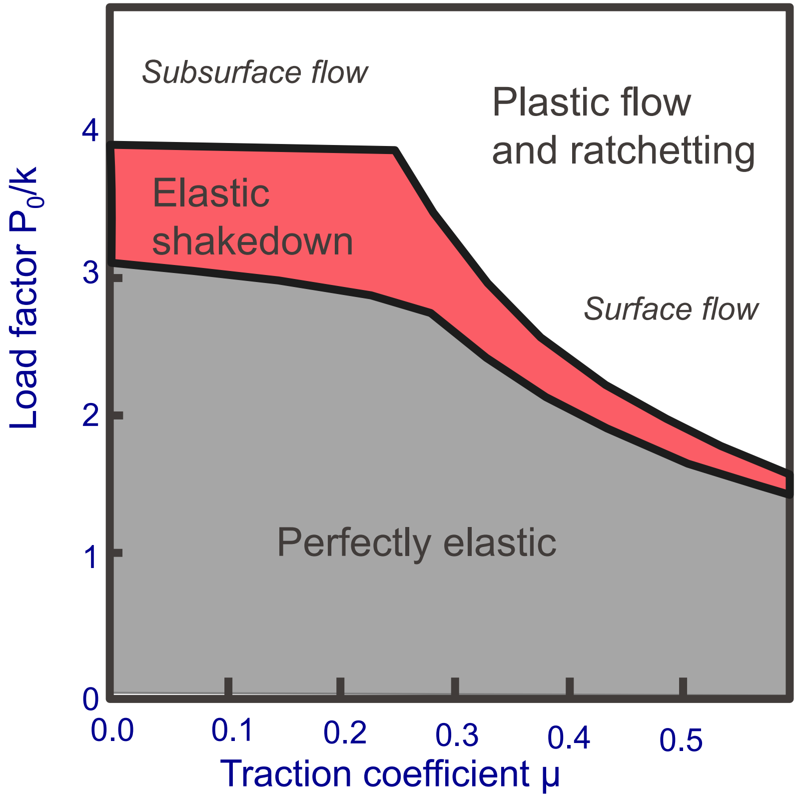
Plastic deformation generates dislocations (as well as other defects) in the metal. The increased concentration of dislocations limits their mobility and thus strengthen the deformed material.



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)

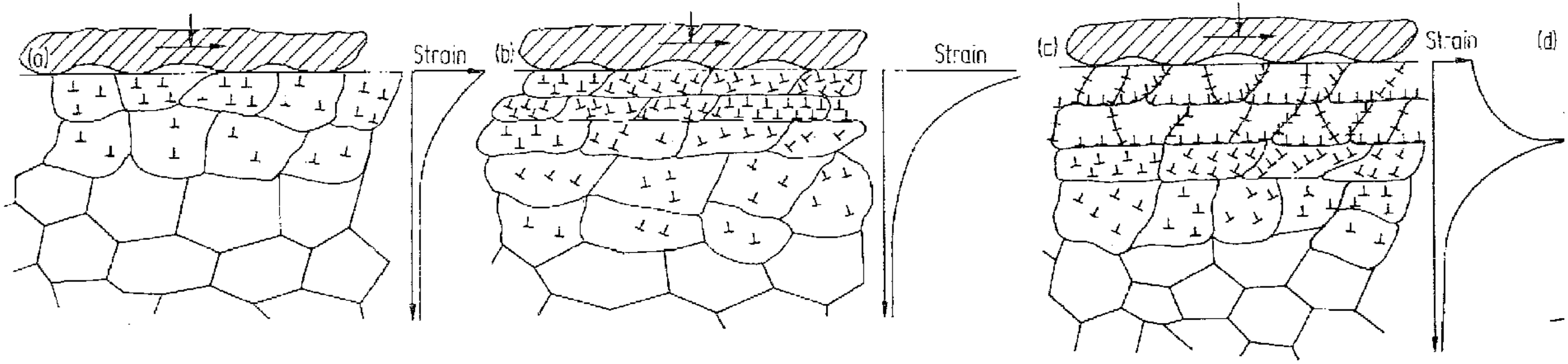
Continuum mechanics approach including work hardening



- P_0: 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



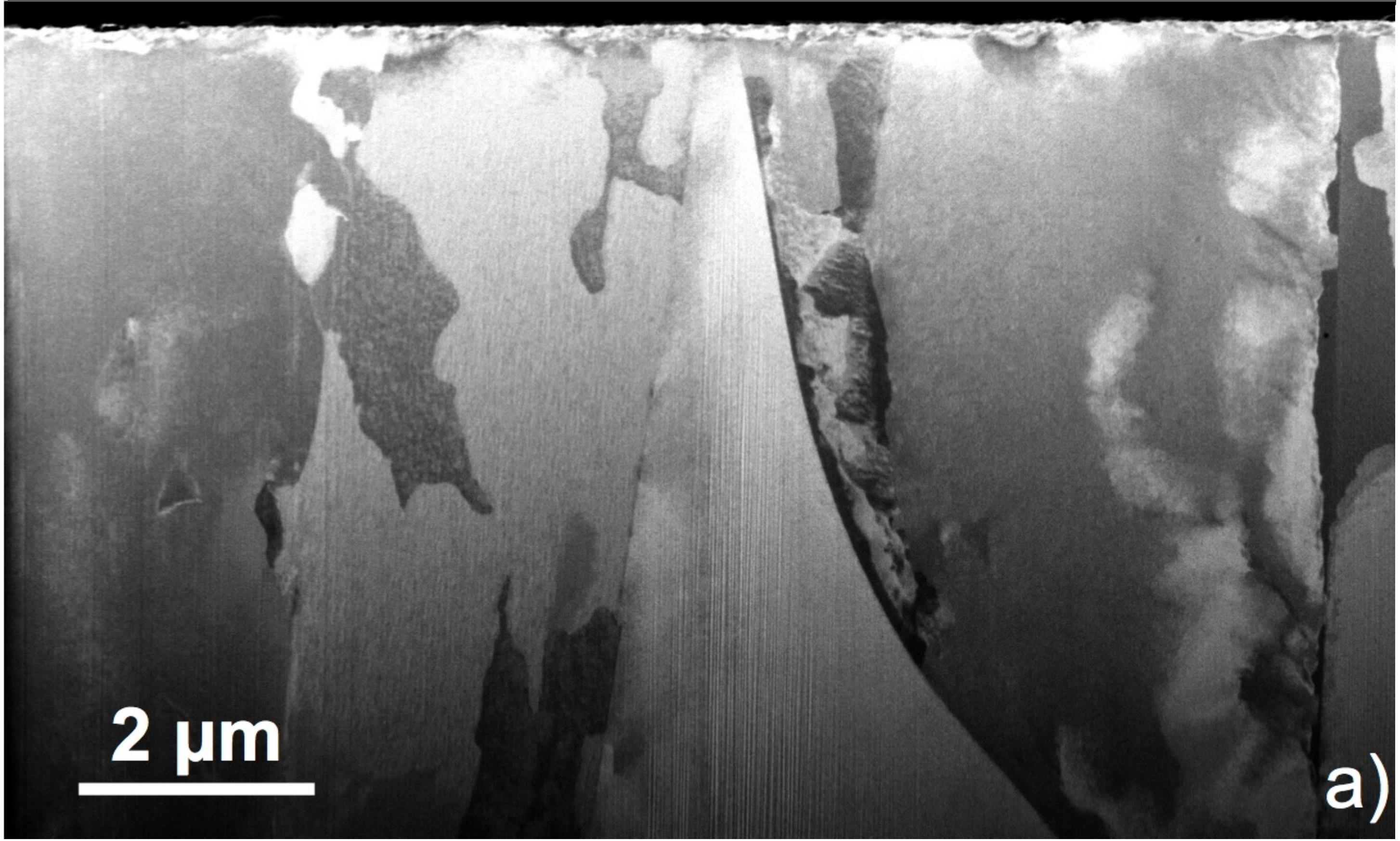
Under the frictional stress, dislocations are generated in the metal below the surface.

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

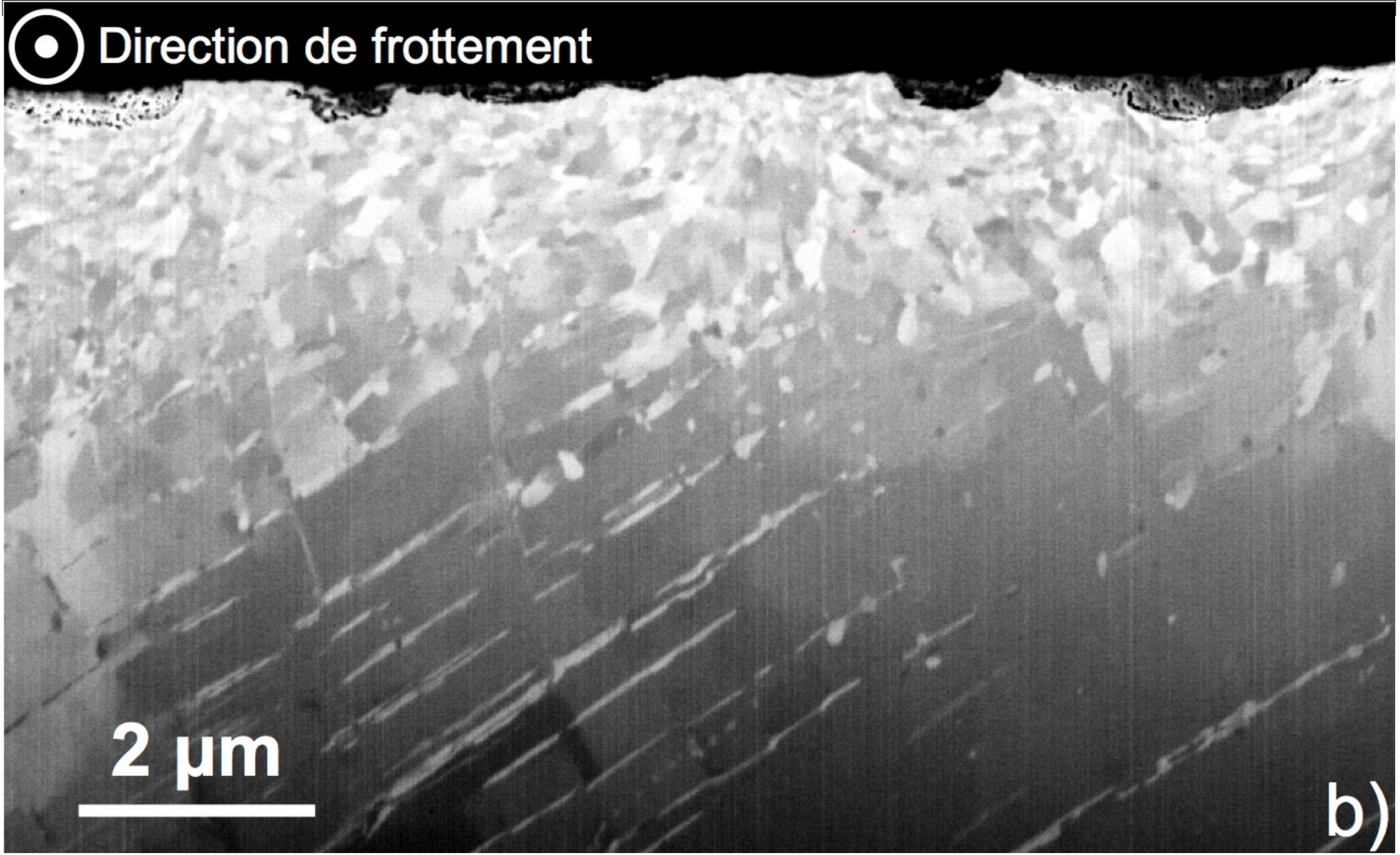
The dislocations rearrange themselves in more energetic favourable configuration and lead to recrystallization in form of smaller grains.

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

FIB cross section of polished, unworn 304L steel

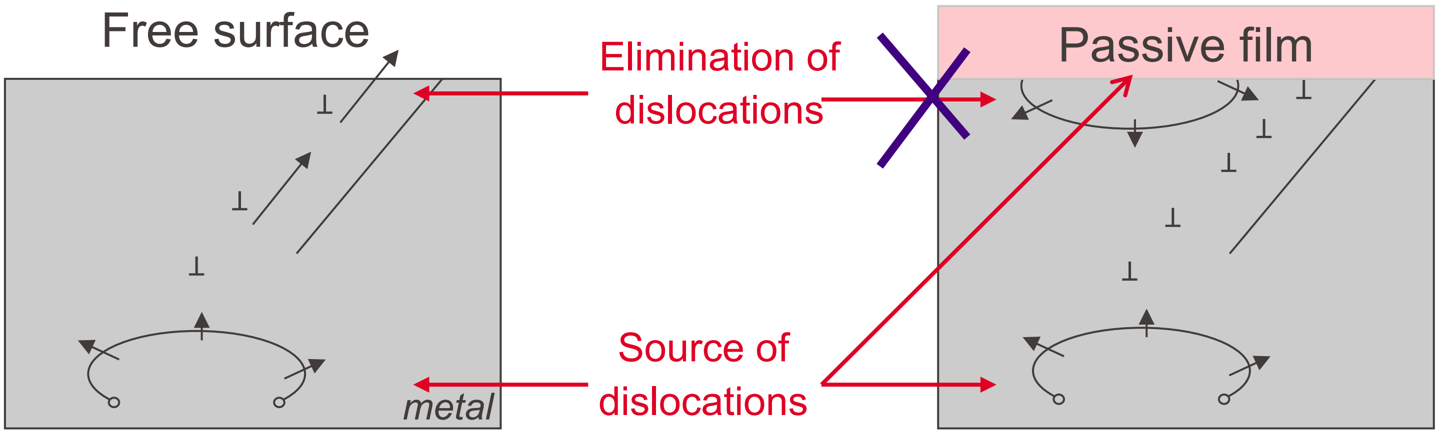


FIB cross section of the wear scar formed in absence of surface film (cathodic polarized in acid)



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

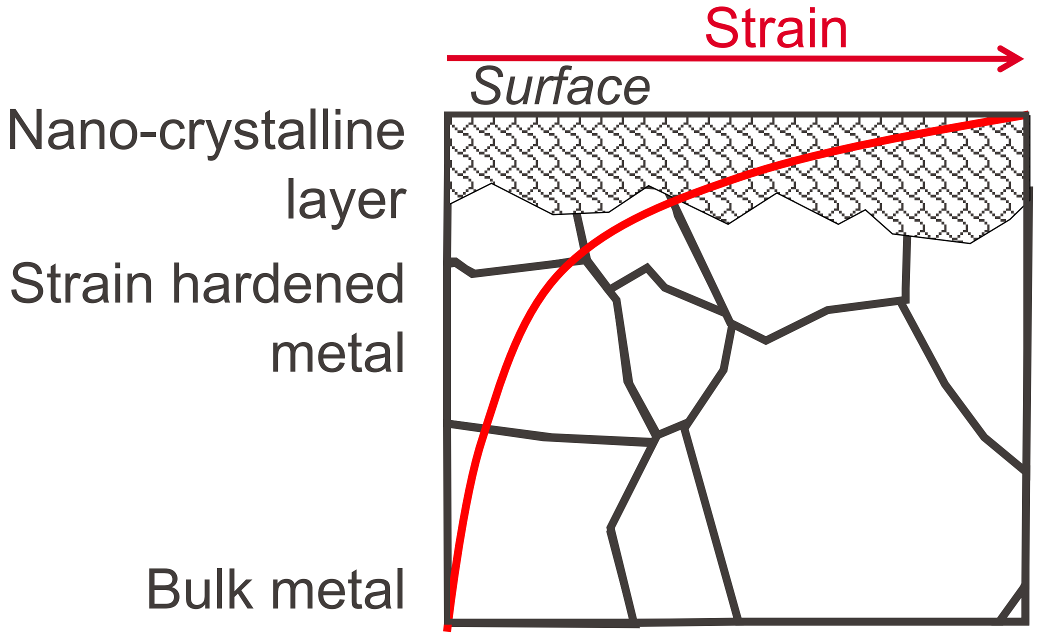
Hypothesis: passive films block and/or generate dislocations



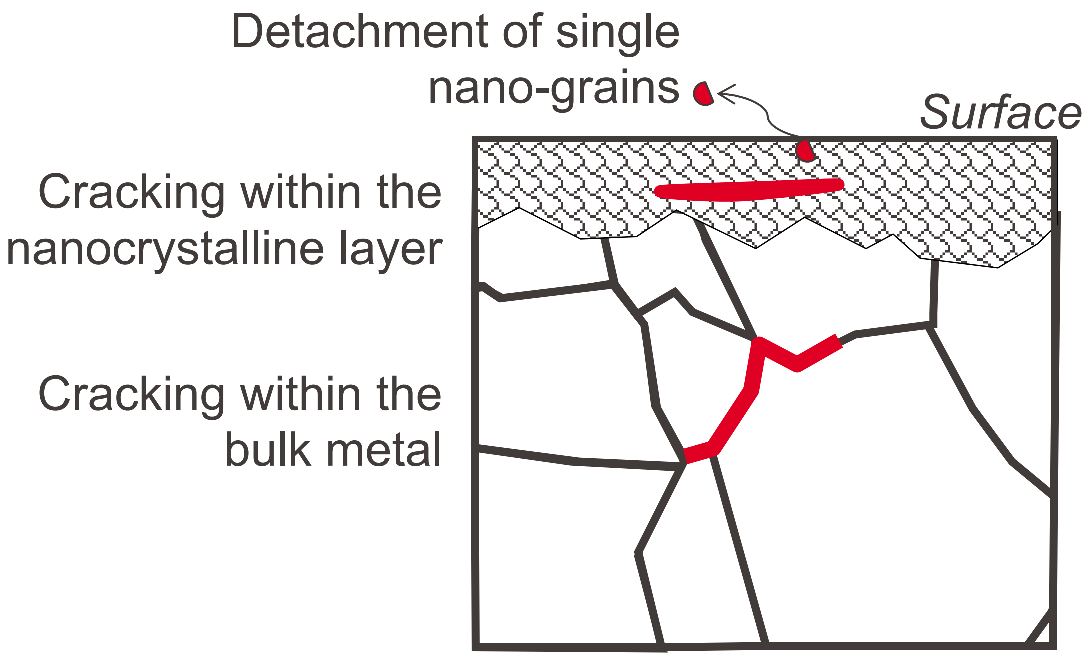
Equilibrium between generation and elimination of dislocations:
limited strain accumulation

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

Tribological Transformed Surface (TTS)



Cracking and particle detachment mechanisms



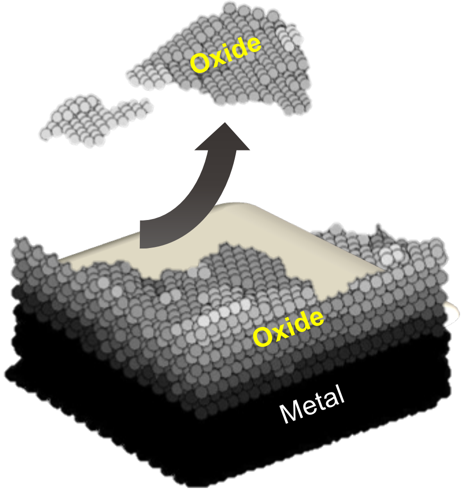
Wear accelerated corrosion

- Many tribological devices operate in aqueous, corrosive environments



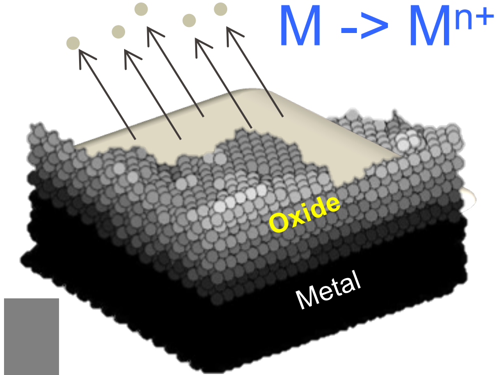

- For such applications, passive alloys (e.g. stainless steel, titanium, …) alloys are used to prevent corrosion.
- However, when rubbing in aqueous solution passive materials undergo severe corrosion due to the periodic abrasion of the passive film

Wear accelerated corrosion of passive metals



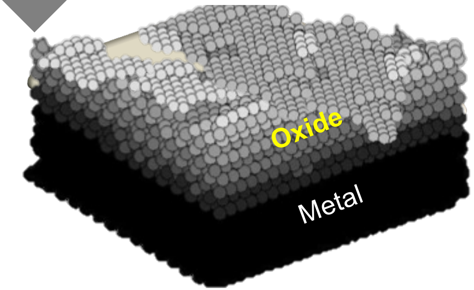
Corrosion

M -> M^{n+} + n e



Re-passivation

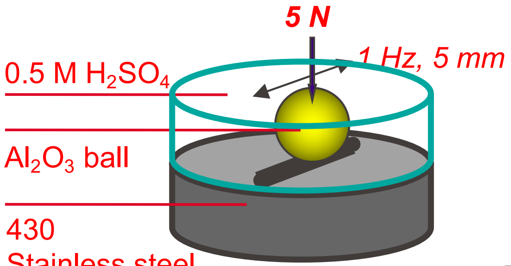
M + n/2 H_2O -> $MO_{n/2}$+ n H^+ + n e



Depassivation by:

- Plastic deformation
- Wear particle generation
- Cracking

Enhancement of corrosion can be recorded using tribo-electrochemical experiments



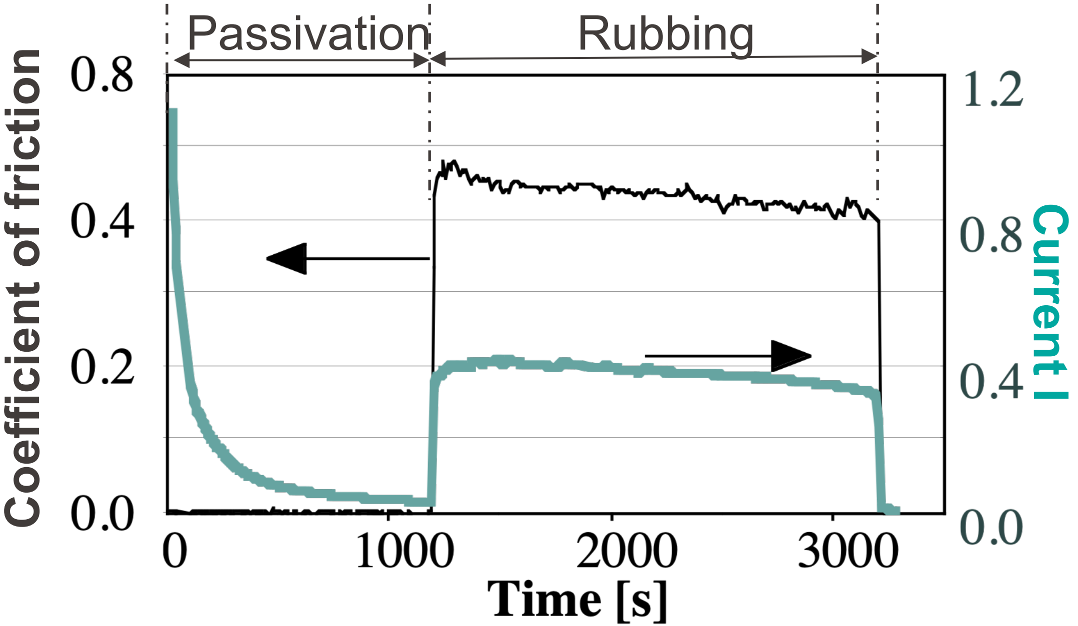
Rubbing duration: 2000 s

Wear accelerated corrosion

Current density (corrosion rate):

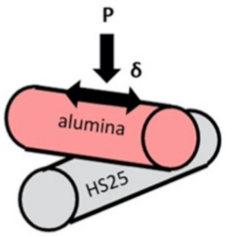
before rubbing ≈ 1 μA/cm^2

during rubbing ≈ 10^5 μA/cm^2

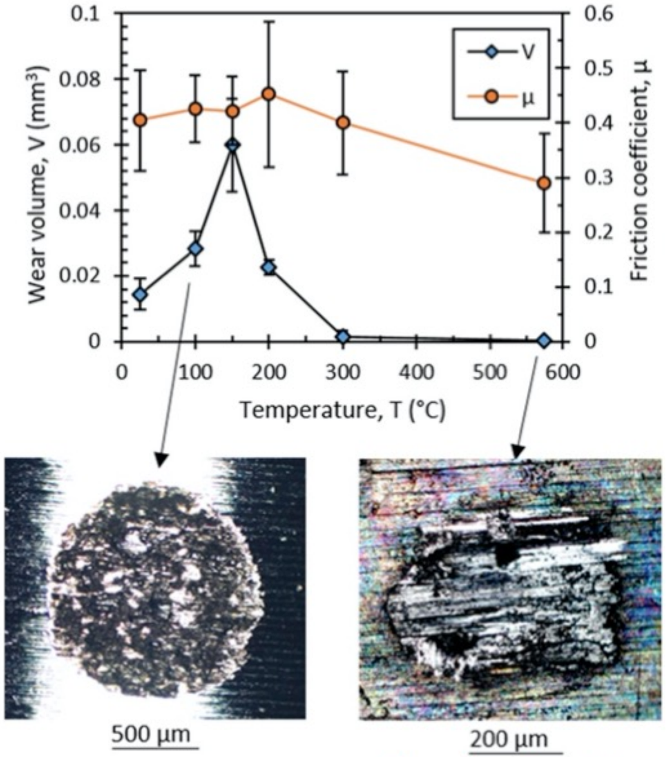


High temperature wear: example of fretting wear of HS25 alloy ($Co_{54}Cr_{26}Ni_{11}W_5Fe_2Mn_2$)

Test configuration (air)



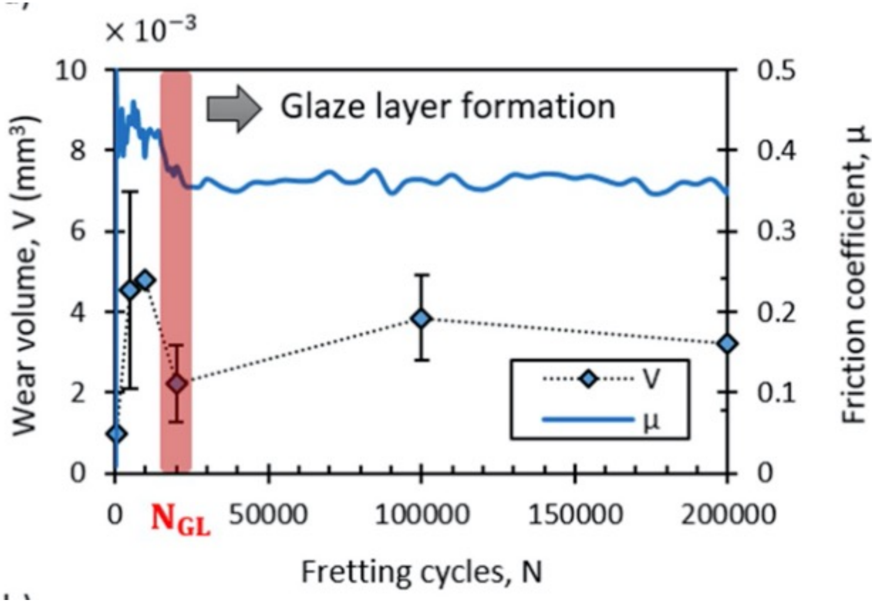
Dreano et al, Wear 440-441 (2019) 203101



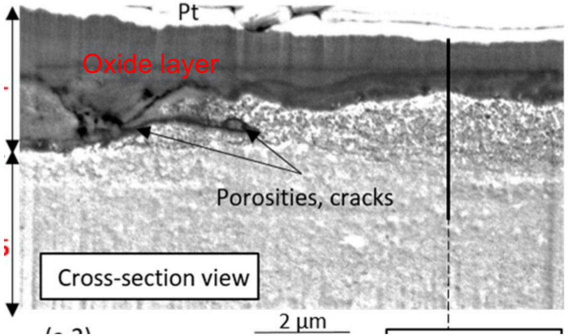
Glaze layer formation

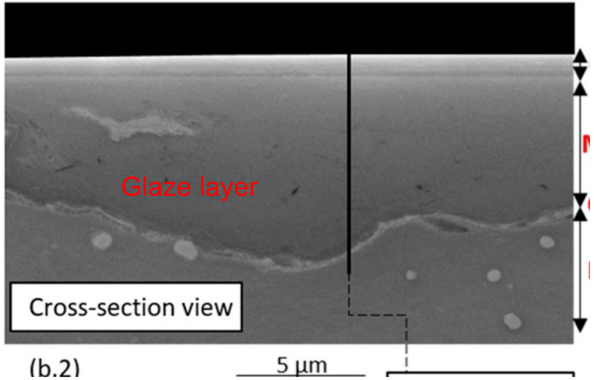
The wear rate increases up to 150°C because of oxidation is faster (tribochemical wear by oxide film particle removal).
At higher temperature, particles start compacting and forming a wear protective layer (glaze layer).

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



after 5000 cycles





after 200000 cycles

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

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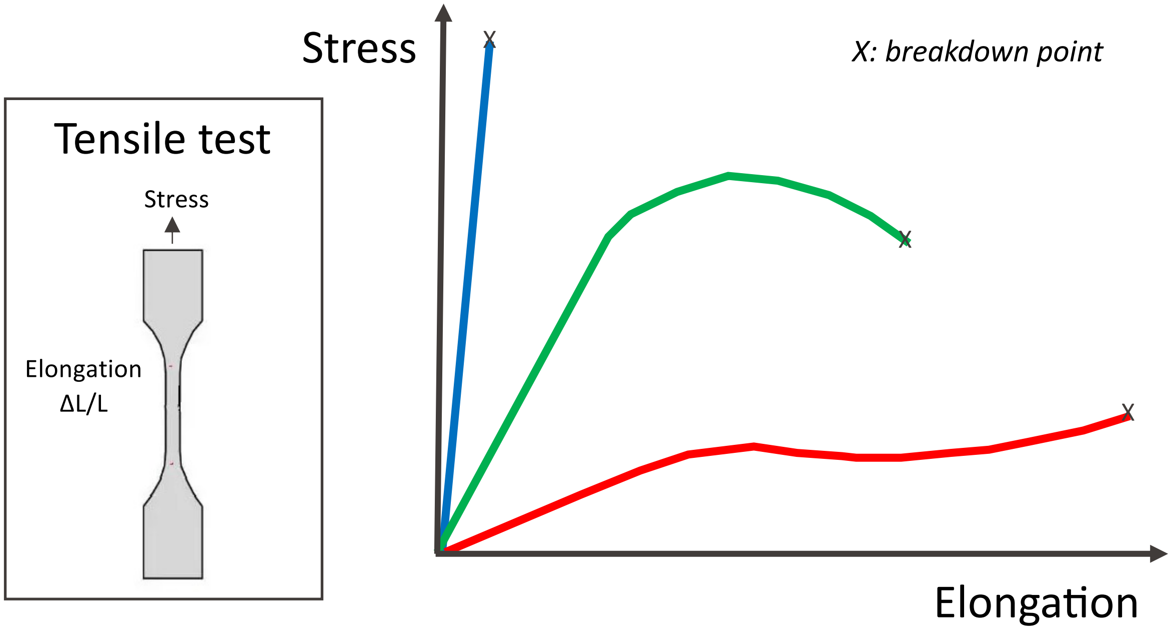
Typical stress-strain curves for different material classes



Ceramics**: elastic deformation and breakdown without plastic flow. **Brittle

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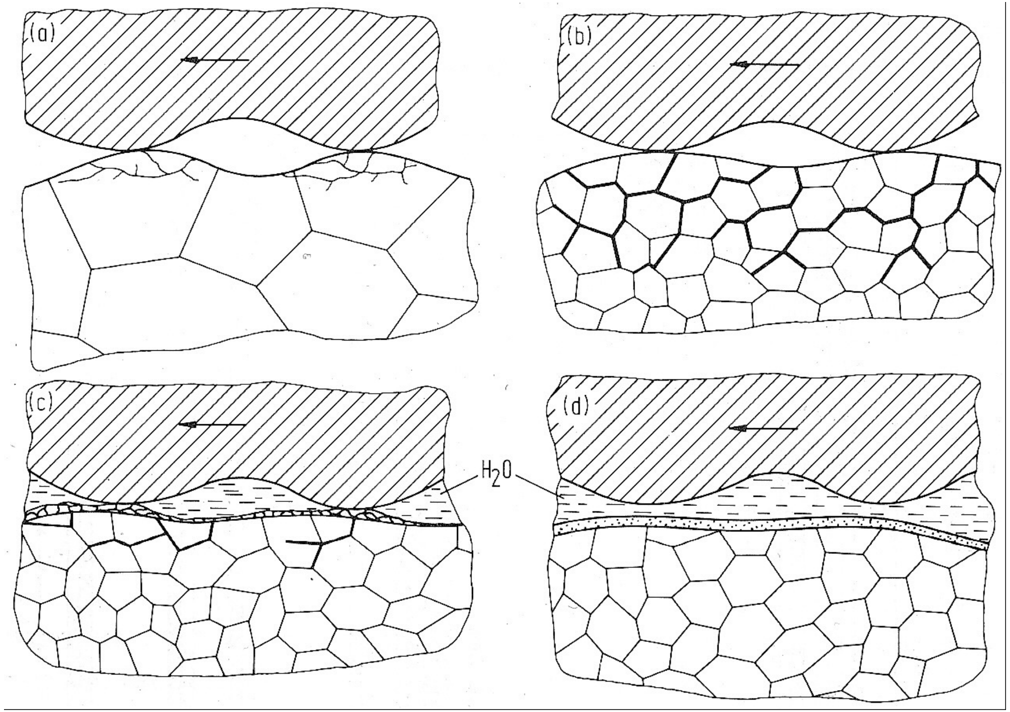
Typical degradation mechanisms of ceramics



a) Transgranular cracking at asperities (low load).

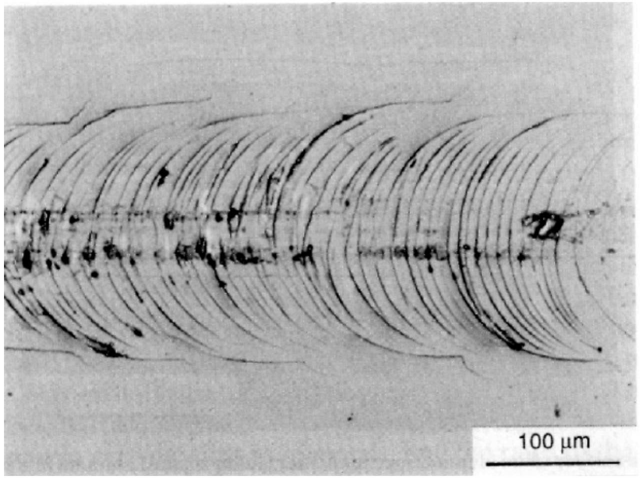
b) Intergranular cracking below the surface (high load).

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

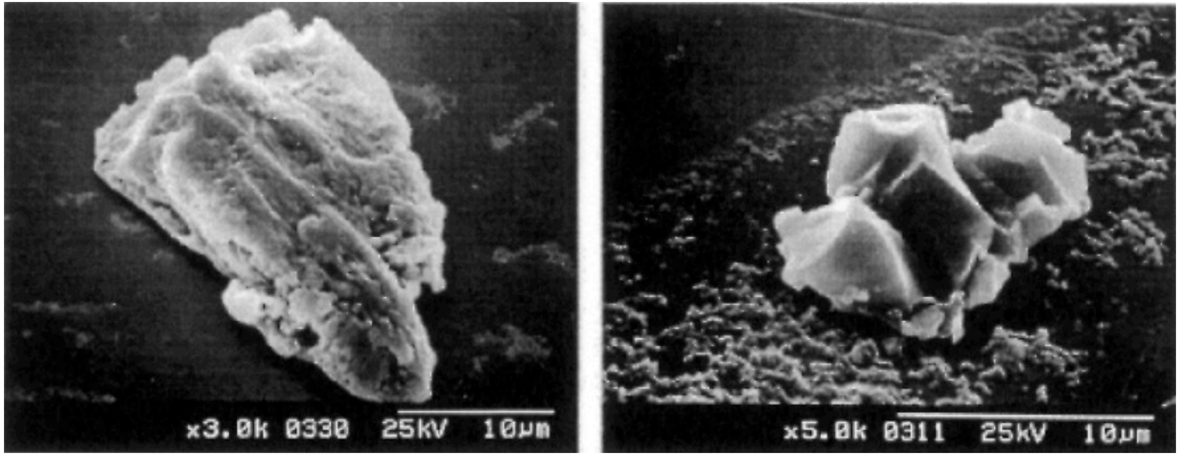
d) A compact layer of reaction products forms (high moisture).

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)

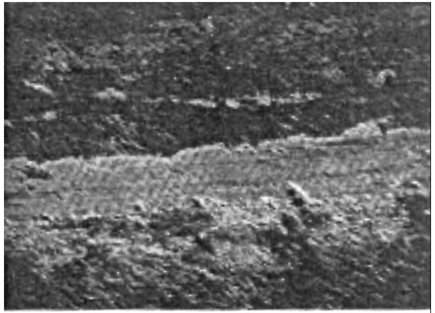


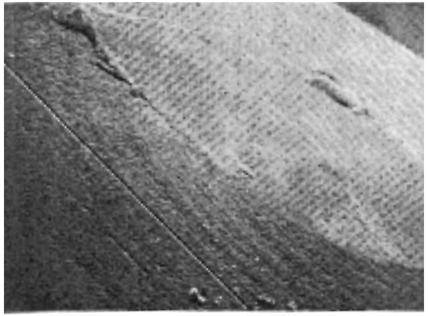
Wear particles formed by transgranular (left) or intergranular (right) fracture of silicon nitride.

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*

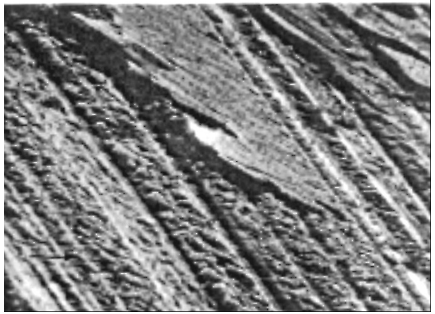
Air, 45% humidity

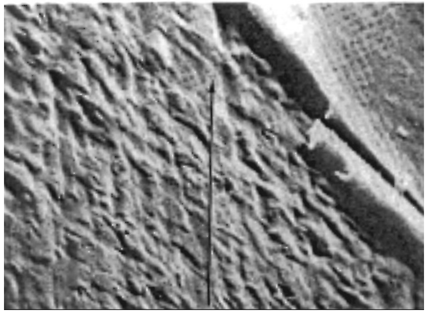




Argon, 98% humidity

Film composed by SiN and reaction products

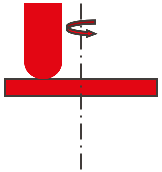




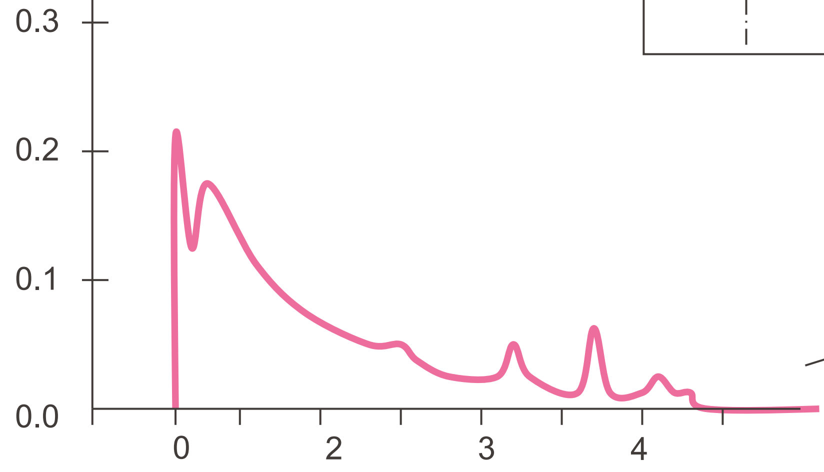
Reaction film comprising only Si and O, but no nitrogen.

Establishment of an hydrodynamic regime by a tribochemical mechanism

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 $\lambda = h / R_q$ ratio.



Si_3N_4-Si_3N_4 contact
0.5 mm/s, 2 N, immersed in water



L. Jordi, Lubrication of ceramics by water, travail de diplôme Stevens Institute New York / EPFIL 2003

Phase transformation: the case of Zirconia ZrO_2

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_2 makes this phenomenon observable at relativly low temperatures (600°C), even at low speed.

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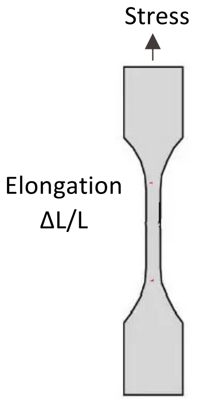
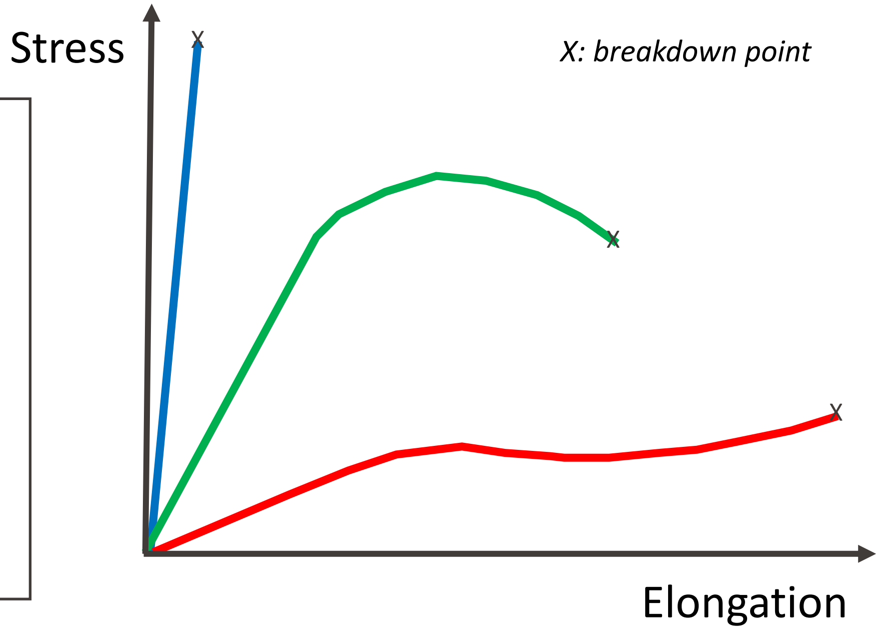
Typical stress-strain curves for different material classes

Tensile test





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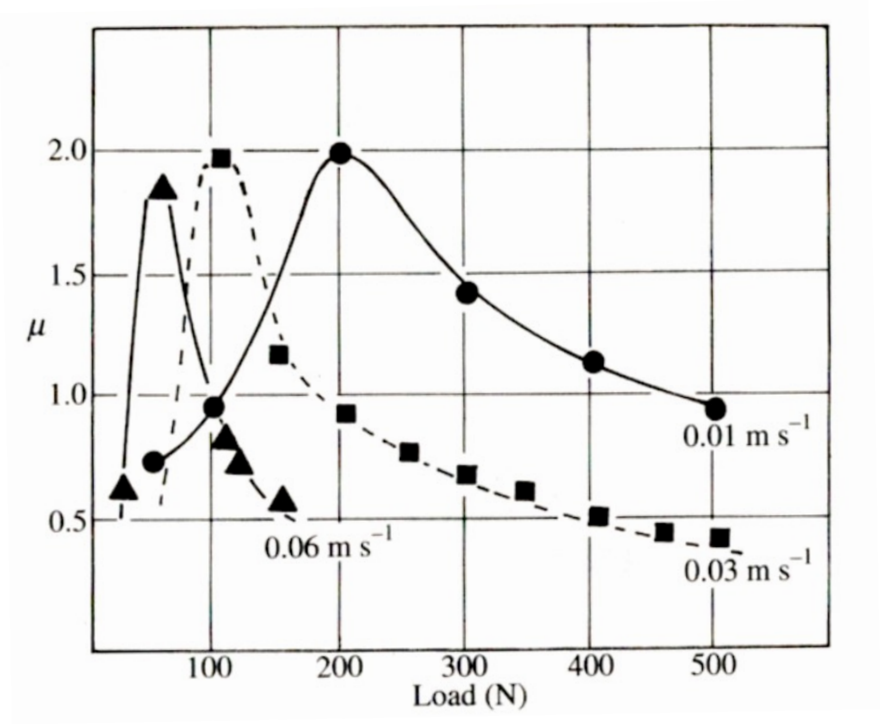
The visco-elastic nature of Polymers influences their frictional behaviour

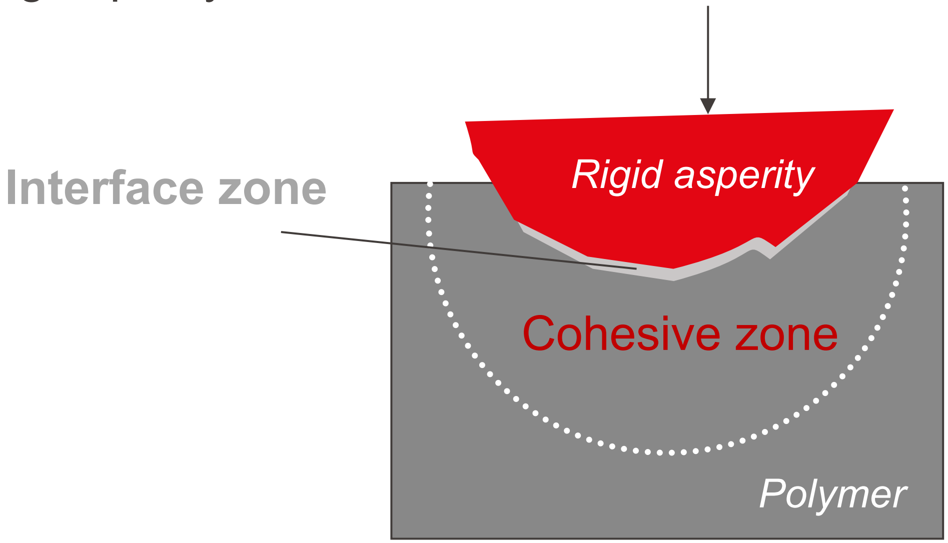
CoF versus normal load for three sliding speeds for nylon on steel:
friction rules (μ independent on load and velocity) are not respected.



Source: Williams "Engineering Tribology" (1994)

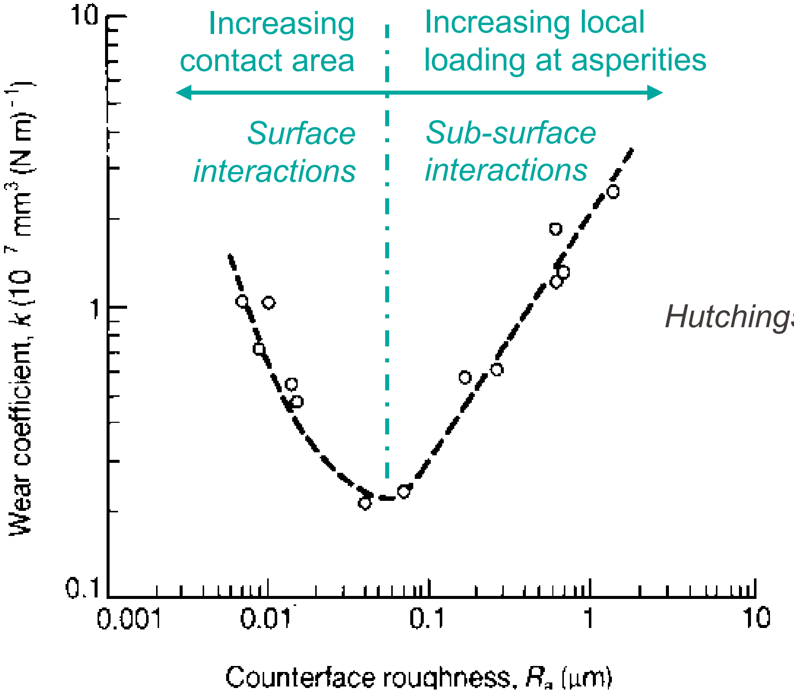
Interfacial and cohesive zones

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



Hutchings, Tribology, Arnold 1992

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

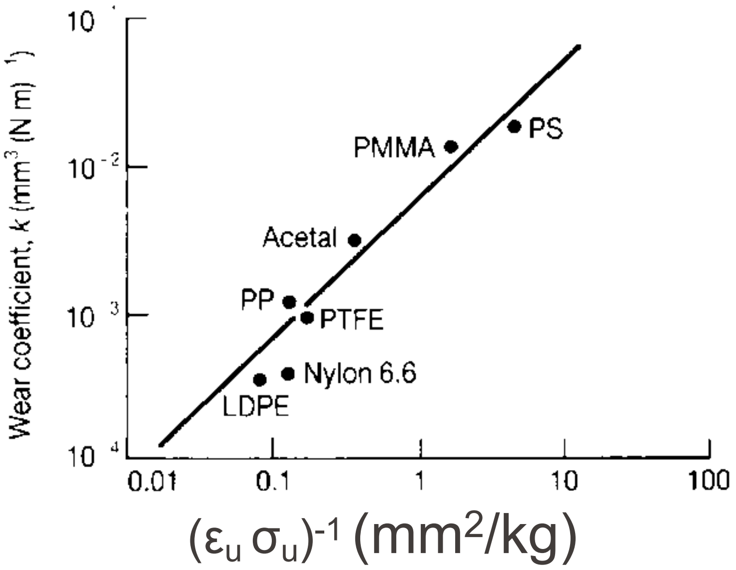
Cohesive wear

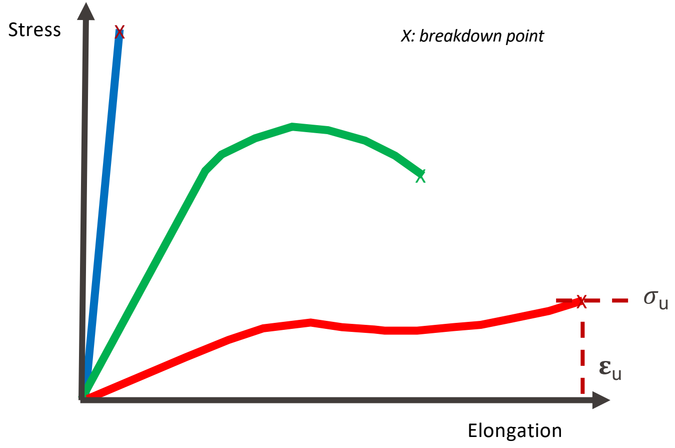
One can distinguish two different situations:

- 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 σ_u and strain ε_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

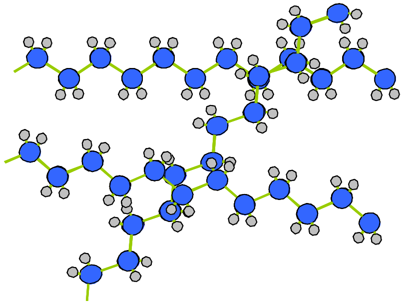
2. **Crack propagation:**

$$da/dN = k\Delta K_I^m$$

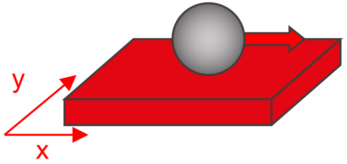
m, k : function of the environment
K_I : function of local stress concentrations

Interfacial wear: alignement of molecules

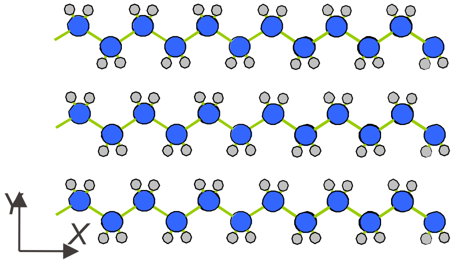
Initial state



Sliding along x

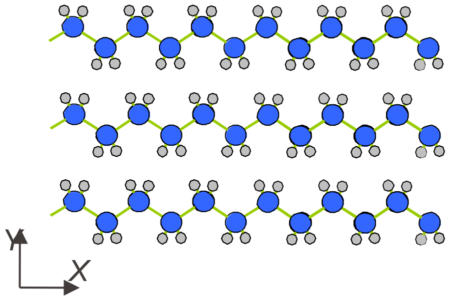


Alignment

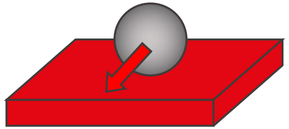


Strong bonds along x: low wear

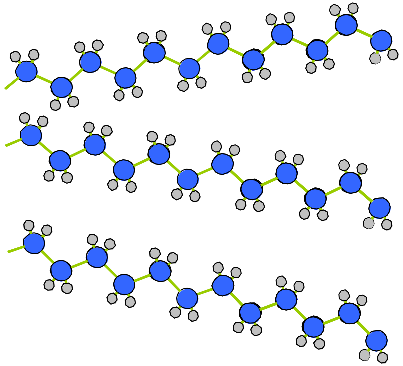
Aligned state:
Weak bonds along y



Sliding along y



Wear



Interfacial wear: melting due to frictional heating

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

Hutchings, Tribology, Arnold 1992

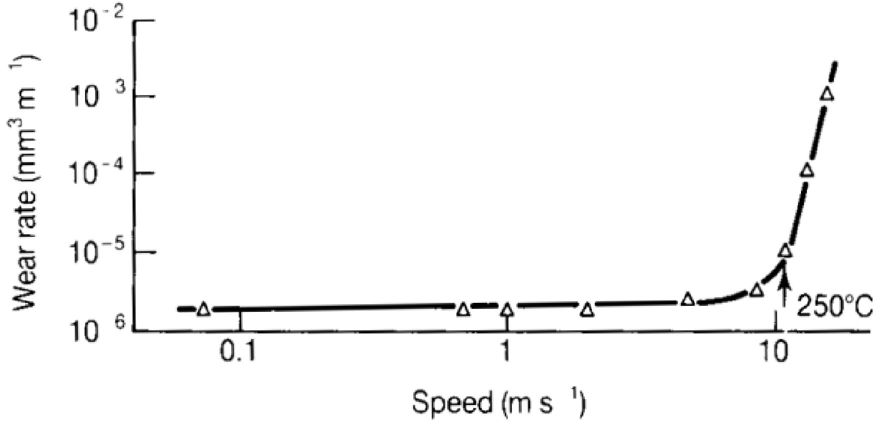


Fig. 5.39 The variation of steady-state wear rate with sliding speed for nylon 6.6 sliding against a smooth mild steel counterface (R_a = 0.15 μm) under unlubricated conditions (from Evans D C and Lancaster J K, in Scott D (Ed.), *Wear, Treatise on Materials Science and Technology*, Academic Press, **13**,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

1 Material classes and their tribological relevant properties

2. Metals

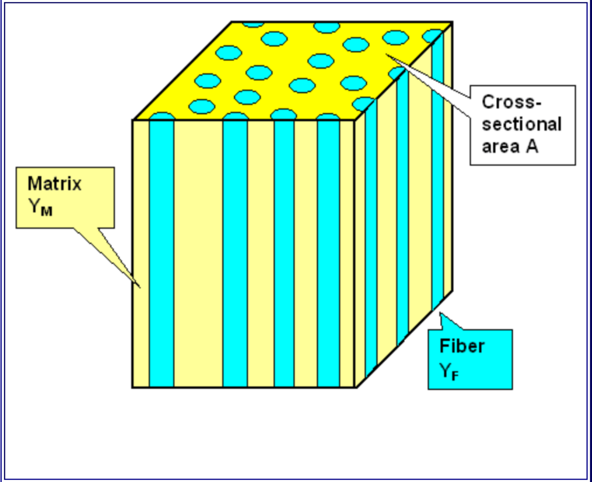
3. Ceramics

4. Polymers

5. Composite materials: the importance of the interface

Composite materials

Reinforcing a material (matrix) with stronger material is the basic idea of composite.

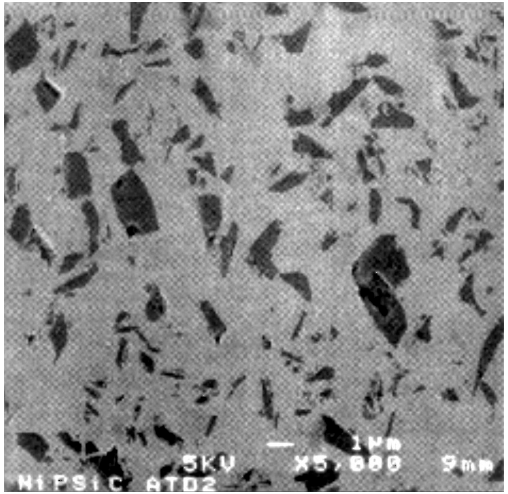


Idealized fiber-reinforced composite material

But the reinforcement takes place only if loads can be transmitted from the matrix to the reinforcement material.

Galvanic composite coatings

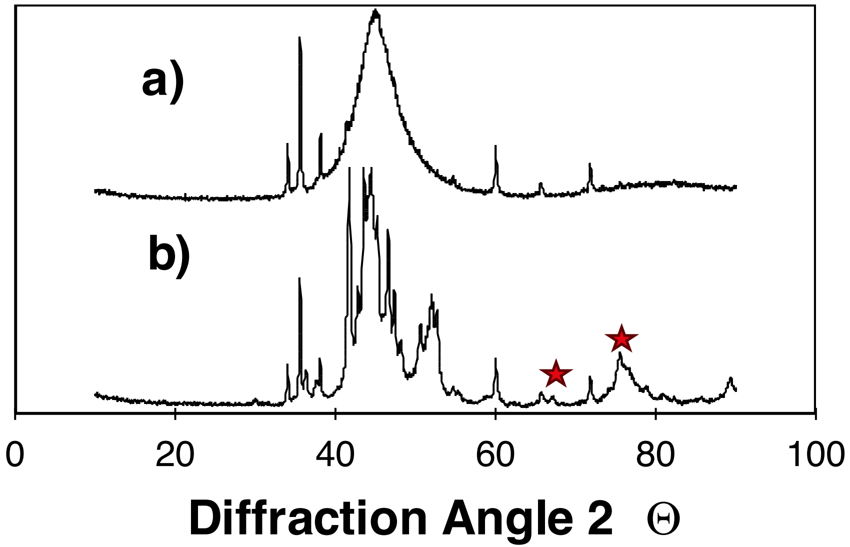
- Ni-P alloy coatings filled with hard SiC particles are used in some industrial applications for their antiwear properties (cylinder liners in engines, paper industry, turbines).



Micro-structure of a Ni-P coating (P 11%) filled with SiC particles (12% vol) of mean size1.7 µm.
EPFL thesis 1504 D. Voltz

Galvanic composite coatings

- **Effect of the thermal treatment**

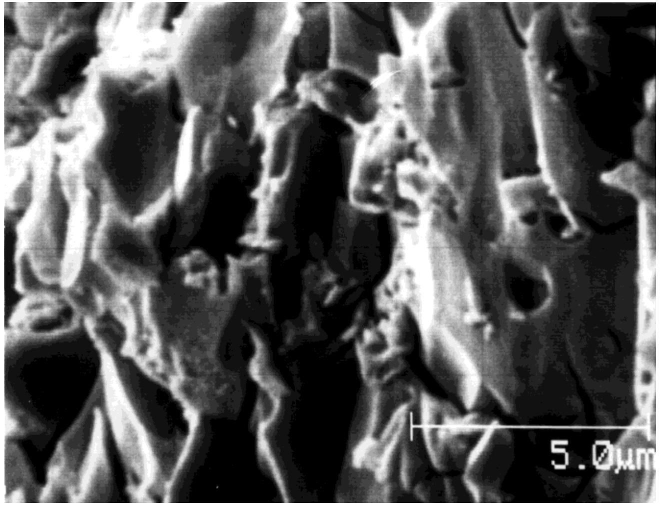


X-rays diffraction spectra of a Ni-P (7,5%) layer filled with 27% volumic SiC.

a) Untreated layer : peaks of a-Sic with a large signal for amorphous Ni-P.
b) After 290°C/5 hours thermal treatment : crystallization of the Ni-P phase and formation of Ni_3Si.★

Fracture morphology (flexion) Ni-P (7,5%) layer with 27% volumic SiC before and after thermal treatment (290°C/2 hours)

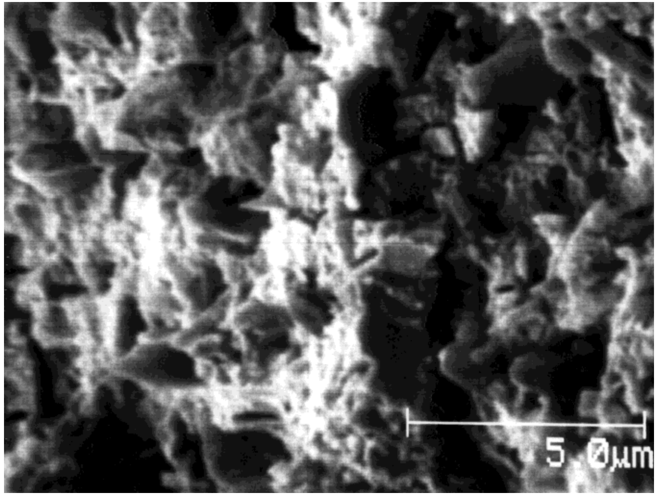
No heat treatment



Poor particle-matrix adhesion:

- Brittle fracture and carbide-matrix interface

Heat treated

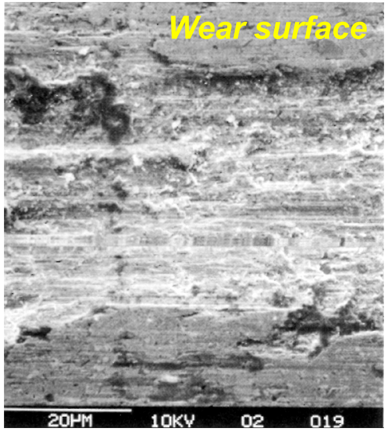


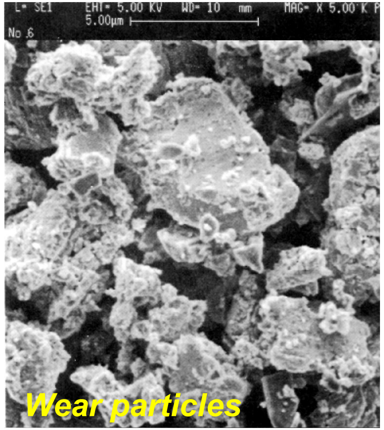
Goodparticle-matrix adhesion:

- Intergranular fracture crossing carbides-matrix interface

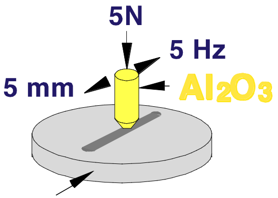
Tribological behavior

Without heat treatment

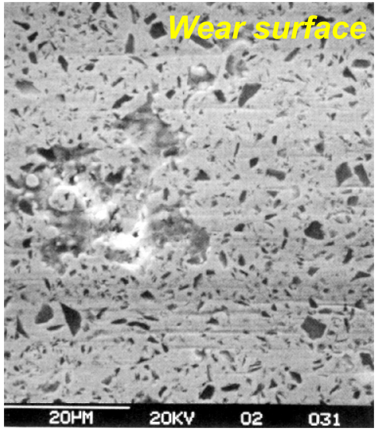


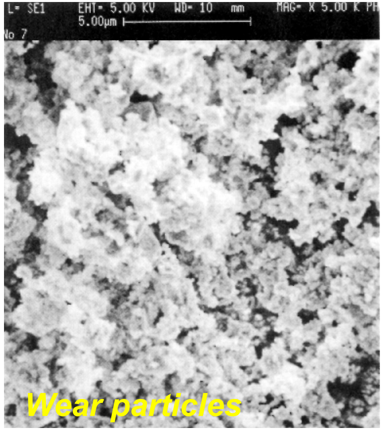


Severe wear with large debris, some corresponding to original SiC particles. Due to poor adherence to matrix, particles were ripped off.



Coated metal





Very mild wear with carbides and matrix jointly carrying the load. Very small oxidized debris particles. Tahnk to good adhesion, no ripping off of carbides.

After heat treatment

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 experienced by the contacting materials.