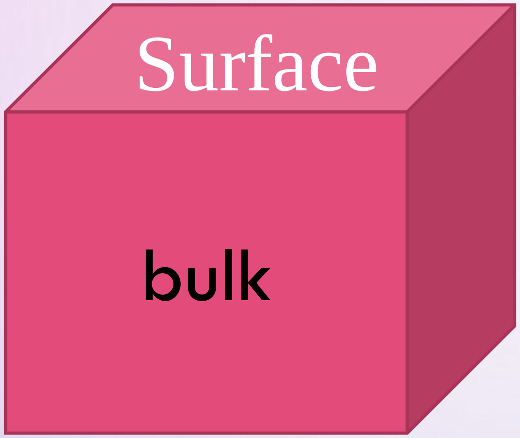
Chương 1. Đại cương về biến tính bề mặt vật liệu (T2)

1.1. Các khái niệm cơ bản

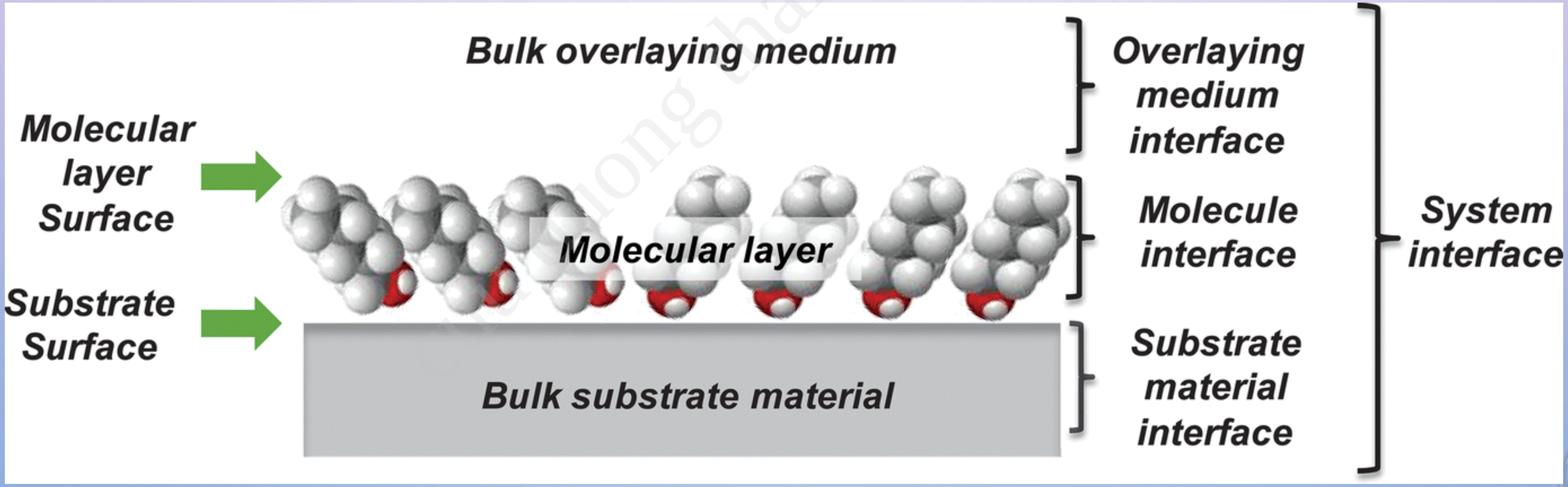
1.2. Các yêu cầu đối với bề mặt vật liệu

1.3. Phân loại và lựa chọn phương pháp biến tính bề mặt vật liệu

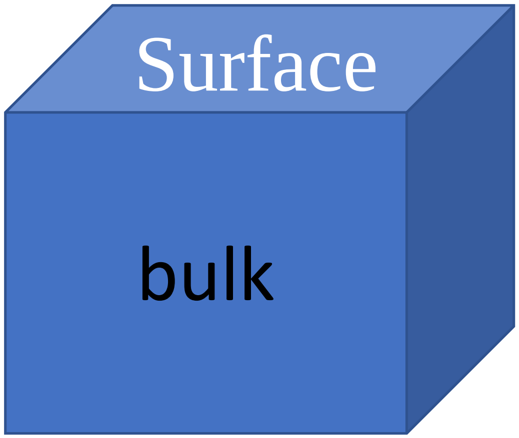
1.4. Phân tích thành phần hoá học và cấu trúc bề mặt


Surface
bulk

Interface


Bulk overlaying medium
Overlaying medium interface
Molecular layer Surface
Molecular layer
Molecule interface
System interface
Substrate Surface
Bulk substrate material
Substrate material interface

Requirements on Part Surfaces



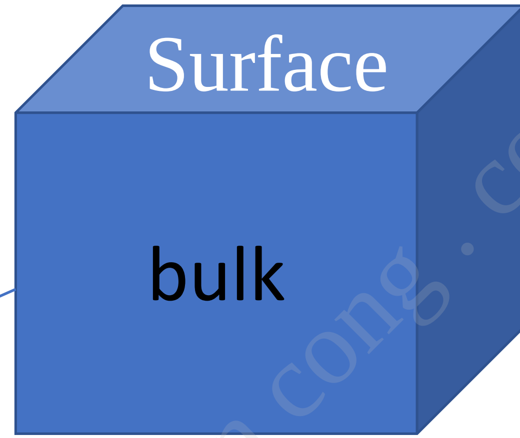
Mechanical
Thermal
Chemical
Electrochemical

interaction ↔ environment

the main functions

- ✓ corrosion resistance
- ✓ wear resistance
- ✓ defined tribological behavior
- ✓ optical behaviour
- ✓ decorative behaviour
- ✓ matched interface behavior (e.g. for joining purposes)

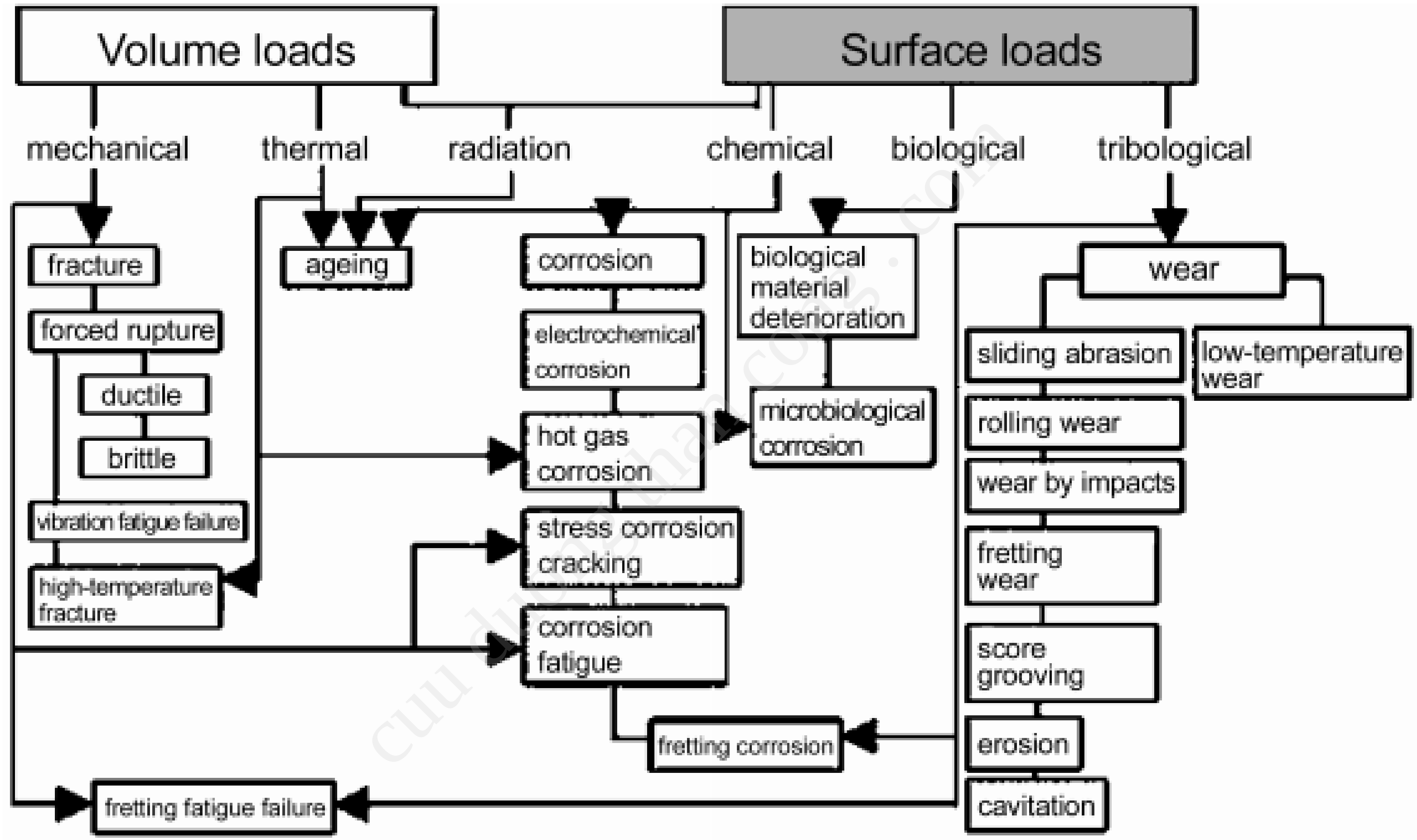
Surface Properties



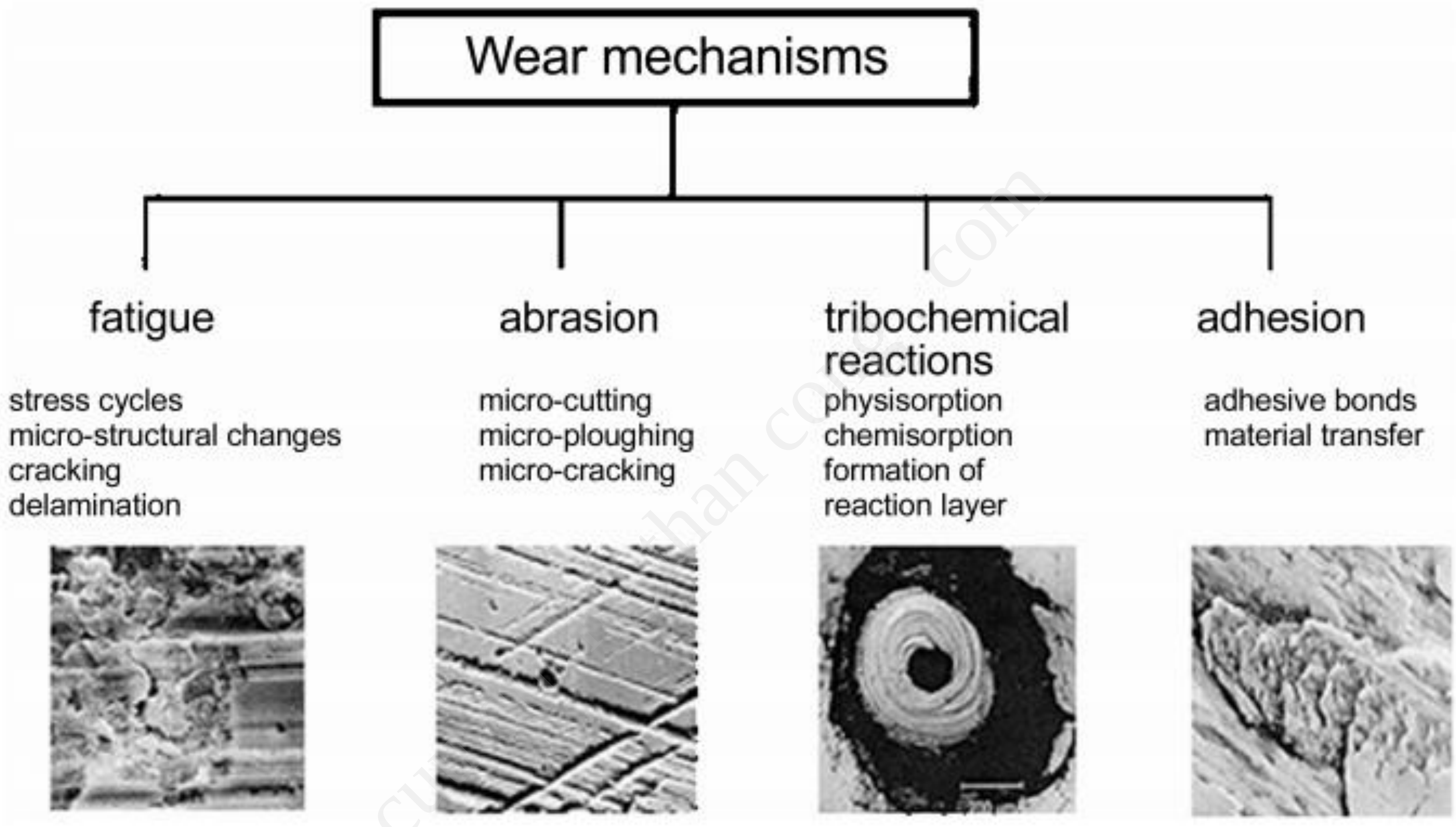
Physical properties:
- ✓ Wettability
- ✓ Crystallinity
- ✓ Roughness
- ✓ Composition
- ✓ Electrical Charge
- ✓ Mobility
- ✓ …

Chemical properties:
facilitate chemical reactions (Chemisorption, Corrosion…)

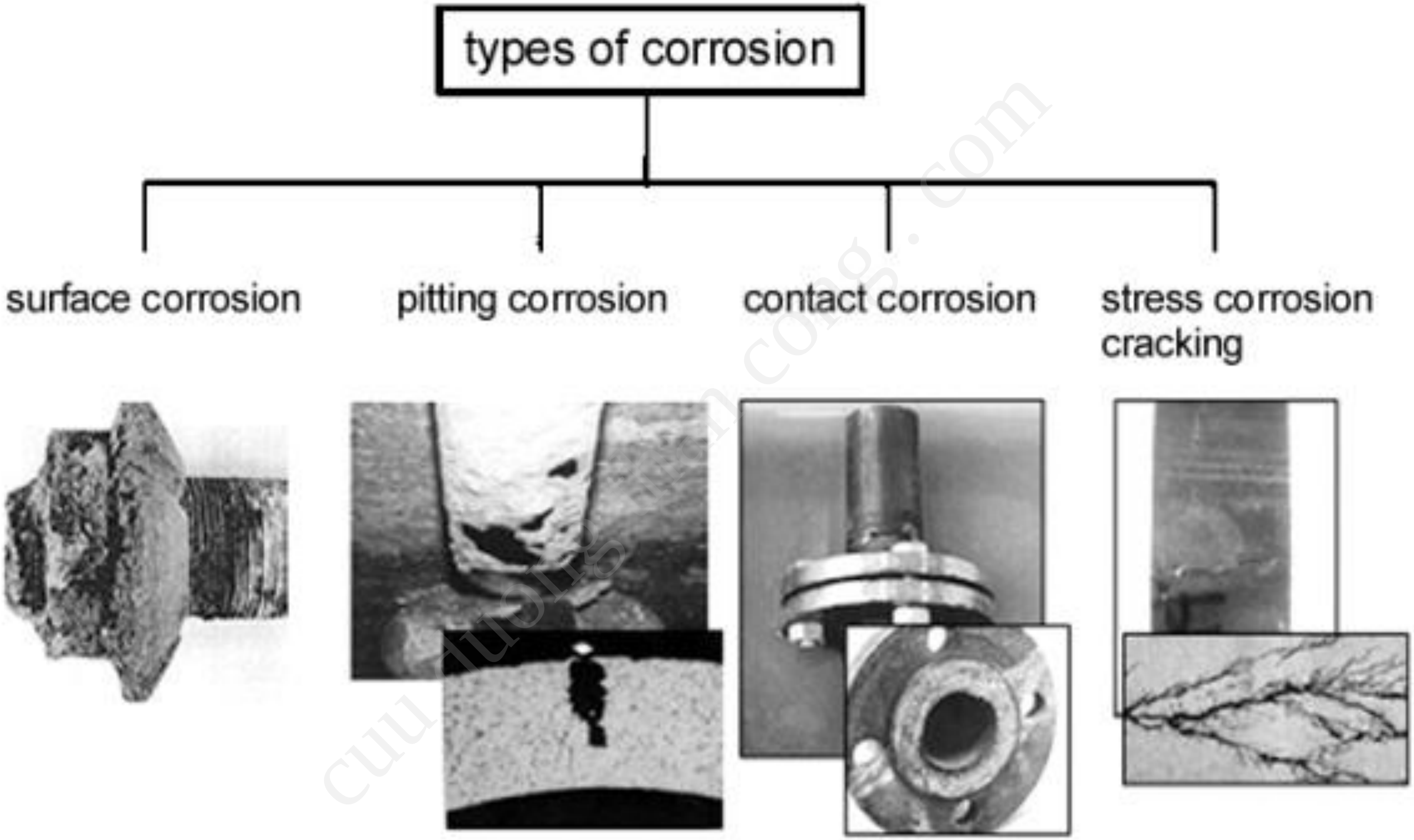
biological properties:
Biological compatibility …



Main volume and surface loads on parts

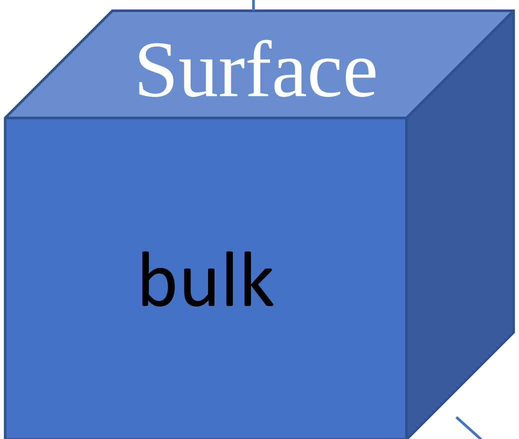


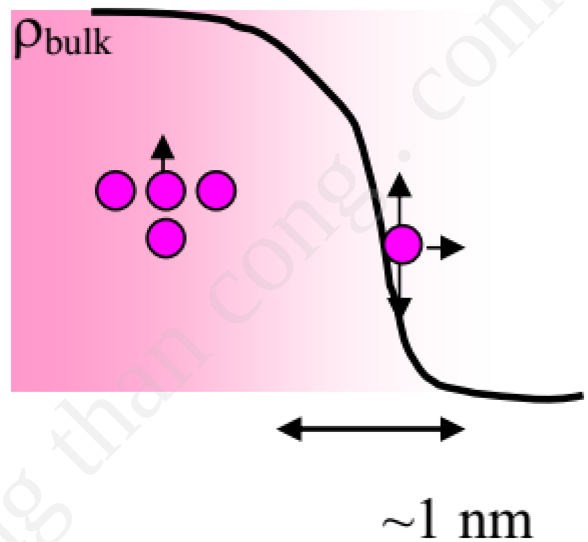
Wear phenomena


types of corrosion
surface corrosion
pitting corrosion
contact corrosion
stress corrosion cracking

1 cm^3 material
10^{23} atoms

Requires special characterization tools





$D = D_0 \exp(-E_a/kT)$

$D_{surf} >> D_{bulk}$

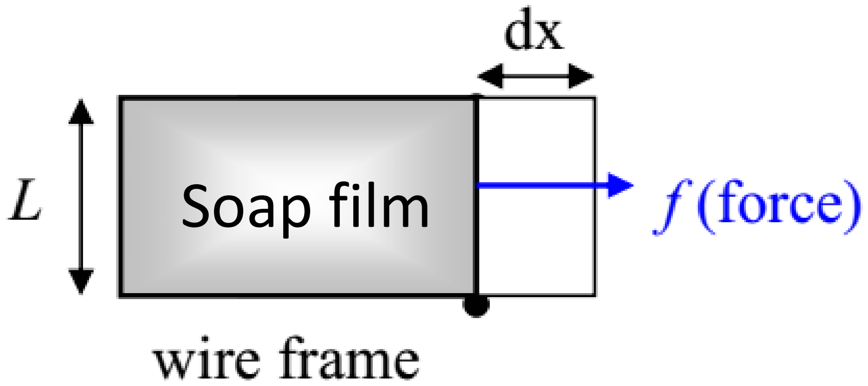
fewer bonds
gradient in density

Higher Energy State (loss of bonds at a surface)

High reactivity and susceptibility to adsorbates

Facilitates rate-limited processes
(phase transformations, crystallization, corrosion…)

Surface tension, γ, is the work required to create unit surface area at constant T,P and composition.



$$dG = -SdT + VdP + \gamma dA$$

G = Gibbs free energy, A = area

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P,n} = \frac{fdx}{2Ldx} = \frac{f}{2L}$$

Work of cohesion: WC = 2γ

Surface Tensions of Materials (*degree of cohesion*)

Material	T (°C)	γ (dyn/cm)
Teflon (PTFE)	20	19
Silicone (PDMS)	20	20
PE	20	36
PMMA	20	41
PEO	20	43
Water	20	73
soda-lime-silicate (*l*)	1350	350
FeO	1400	580
Al_2O_3	1850	950
TiC	1100	1190
Ti (*l*)	1660	1550
δ-Fe (bcc)	1400	1900

1 dyn/cm = 1 mJ/m^2 = 1 erg/cm^2

Trends: high γ materials: (>200 dyn/cm) – metals, carbides, oxides
low γ materials: polymers, organics

Surface Phenomena

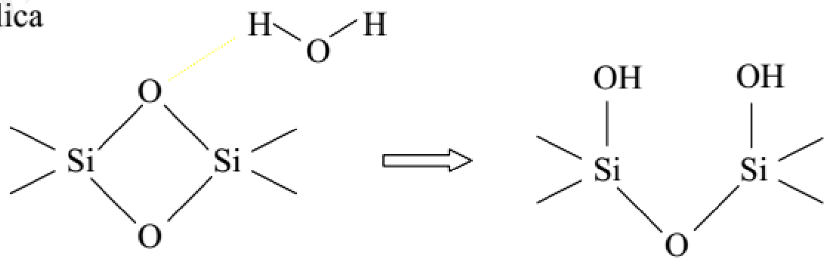
Surface phenomena are driven primarily by an associated reduction in surface free energy.

Adsorption phenomena

Chemisorption: strong modifications to electronic structure/electron density of adsorbate molecule (> 0.5 eV/surface site)

Example: H_2O on silica

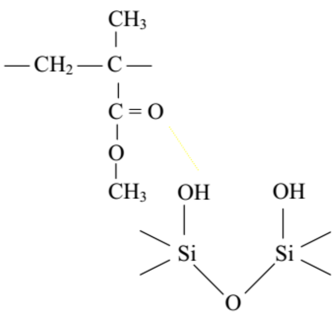
E_{ads} = 1.7 eV



Higher energy surfaces are quickly coated/contaminated by lower energy species

Water on glasses, metals or oxides
Hydrocarbons on inorganic surfaces
Surfactants at air/water interface

physisorption – adsorbate weakly adherent via secondary (i.e., van der Waals') interactions (< 0.25 eV/surface site)



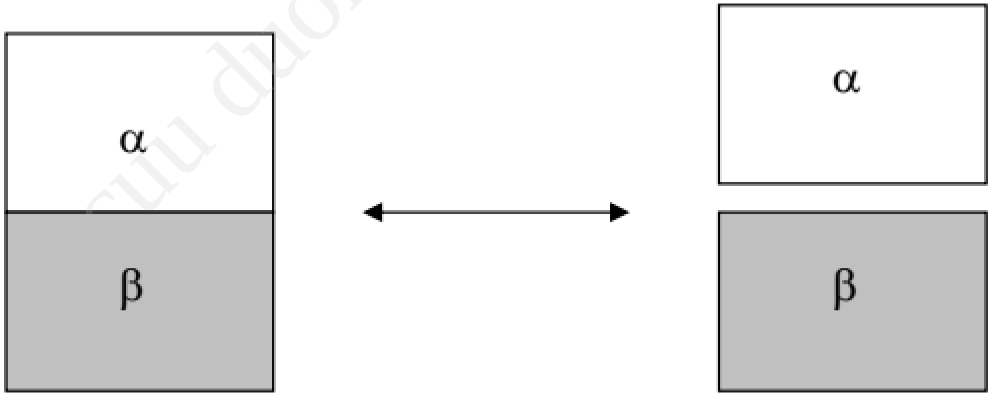
PMMA on silica

1 eV/molec = 96.5 kJ/mol
kT_{293} ≈ 0.025 eV

Such adsorption phenomena are examples of "thermodynamic adhesion"

Adhesion – state in which 2 dissimilar bodies are held together in intimate contact such that a force can be transferred across the interface.

Thermodynamic adhesion is driven by interfacial forces associated with reversible processes.



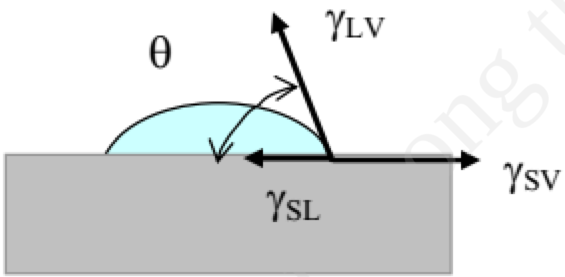
Work of Adhesion (W12): the work required to separate a unit area of interface between 2 phases.

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad W_{12} > 0 \Rightarrow \text{adhesion}$$

$\gamma_{12} = \alpha/\beta$ interfacial tension

(for $\alpha = \beta$, $W_{12} = W_C = 2\gamma_1$)

The *hydrophilicity* of a surface can be gauged by measuring the *contact angle* of a droplet of water on the surface. The balance of interfacial forces is described by *Young's Equation*:



$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$$

$$W_{SL} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$$

$$\Rightarrow W_{SL} = \gamma_{LV}(1+\cos\theta)$$

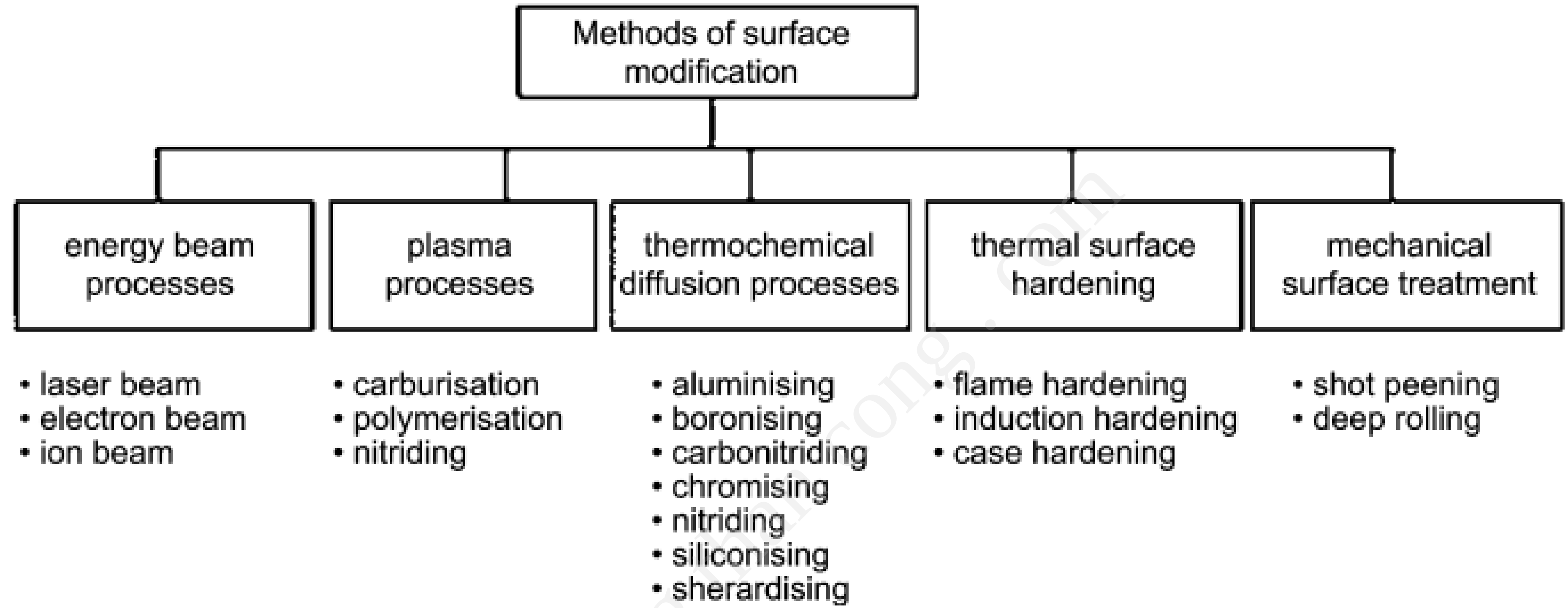
θ	Wettability
0	Complete
<90	Partial
>90	Non wetting

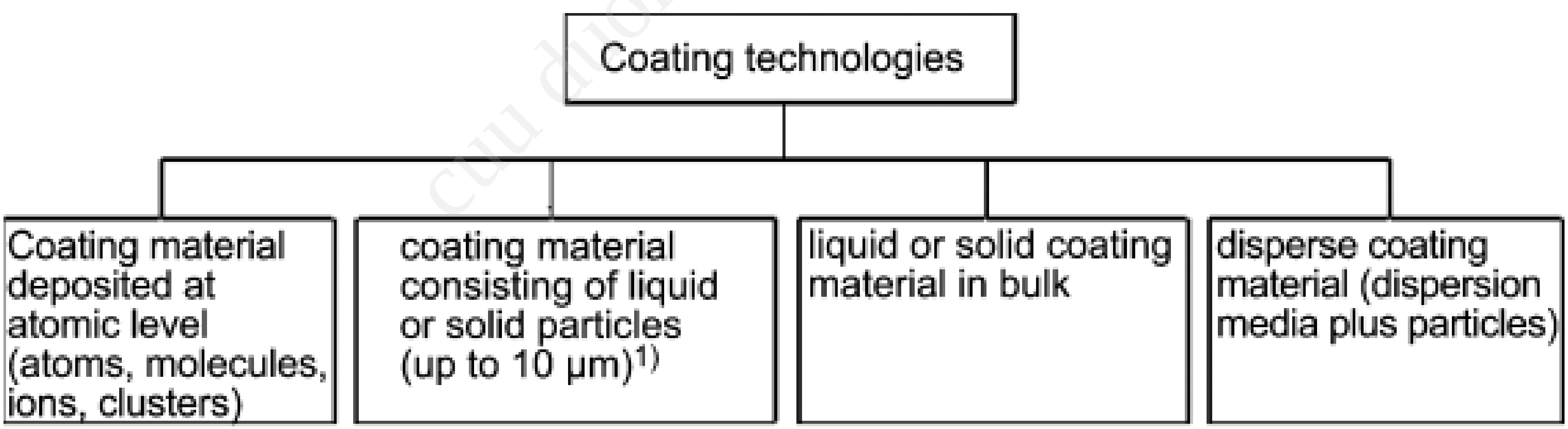
Surface Modification Methods

- Plasma treatment and deposition

radiation grafting

- chemical reaction of the surface
- ozonolysis
- photoreaction
- ion implantation
- ion etching
- solvent cast films
- surface active modifiers (low and high MW)
- metalization
- self assembly
- micro-contact printing
- immobilization of biomolecules


Methods of surface modification
energy beam processes
plasma processes
thermochemical diffusion processes
thermal surface hardening
mechanical surface treatment
• laser beam
• electron beam
• ion beam
• carburisation
• polymerisation
• nitriding
• aluminising
• boronising
• carbonitriding
• chromising
• nitriding
• siliconising
• sherardising
• flame hardening
• induction hardening
• case hardening
• shot peening
• deep rolling


Coating technologies
Coating material deposited at atomic level (atoms, molecules, ions, clusters)
coating material consisting of liquid or solid particles (up to 10 μm)1)
liquid or solid coating material in bulk
disperse coating material (dispersion media plus particles)

Surface Materials

Surface chemistry

chemical composition

functional groups

- Fourier transform infrared spectroscopy
- Attenuated total reflection (metallic, polymeric, and ceramic biomaterials)
- Specular reflectance (thin films)
- X-ray photoelectron spectroscopy
- Secondary ion mass spectrometer

Surface wettability

- Contact angle goniometry

Surface texture

- Scanning electron microscopy
- Atomic force microscopy
- Profilometry techniques

Surface charges

- Zeta potential analysis