



Une fois l'alliage métallique obtenu, viennent le **contrôle** et la maîtrise des **propriétés en conditions d'usage**. Certaines de ces propriétés sont dictées par la nature de l'environnement dans lequel le matériau est appelé à fonctionner :

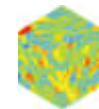
1. **chimie de la corrosion**, —→ **électrochimie**
2. chimie de l'oxydation (chimie des solides)
3. chimie de la catalyse. (réactivité des solides)

A. Bases

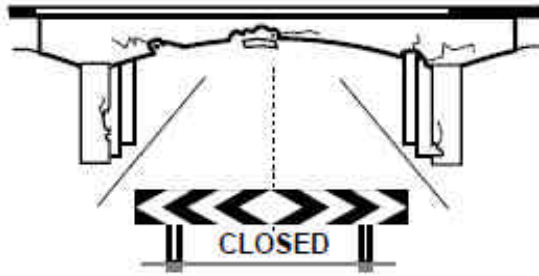
La corrosion : B. Exemples emblématiques

C. Défis

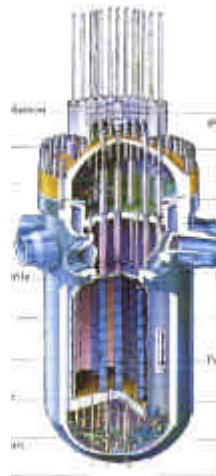
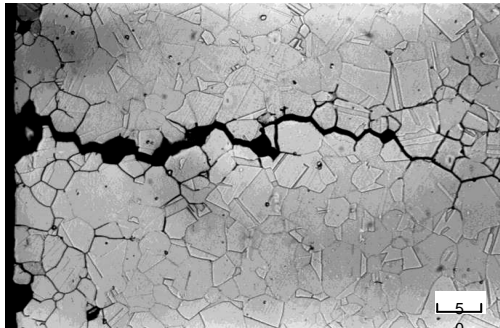
**Quelques exemples illustrant le couplage des connaissances en métallurgie et en électrochimie**



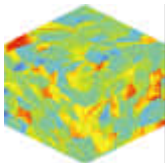
processus d'oxydation



anti-corrosion



limites



La corrosion est définie comme l'interaction physico-chimique entre la **partie métallique** d'une structure et le milieu environnant entraînant une **dégradation fonctionnelle** de la structure dans son ensemble.

**A. Bases**

*B. Exemples emblématiques*

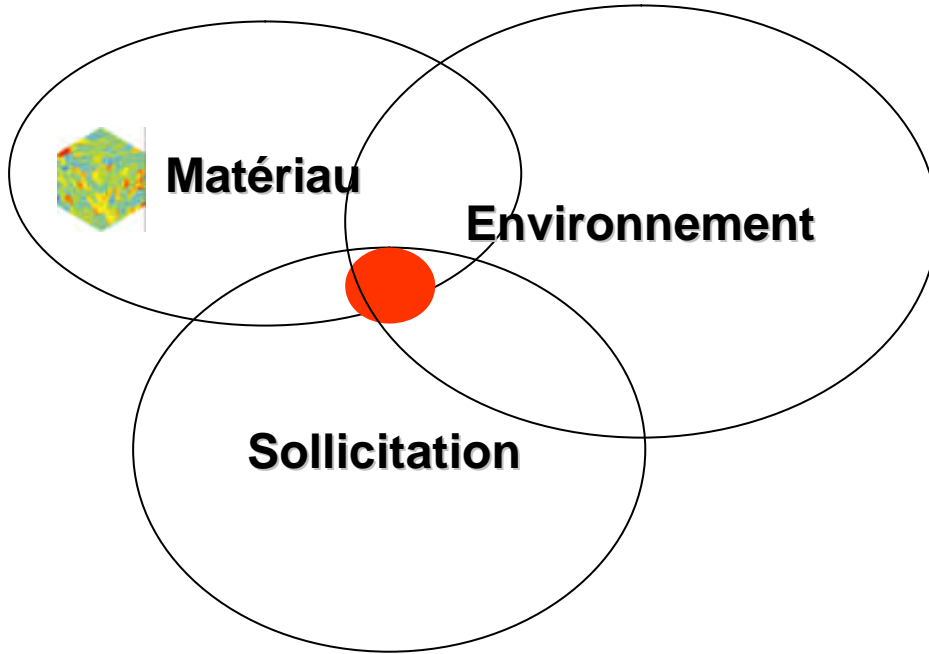
*C. Défis*

*D. Conclusion*

*processus d'oxydation*

*anti-corrosion*

*limites*

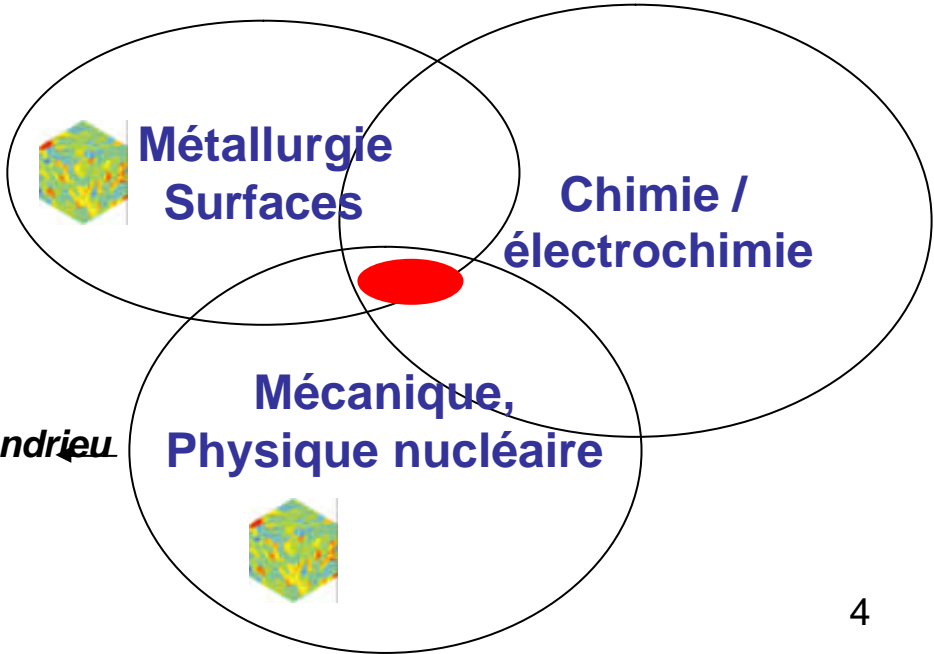
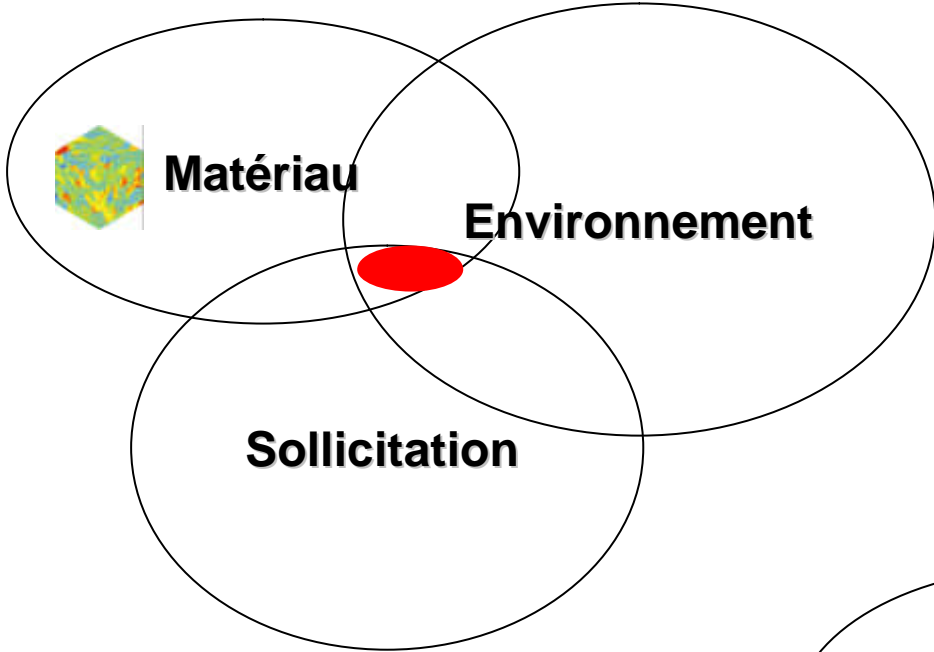


<b>A. Bases</b>	<i>B. Exemples emblématiques</i>	<i>C. Défis</i>	<i>D. Conclusion</i>
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*processus d'oxydation*

*anti-corrosion*

*limites*



*Voir exposé Eric Andrieu (couplage)*



## 2 *simultaneous* reactions :

↓ **Oxidation** of the metal (Fe, Ni, Cu, ...)

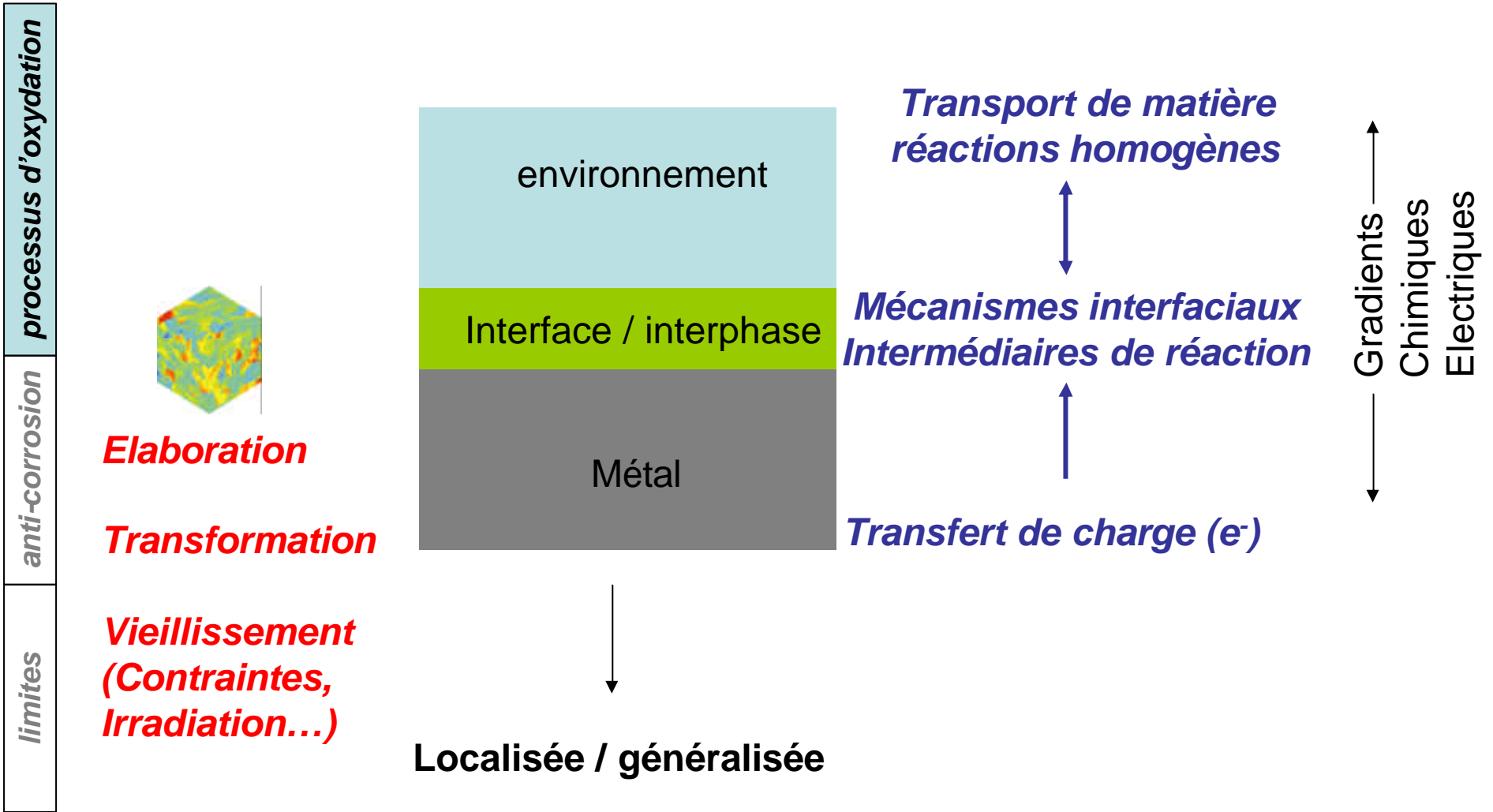


↓ **Reduction** of an oxidizing species present in the medium (acid, oxygen, ...)



Always a galvanic process

<b>A. Bases</b>	<i>B. Exemples emblématiques</i>	<i>C. Défis</i>	<i>D. Conclusion</i>
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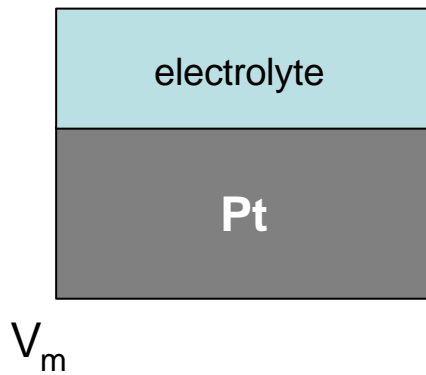
*(schéma sans échelle: spatiale ou temporelle)*

**Electrochimie**

Transfert d'électrons entre une électrode métallique et une espèce chimique en solution dépend de l'écart entre :

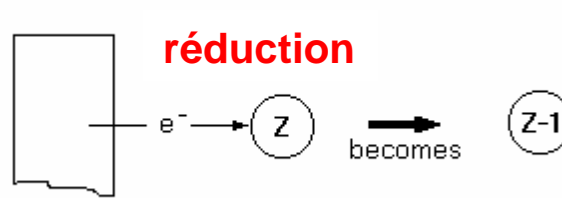
l'énergie des  $e^-$  dans le métal  $E(e^-)_M$  (niveau de Fermi)

et  
l'énergie (pour l'espèce en solution)

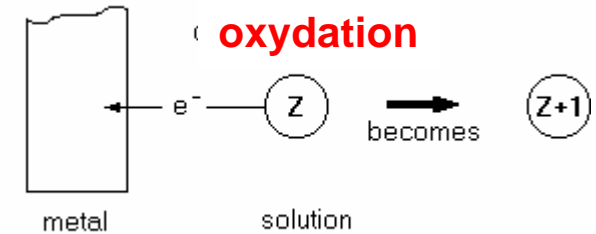


soit du plus bas niveau des orbitales non occupées  $E_{un}(e^-)_{sol}$

soit du plus haut niveau des orbitales occupées  $E_{oc}(e^-)_{sol}$



$$E(e^-)_M > E_{un}(e^-)_{sol}$$



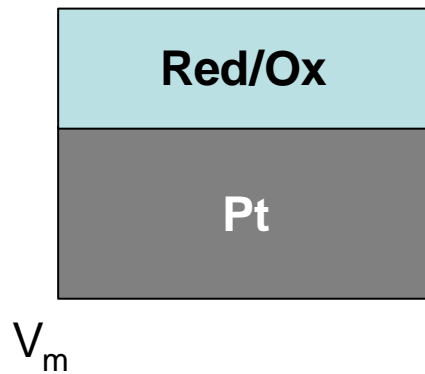
$$E(e^-)_M < E_{oc}(e^-)_{sol}$$

processus d'oxydation

anti-corrosion

limites

### Thermodynamique (équilibre électrochimique)



Nernst equation

$$E_{\text{rev}} = E^{\circ}_{(\text{Ox/Red})} + (RT/nF) \ln [a_{(\text{Ox})}/a_{(\text{Red})}]$$

↓  
(~ C<sub>ox</sub>/C<sub>red</sub>)

Potential vs a reference electrode



**Thermodynamique (équilibre électrochimique + chimique)**

**processus d'oxydation**

$$O + ne \xrightleftharpoons[k_2]{k_1} R$$

Équilibres électrochimiques

+

Equilibres chimiques

$\Phi$

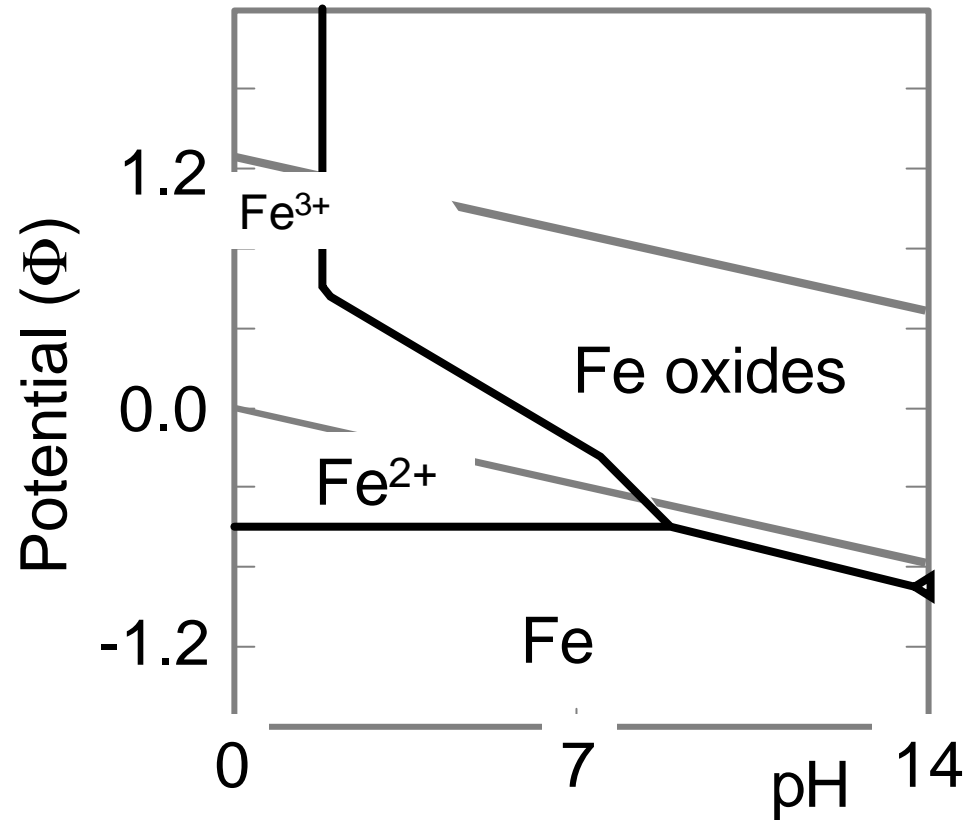
**S espèces MX**

**métal M**

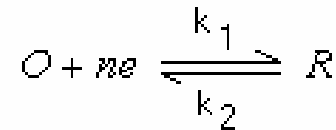
**anti-corrosion**

**limites**

$V_m$



## Cinétique électrochimique (hors équilibre)



$$\bar{v} = k_1 c_O \quad \text{and} \quad \bar{v} = k_2 c_R$$

$$\bar{i} = nFk_1 c_O$$

Loi de Faraday

$$\bar{i} = nFk_2 c_R$$

$$i = \bar{i} - \bar{i}$$

I (courant) = f [E] (potentiel)

$$i = nFk^0 \left\{ c_O \exp \left[ -\frac{\alpha nF(E - E^0)}{RT} \right] - c_R \exp \left[ \frac{(1 - \alpha)nF(E - E^0)}{RT} \right] \right\}$$

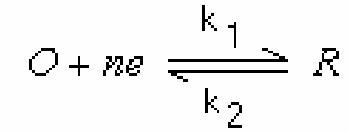
Equation de Butler – Volmer

processus d'oxydation

anti-corrosion

limites

A l'équilibre (et à la surface de l'électrode)



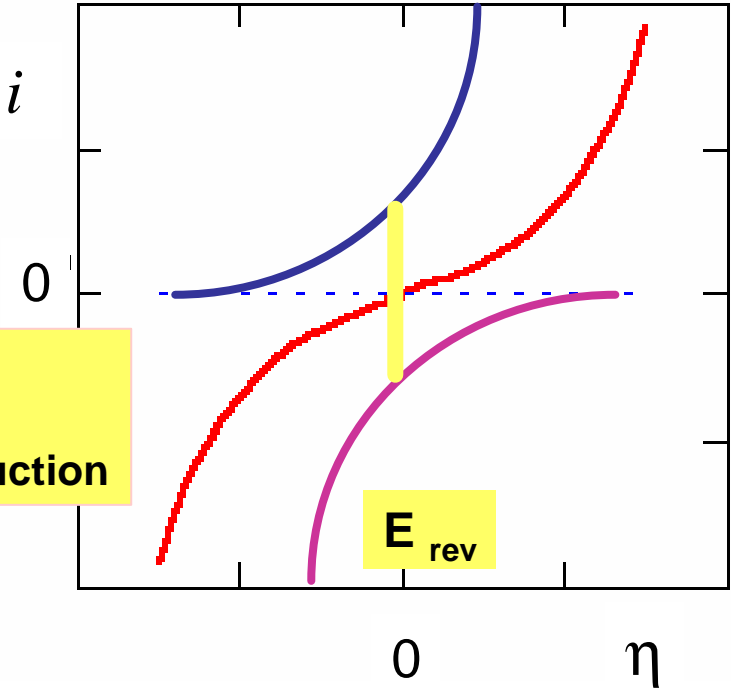
$$i = nFk^0 \left\{ c_O \exp \left[ -\frac{\alpha nF(E - E^0)}{RT} \right] - c_R \exp \left[ \frac{(1 - \alpha)nF(E - E^0)}{RT} \right] \right\}$$

processus d'oxydation

anti-corrosion

limites

Flux égaux  
Oxydation = réduction



$$E - E^0 = h$$

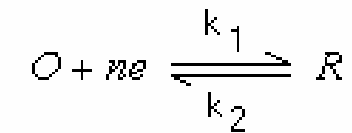
Courbe de polarisation

Courant d'échange

$$I_o = n F A k^\ominus [c_R(\infty)]^{1-\alpha} [c_O(\infty)]^\alpha$$

$$C_{surf} = C \quad (8)$$

Equation de Butler-Volmer



$$I = I_o \left[ e^{\alpha n F \eta / RT} - e^{-(1-\alpha) n F \eta / RT} \right]$$

Courant d'échange



## Cinétique électrochimique (corrosion)

processus d'oxydation

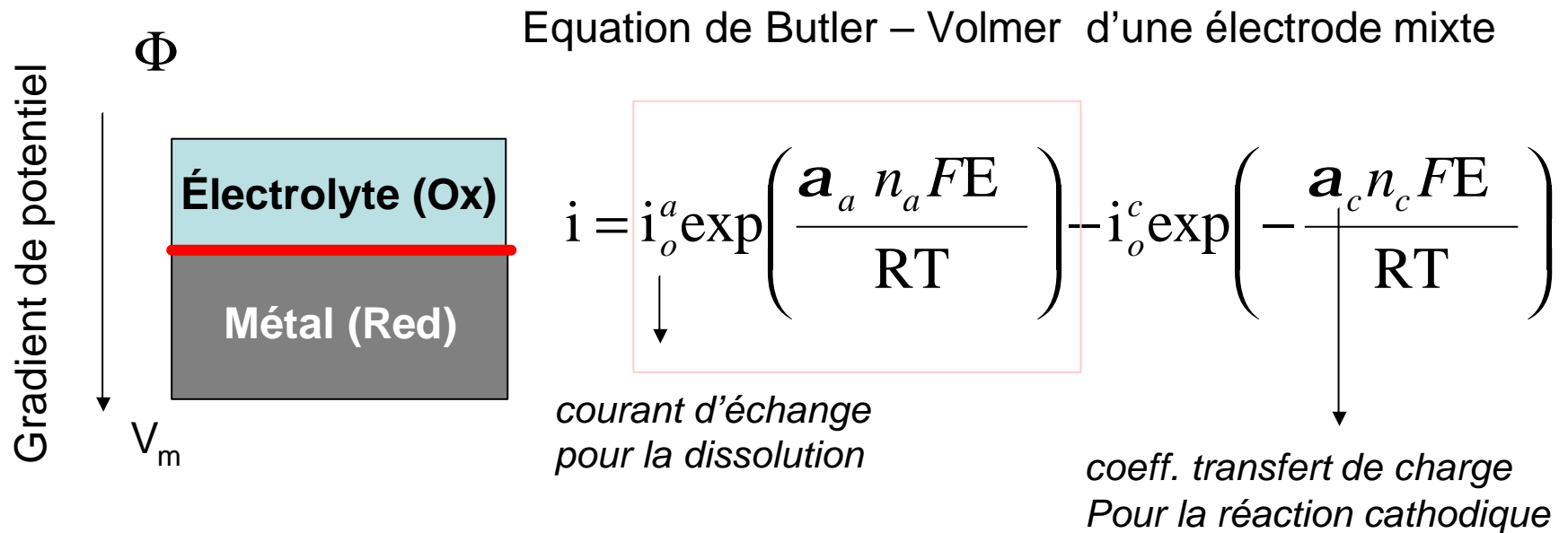
anti-corrosion

limites

réaction "cathodique" réduction d'un composé chimique (Ox)  
présent dans le milieu

mixte =

réaction "anodique" qui est l'oxydation du métal

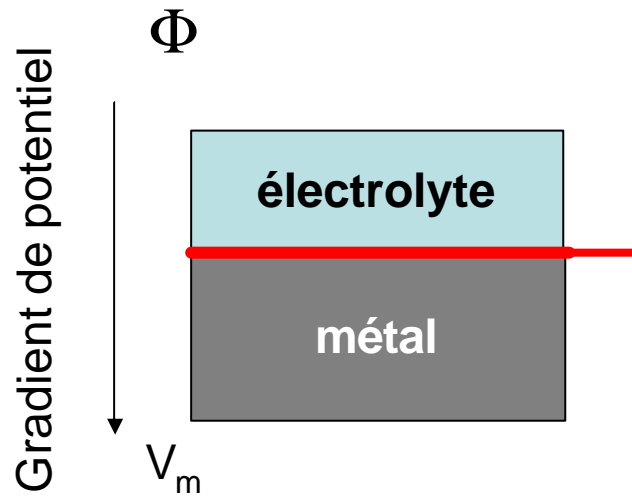


→ Interface  $E = V_m - F$

↘ Réactions homogènes (en solution)

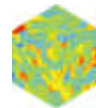
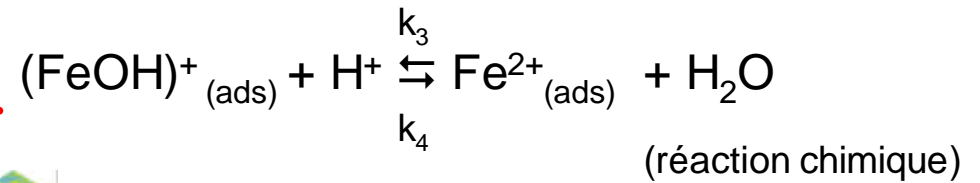
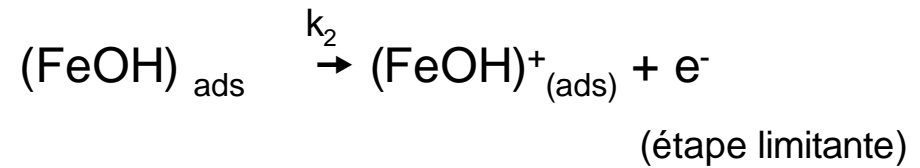
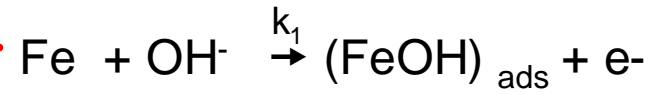
Mécanismes

processus d'oxydation  
anti-corrosion  
limites



→ Interface  $E = V_m - F$

Réaction globale =  $Fe \rightarrow Fe^{2+} + 2e^-$



= f (pureté, cristallographie, ...)

les produits intermédiaires :  $(FeOH)^+$  et  $(FeOH)_{ads}$

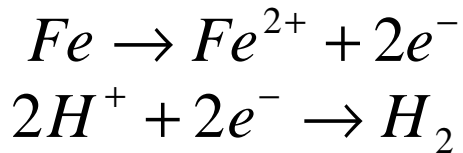
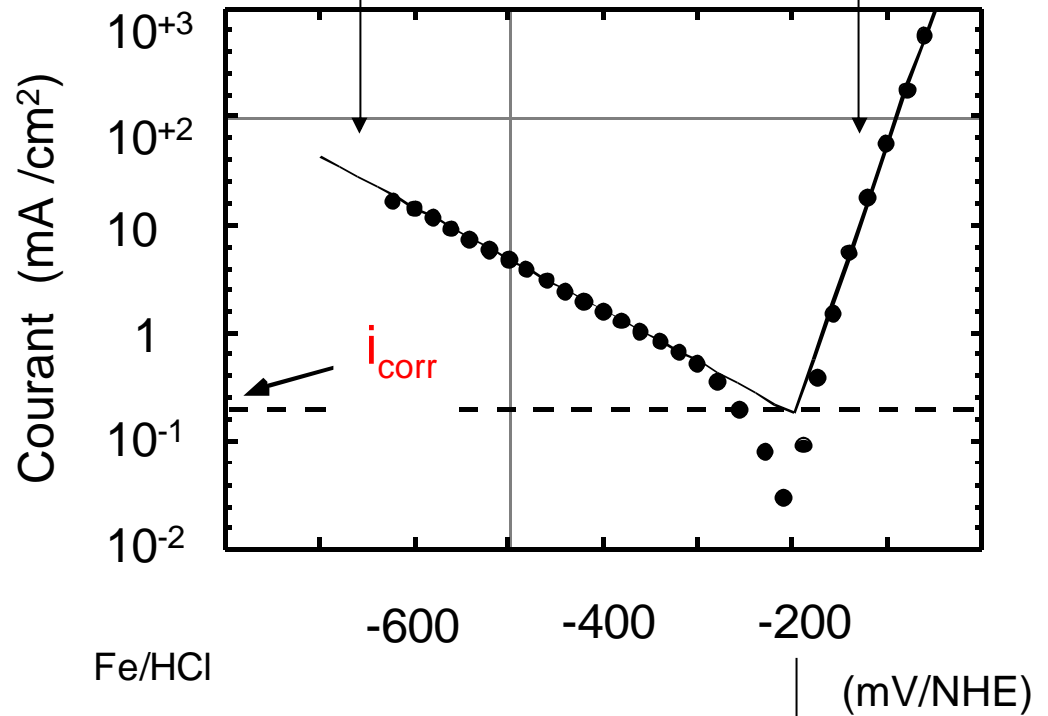
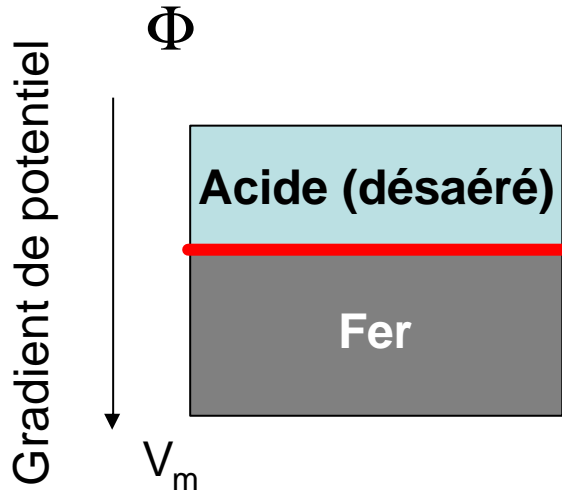
la dépendance en fonction du pH



Courbe de polarisation

$$i_{Fe} = i_{Fe}^0 C_{H^+}^{nH} \exp\left(\frac{a_{Fe} F (V_m - \Phi)}{RT}\right)$$

$$i_{H^+} = -i_{H^+}^0 C_{H^+} \exp\left(-\frac{a_{H^+} F (V_m - \Phi)}{RT}\right)$$

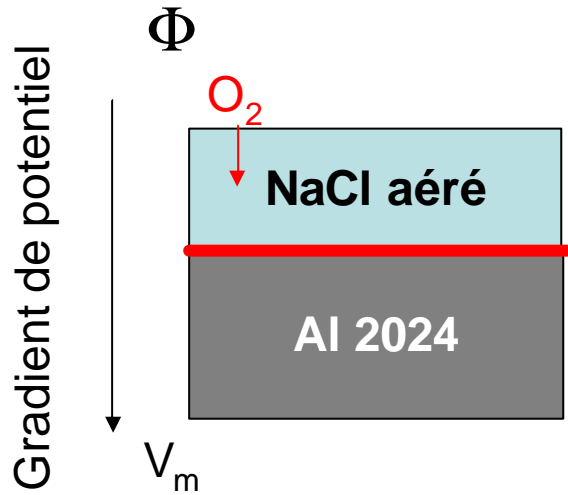


$E_{corr}$  16

processus d'oxydation  
anti-corrosion  
limites

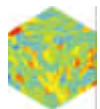
Transport de matière

2024 / NaCl 0.5M

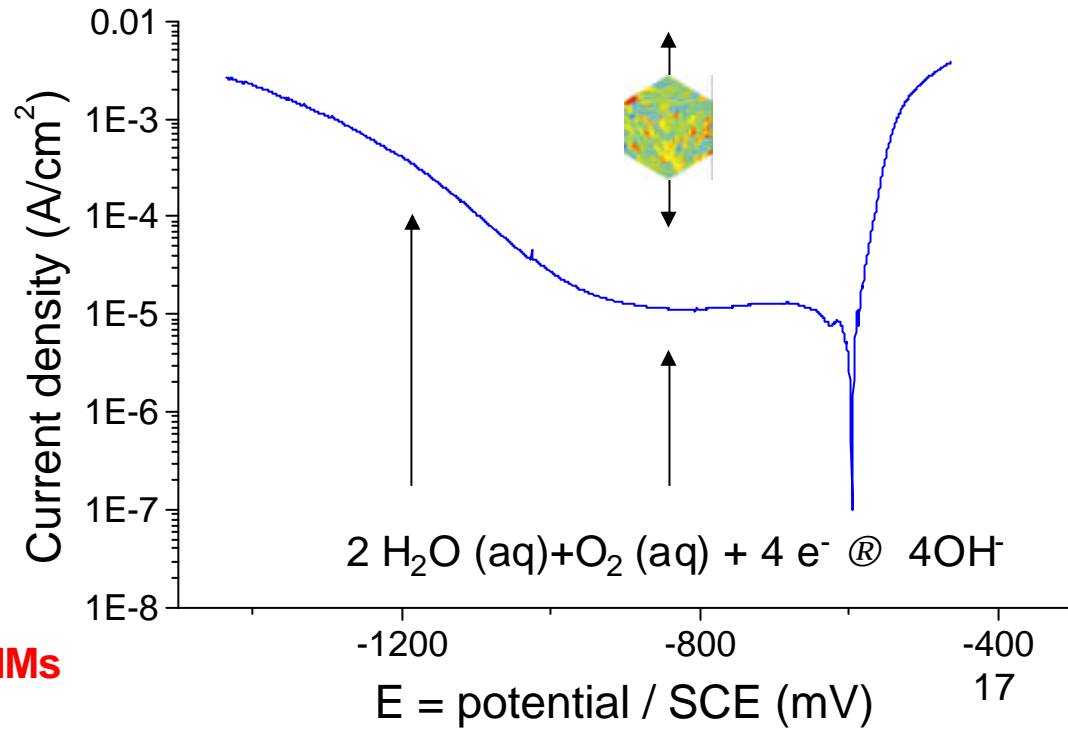
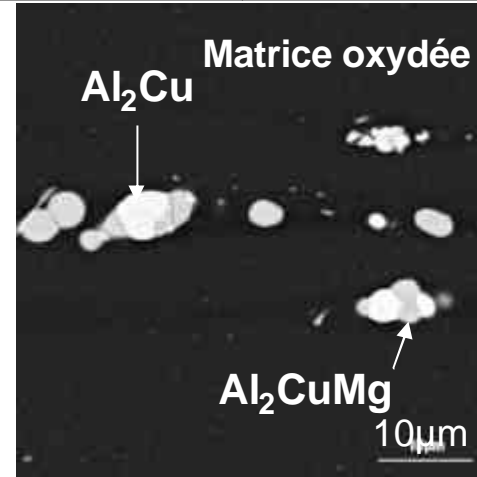


Gradient concentration

→ Interface



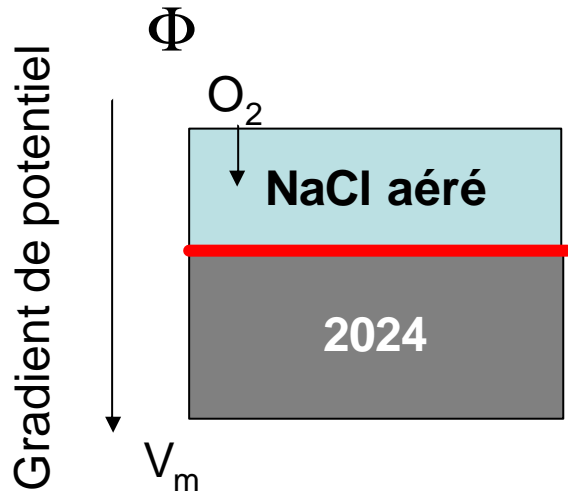
Matrice passivée  
dissolution sélective des IMs



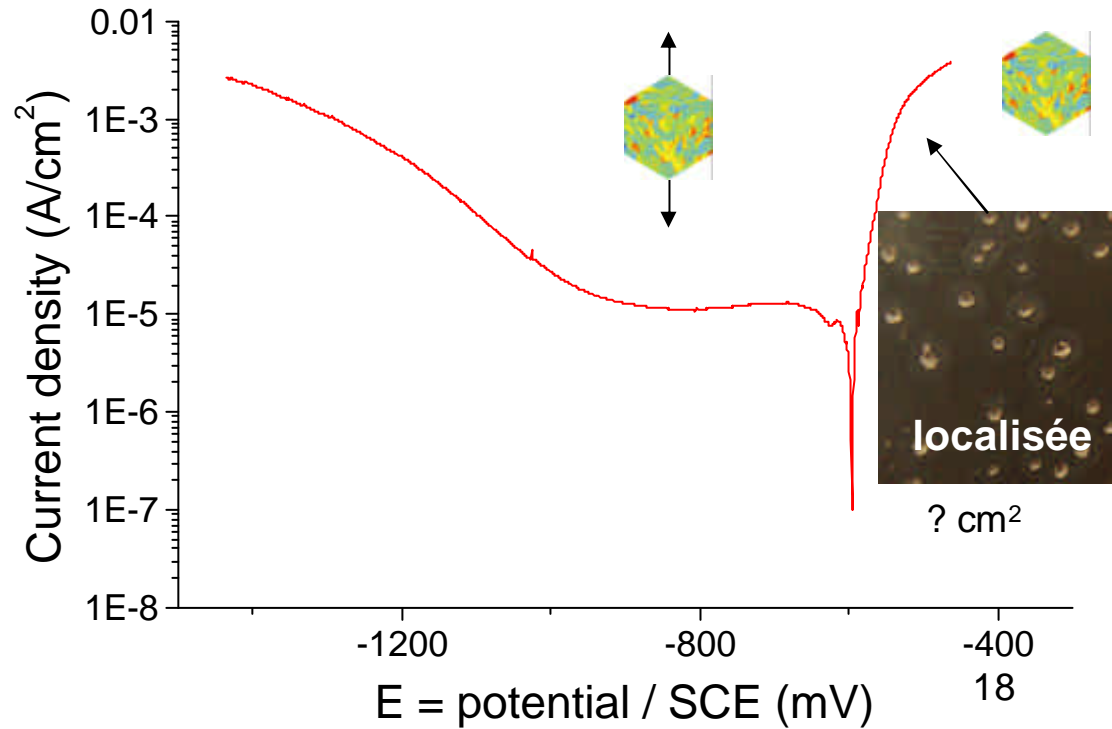
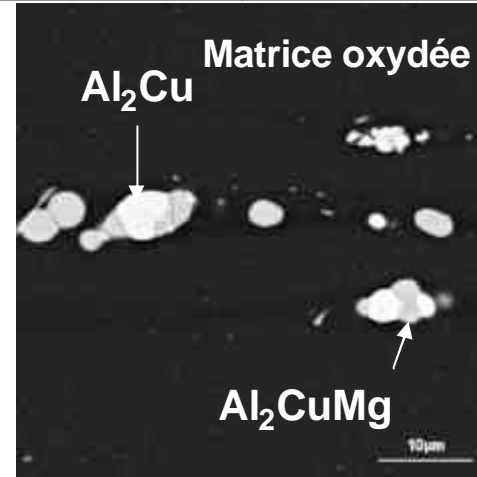
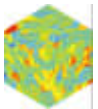
processus d'oxydation  
anti-corrosion  
limites

Distribution anodes

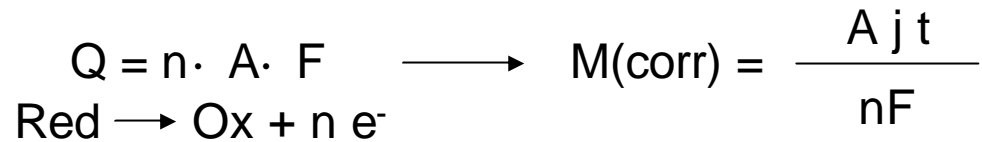
2024 / NaCl 0.5M



→ Interface = corrosion par piqûres



Loi de FARADAY : permet d'accéder à la vitesse de corrosion

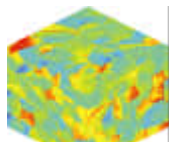


A = masse atomique (g/mol)

j = densité de courant (A/cm<sup>2</sup>)

F = 96 500 C

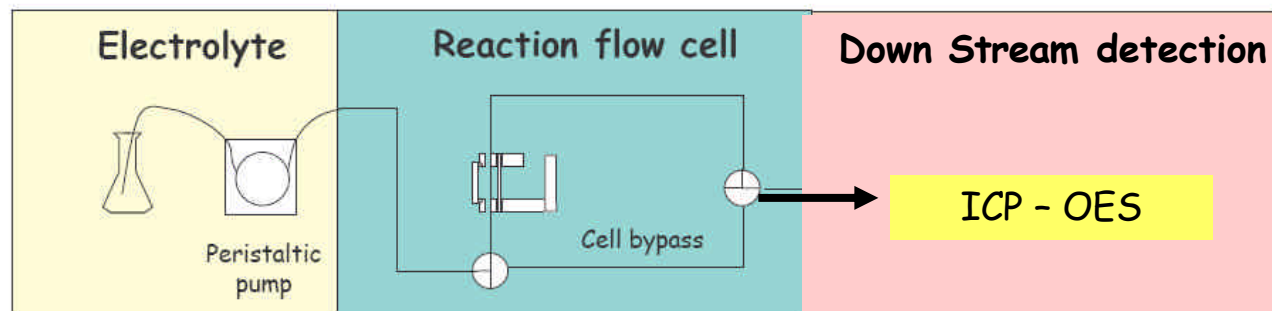
T = temps (s)



? Dissolution sélective ou non

? Interfacial process

### ICP Atomic Emission Spectroelectrochemistry (ECICP)



processus d'oxydation

anti-corrosion

limites

**A. Bases**

**B. Exemples emblématiques**

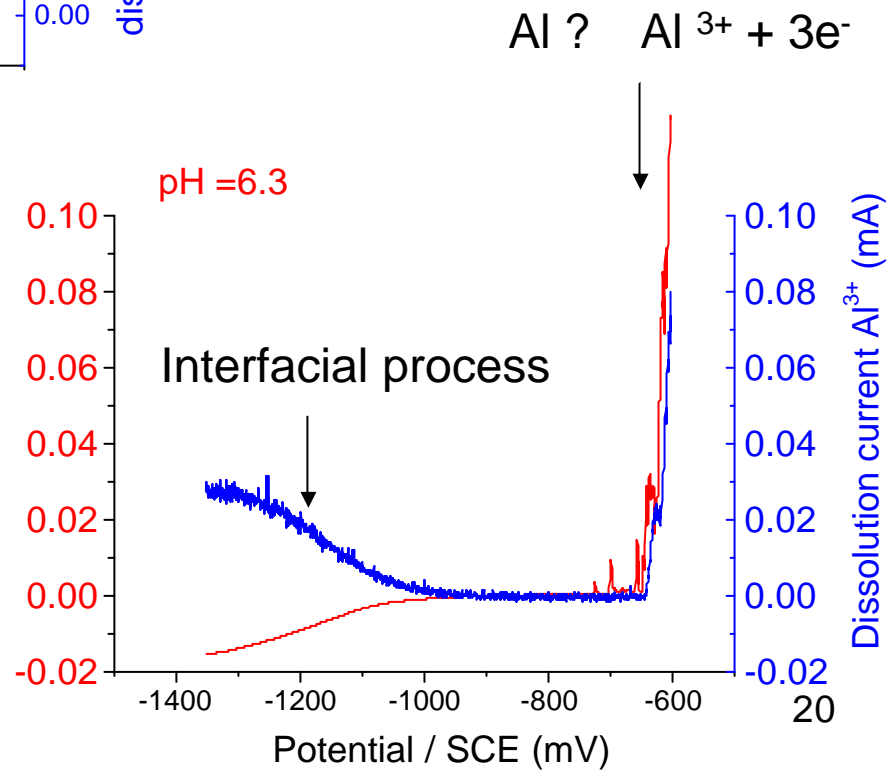
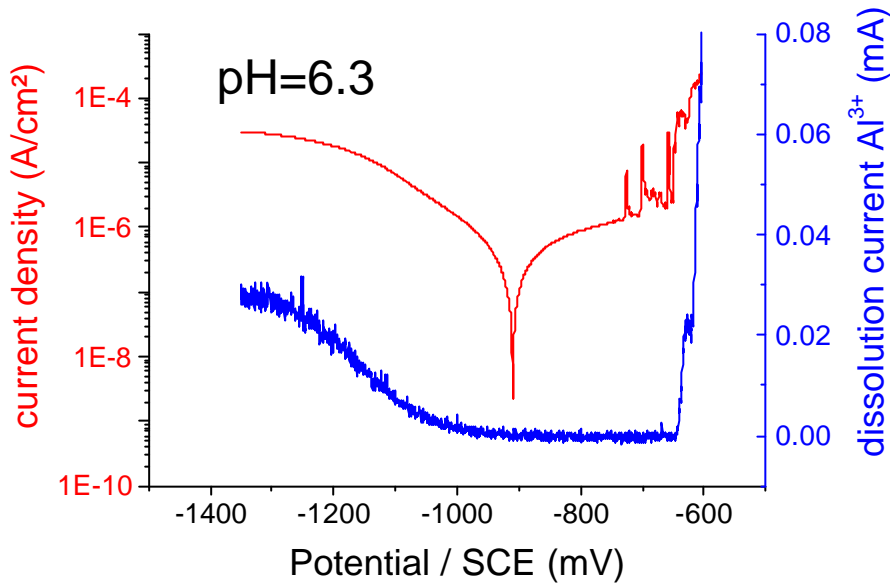
**C. Défis**

**D. Conclusion**

processus d'oxydation

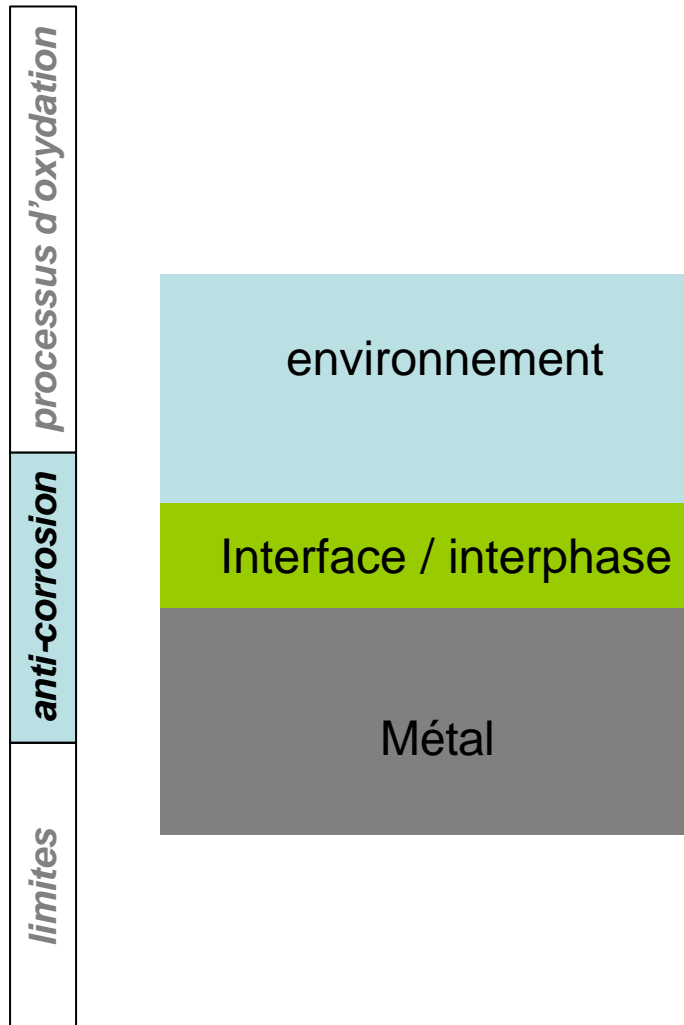
anti-corrosion

limites





*Anti-corrosion : R&D conditionnée par engineering + sociétal*

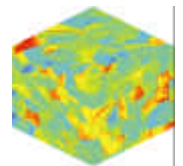
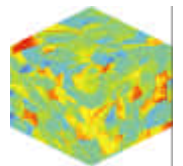


➤ *Inhibiteurs en solution*

➤ *Traitements de surface* (inorganiques ou organiques) : self healing ou autocicatrisation avec des mécanismes comme la conversion chimique

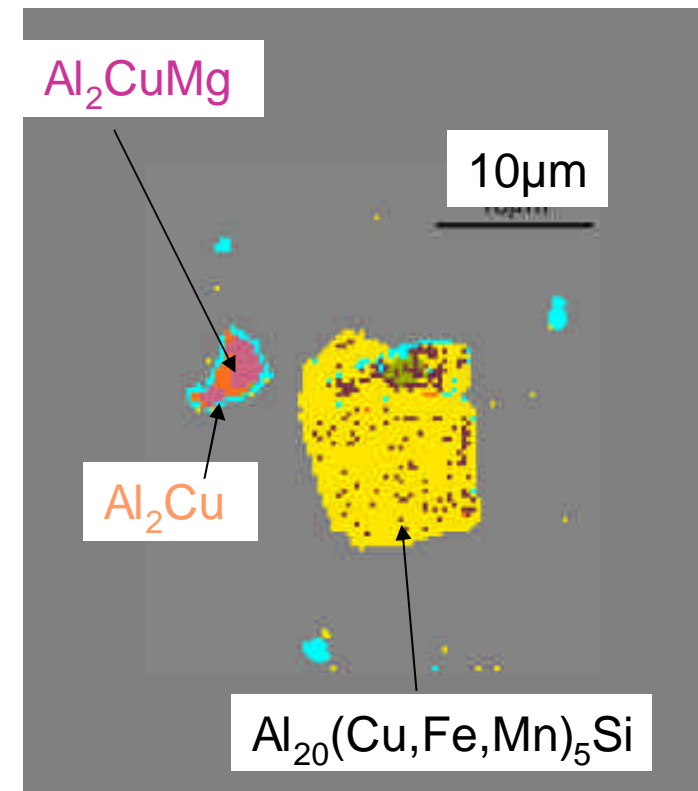
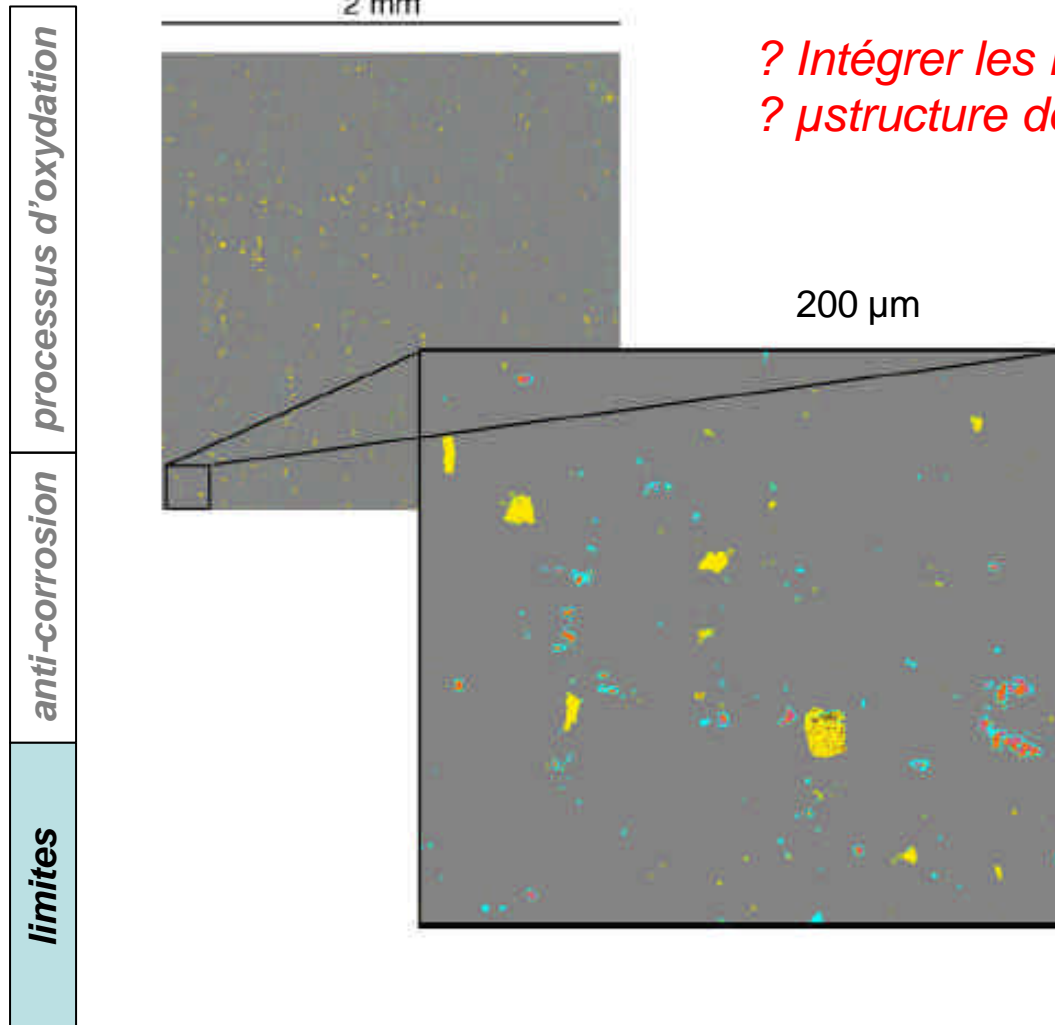
➤ *aspect sacrificiel* = revêtements métalliques le métal protège le métal. C'est une voie de recherches car il y a des inquiétudes quant à la disponibilité de certains métaux sacrificiels comme le Zn

➤ *surface du métal* = oxyde (l'exemple le plus démonstratif : les aciers inoxydables : au sens plus large les matériaux passivables)



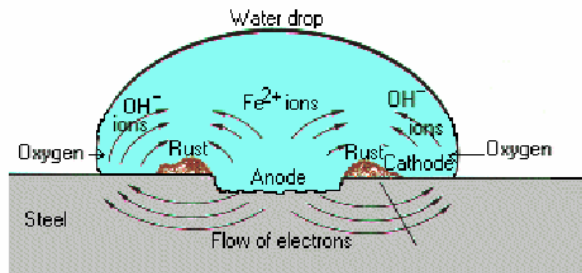
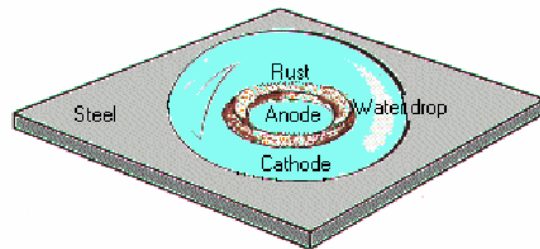
2024 Al

Microstructure de coulée

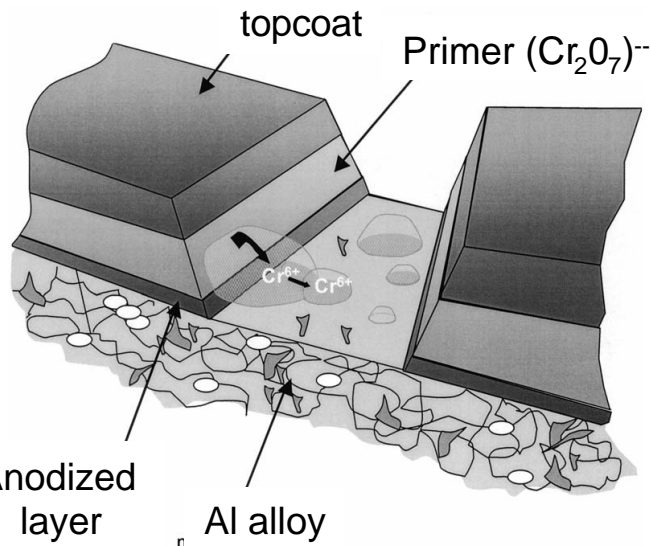
*? Intégrer les interactions**? μstructure de transformation*

How complex is the microstructure of AA2024-T3?  
 A.E. Hughes and coll., *Corrosion Science* 51 (2009) 1565–1568

processus d'oxydation



anti-corrosion

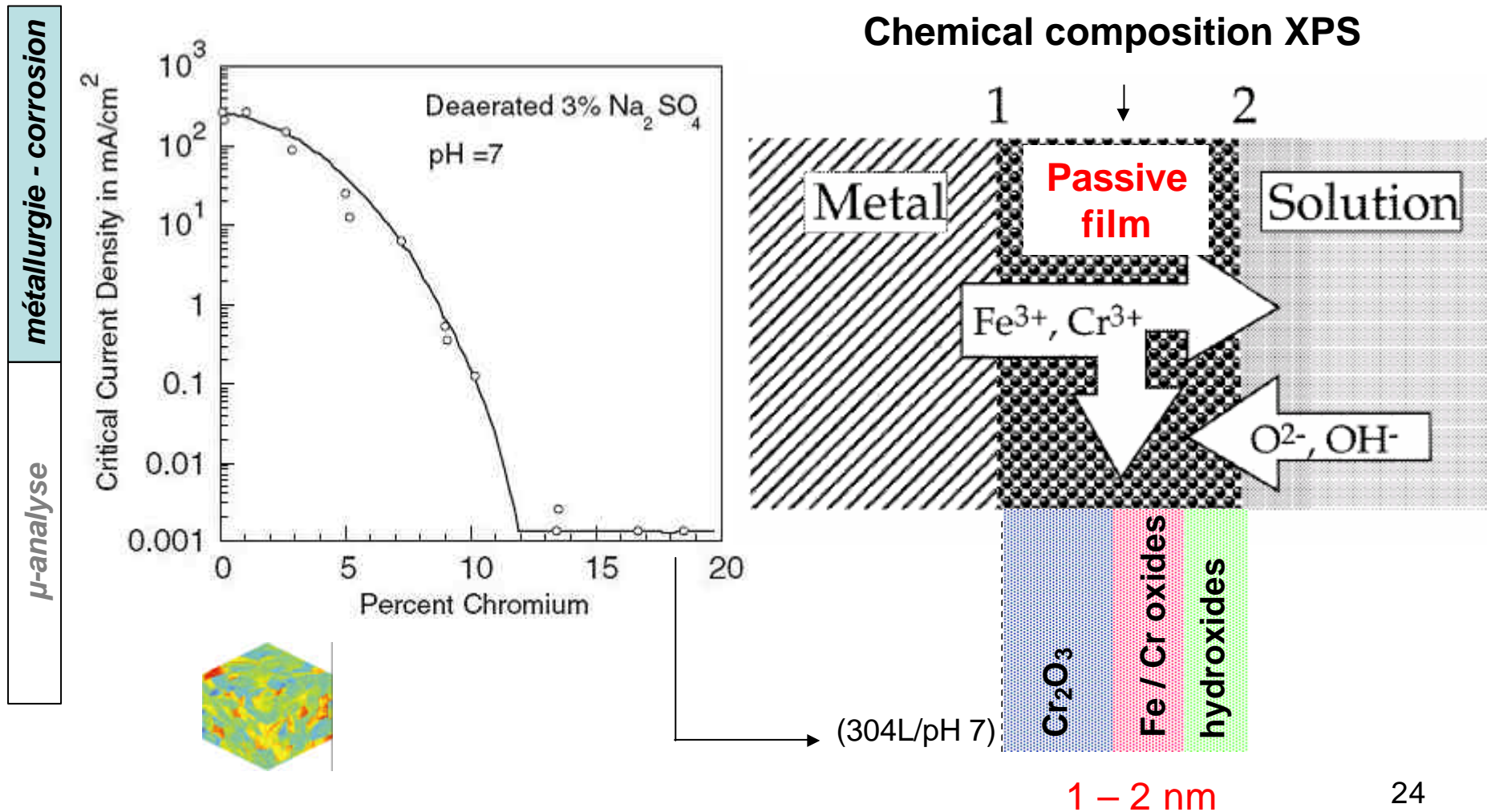


limites

Schéma issu d'un article publié en 1926 par Evans (U. R. Evans, *The Ferroxy Indicator in Corrosion Research, The Metal Industry* (1926) 481-482)

Objectif = modéliser le processus d'auto-cicatrisation via le transport de matière dans des gouttelettes qui vont coalescer

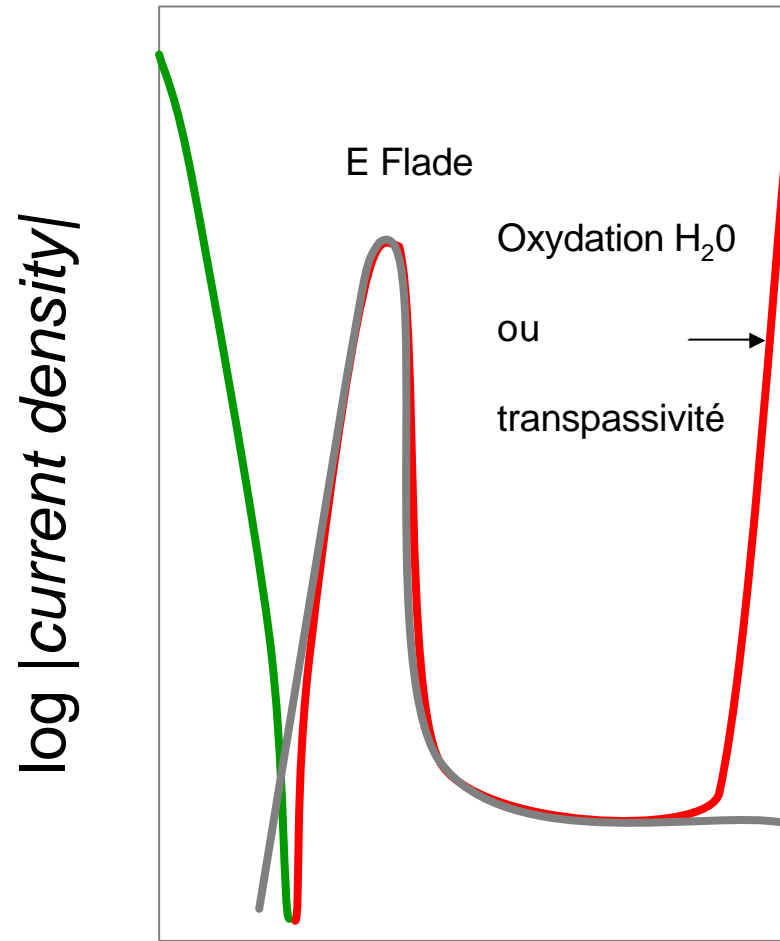
Métaux passivables (Aciers inoxydables, Ni alloys, ...)



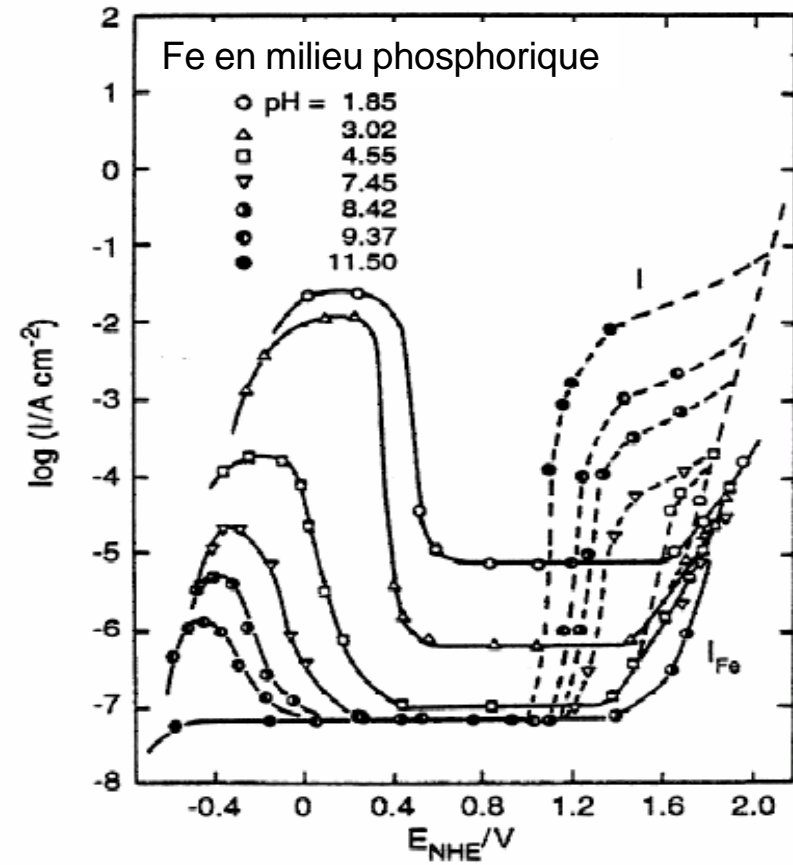
$I = f(E)$  - passivation

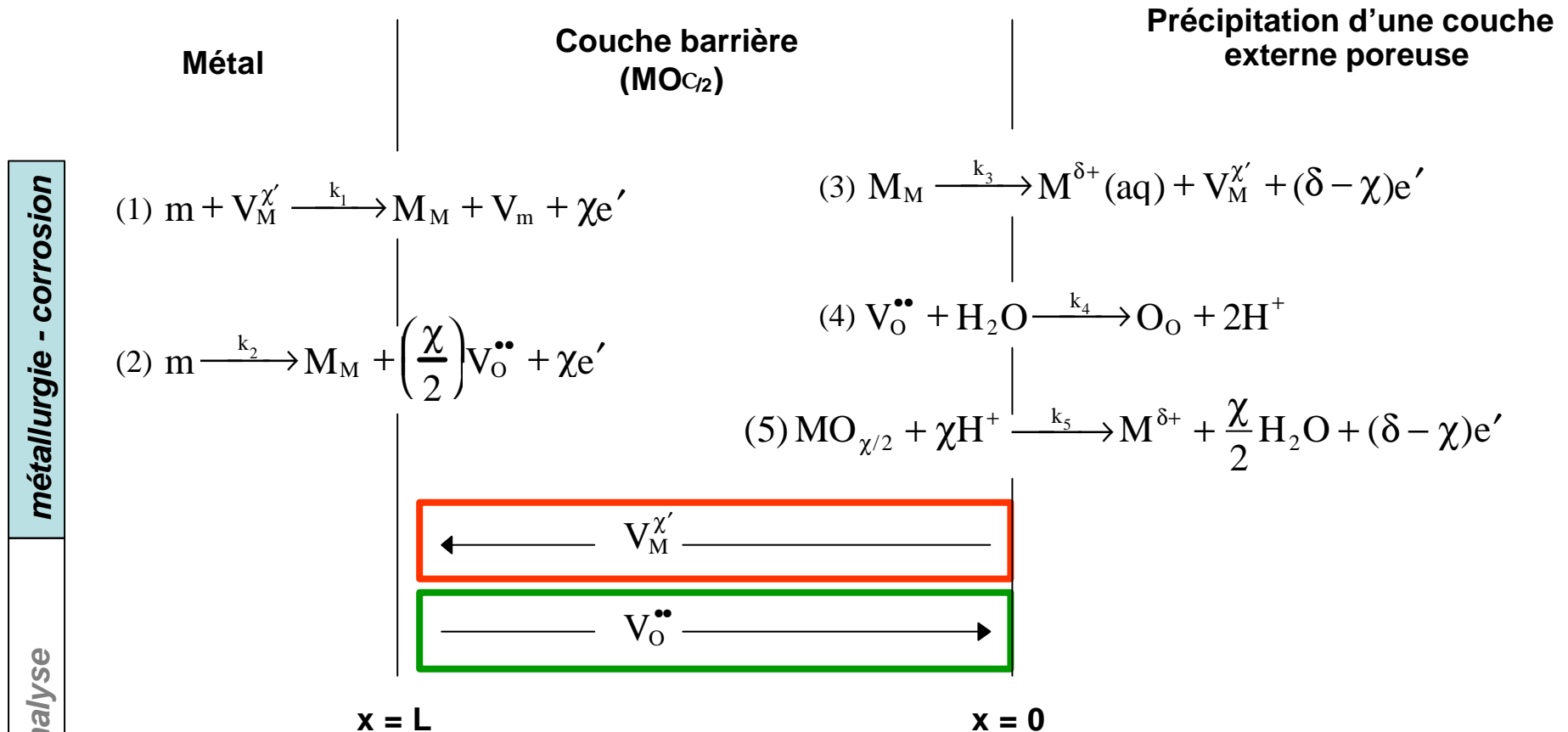
métallurgie - corrosion

$\mu$ -analyse



Electrode Potential





Des lacunes anioniques sont créées à l'interface métal / film et consommées à l'interface film / solution.

Des lacunes cationiques formées à l'interface film / solution sont consommées à l'interface métal / film.

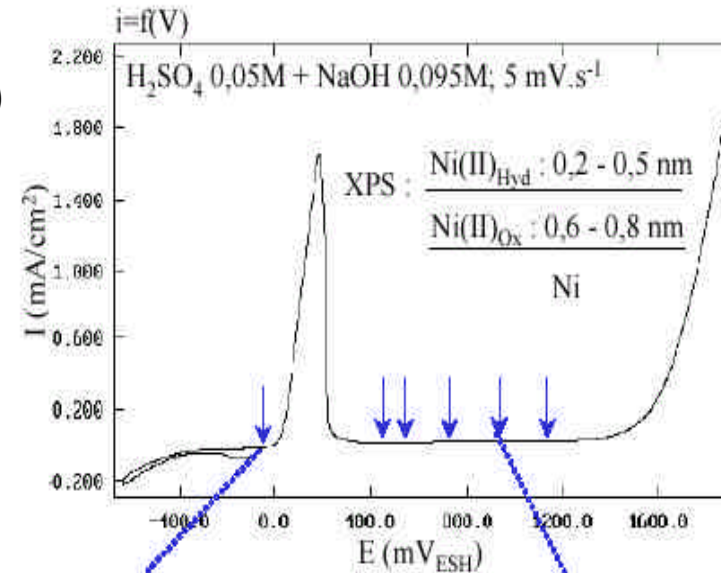


## In situ atomic level microscopy (STM)

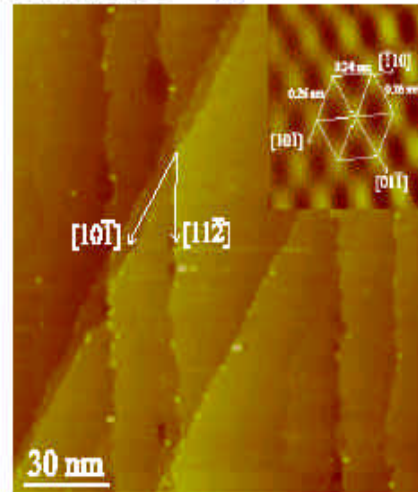
métallurgie - corrosion

Ni (111) passivé

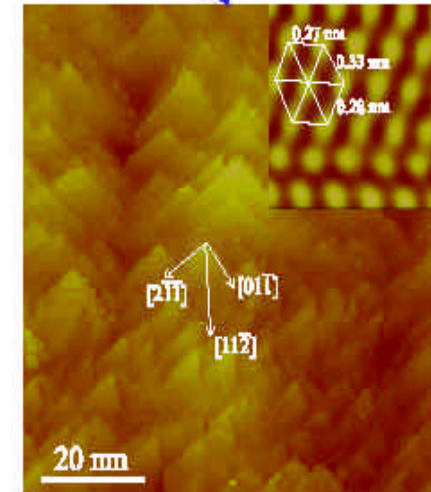
- ⇒ XPS : modèle bicouche oxyde/hydroxyde
- ⇒ STM : structure cristalline indépendante du potentiel, attribuée à NiO orienté (111) et stabilisé par la couche d'hydroxyde superficielle
- ⇒ STM : facettes résultent d'une épitaxie inclinée (3 à 13°) entre réseaux de l'oxyde et du métal, confirmée par SXRD



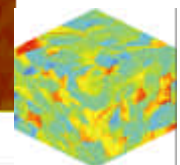
STM *in situ* :



Surface métallique

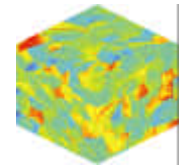
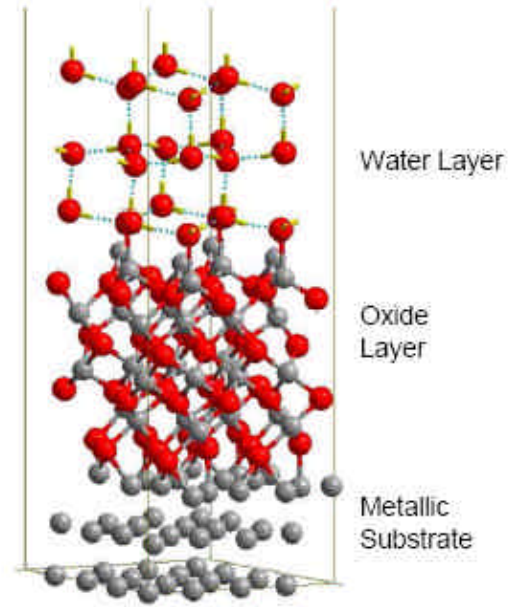
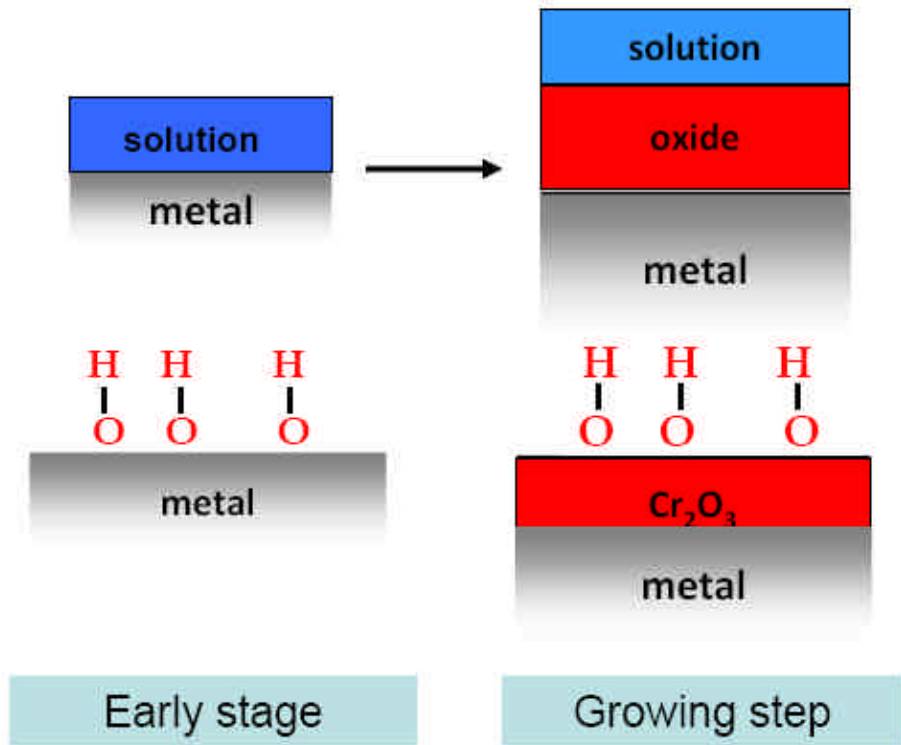


Surface passivée



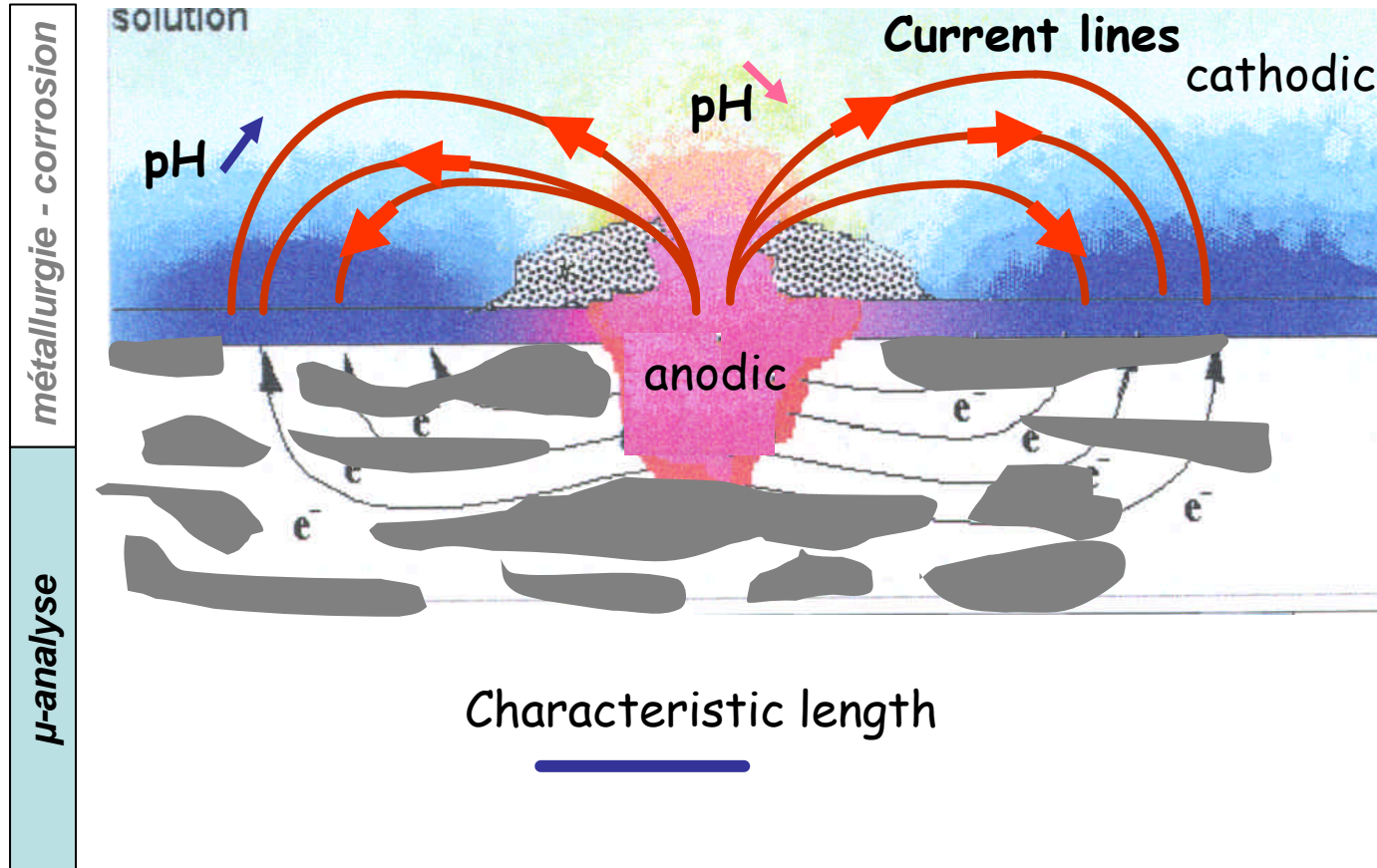
### Atomistic simulations (DFT)

métallurgie - corrosion  
 μ-analyse

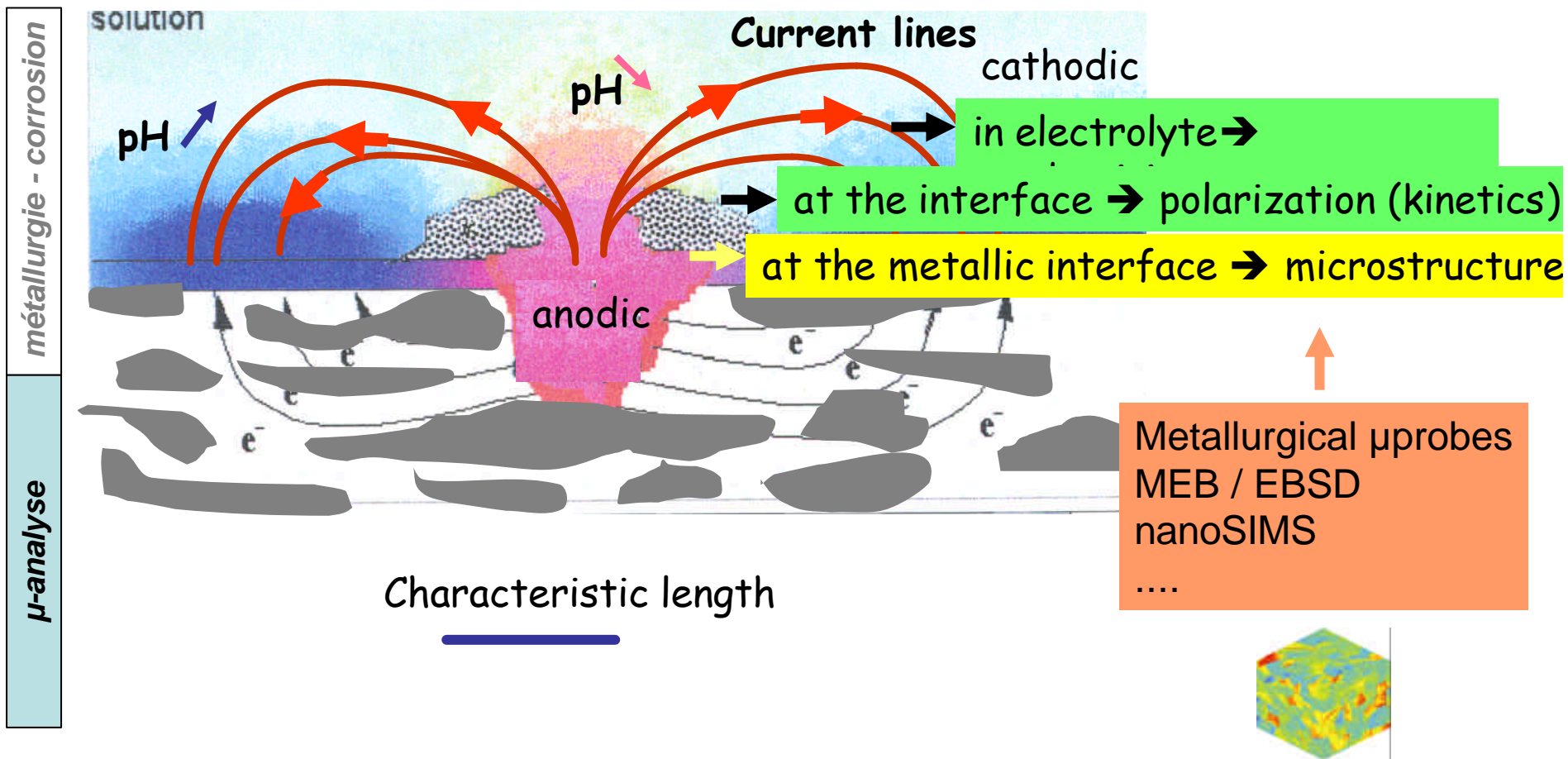




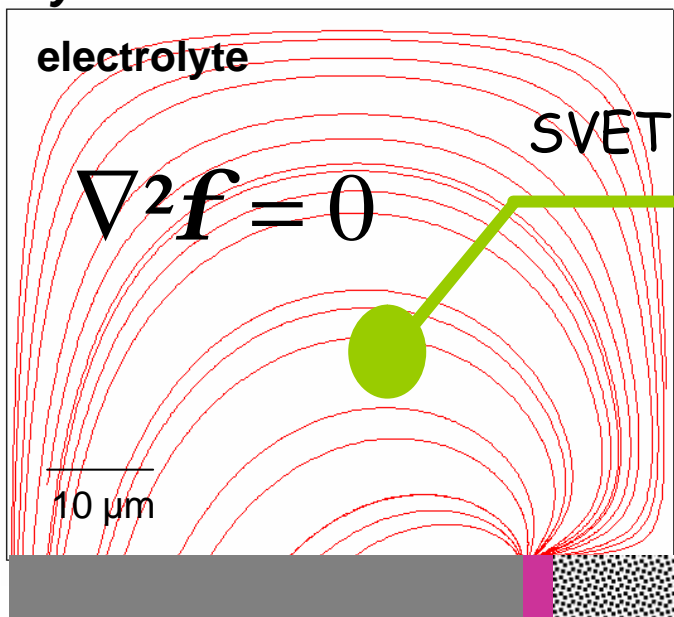
*μanalyse & corrosion localisée*



### *μanalyse & corrosion localisée*



*μanalyse & corrosion localisée*

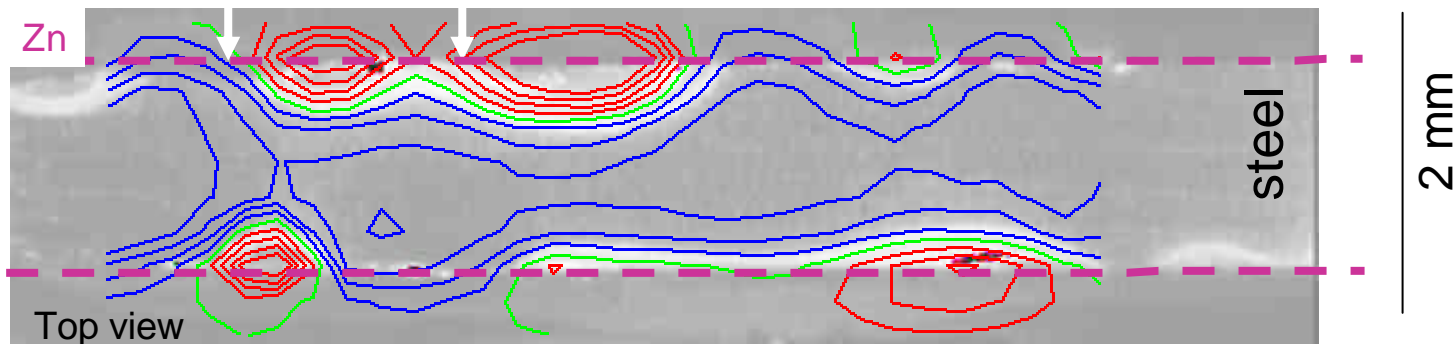


Conductivité  
+  
géométrie } → la distribution de courant

Densité de courant normale à la surface :  
- anodique → **corrosion**  
- cathodique → **protection**

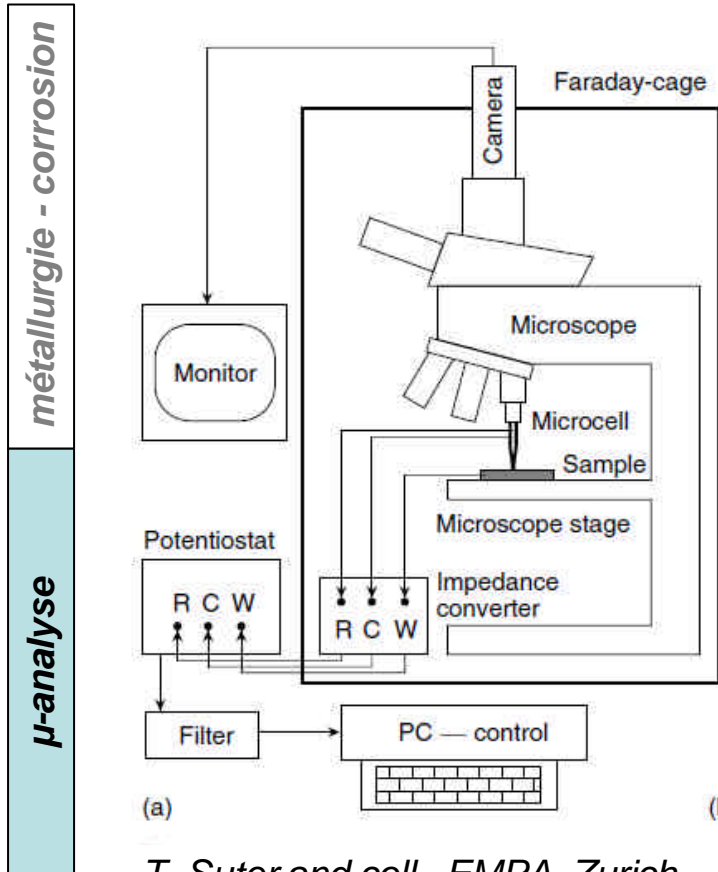
métallurgie - corrosion

μ-analyse

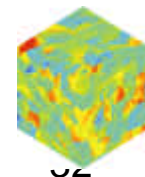
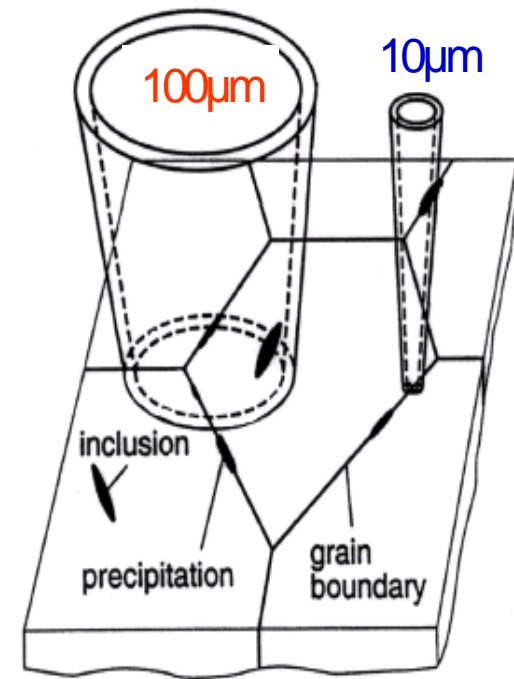


# Métallographie & Electrochimie

Multi-phases Single phase

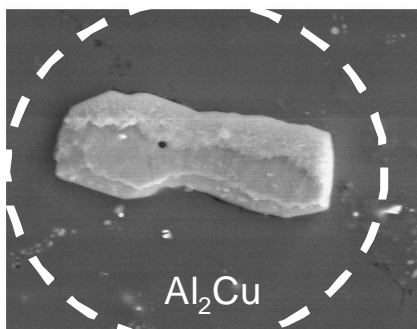


T. Suter and coll. EMPA Zurich



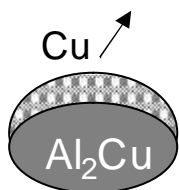
métallurgie - corrosion

$\mu$ -analyse

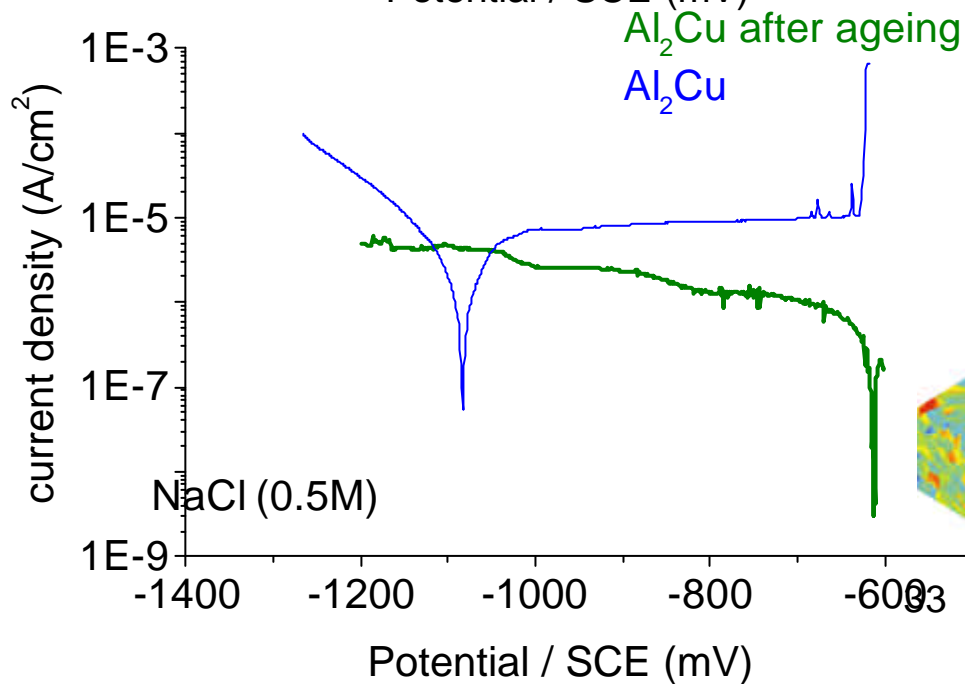
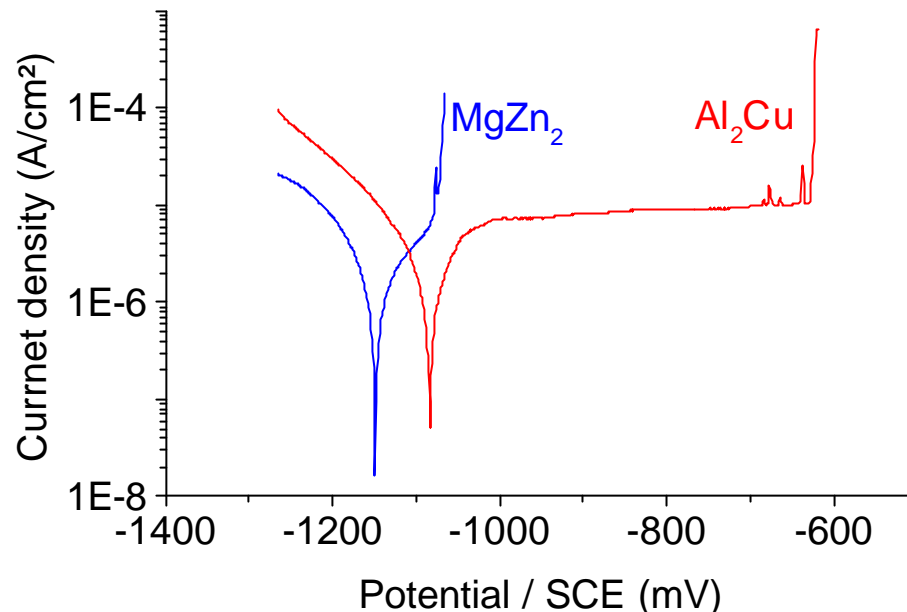


10  $\mu$ m

dealloying



Cathodic behaviour of IM

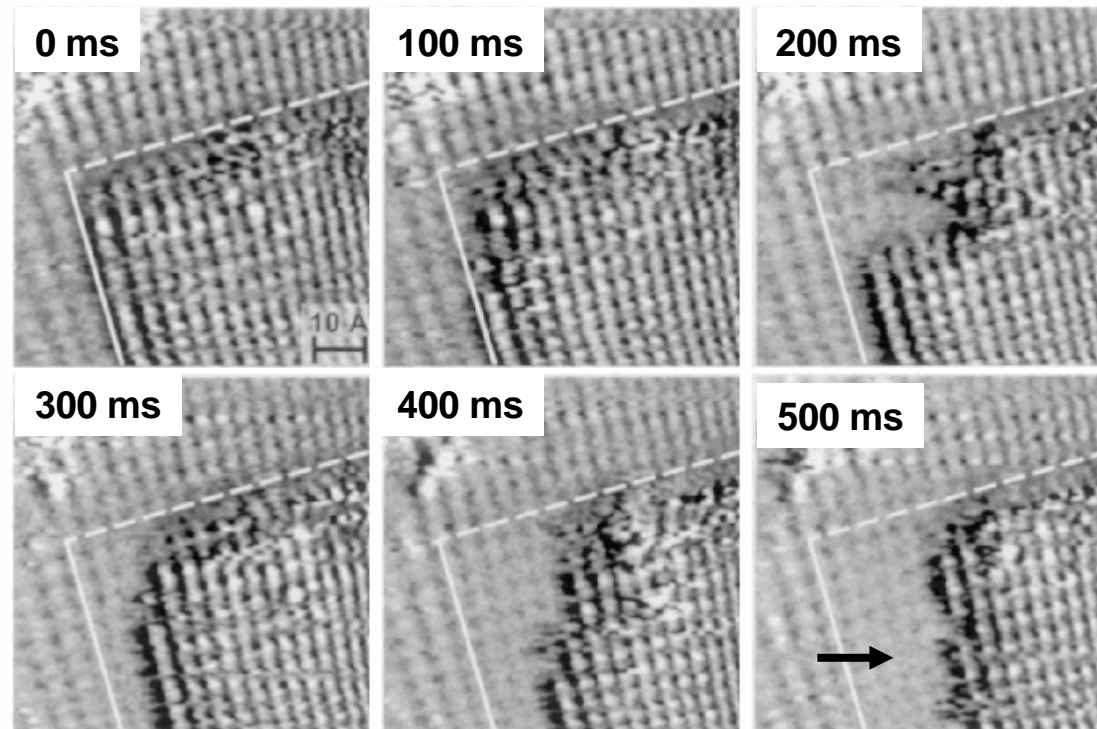




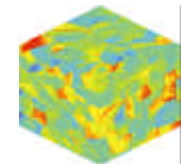
Progressing dissolution of a Cu terrace observed by in-situ video-STM

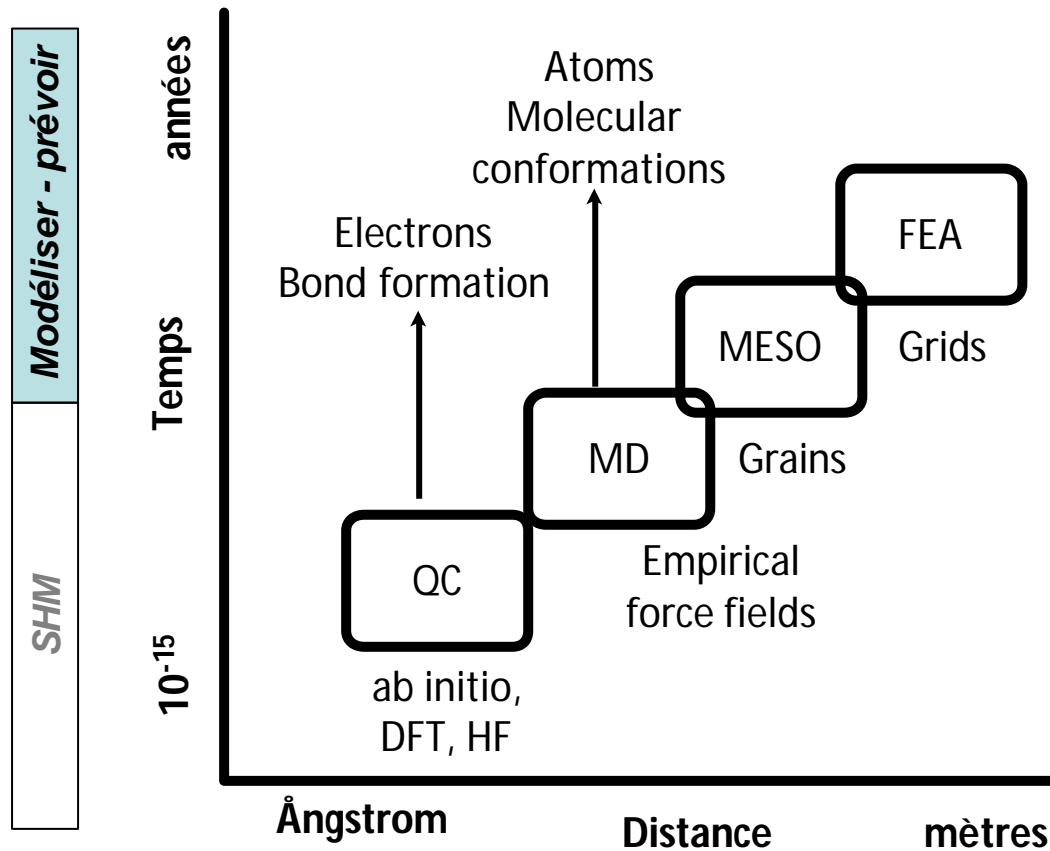
métallurgie - corrosion

$\mu$ -analyse



Cu(100) in 0.01 M HCl / Potential imposed





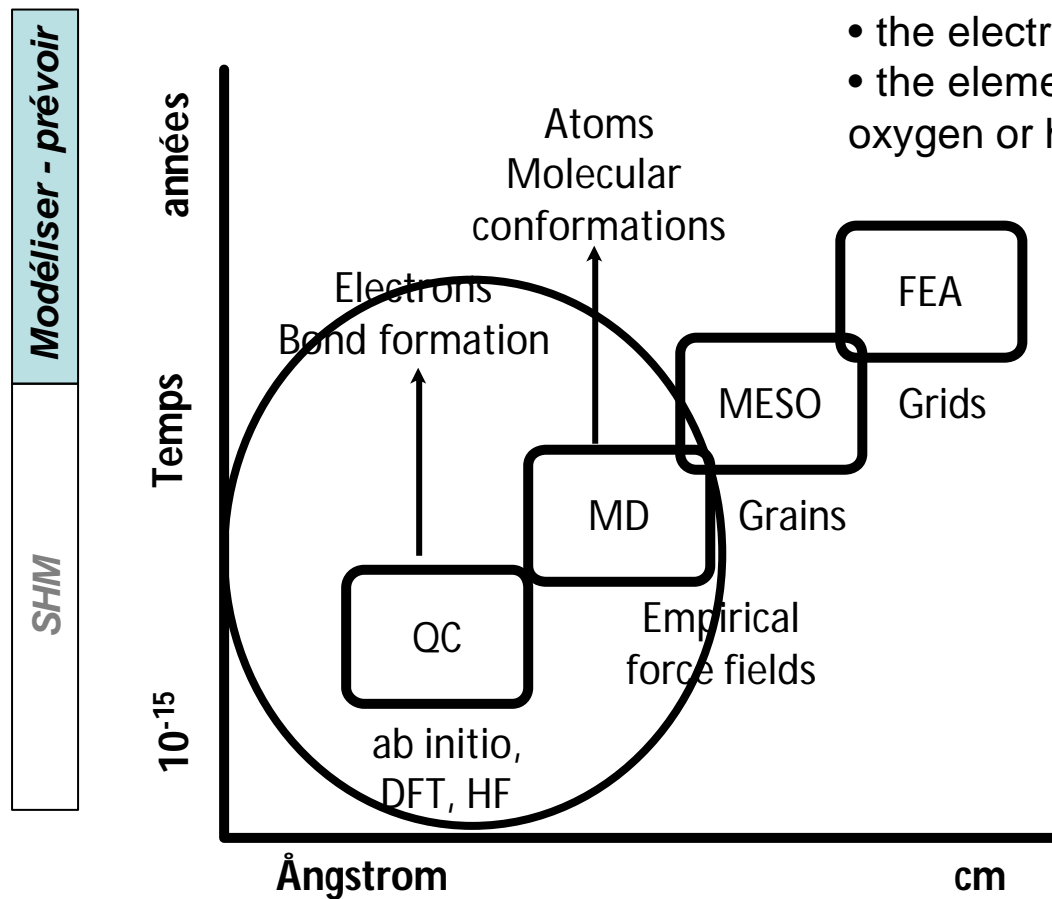
*Future perspectives of corrosion science*

*G.S. Frankel, G. S., M. Stratmann, Corrosion Engineering, Science and Technology, 44, (2009)328-331*

For the systems this understanding might be achieved by ab-initio modeling using for example DFT methods.

well suited for modeling

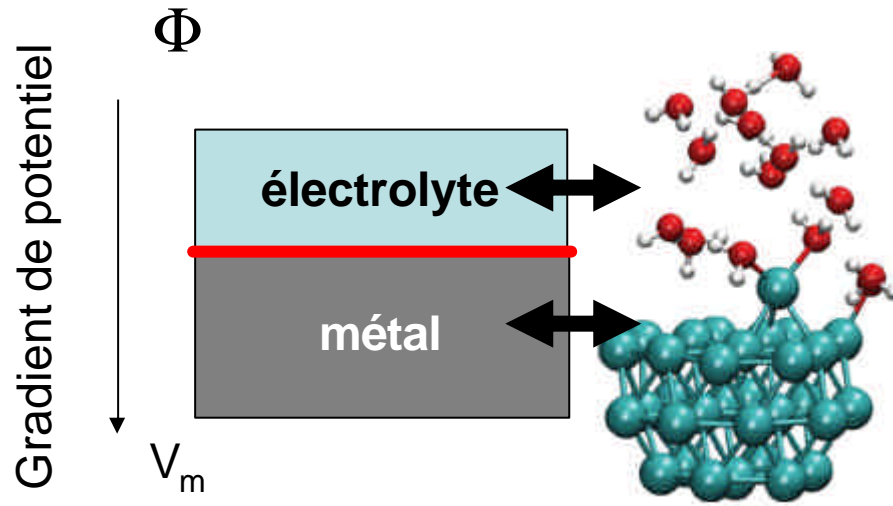
- the electronic properties of passive films
- the elementary electrochemical reactions like the oxygen or hydrogen cathodic reactions.



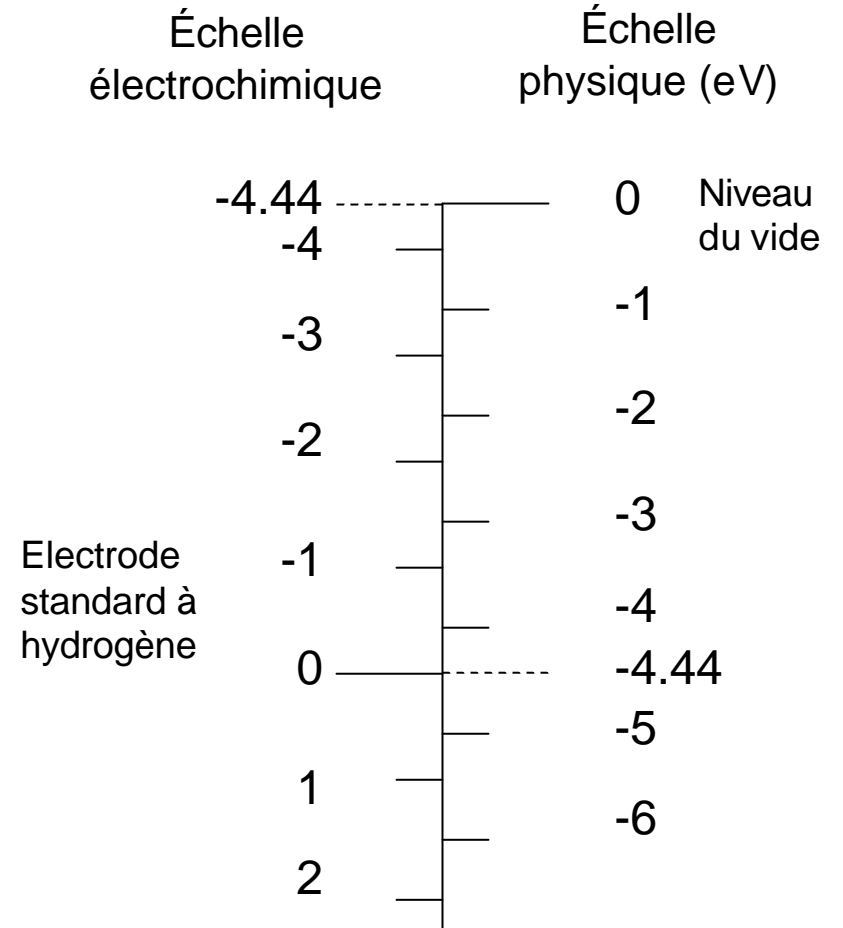


Modéliser - prévoir

SHM



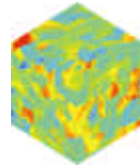
→ Interface  $E = V_m - F$



Travaux issus de la physique des interactions métal-électrolyte

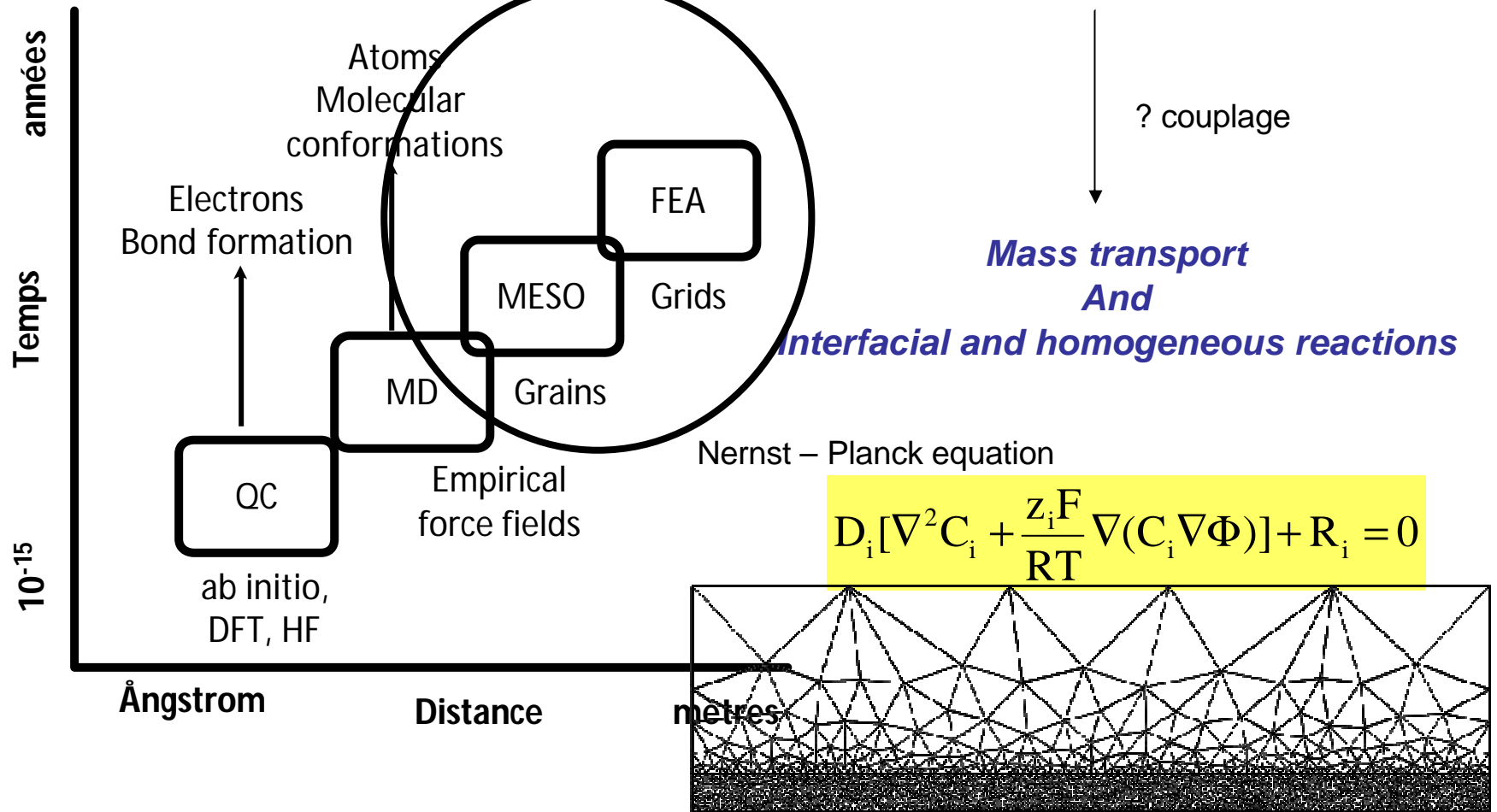
? Notion de vitesse de réaction

Integrated modeling of FSW of 6xxx series  
 Al alloys: Process, microstructure and properties



*A. Simar, Y. Bréchet, B. de Meester, A. Denquin  
 C. Gallais, T. Pardoën  
 Progress in Materials Science 57 (2012) 95–183*

SHM  
 Modéliser - prévoir



Nernst – Planck equation

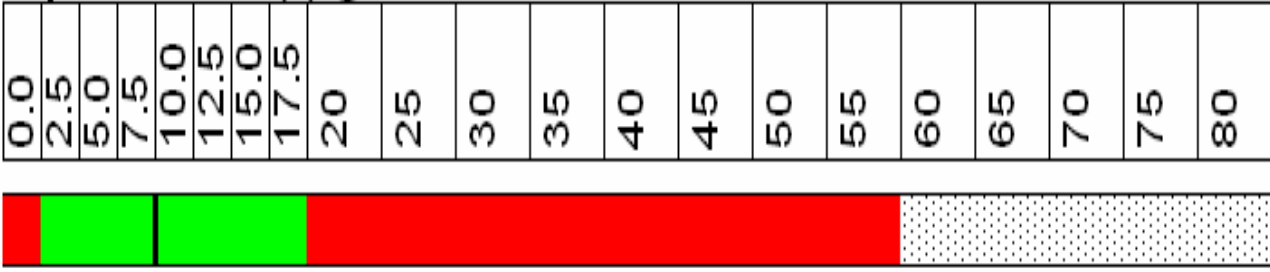
$$D_i \left[ \nabla^2 C_i + \frac{z_i F}{RT} \nabla(C_i \nabla \Phi) \right] + R_i = 0$$

Modéliser - prévoir

SHM

Alloy 2050

**Equivalent time (h) @ 175°C**



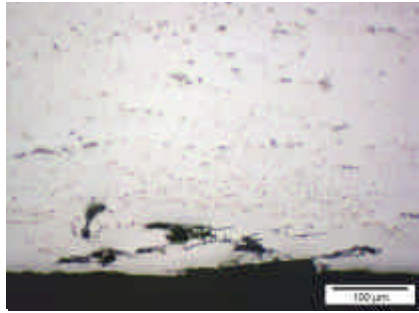
immune to IGC  
 IGC sensitivity  
 no data  
 mark | corresponds to peak aged.

Modéliser - prévoir

SHM

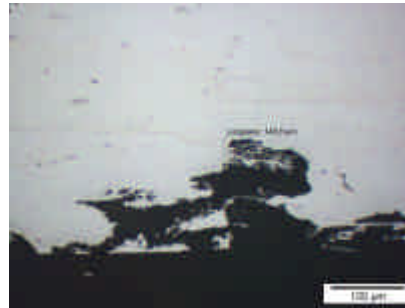
ASTM G110  
IGC testing

**AlCuLi (underaged)**



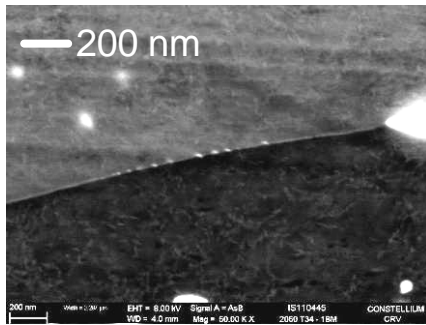
Intergranular corrosion

**AlCuLi (peak aged)**

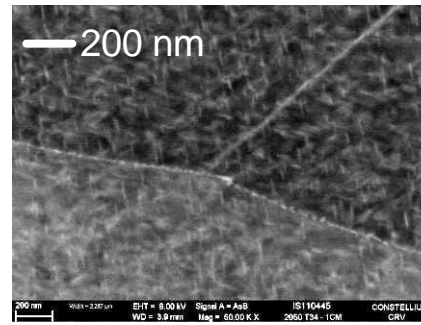


Transgranular corrosion

FEG  
observations



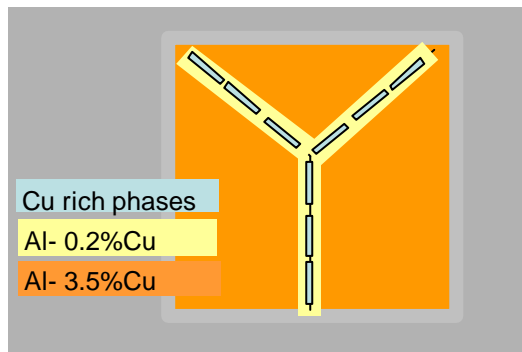
T1 precipitation at gb



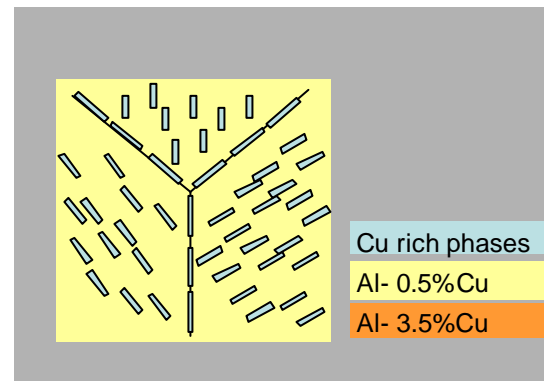
T1 precipitation in the matrix

T1 Al<sub>2</sub>CuLi

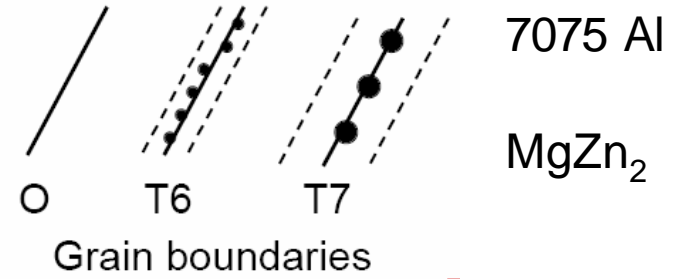
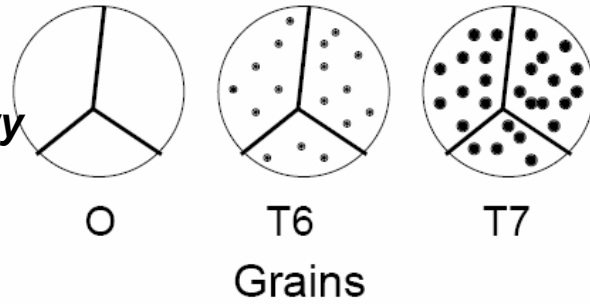
Localised  
corrosion of  
Cu depleted  
zone at grain  
boundary



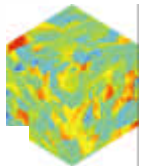
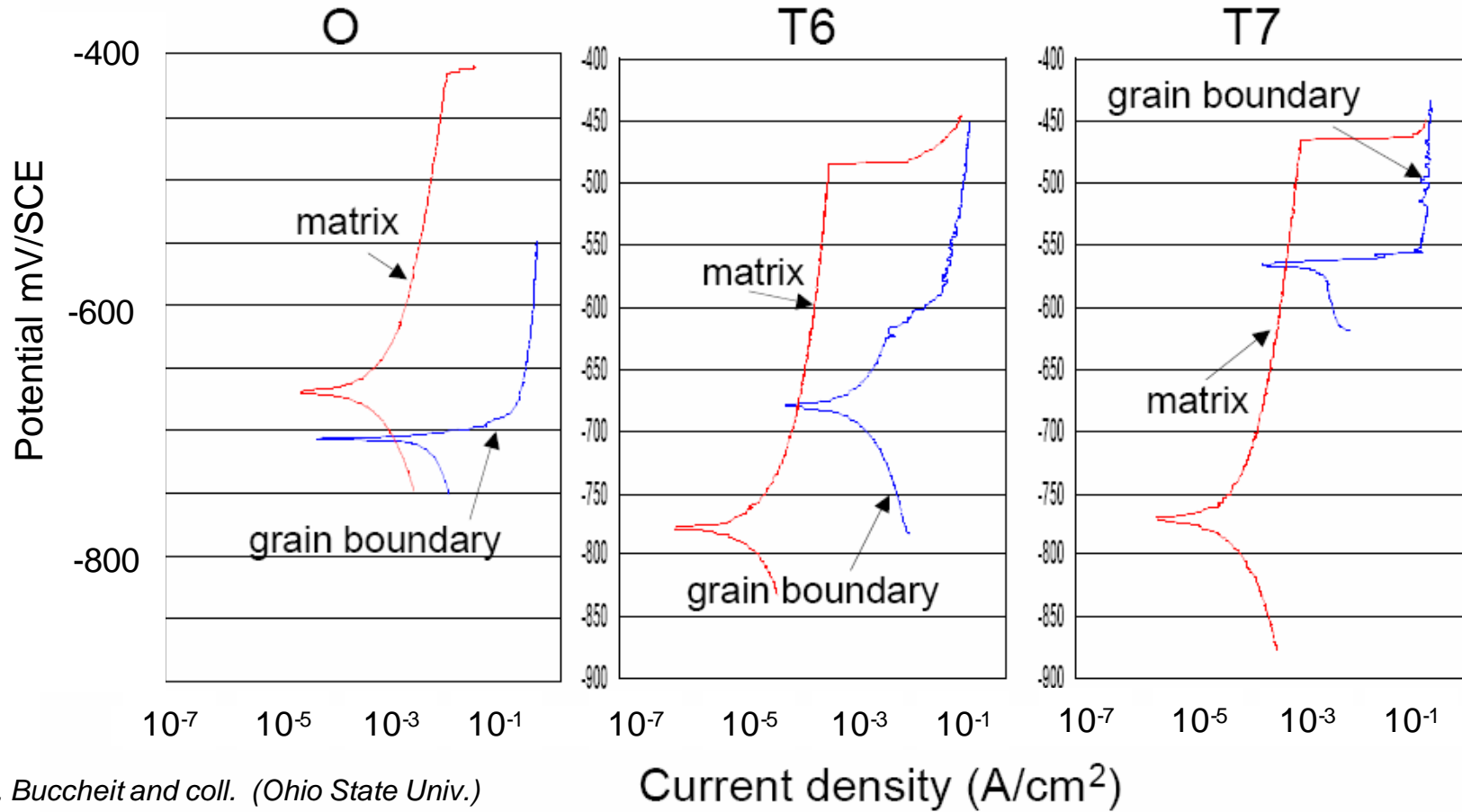
Generalised  
corrosion of  
depleted zone  
of the matrix



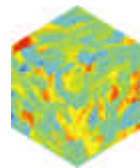
? Limit of  $\mu$ -electrochemistry



SHM      Modéliser - prévoir

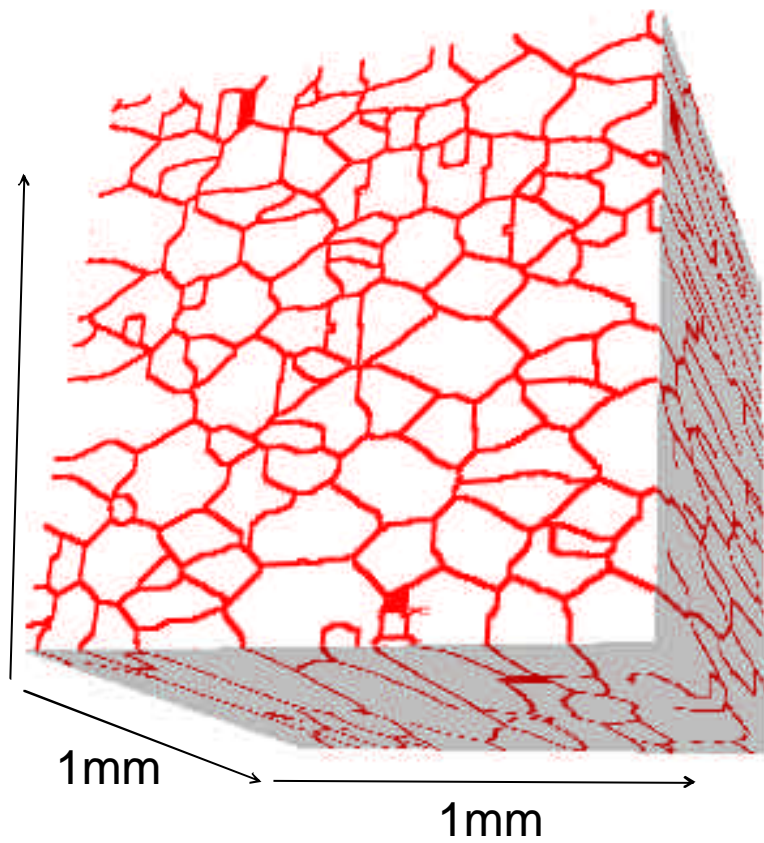
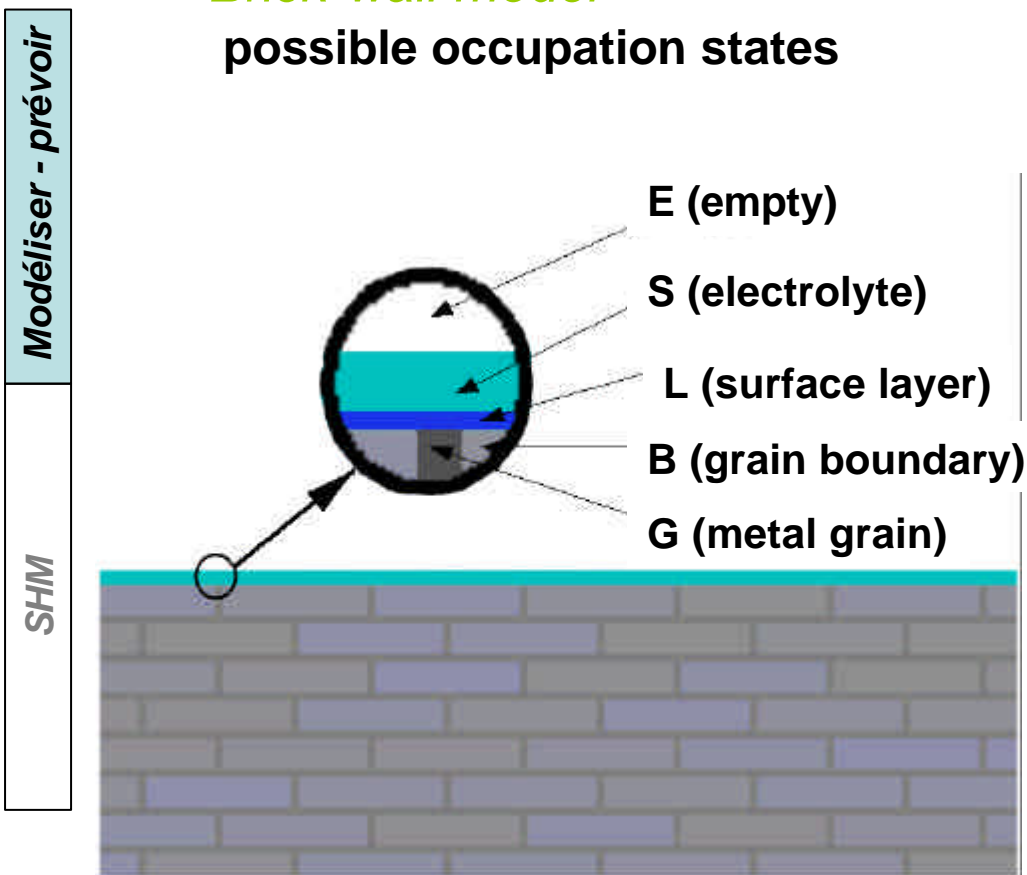


Probabilistic model



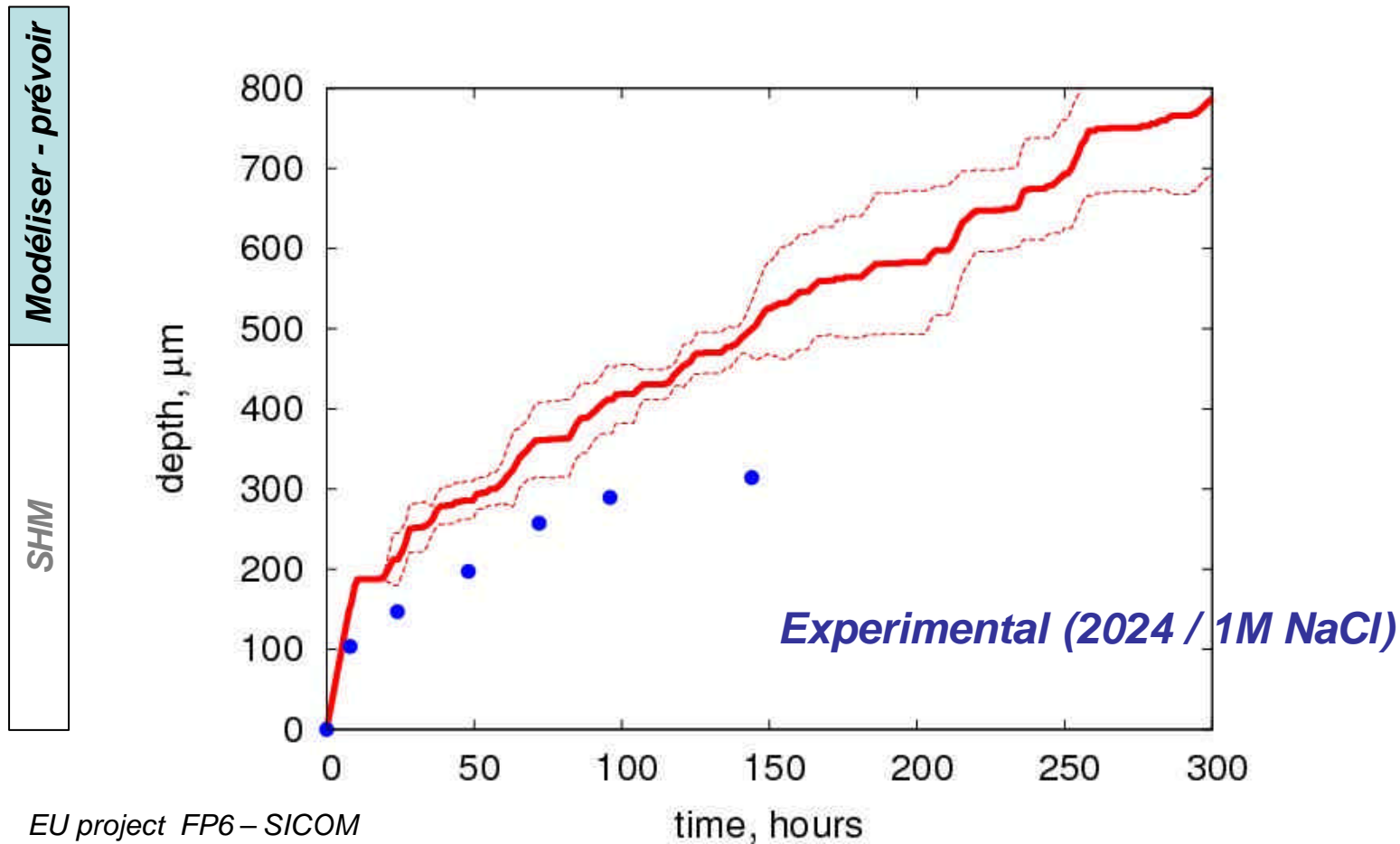
*Brick-wall model*

possible occupation states



Probabilistic model

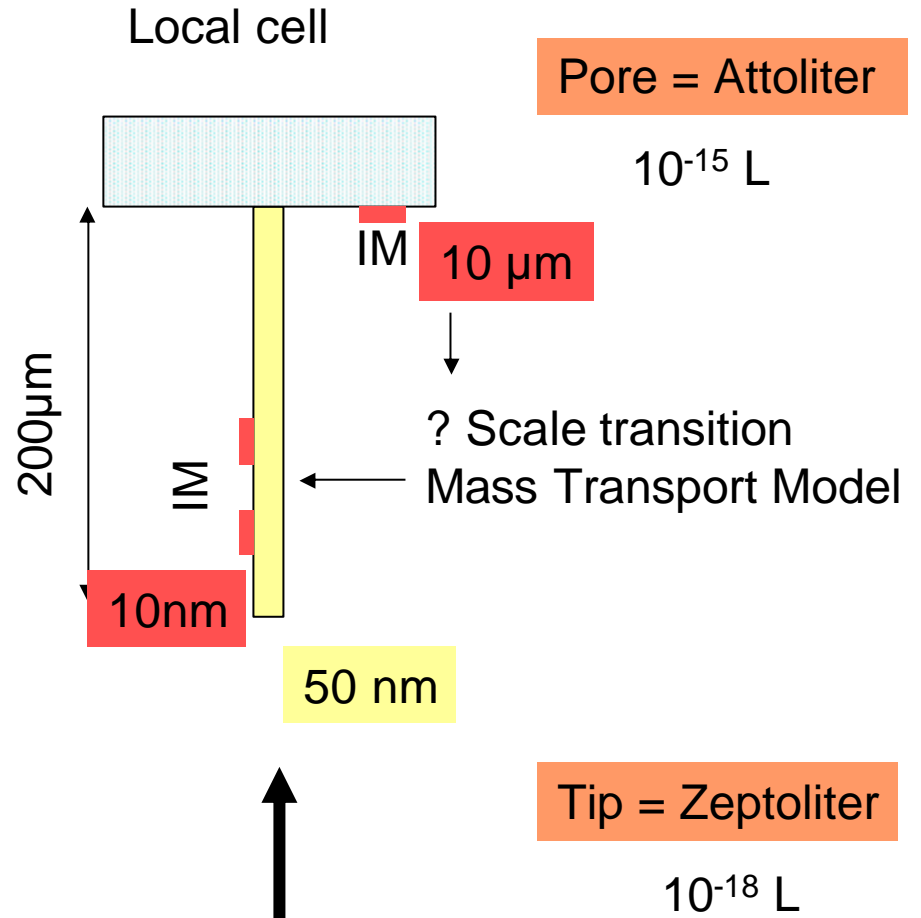
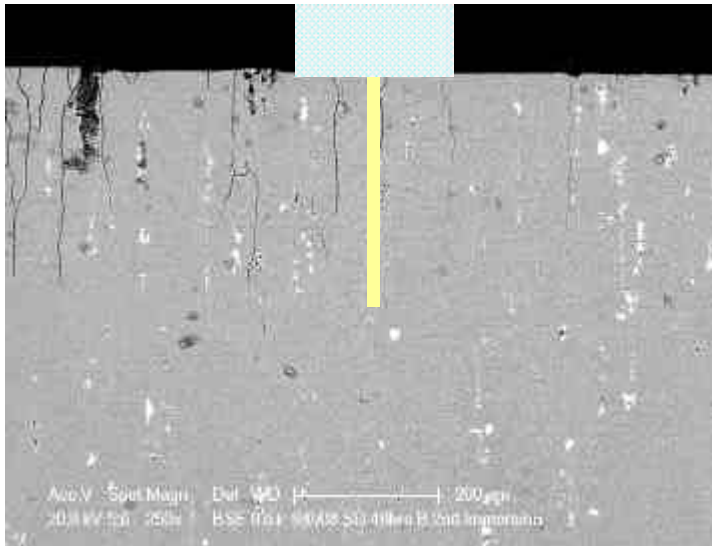
Maximum corrosion depth determined using a set of probabilities



Modéliser - prévoir

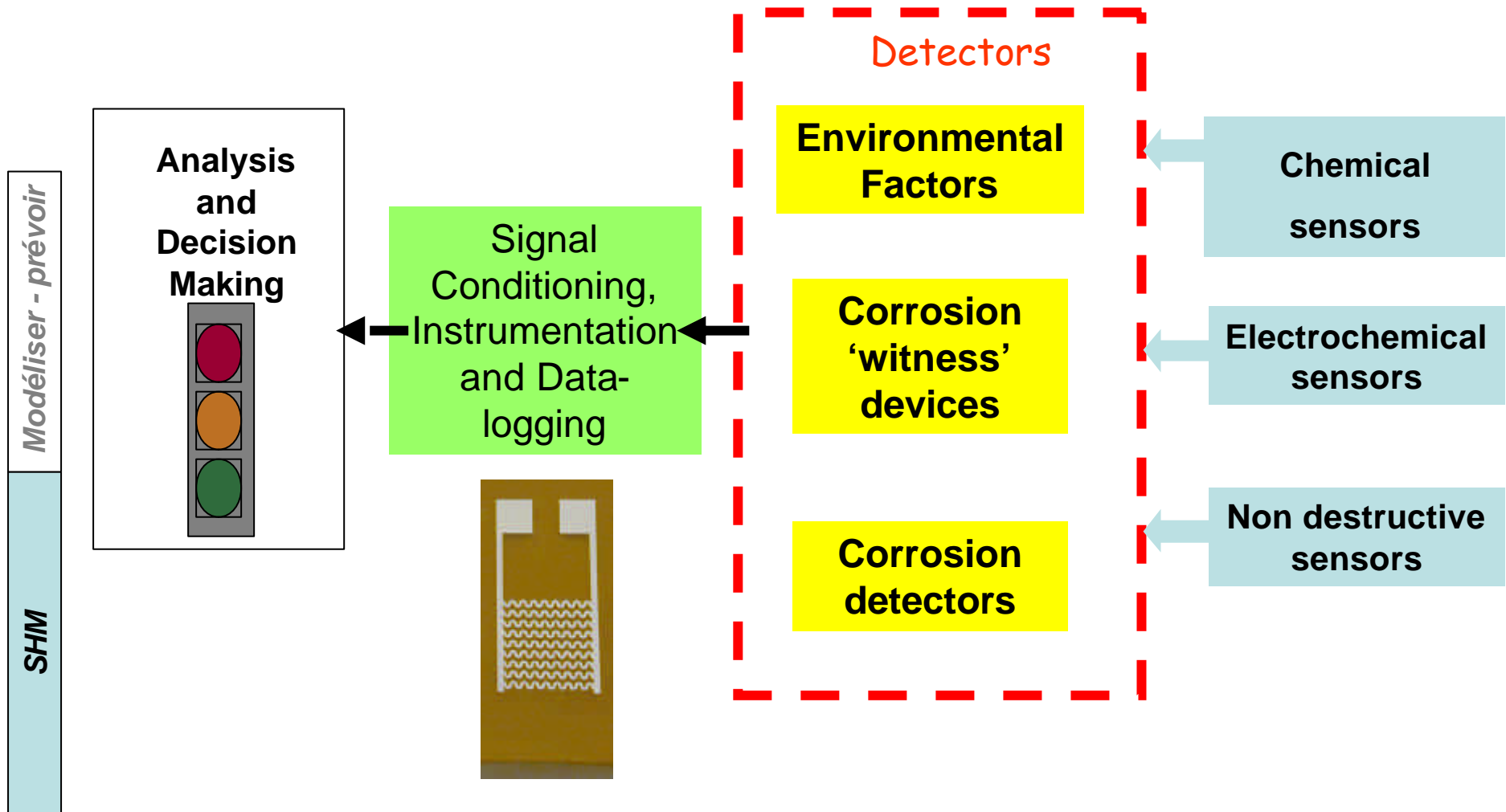
SHM

Propagation



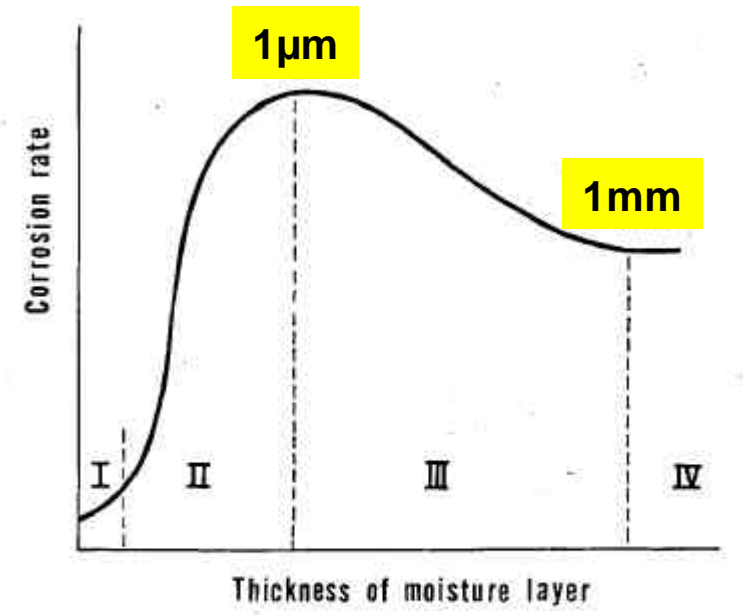
Nernst-Planck (N-P) equation : ? validity



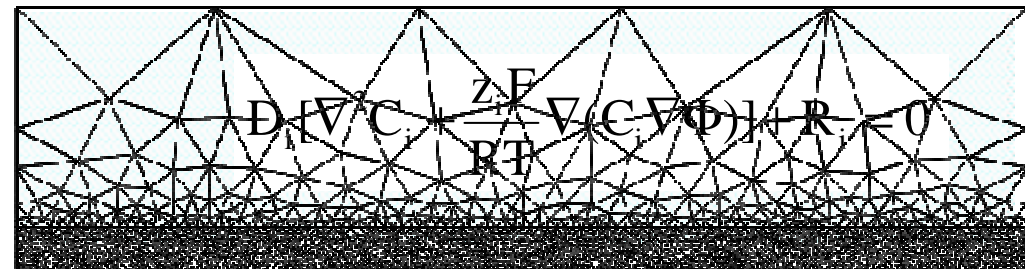




N.D. Tomashov, Corrosion 20 (1964) 7.



**Transport de Matière  
et  
Réaction aux interfaces et en solution**

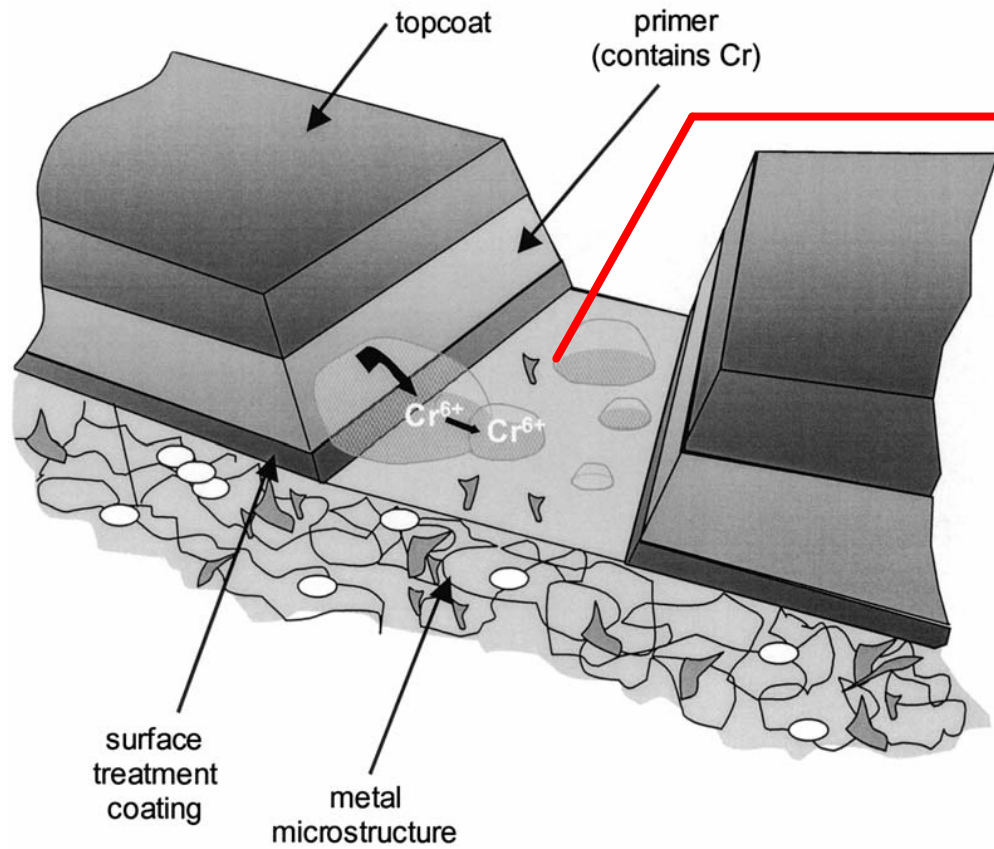


R. Oltra et coll (LICB Dijon).

Modéliser - prévoir

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SHM



1 cm

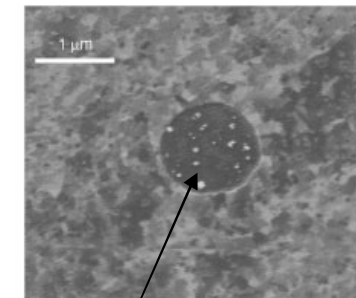
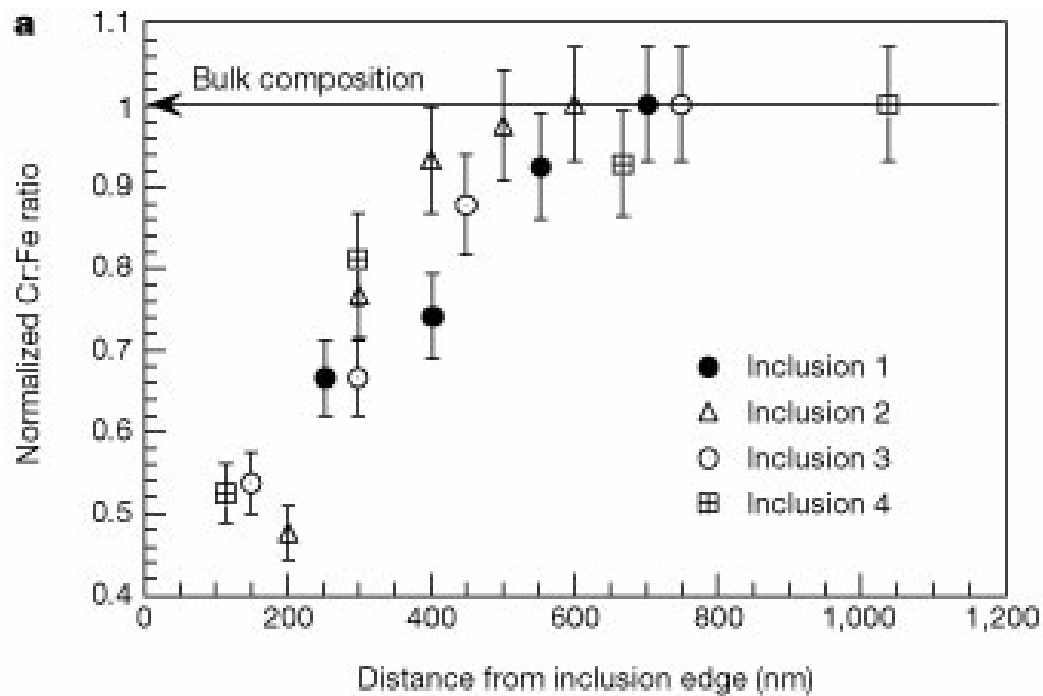
Capteur SENTINEL®

BAE Systems

Effet cicatrisant (self-healing) des inhibiteurs (peintures)

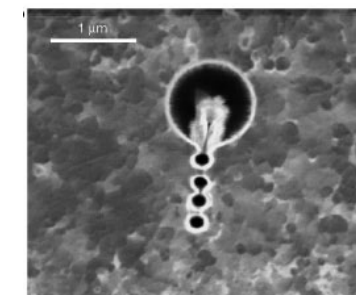
M.P. Ryan, D.E. Williams, R.J. Chater, B.M. Hutton, D.S. McPhail, Why stainless steel corrodes, *Nature* 415 (2002) 770–774.

Transmission des connaissances

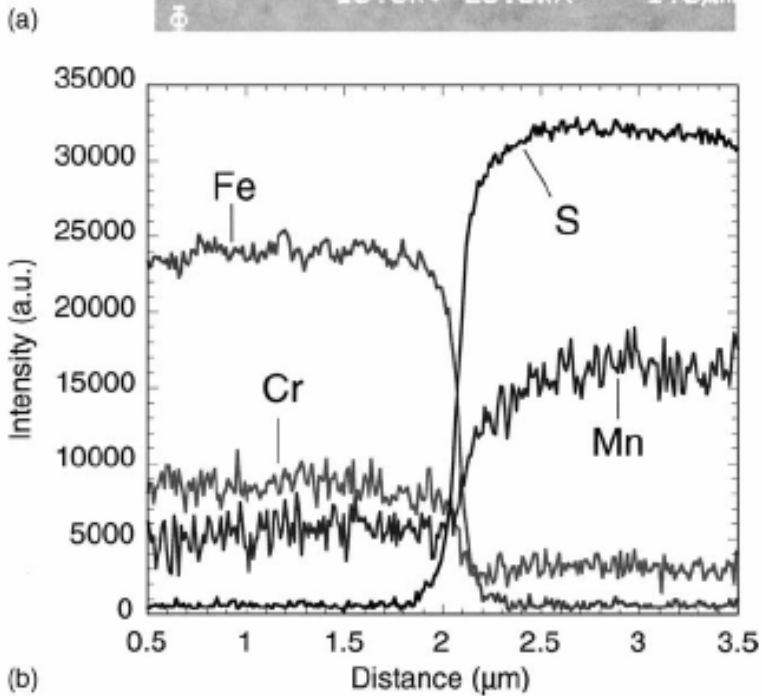
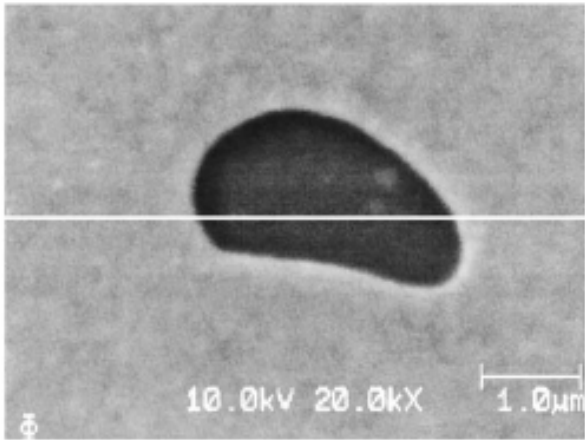


MnS(Fe, Cr)

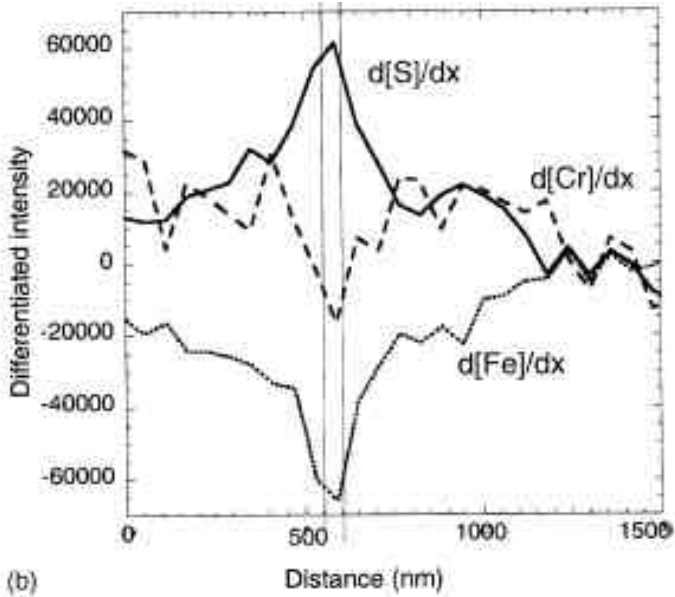
→ déchromisation



Transmission des connaissances



*Microstructure de coulée*

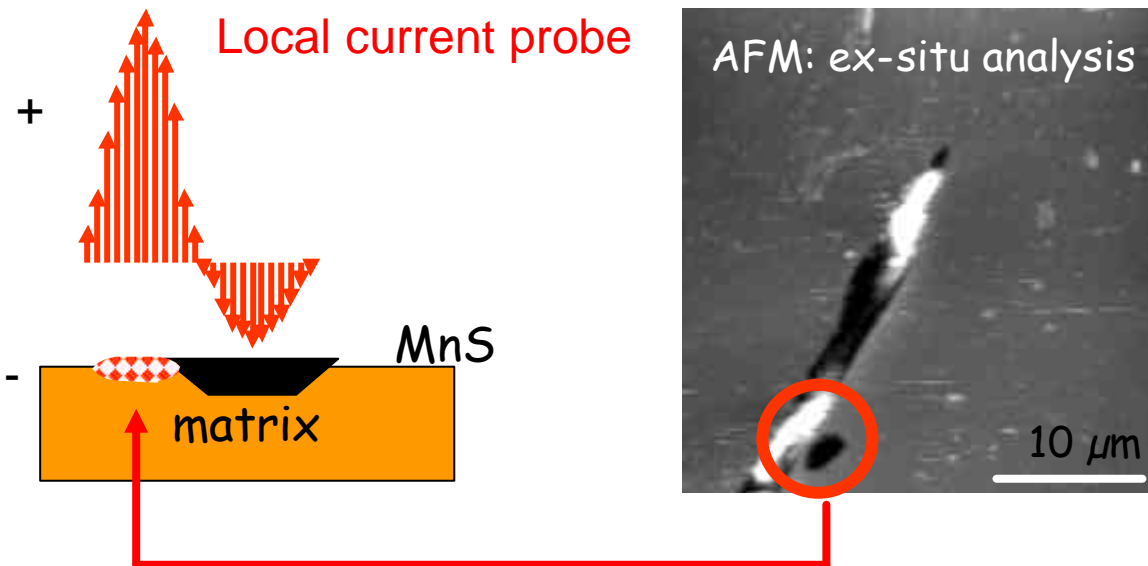


*No Cr depletion*

**Microstructure de coulée (pas –ou très rare – déchromisation)**

**Microstructure de vieillissement / transformation**

Transmission des connaissances



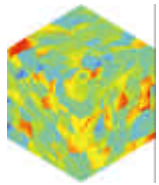
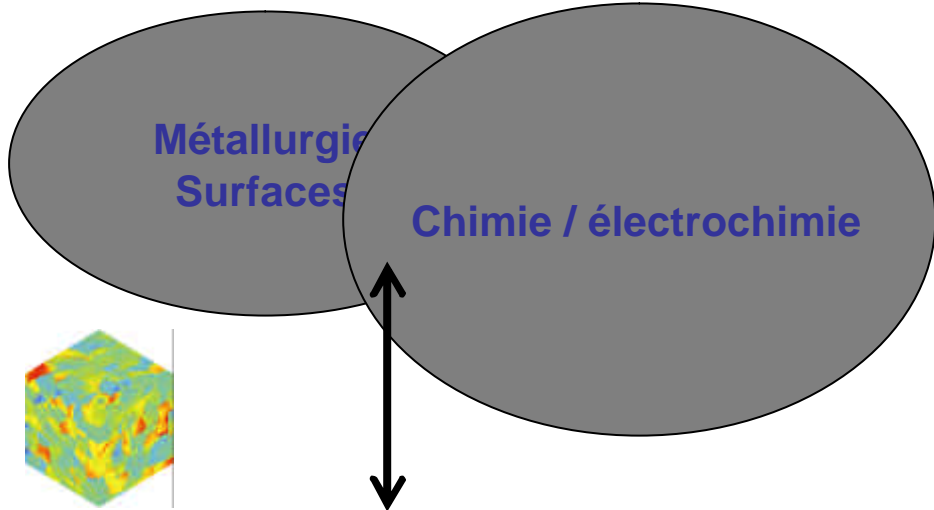
anodic currents on the surrounding matrix due to local depassivation by sulphur contamination

B.Baroux, d.Gorse, R.Oltra

*Pitting corrosion of stainless steel: The importance of being a metallurgist*

*Critical Factors in Localized Corrosion IV*, Eds.S. Virtanen, P. Schmuki, and G. S. Frankel, The Electrochemical Society, PV 2002-24, (2002), p.335-346

A.Bases	B.Exemples emblématiques	C. Défis	D. Conclusion
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*Échelle moléculaire*

*Interface: réactions élémentaires*

*Sondes locales in situ*

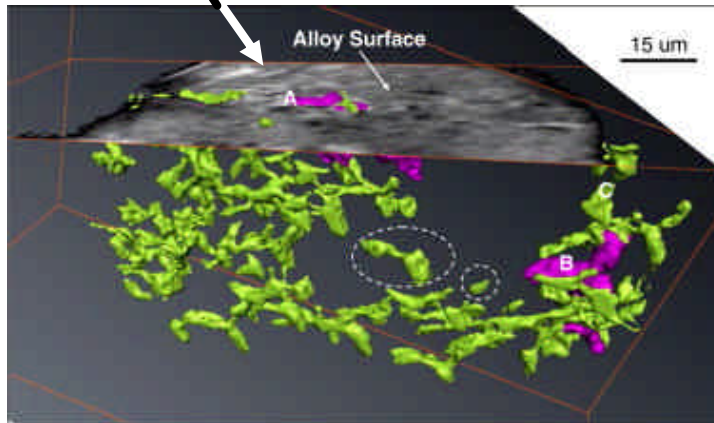
*Transport de matière*

**Couplage microstructure 2D à l'échelle élémentaire**

? *Interaction 2D*

? *3D*

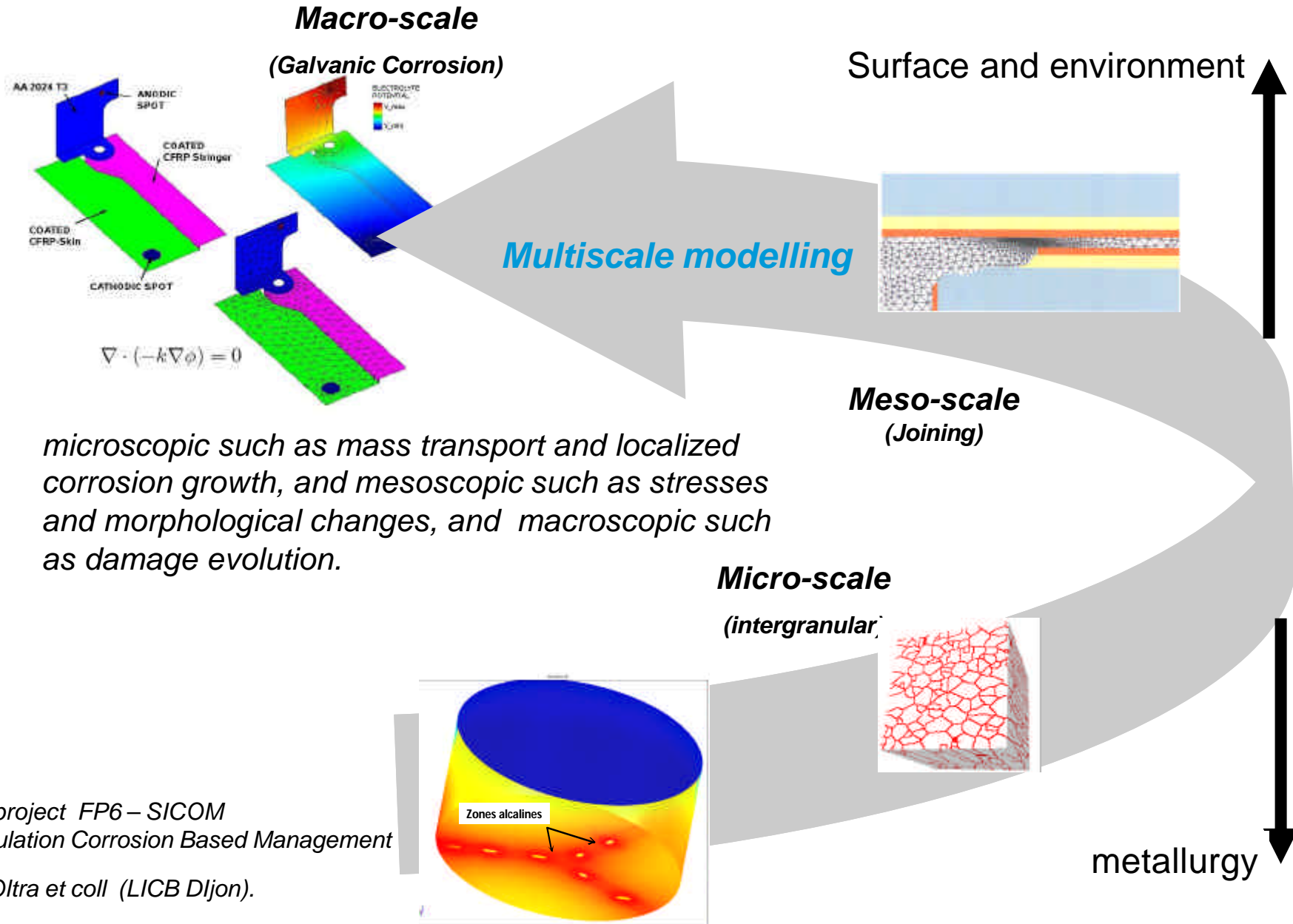
? *cinétique*



*(environnement humide)*

X-Rays tomography (Corr;Sci. 2012)





EU project FP6 – SICOM  
Simulation Corrosion Based Management

R.Oltra et coll (LICB Dijon).



- "Corrosion et protection des métaux", G. Béranger, F. Dabosi, Les Houches, 1981.
- "Corrosion des matériaux à haute température", G. Béranger, J.-C. Colson, F. Dabosi, C. Lemaître, J.-A. Petit, Piau-Engaly, 1885.
- "Traitements de surface et protection contre la corrosion", S. Audisio, M. Caillet, A. Galerie, H. Mazille, Aussois, 1987.
- "Caractérisation des surfaces : matériaux, méthodes et technologies", R. Caplain, D. David, St-Valéry sur Somme, 1988.
- "Les aciers inoxydables", B. Baroux, G. Béranger, J. Lefèvre, P. Pedarre, St-Jorioz 1989.
- "Corrosion sous contrainte : phénoménologie et mécanismes", D. Desjardins, R. Oltra, Ed. de Physique, Bombannes, 1990, 870 p.
- "La corrosion localisée", F. Dabosi, G. Béranger, B. Baroux, Ed. de Physique, Banyuls, 1992, 697 p.
- "Biodétérioration des matériaux", C. Lemaître, N. Pébère, D. Festy, St-Avit, 1995.
- "Revêtements et traitements de surface : Principe et fonctionnalité, durabilité et procédé", S. Audisio, M. Caillet, A. Galerie, H. Mazille, Ed. Presses Polytechniques et Universitaires Romandes, 1998, 763 p.
- "Prévention et lutte contre la corrosion - Une approche scientifique et technique", B. Normand, N. Pébère, C. Richard, M. Wéry, Ed. Presses Polytechniques et Universitaires Romandes, Coll. METIS Lyon Tech, 2004, 775 p.
- "Anticorrosion et durabilité dans le Bâtiment, le Génie Civil et les Ouvrages Industriels", Ed. des Presses Polytechniques et Universitaires Romandes, Coll METIS Lyon Tech, 2010, 744 p.

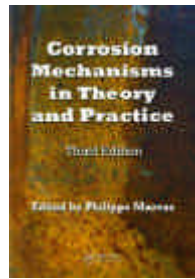
**ThemaCorr 2013****Mesure de la corrosion :  
De la conceptualisation à la méthodologie**

29 Septembre au 4 Octobre 2013  
Haute Corse - Furiani

TRAITE DES MATERIAUX



**Traité des matériaux Vol 12 : Corrosion et chimie de surface des métaux** (552 p),  
Editeur D. Landolt, Presses Polytechniques et Universitaires Romandes  
(1993)



**Corrosion mechanisms in theory and practice** ( 941p)  
Editeur P. Marcus, CRC Press (2011)



**Corrosion** (2 volumes d'environ 1000 p),  
Editeurs L.L. Shreir, R.A. Jarman, G.T. Burstein,  
Editions Butterworth - Heineman (1994)  
Vol 1 : Metal / environment reaction  
Vol 2 : Corrosion control



**Surface Electrochemistry: A Molecular Level Approach** (1014p)  
John O'M. Bockris , Shahed U.M. Khan  
Plenum Press ( 1993)



**Les aciers inoxydables** (1011 p)  
Editeurs P. Lacombe, B. Barroux, G. Beranger,  
Les Editions de physique (1990)



**Corrosion localisée** (697 p),  
Editeurs F. Dabosi, G. Beranger, B. Barroux,  
Les Editions de physique (1994)



**Corrosion sous contrainte** (870 p),  
Editeurs D. Desjardins, R. Oltra,  
Les Editions de physique (1992)



**Prévention et lutte contre la corrosion** (798p)  
Editeurs B. Normand , N. Pébère , C. Richard , M. Wéry  
PPUR (2004)



**Centre Français de l'Anticorrosion (CEFRACOR)-**  
[www.cefracor.org](http://www.cefracor.org)



**Corrosion doctors:** <http://www.corrosion-doctors.org/>