Introduction in the topic of passivation

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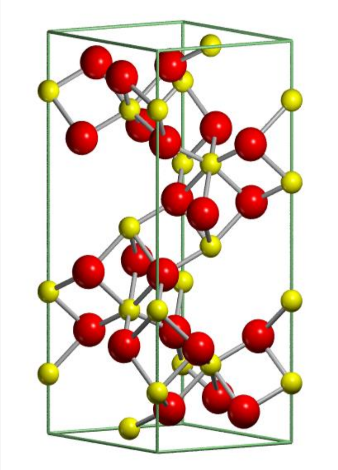


INSIGHT Fachtagung, Swiss Medtech Veranstaltung

16.02.2021

Outline

- **Introduction about fundamentals of passivation**

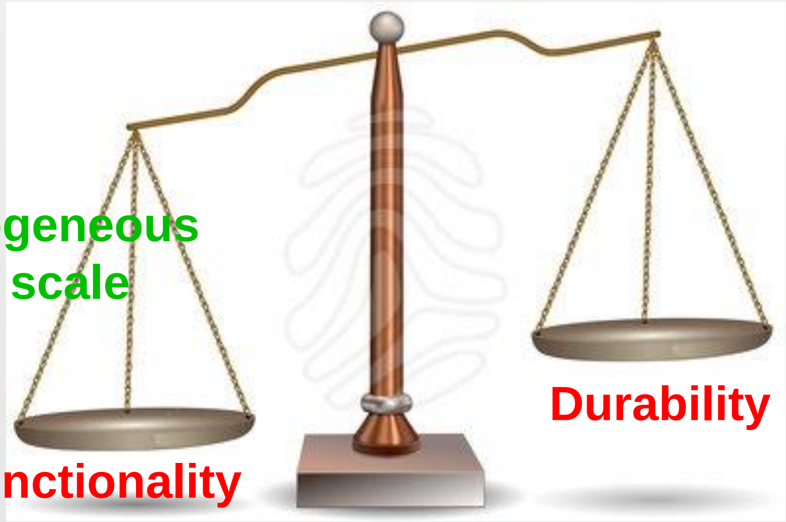
- **Surface analysis of nm-thick “passivated” films**

  - Principle of X-Ray Photoelectron Spectroscopy
  - Passive films on Steel

- **Facts about localized corrosion resistance**

  - Corrosion resistance and alloying elements

- **Summary**



Electrochemistry at metallic surfaces

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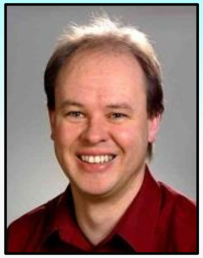
Core competences of the group

- Passivation of reactive metal surfaces
- Electrochemical characterizations
- Biocompatibility of functional metallic surfaces



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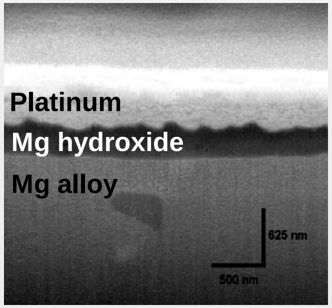
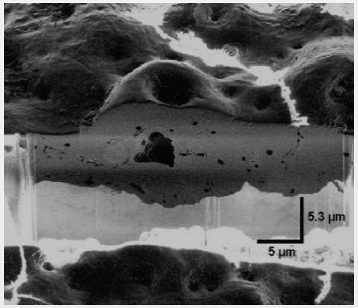
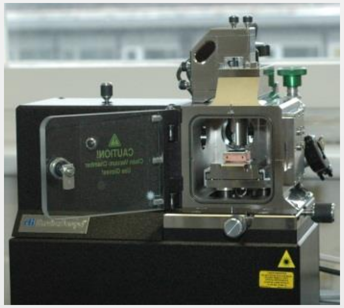
Micro and Nano Electrochemistry	Electrochemical surface Modification	Surface analytical characterizations
N. Ott / J.Kollender	**M. Khokhlova / R. Han**	**R. Hauert / C. Cancellieri**







FIB sections: Ion beam images

- Microcapillary electrochemistry
- SEN nanoelectrochemistry
- Synchrotron “electrochemical“ tomography

- EPMA, SEM (EDX)
- Anodizing
- Electrodeposition
- Photo-electrochemistry

- Environmental AFM
- XPS /AES spectroscopies
- Synchrotron methods (HAXPES / EXAFS)

What is passivation !!!

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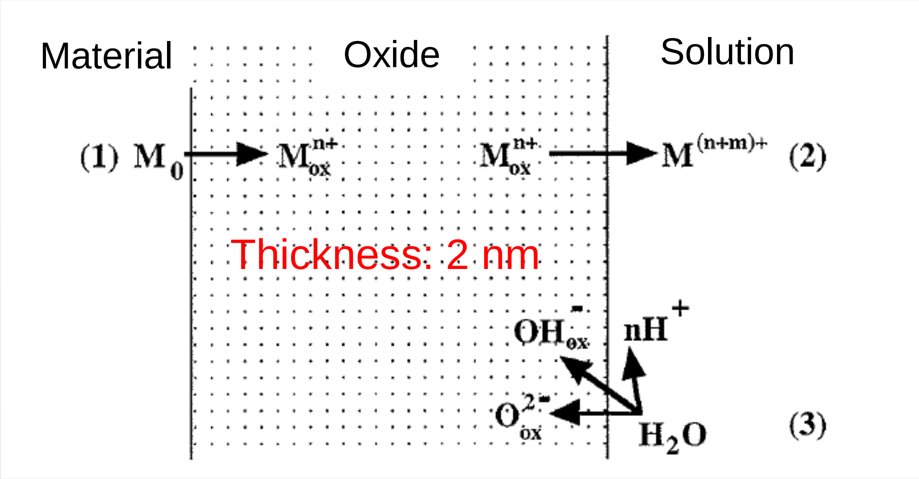
Material science

- Spontaneous formation (milliseconds in atmospheric / aqueous environment) of a nm-thick protective layer
- **Thickened by Laser Treatments**



Chemical passivation

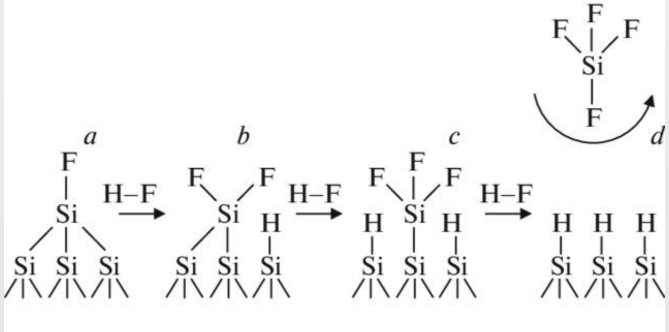
- Reinforcement (homogenization) of an existing nm-thick oxide layer

Reactions involved

1) Metal oxidation
2) Metallic ion dissolution
3) Water splitting and anion incorporation

Microelectronics

- Hydrogen surface termination of silicon to avoid formation of a nm-thick oxide



Iron oxide thermodynamic stability

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Passivation is linked to the possibility to form stable oxide.

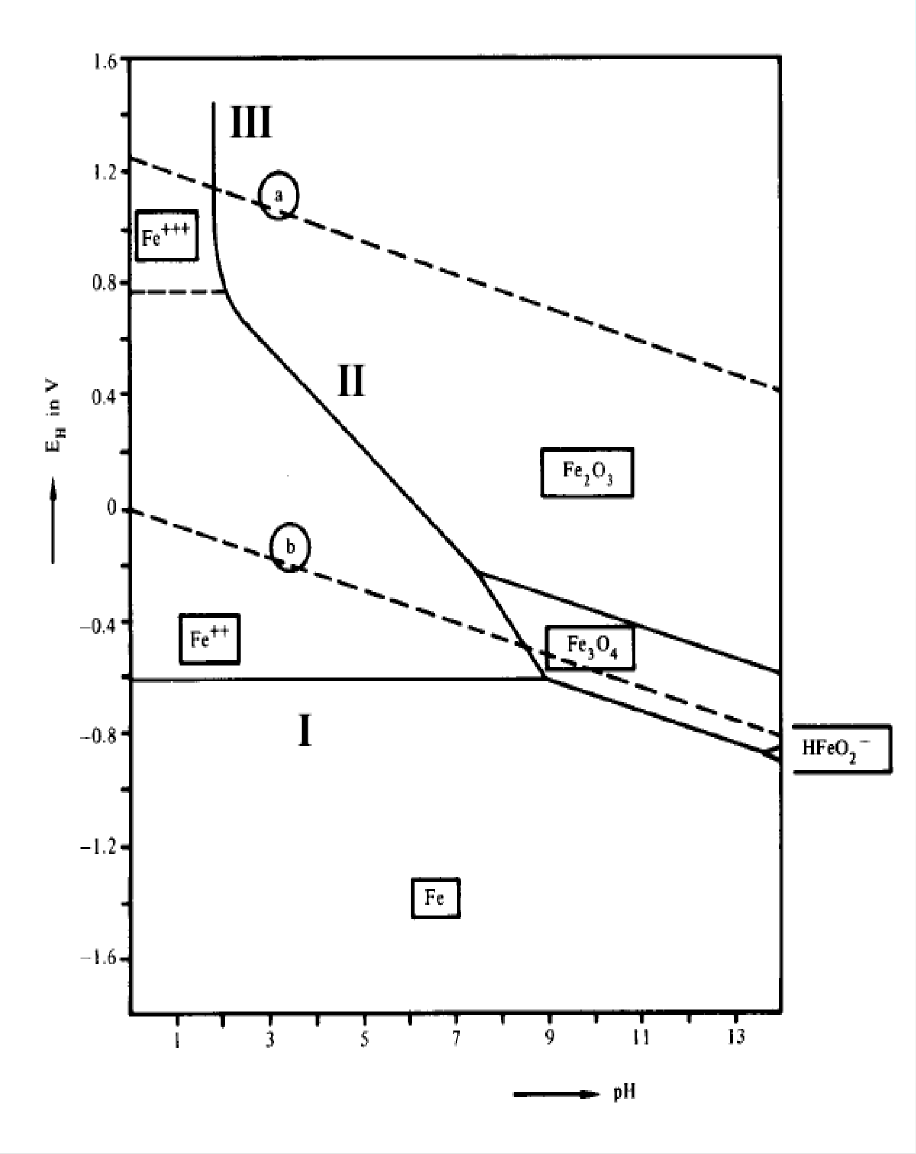
Your first reflex should be to consult the relevant **Pourbaix diagram (e.g: iron in water):**

Reaction considered:

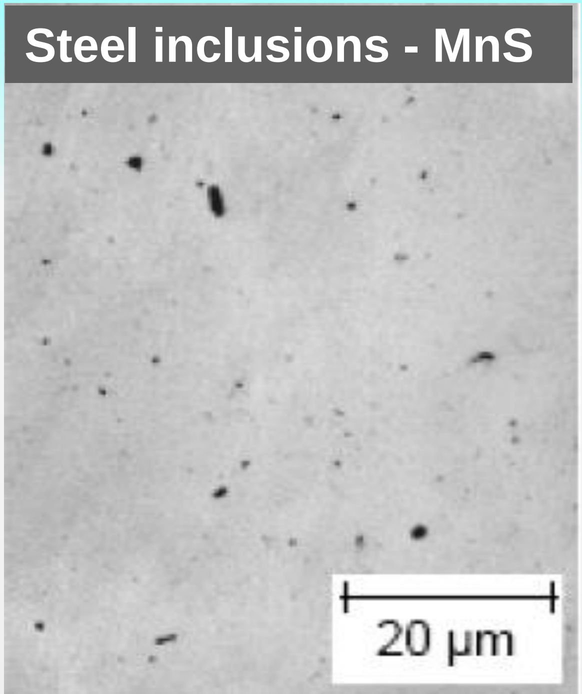
I: Electrochemical equilibrium (Redox potentials)

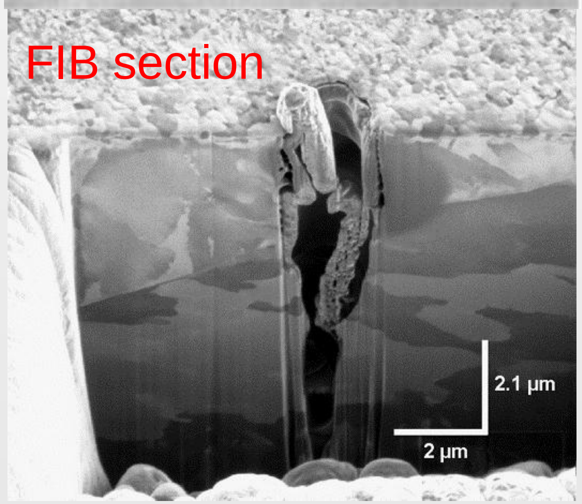
II: Electrochemical equilibrium involving reaction with water

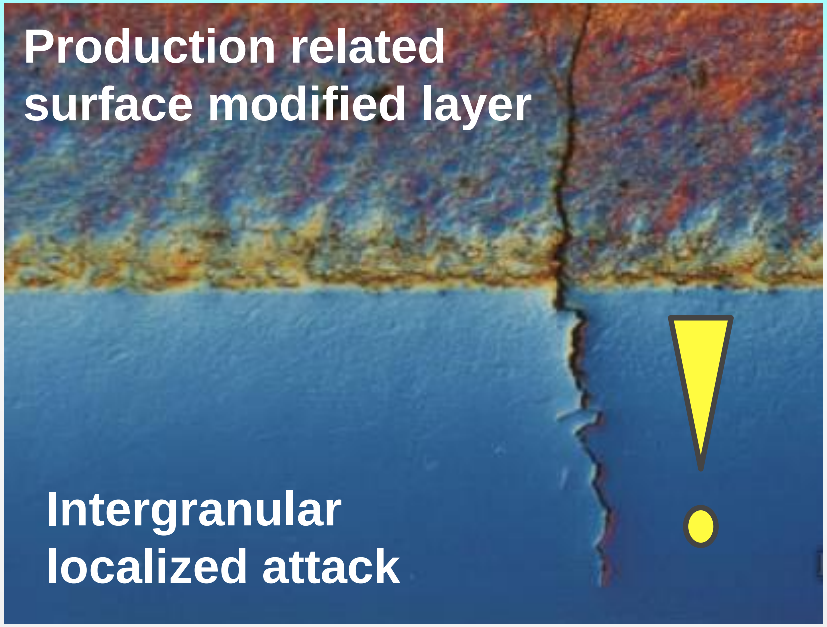
III: Chemical equilibrium

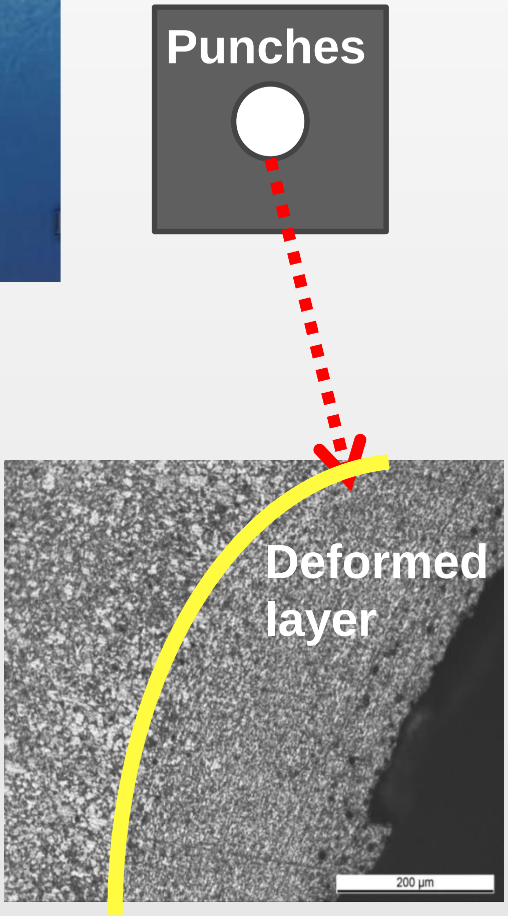


Complex microstructure and surface defects





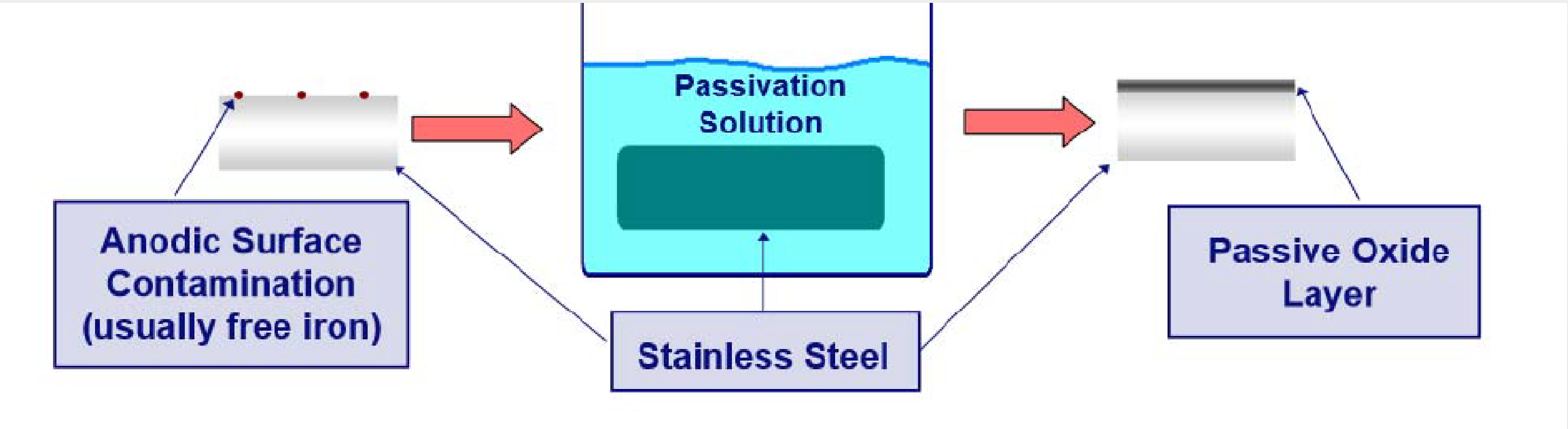




Acidic chemical treatment

What can be reached depending from natural passive film stability ?

- Etching/cleaning (for low alloyed steel)
- Alloying element enrichment in oxide (around the natural passivation threshold)
- Improved corrosion resistance / removal of surface defects
- Oxide surface functionalizing
- Surface cleaning (Ti alloys)



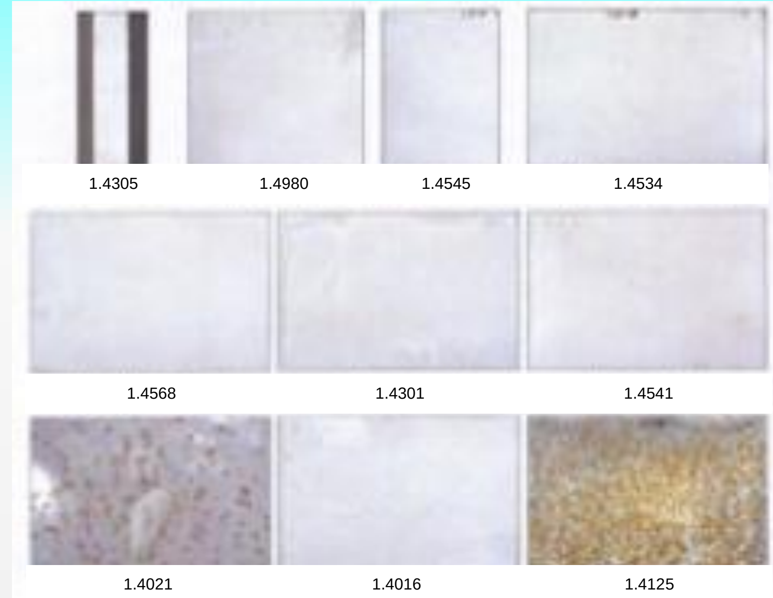
Classical salt spray testing

- Corrosion management
  (failure analysis network @ Empa)

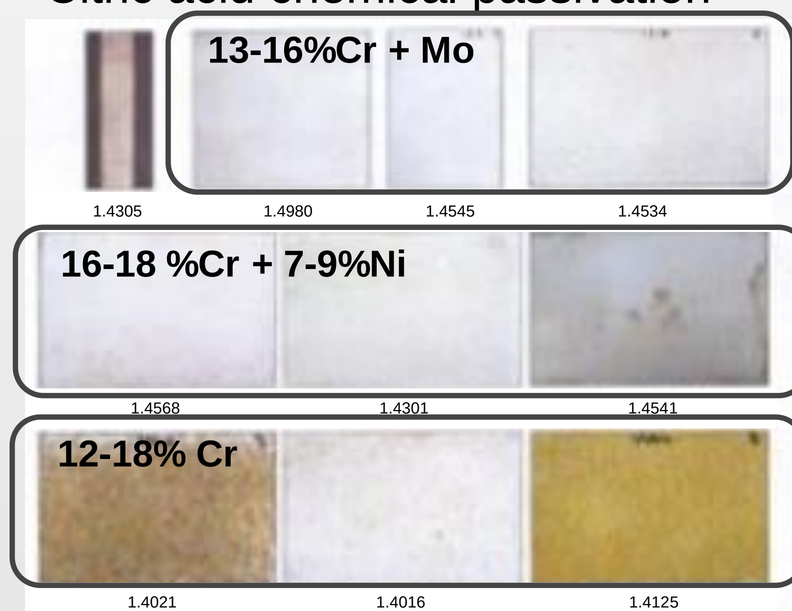
- Accelerated corrosion tests

condensation-water	(EN ISO 6270-2)
ditto + SO_2	(EN ISO 6988)
salt spray test	(EN ISO 9227)

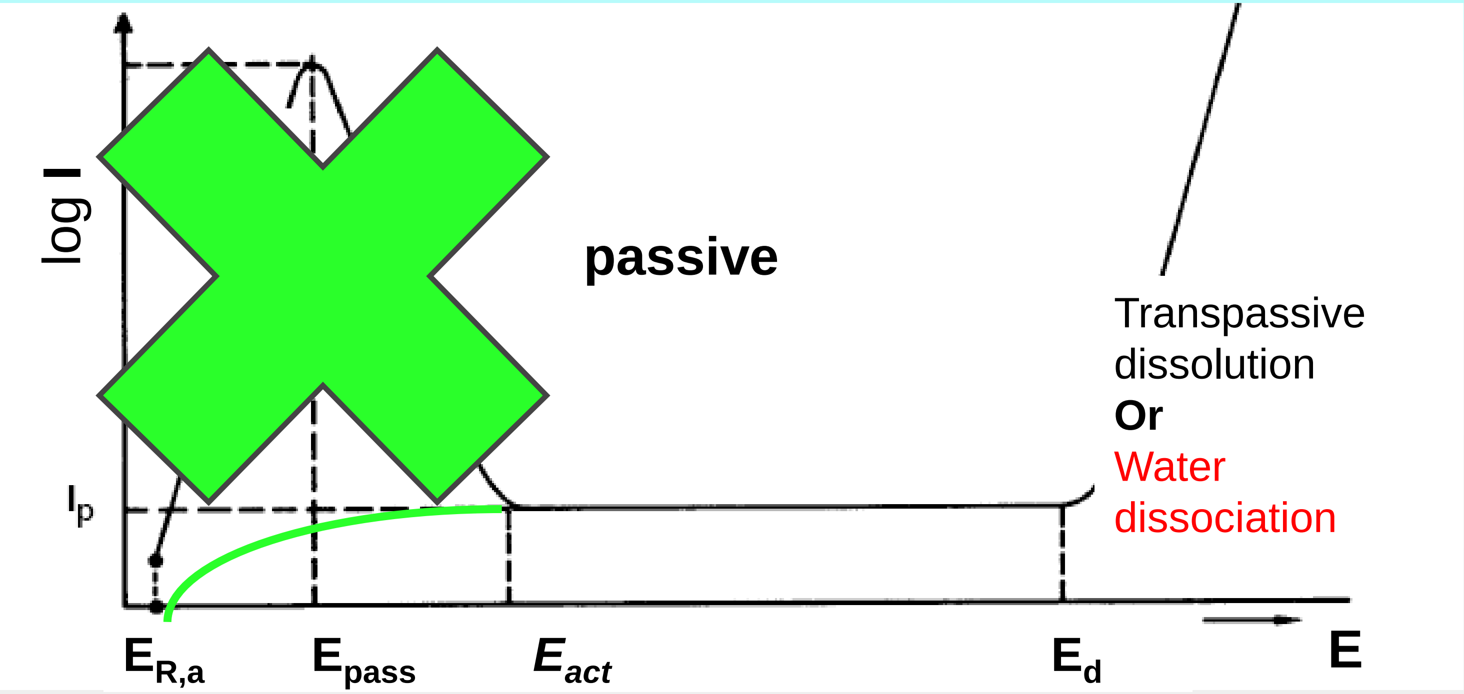
Nitric acid chemical passivation



Citric acid chemical passivation



Passivation: important parameters



$O_2 + 2H_2O + 4e^- \;=\; 4OH^-$ **$E_{rev,O2}$ = 1.23 - 0.059 pH [V]**

On an anodic polarization measurement, following domains are important:

Active: very rapid current increase (charge transfer controlled)

Active–passive transition: order of magnitude decrease of current

Passive: current in the microampère/cm^2 domain, stable surface

Most used passive metals

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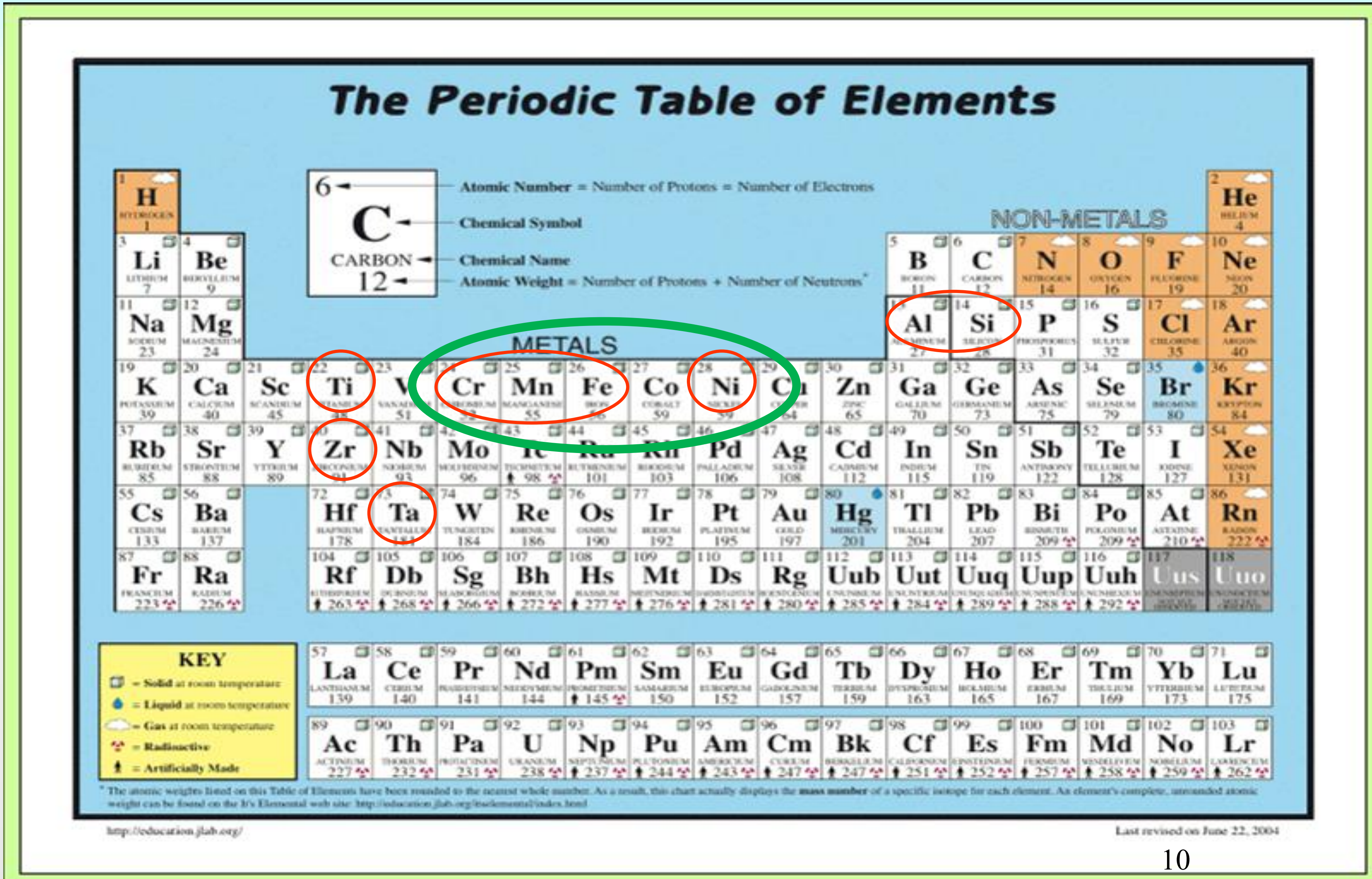

X-Ray photoelectron spectroscopy

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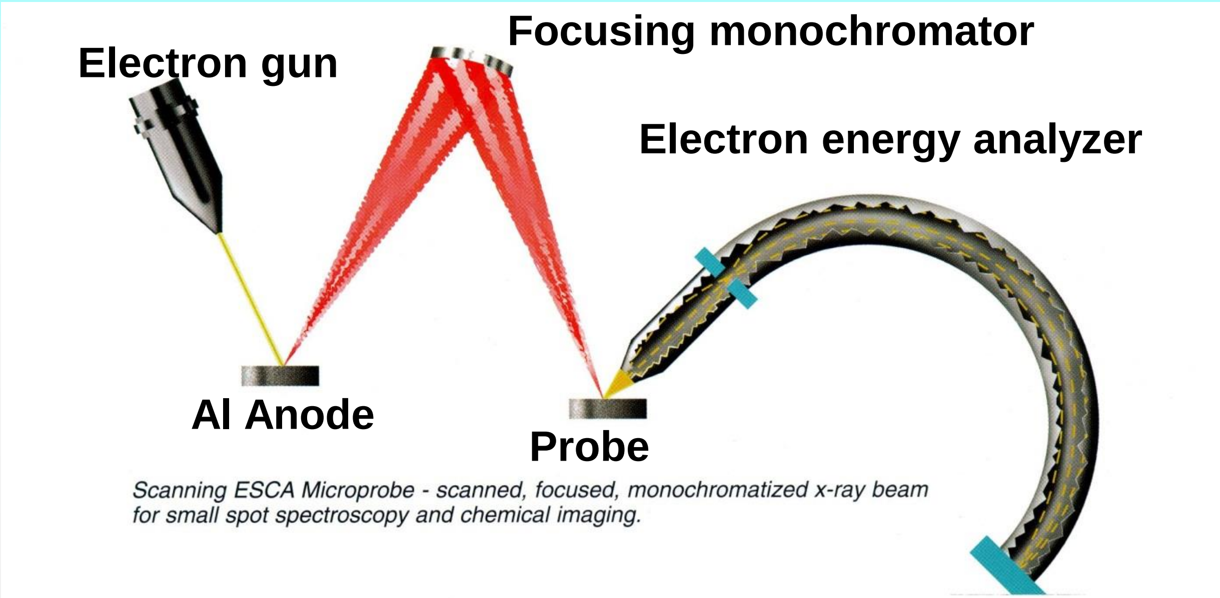

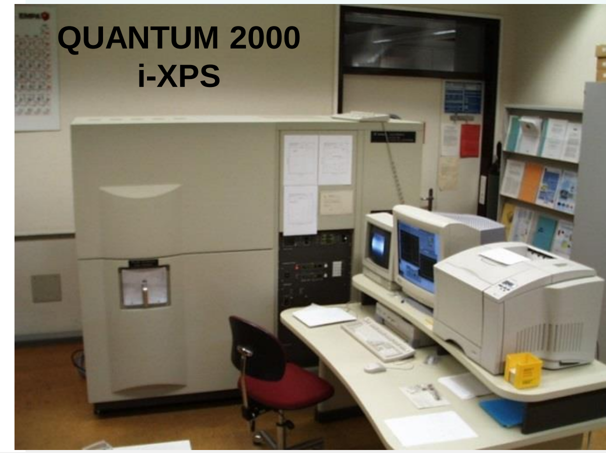

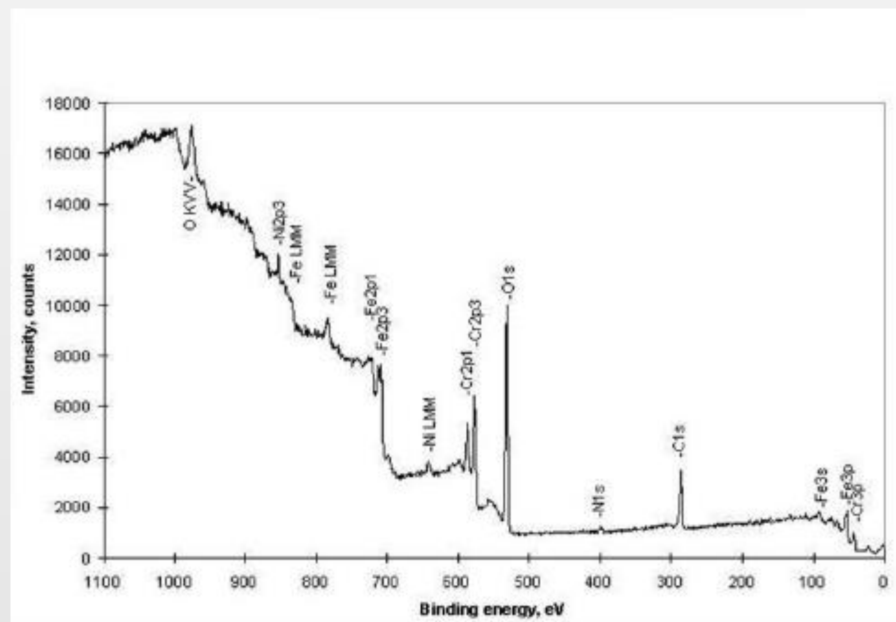

Scanning XPS (ESCA):

Focused monochromatized X-Ray source for point analysis and chemical mapping

Measurement:

- **All elements except H**
- **Measurement depth ca. 2-4 nm (inelastic mean free path)**

Surface analysis : XPS and Auger spectroscopies

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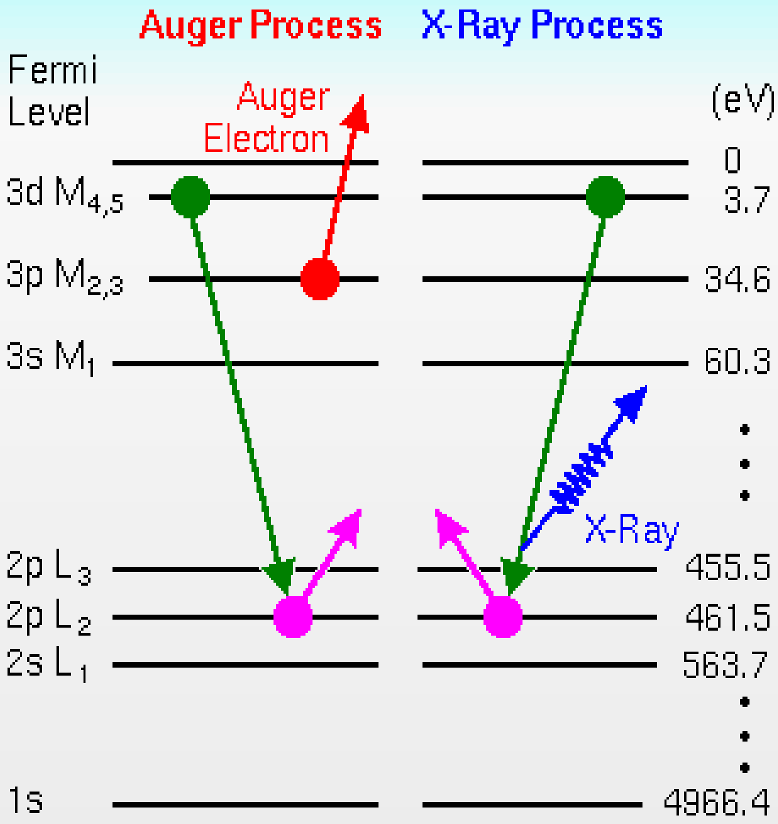

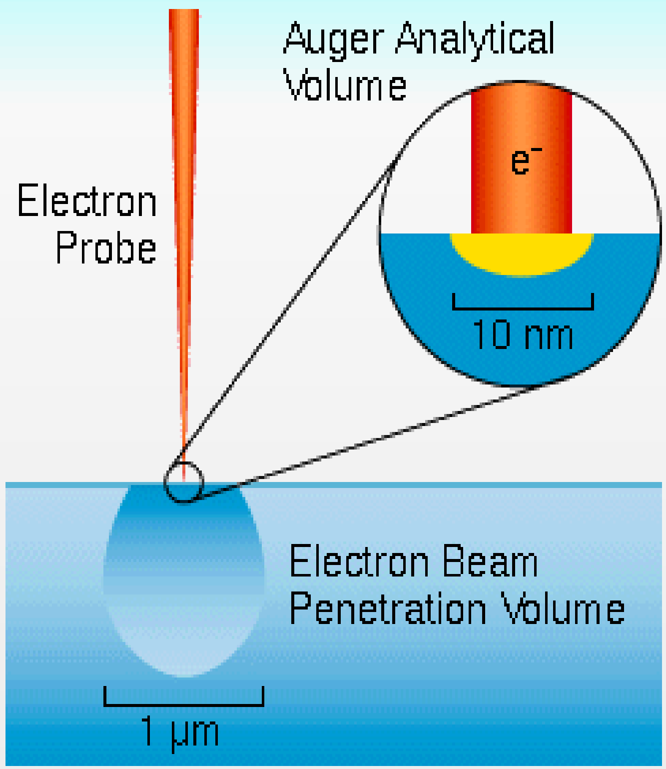

- Electron energy is element specific

- AES with focused electron beam (good lateral resolution)

- XPS poorer lateral resolution because of the X-Rays but easier access to chemical information

Where is the chemical information ?

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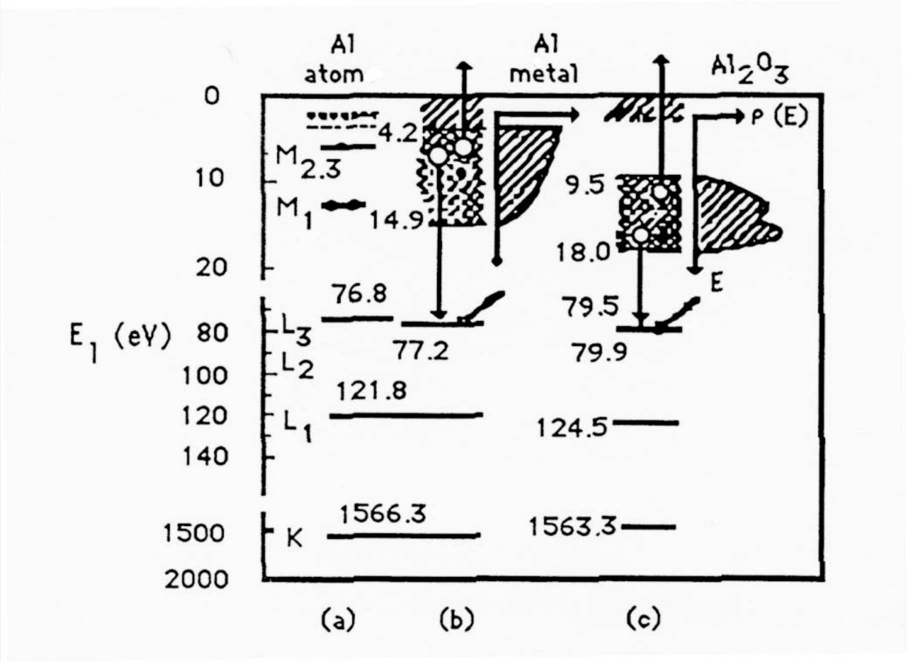
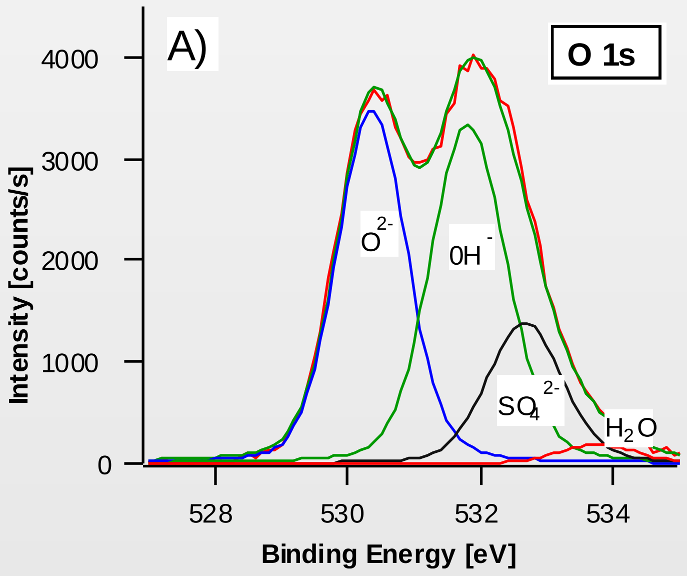
- Oxidation state can be characterized by energy shifts because of the different amount of electrons surrounding an atom in ions
- Oxides and hydroxide can be very well distinguished because the influence of the proton (H^+) on O^{2-} energy level is stronger than the influence of the surrounding metallic ions.





XPS spectra of chromium 2p level

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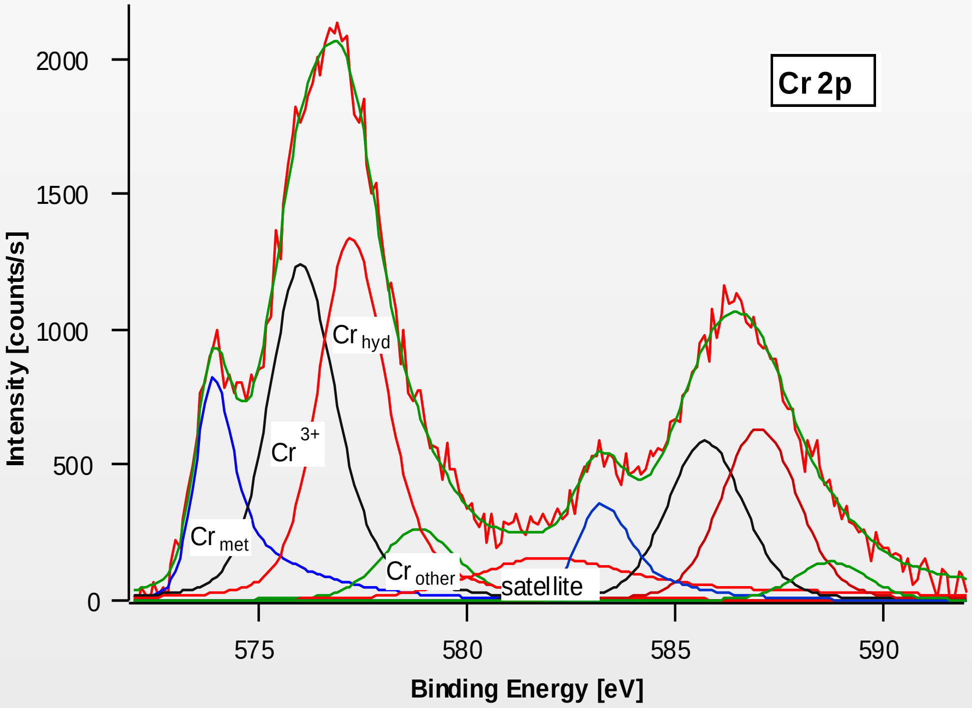
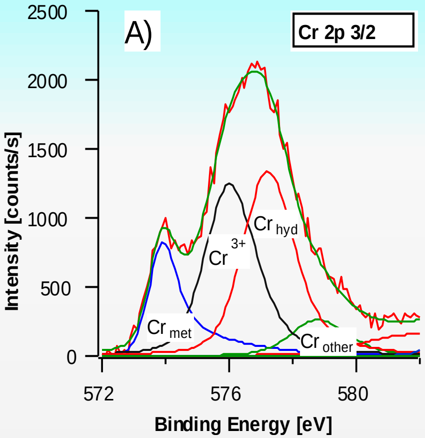
Fe25Cr alloy passivated at 0.5V SHE during 5 minutes (solution: 0.1M H_2SO_4 + 0.4M Na_2SO_4).

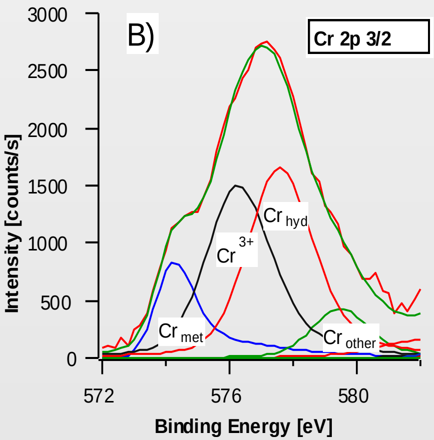




Detail of the Cr 2p3/2 peak as a function of the X-Ray source used:

a) Al ka monochromatized, pass energy 5.85 eV

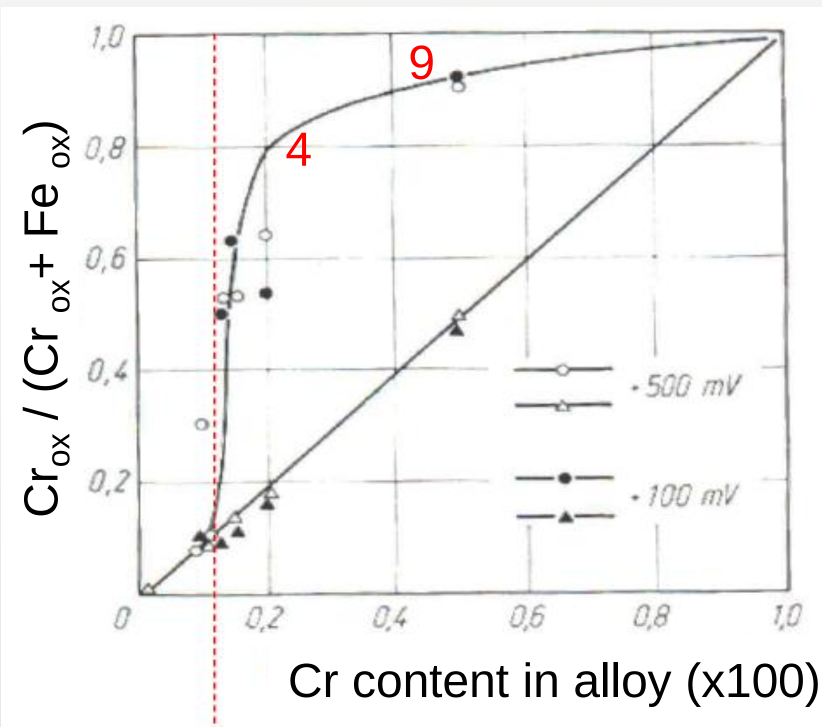
b) Al ka standard, pass energy 5.85 eV

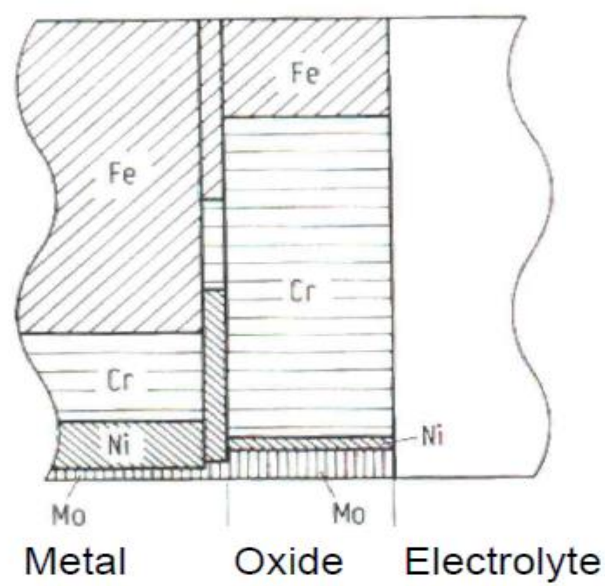


Large amount of Chromium 3+ in oxide and hydroxide form is found in the passive film

XPS: passivation of stainless steel

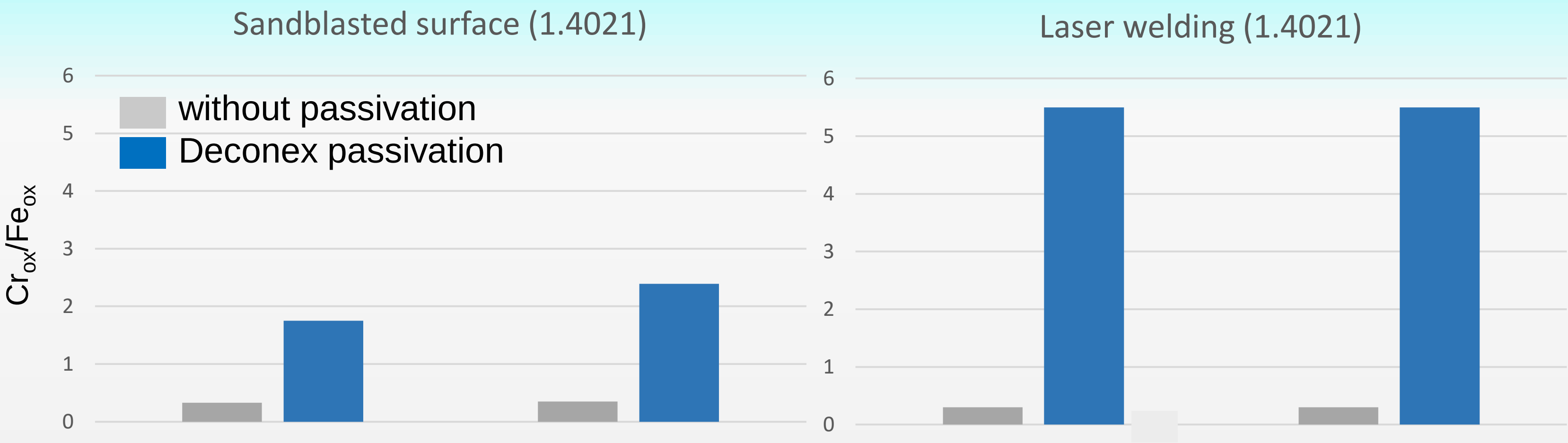
- **Chromium** is the important element to build a stable passive film (an amount of 12% is necessary to reach is significant enrichment in the passive layer in acidic media)
- Often quantified in terms of $Cr_{ox}/(Cr_{ox} + Fe_{ox})$ or $\mathbf{Cr_{ox}/Fe_{ox}}$ ratio
- Ni and Mo are almost not present in the passive oxide film



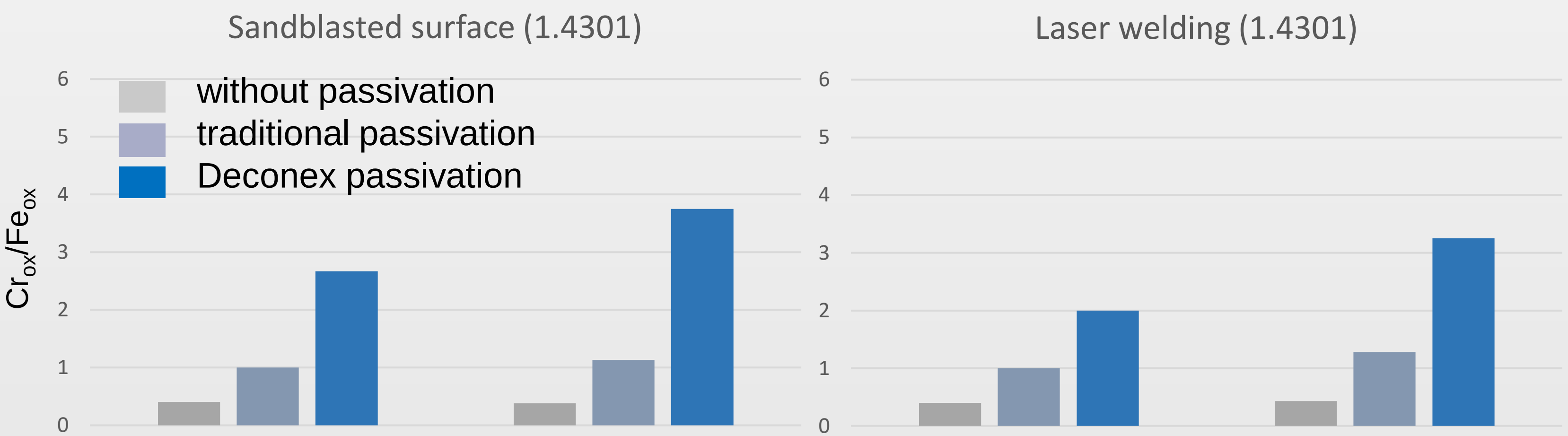


Chemical passivation: efficiency and industrial use

- Material: 1.4021 (X20 Cr13)



- Material : 1.4301 (X5 CrNi18-10)

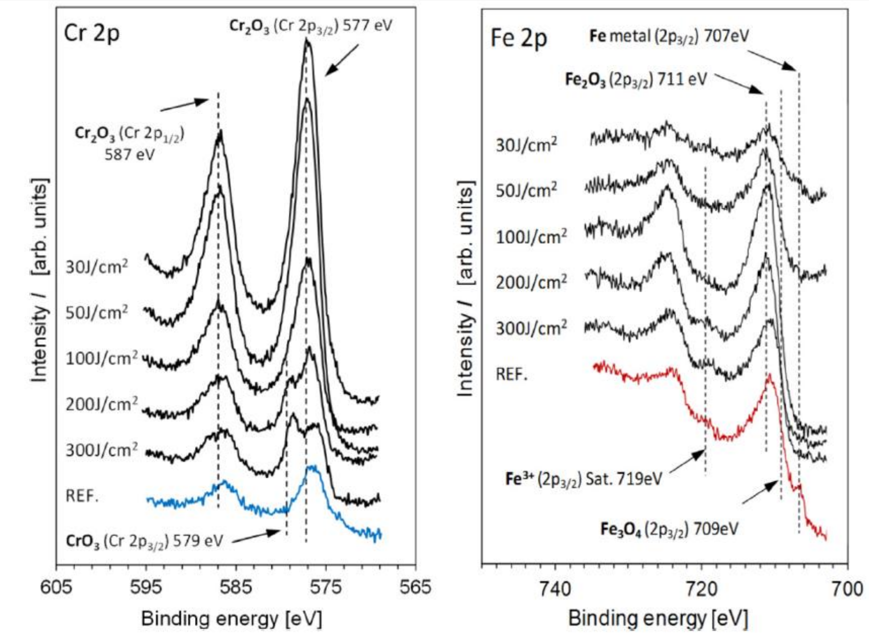


borer
advanced cleaning solutions

Laser induced surface oxidation ?

Stainless steel

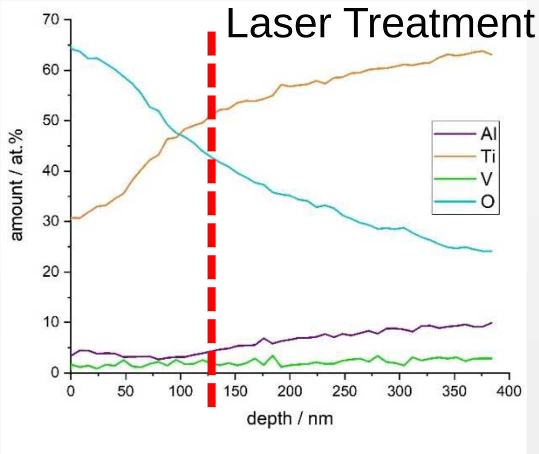
• Thicker surface oxide requiring modified chemical treatment to remove thicker Fe-oxide (or not if preferential Cr-oxidation can be obtained)



K. M. Łęcka et al. Journal of Laser Applications **28**, 032009 (2016)

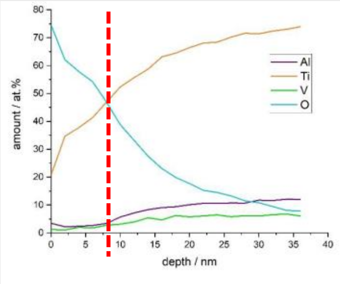
Titanium and Ti-alloys

• Extreme case due to high oxygen affinity of Ti crystal structures



Surface treatment	Oxide thickness
Machined	8 nm
Laser treated	around 100 nm

Passive surface



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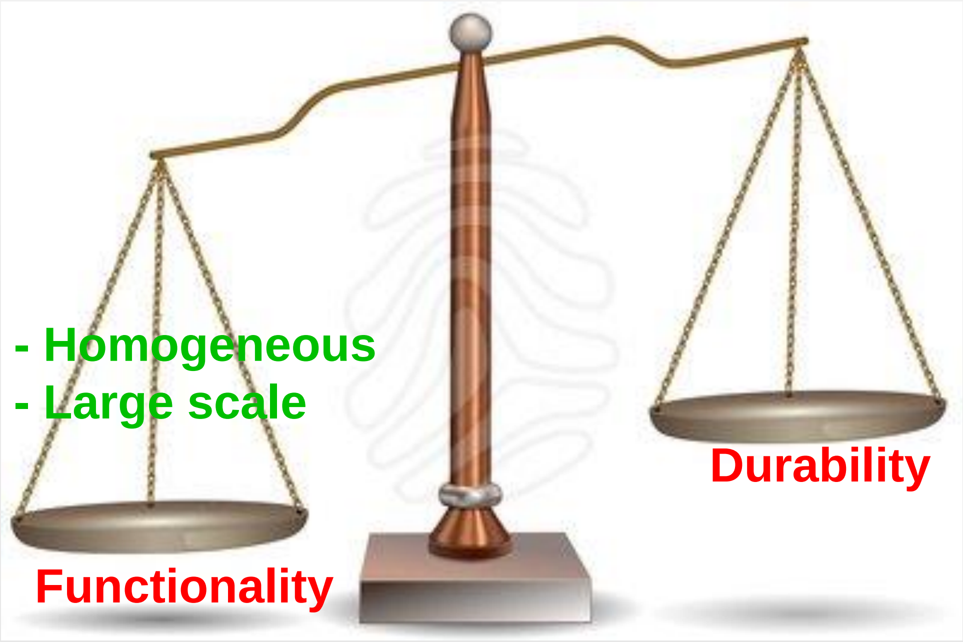
- Is an alloying element enrichment in the passive oxide sufficient ?

  - What about corrosion behavior of passivated surfaces ?

Electrochemical characterization of oxide breakdown behavior is necessary because a good passivation induces a risk of localized corrosion

- **Weakest spot**
- **Local methods**



Localized corrosion

For a passive metal to become susceptible to localized corrosion…

Two conditions have to be fulfilled:

1) Presence of aggressive anions (element: Cl, F, Br, I)

→ **local attack (dissolution) of the passive film**

2) The equilibrium potential of the material must be higher than a characteristic potential

→ **Pitting potential**

Pitting of Cr-Ni stainless steel in HCl

Important stages of localized attacks

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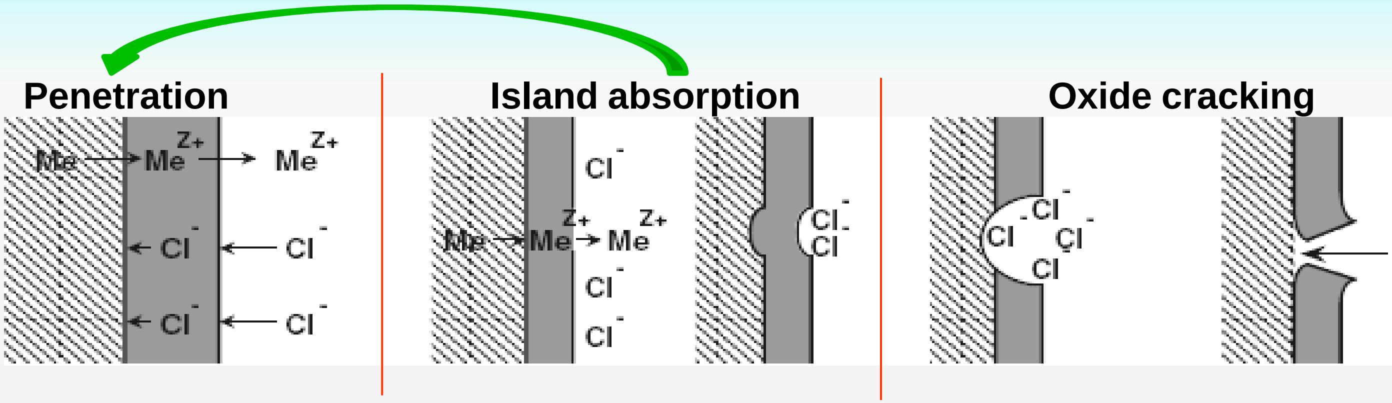
- **Pit initiation**



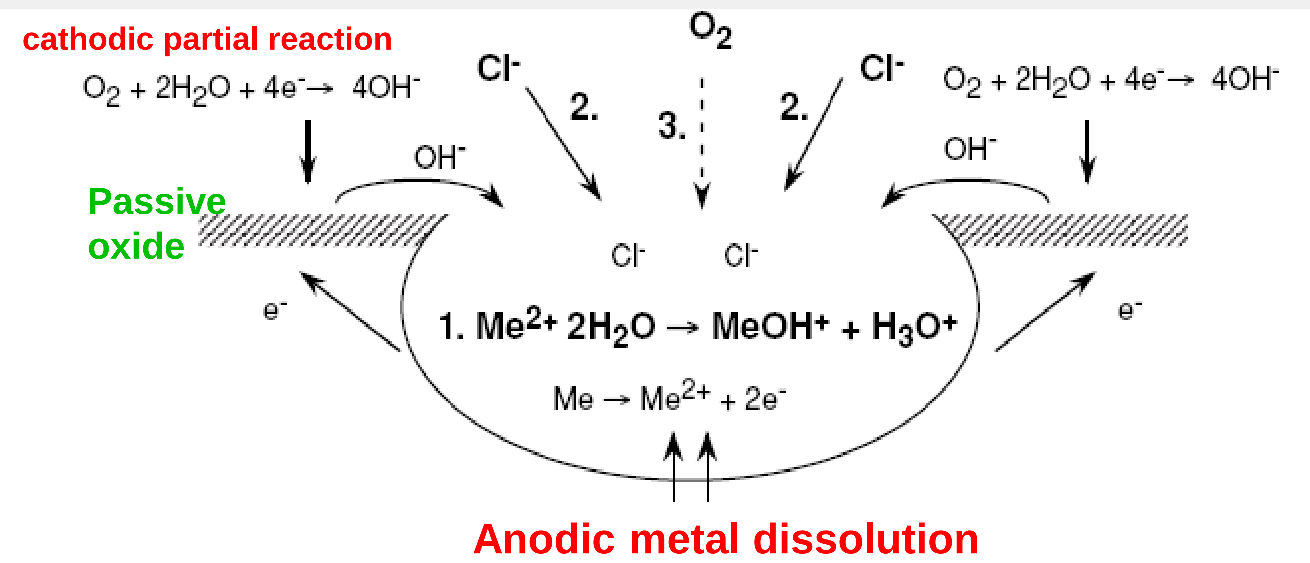
Increase

Cr_{ox} / Fe $_{ox}$ ratio

- **Metastable pitting**
- **Pit growth**

Increase

Stainless steel substrate alloying



Typical pitting potentials

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The base material influence:

• stability of the passive film /

or

• presence of defects

Pitting potential of different metallic materials in 0.1M NaCl, T= 25°C

Metal	Pitting potential (SHE)
Aluminum	-0.37
Nickel	0.28
Zirconium	0.46
18/8 CrNi steel (DIN 1.4301)	0.26
12% Cr steel	0.20
30% Cr Steel	0.62
Chromium	>1.0
Titanium	>1.0 (1M NaCl)

Really good localized corrosion resistance, if

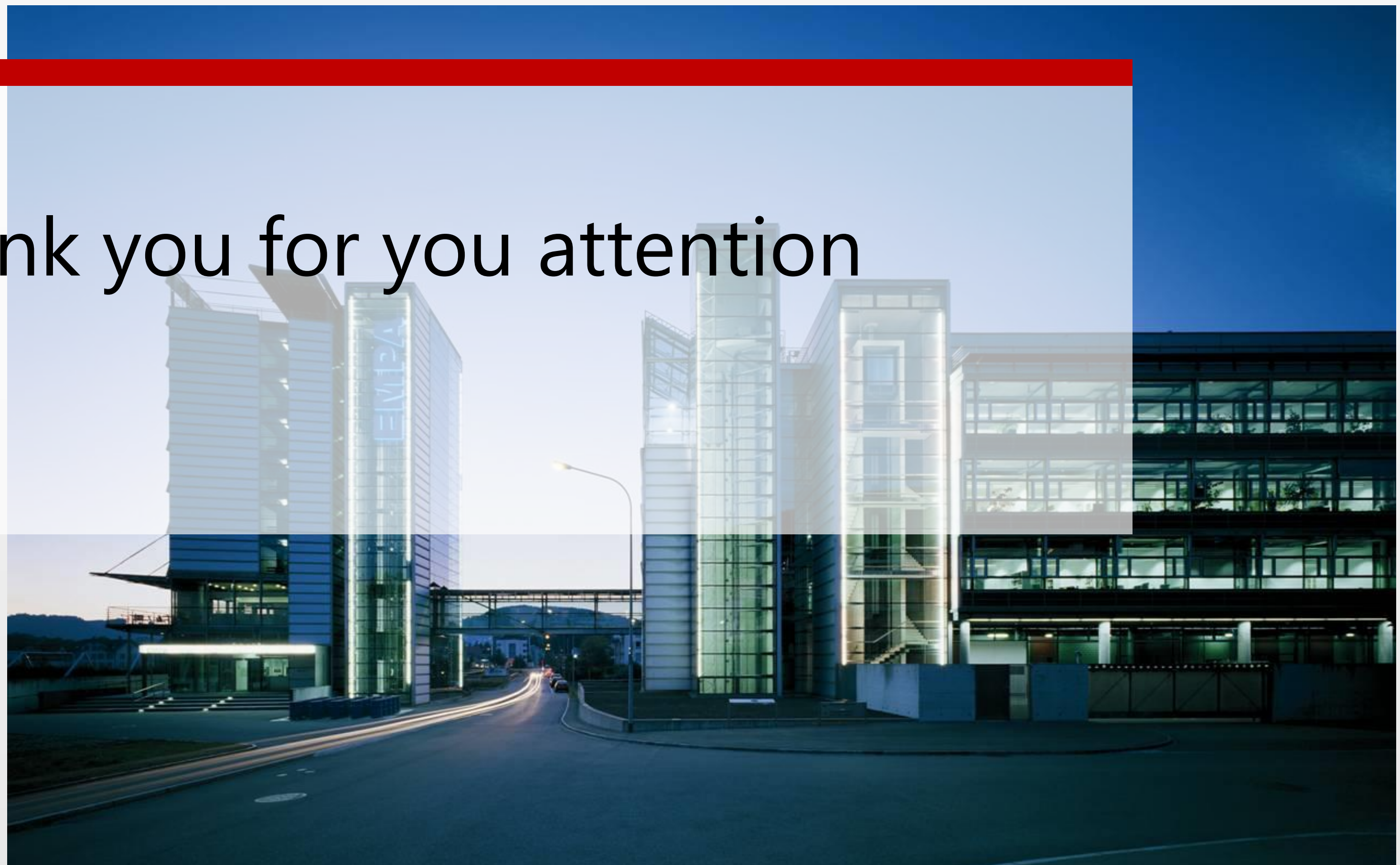
$O_2 + 2H_2O + 4e^- = 4OH^-$

Epit > $E_{rev,O2} = 1.23 - 0.059\ pH[V]$

Conclusions

- Corrosion resistance of steel (stainless steel) is obtained by chromium cation enrichment in the passive oxide with an alloy threshold value of 12%. This process happens naturally in acidic media
- Below this composition threshold value, only surface etching/cleaning effects can be obtained
- In this «transition» composition domain (around 12% Cr), additional strengthening/ functionalizing of the oxide can be obtained by a targeted acidic chemical passivation (increase Cr_{ox}/Fe_{ox} ratio)
- A really stable oxide on stainless steel in very acidic environment can only be obtained with high chromium alloy concentration. In this case, additional chemical passivation can only bring some surface functionalities
- Localized corrosion resistance in presence of chlorides ($E_{pit} > E_{rev,O2}$) is difficult to obtain by passive film engineering and is enhanced by adding slowly dissolving element like Molybdenum

Thank you for you attention



- Alloying element, corrosion resistance and field of application of various stainless steels

Advanced passivation characterization

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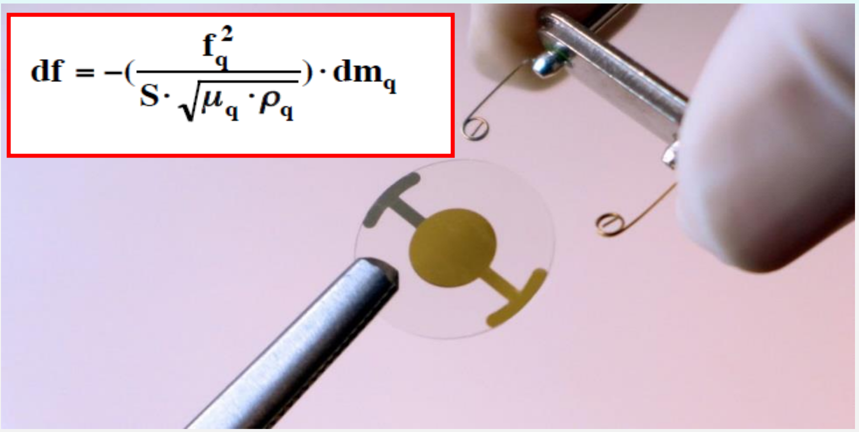
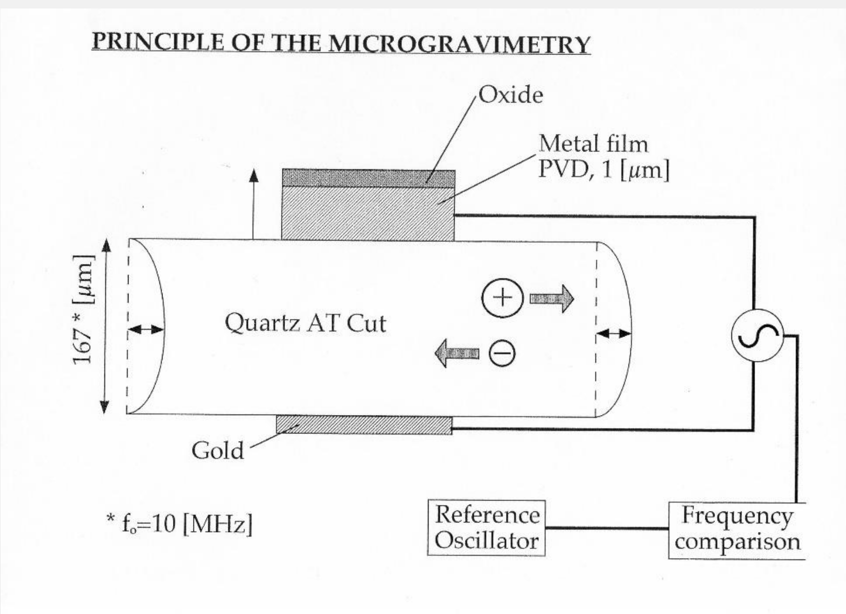
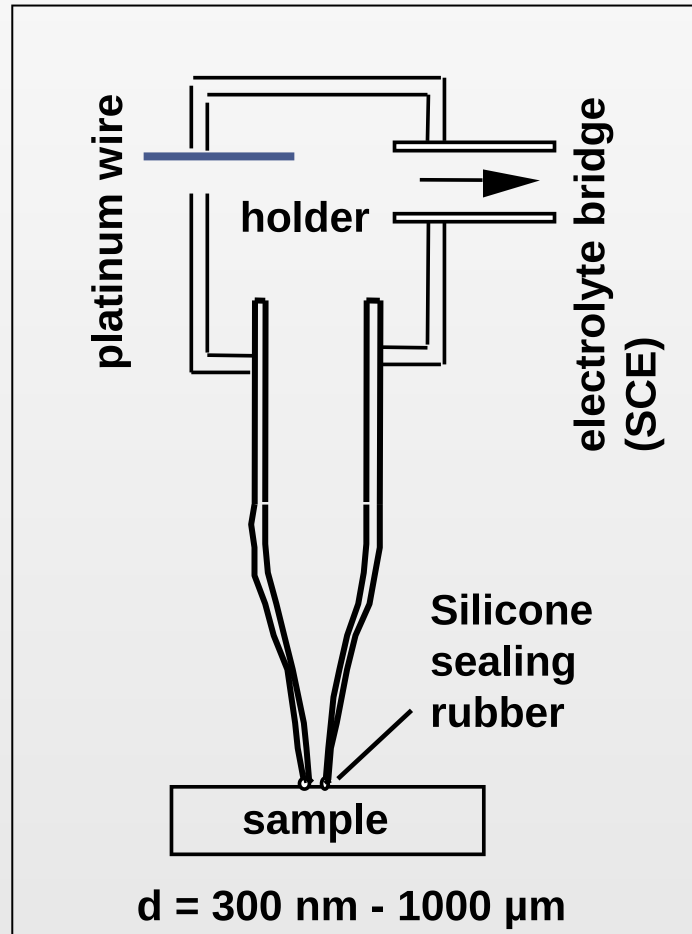
Oxide stability (EQCN)



$$df = -\left(\frac{f_q^2}{S \cdot \sqrt{\mu_q \cdot \rho_q}}\right) \cdot dm_q$$



Oxide lateral homogeneity (Microcapillary cell)



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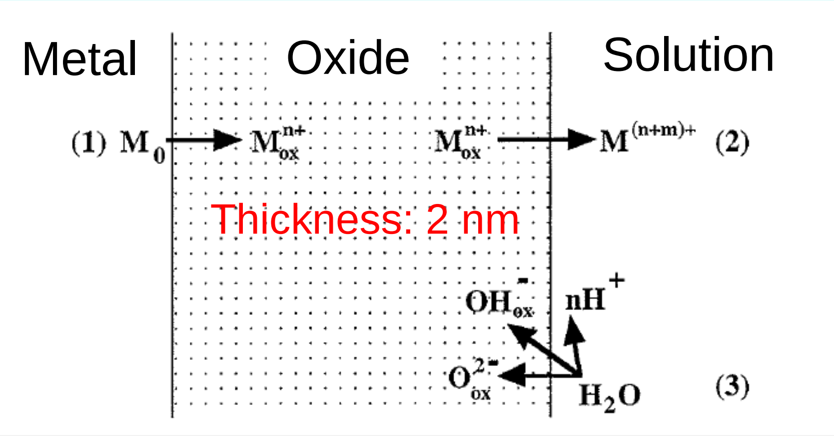
Type of steel	Corrosion resistance	Abbreviated name	Material no.	PREn	Applications
CrNi steels	I	X5CrNi18-10	1.4301	18	humid areas
		X4CrNi18-12	1.4303	18	
		X6CrNiTi18-10	1.4541	18	
		X2CrNi19-10	1.4306	19	
CrNiMo steels	II	X5CrNiMo17-12-2	1.4401	24	mild outdoor climate, weathered
		X6CrNiMoTi17-12-2	1.4571	24	
		X2CrNiMo17-12-2	1.4404	24	
		X3CrNiMo17-13-3	1.4436	26	
		X2CrNiMo18-14-3	1.4435	27	
		X2CrNiMoN17-11-2	1.4406	30	
		X2CrNiMoN17-13-3	1.4429	32	
	III	X2NiCrMoCu25-20-5	1.4539	35	outdoor climate, unweathered industrial atmosphere, weathered
		X2CrNiMoN17-13-5	1.4439	37	
		X2CrNiMoN22-5-3	1.4462** *)	37	
	IV	X1NiCrMoCuN25-20-7	1.4529	47	aggressive media indoor swimming pools, tunnels, sewage treatment plants
		X1CrNiMoCuN20-18-7	1.4547	48	
		X2CrNiMnMoNbN25-18-5-4	1.4565	50	
Special materials		NiCr21Mo14W	2.4602	(66)	Combination of aggressive media chemicals industry
		NiMo16Cr15W	2.4819	(68)	
		NiMo16Cr16Ti	2.4610	(69)	

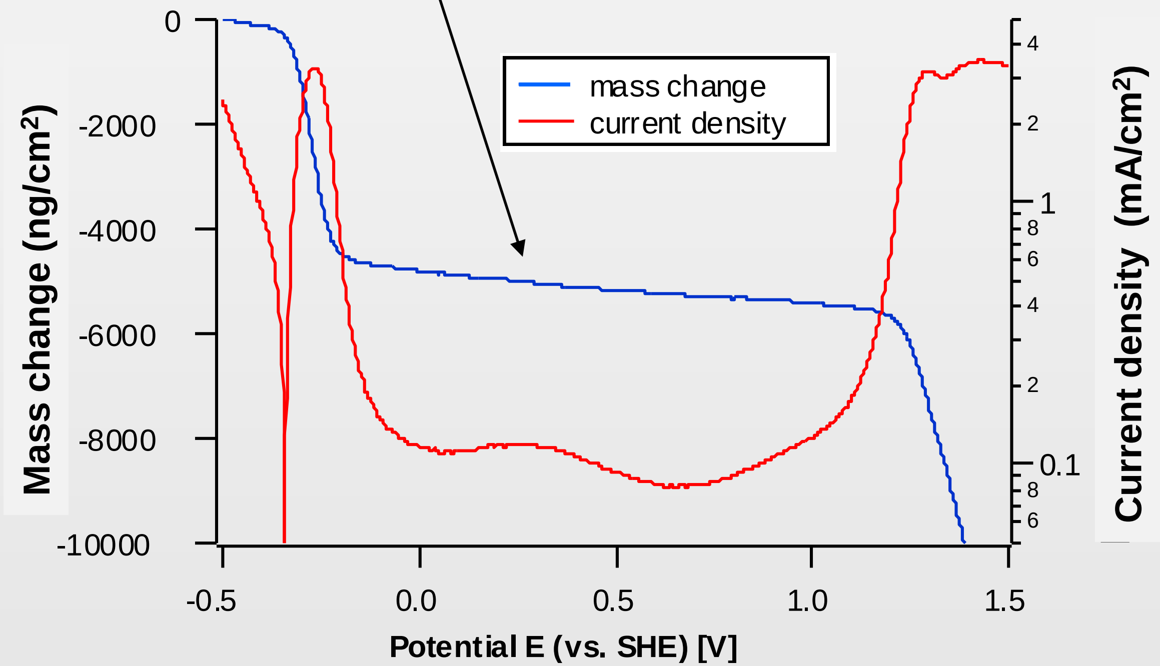
- Online “chemical passivation” characterization electrochemical method

EQCN: “Passive” oxide film stability

Ferritic Stainless Steel: Fe25Cr
in 0.1M H_2SO_4 + 0.4M Na_2SO_4



- Mass decrease (oxide dissolution in the passive domain) on the electrode



- mA/cm^2 current densities measured still represent mm/year dissolution
- Larger amount of chromium are necessary in the alloy to stabilize the oxide

- Laterally resolved electrochemical defect identification / characterization

Lateral defect distribution on Steel

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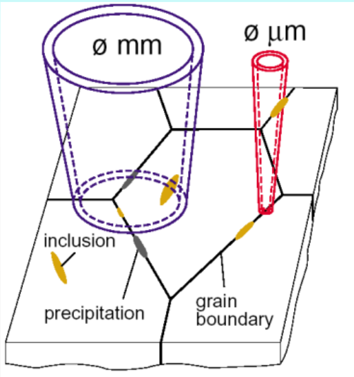
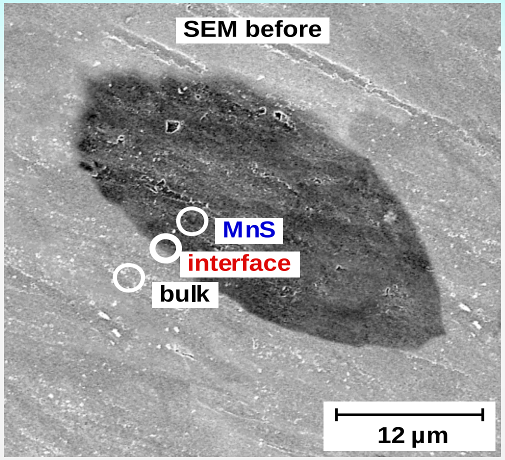


1.4301 Stainless Steel with 0.017% S

- MnS inclusions form and are preferential sites for localized corrosion attack
- Size dependent analysis: defect distribution



Pitting potential as function of measured area