Corrosion of metals

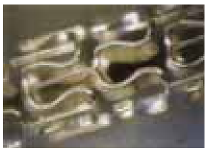
MB - JASS 09

Flavius Deleanu
Kathrin Lorenz
Christina Engelhardt

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Outline

- corrosion of metals in aqueous solutions
- corrosion processes
  (material, biomaterial, current density potential diagram)
- Pourbaix-diagram
- different types of corrosion
  - surface corrosion
  - pitting corrosion
- corrosion of metals
  - titanium
  - ion
  - 316L
  - magnesium
- Stents
  - ion
  - magnesium



Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Corrosion

What is corrosion?

Definition (DIN 50900):

→ Reaction of a material with the environment

→ Measurable change (properties, behavior)

→ Probably damage of a function or system

Appearance:

Basically electrochemical

Corrosion

Generic chemical formula for **anodic metal loss**:

$$M \rightarrow M^{+} + e^{-} \quad \text{(Oxidation)}$$

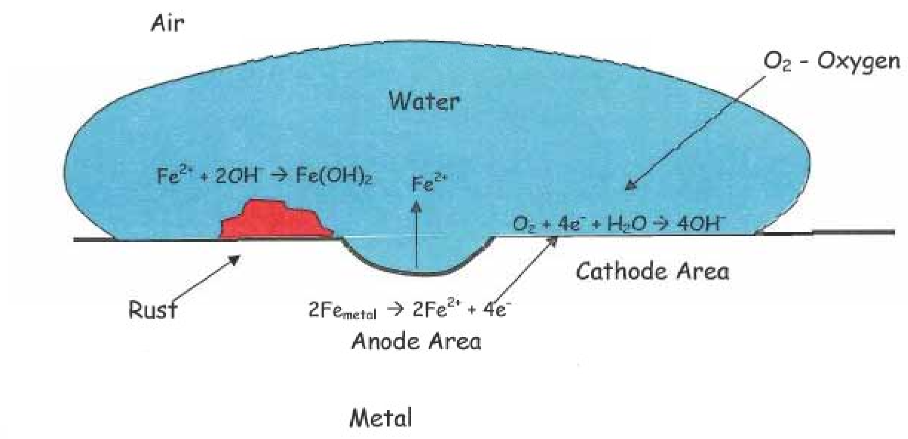
The produced **electrons** are **consumed** at the **cathodic side**:
→ 2 possibilities in aqueous solution:

I) $2\,H^{+} + 2\,e^{-} \rightarrow H_2$ (Reduction)

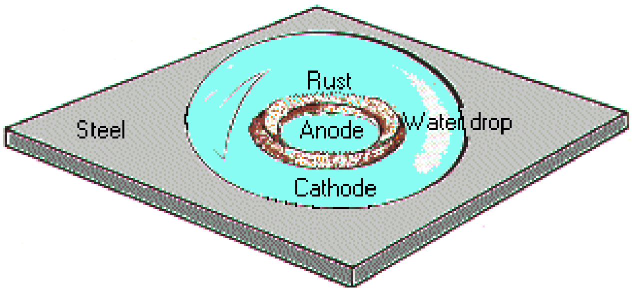
II) $O_2 + 2\,H_2O + 4e^{-} \rightarrow 4\,OH^{-}$ (Reduction)

Corrosion

Corrosion of iron (Fe) :



Corrosion



Anode: Fe → Fe^{2+} + $2e^-$

Cathode: $O_2 + 4e^- + 2H_2O \rightarrow 4\ OH^-$

Formation of **rust**: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Corrosion

Only noble metals are stable in aqueous environment

→ **Oxidation-potential** (noble metal) > **Reduction-potential** (environmental species)

Other reason for stability:

→**PASSIVITY**: stable non-dissolvable **oxide-layer** on the surface
→ primarily **titanium**!

Corrosion

Electrode		Electrode reaction	E^0/V
Au	Gold	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.43
Ag	Silver	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Cu	Copper	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
H	Hydrogen	$H^+ + e^- \rightleftharpoons H$	0
Pb	Lead	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
Sn	Tin	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
Ni	Nickel	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25
Cd	Cadmium	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.40
Fe	Iron	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
Zn	Zinc	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
Ti	Titanium	$Ti^{2+} + 2e^- \rightleftharpoons Ti$	−1.63
Al	Aluminium	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
Mg	Magnesium	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
Na	Sodium	$Na^+ + e^- \rightleftharpoons Na$	−2.71
K	Potassium	$K^+ + e^- \rightleftharpoons K$	−2.93
Li	Lithium	$Li^+ + e^- \rightleftharpoons Li$	−3.05

↑: noble metals, cathode

↓: base metals, anode

$\Delta U = E_{anode} - E_{cathode}$

< 0 → reaction possible!

→ Actually **titanium** is **less noble,**
but: high O_2-affinity: formation of a **protective oxide-layer**

Corrosion

Correlation: Current Flow and Weight Loss

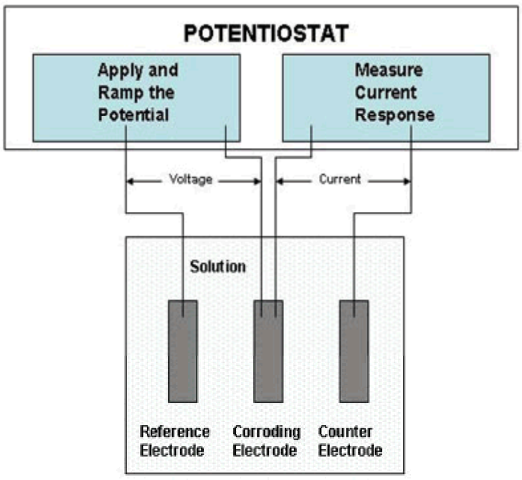
→ Metal loss is proportional to the produced electrons

→ Metal loss is proportional to the current flow

→ Corrosion-rates can be determined by applying **current (j) against potential (E)**

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Corrosion



Measurement of j/E-curve:

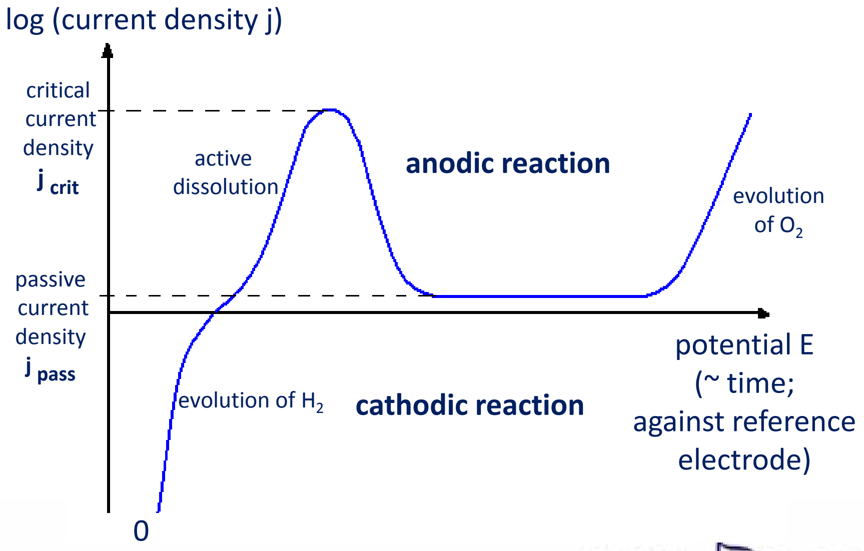
→ **Voltage**-setting between **corroding electrode** and **reference electrode**

→ **Current** between **corroding electrode** and **counter electrode**

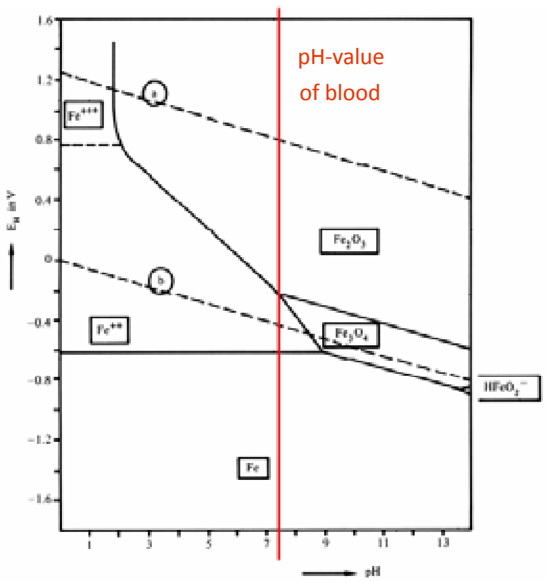
→ The **reference electrode** keeps its potential (high-ohmic input)

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Corrosion



Corrosion – Pourbaix-diagram



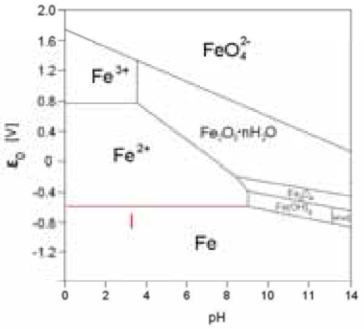
Pourbaix- diagram:

electrochemical equilibrium diagram

→valid only for endless time!

→ no information about reaction rate!

Corrosion – Pourbaix-diagram



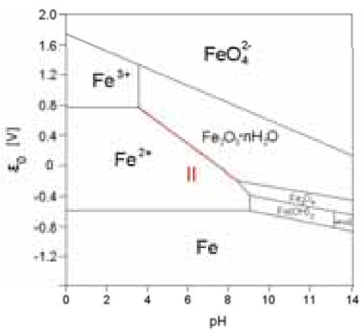
$$Fe \rightarrow Fe^{++} + 2e^{-}$$

$$E_{Fe/Fe^{++}} = E^{0}_{Fe/Fe^{++}} + \frac{0{,}059}{2} \cdot \lg c_{Fe^{++}}$$

$$E_{Fe/Fe^{++}} = -0{,}62 Volt$$

→ No pH-value depandance: horizontal line I

Corrosion – Pourbaix-diagram



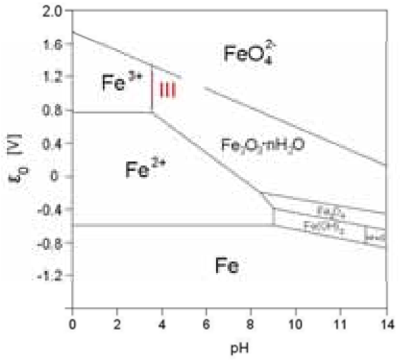
$$2Fe^{++} + 3H_2O \rightarrow Fe_2O_3 + 6H^{+} + 2e^{-}$$

$$E_{Fe/Fe_2O_3} = E^{0}_{Fe/Fe_2O_3} + \frac{0{,}059}{2} \cdot \lg \frac{c^{6}_{H^{+}}}{c^{2}_{Fe^{++}}}$$

$$E_{Fe/Fe_2O_3} = 1{,}09 - 0{,}18\,pH$$

→ pH-value-depandance: line II

Corrosion – Pourbaix-diagram



$$2Fe^{+++} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$$

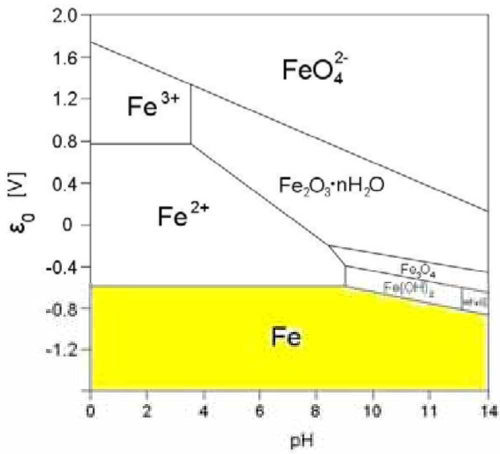
$$\frac{c_{H^+}^6}{c_{Fe^{+++}}^2} = K = 10^{1,45}$$

$$pH = 1,76$$

→ pure chemical reaction: vertical line III

Corrosion – Pourbaix-diagram

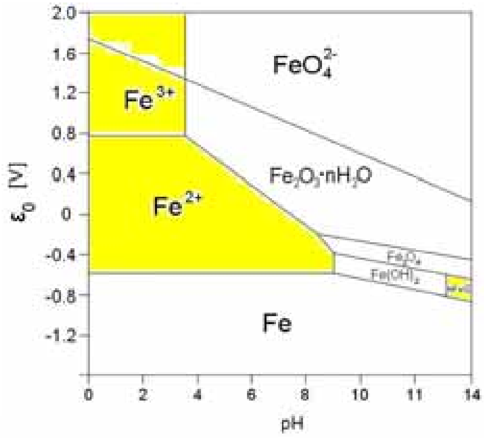
Yellow: inert area



Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Corrosion – Pourbaix-diagram

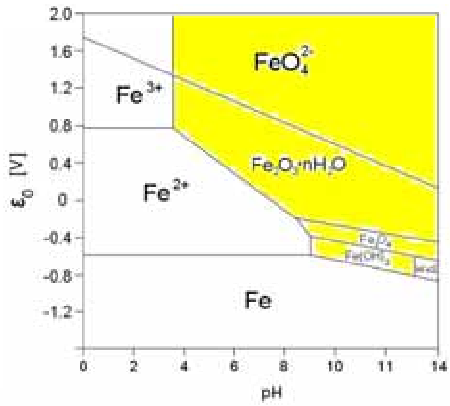
Yellow: corrosion area



Max Schaldach - Stiftungsprofessur
Biomedizinische Technik MSBT

Corrosion – Pourbaix-diagram

Yellow: areas with stable oxides



Max Schaldach - Stiftungsprofessur
Biomedizinische Technik MSBT

Corrosion

Corrosion of implants in human body:

→ **Blood = complex electrolyte**
* pH = 7,4 (±0,05)→ generated with a buffer-system
* blood consists of cells and plasma (proteins and electrolytes like *Cl^- or PO_4^{3-} dissolved in water*)
→ **more aggressive than seawater**!

→Corrosion increased at areas with **mechanical stress**

→ Can provoke an **inflammation**

Corrosion

How do metallic ions damage the tissue?

I) Ph- value and the oxygen partial pressure can diversify and this can **change the chemical environment** (metal-ions form heavily solvable compounds)

II) Metallic ions can **change the cell-metabolism**

Different types of corrosion

corrosion

- surface corrosion
- atmospheric corrosion
- galvanic (contact) corrosion
- …

types of local corrosion

- pitting corrosion
- crevice corrosion
- stress-cracking corrosion
- intercrystalline corrosion
- …

Surface corrosion

mechanism:

$Fe \rightarrow Fe^{++} + 2e^{-}$

$2H^{+} + 2e^{-} \rightarrow H_2$ acid medium

$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$ alcaline medium

preconditions:

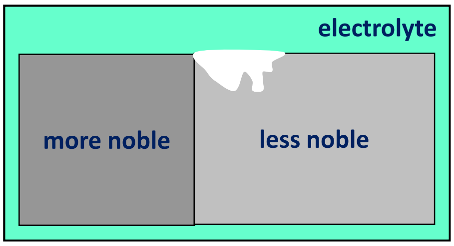
- conductive surrounding (even a very thin water film is enough)
- homogeneity of surrounding & material

! anodic and cathodic reactions are parallel !

Galvanic corrosion

→ dissimilar conducting materials are connected electrically and exposed to an electrolyte

preconditions:
- electrochemically dissimilar metals
- metals are in electrical contact
- metals are exposed to an electrolyte



metals in electrolyte → different corrosion potentials of different metals
→ potential difference = driving force for galvanic current flow

less noble material	**= anode**	**→ acceleration of corrosion**
more noble material	**= cathode**	**→ reduction of corrosion**

Pitting corrosion

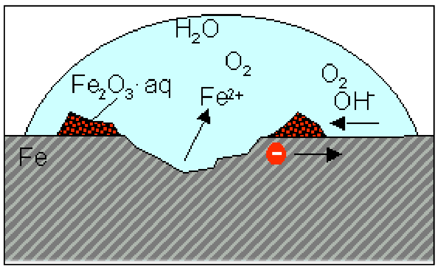
→ Kathodic reaction at the periphery of the drop

→ Passivation of border area by increasing pH

→ Low pH & low O_2-concentration in the middle → dissolving of ion

→ around anodic area: formation of rust

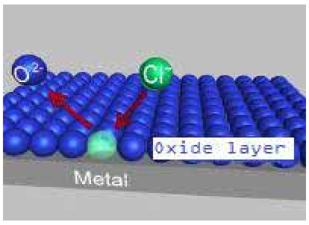
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2$$
$$4Fe(OH)_2 + O_2 \rightarrow 4FeO(OH) + 2H_2O$$



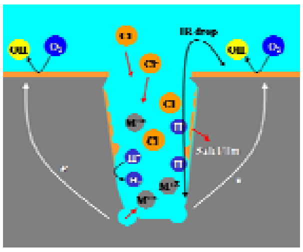
↑Corrosion with **↓O_2 concentration**

Pitting corrosion

Initiation:
Oxide layer
breakup



Processes in the pit



pitting corrosion on surface of cast iron bathtub

$FeCl_2 + H_2O \rightarrow FeClOH + H^+ + Cl^-$

[23] [24]

Influences on corrosion

- **pH**	→ Porbaix-diagram
- **microstructure**	→ galvanic elements
- **temperature**	→ ↑diffusion constant
	→ ↓ O_2-conc. in open systems
- **O_2-concentration**	→ drop-model
- **velocity of flow**	
- **salt-concentration**	

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Corrosion of metals

Examples:
titanium
iron
316L
magnesium

Titanium

Implants

properties	bone	magnesium	Ti-alloy	Co-Cr-alloy	316L
density (g/cm^3)	1,8-2,1	1,74-2,0	4,4-4,5	8,3-9,2	7,9-8,1
Young´s modulus (GPa)	3-20	41-45	110-117	230	190
fracture toughness (MPam$^{1/2}$)	3-6	15-40	55-115		0,7

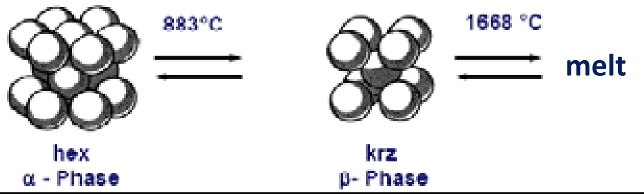
Titanium

rutil

anatas

brookit

structures



Titanium

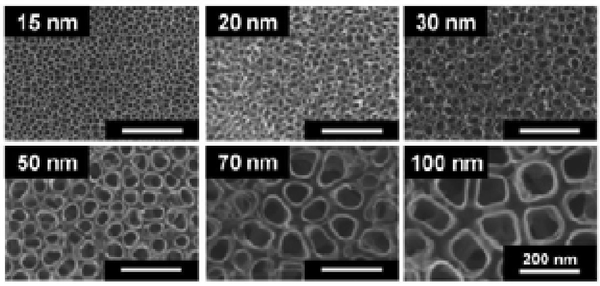
Corrosion Resistance ?

Titanium

Ti: creation of a titanium oxide layer
→ **good corrosion resistance**

Ti	→ **$Ti^{2+} + 2e^-$**	**-1.75V**
$Ti^{3+} + 3H_2O$	→ **$TiO^{2+} + 2H_3O^+ + e^-$**	**+0.10V**

TiO_2
→ n-type semicondu
→ amorphous
→anodisation: crysta
= under specific electro

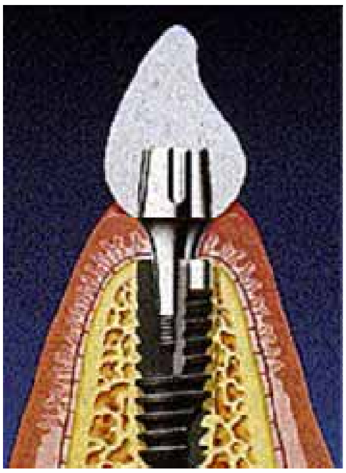


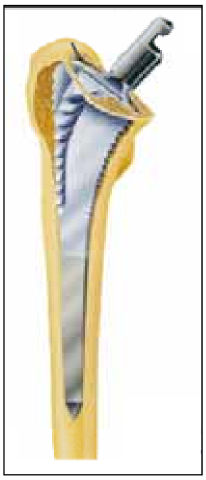
Passivation of Titanium

→ **titanium oxide layer TiO_2**

→ highly stable surface oxide layer provides excellent corrosion resistance

Titanium - applications





Iron

Max Schaldach - Stiftungsprofessur
Biomedizinische Technik MSBT

Iron (Fe)

- 4,7 wt.-% of earth crust
- **Resistant** in dry air, in dry Cl, concentrated sulforic acid and in alkaline medium (except NaOH) with **pH > 9**

Max Schaldach - Stiftungsprofessur
Biomedizinische Technik MSBT

Iron (Fe)

The more active metal in the galvanic couple becomes the anode and gets oxidized. The noble metal is the cathode.

Cathodic (noble)
↑
platinum
gold
graphite
titanium
silver
zirconium
AISI Type 316, 317 stainless steels (passive)
AISI Type 304 stainless steel (passive)
AISI Type 430 stainless steel (passive)
nickel (passive)
copper-nickel (70-30)
bronzes
copper
brasses
nickel (active)
naval brass
tin
lead
AISI Type 316, 317 stainless steels (active)
AISI Type 304 stainless steel (active)
cast iron
steel or iron
aluminum alloy 2024
cadmium
aluminum alloy 1100
zinc
magnesium and magnesium alloys
↑
Anodic (active)

316L

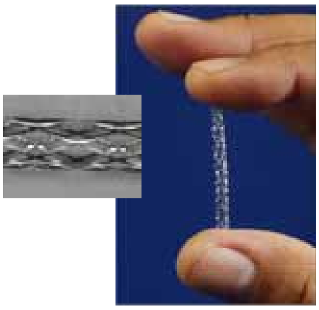
316 L

Surgical stainless steel is an specific type of stainless steel, used in medical applications

Elemental composition

Wt.-%

	316L
C	≤ 0.03
Cr	17–20
Ni	12–14
Mo	2–4



→ Low content of C

→ High addition of Cr and Ni

316 L

Corrosion Resistance ?

316 L

Formation of a **compact oxide layer** (Cr_2O_3)
→ protection against corrosion

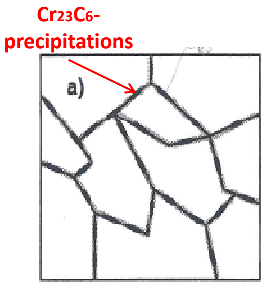
but…

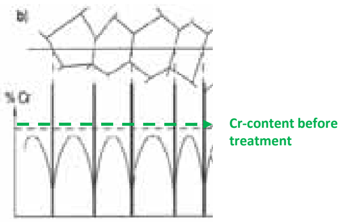
Thermal treatments (welding, annealing) lead to $Cr_{23}C_6$-precipitations in the grain boundaries

$$23\ Cr + 6\ C \rightarrow Cr_{23}C_6$$

→ Inside the grain decreased Cr-concentration

316 L

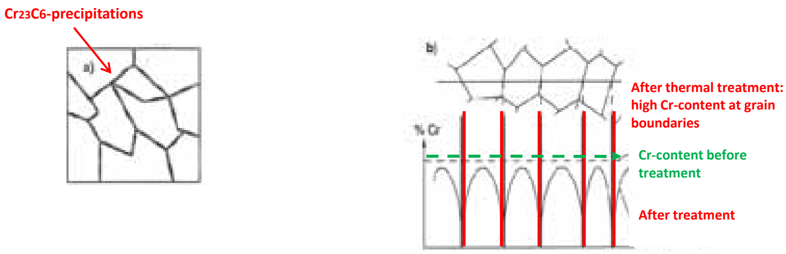




- Cr-precipitations at the grain boundaries

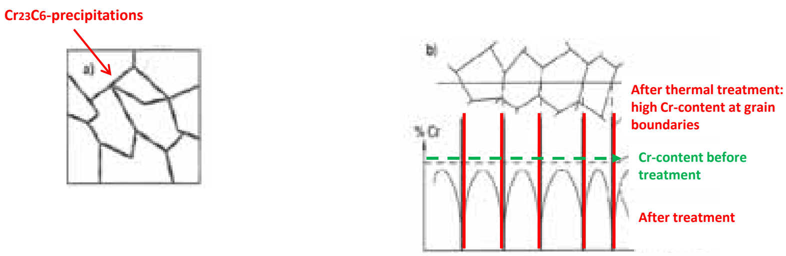
→ Less Cr near the grain boundaries

316 L



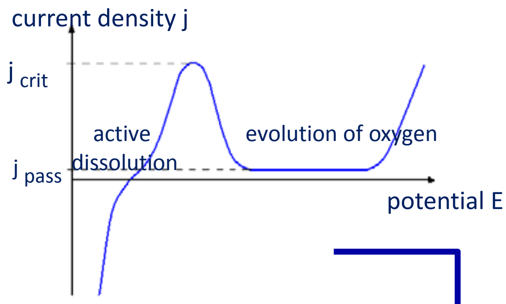
- Less Cr near the grain boundaries
  - → Critical passivation current density increases
  - → **Possibility to lose passivation**

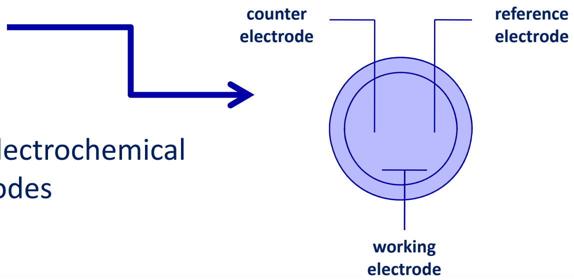
316 L



- Different concentrations near the grain boundaries and in the grain boundaries
  - → **Danger of contact corrosion**

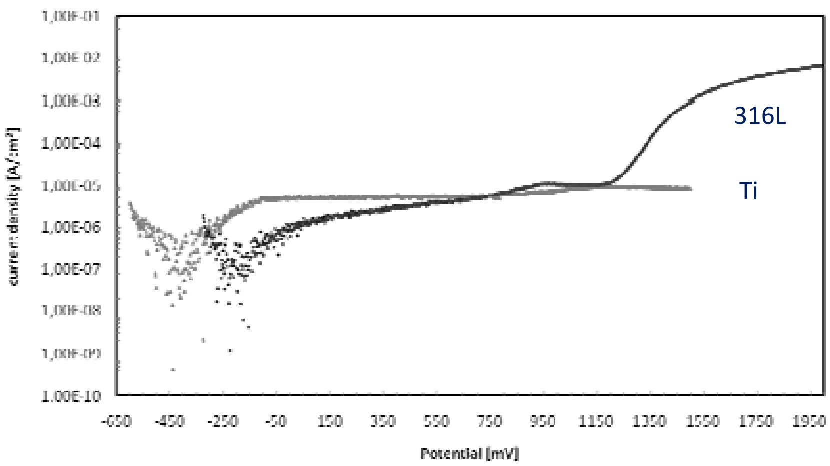
Current density potential diagram





Measurement: electrochemical cell with 3 electrodes

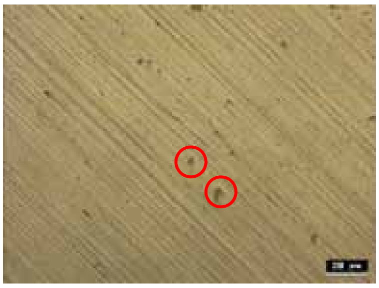
j/E-curves



Electrolyte: 0,14 M NaCl, pre-treatment: grinding (1200)

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

316L



Microscopic picture of 316L after electrochemical treatment

→ **mainly protection**

but

→ **pitting** caused by chloride-ions

Titanium

Microscopic image of Ti after electrochemical treatment

→ Leveling of grinding grooves because of grown oxide layer

Magnesium

Implants

properties	bone	magnesium	Ti-alloy	Co-Cr-alloy	316L
density (g/cm^3)	1,8-2,1	1,74-2,0	4,4-4,5	8,3-9,2	7,9-8,1
Young´s modulus (GPa)	3-20	41-45	110-117	230	190
fracture toughness ($MPam^{1/2}$)	3-6	15-40	55-115		0,7

Magnesium

magnesium
1.74 g/cm³

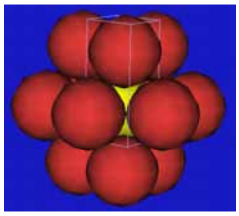
12 24,305

1107
651

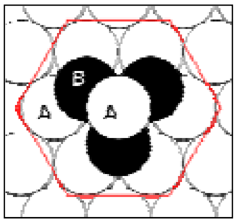
Mg

Magnesium

atomic number
atomic mass
symbol
name
boiling temperature
melting point



Hexagonal-closed-packed

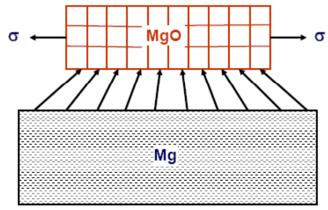


Magnesium

Corrosion Resistance ?

Magnesium

Mg: highly negative electrochemical potential of -2.38 V
→ **low corrosion resistance**



MgO: no formation of protection layer
WHY? → difference in molar volume of Mg & MgO
→ flaking off caused by tensile & compression stresses

Mg → corrosion even in water
Mg in acids → highest corrosion

increase of corrosion rate by impurities in Mg – especially Fe, Ni, Cu
→ **galvanic corrosion**

Magnesium

corrosion reactions of magnesium

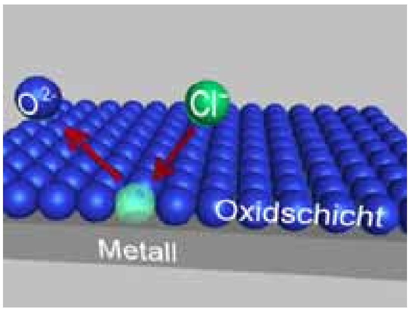
$$Mg(s) + 2H_2O \rightarrow Mg(OH)_2(s) + H_2(g),$$

$$Mg(s) + 2Cl^- \ (aq) \rightarrow MgCl_2,$$

$$Mg(OH)_2 \ (s) + 2Cl^- \rightarrow MgCl_2.$$

M.P. Staiger et al. / Biomaterials **27** (2006) **1728–1734**

Magnesium-corrosion

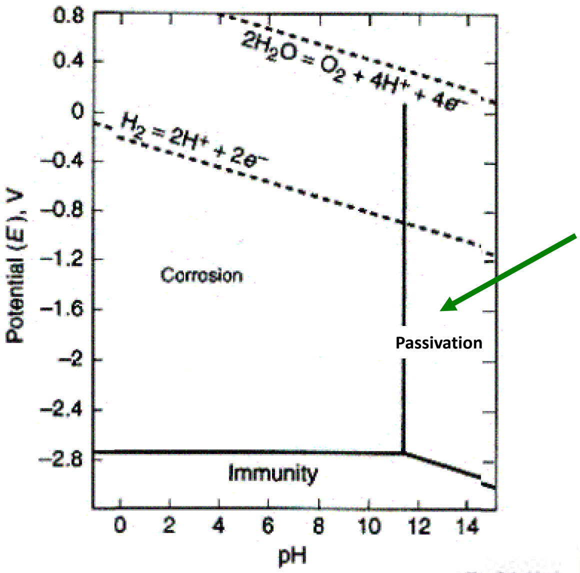


- local corrosion of passive layer by Cl^-
- rapid increase of corrosion rate

→ **pitting corrosion**

	Na^+	K^+	Mg^{++}	Cl^-
Blut [mmol/l]	142,0	3,6-5,5	1,0	95,0-107,0

Pourbaix-diagram of Mg



Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Magnesium

Mg-corrosion in the body?

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

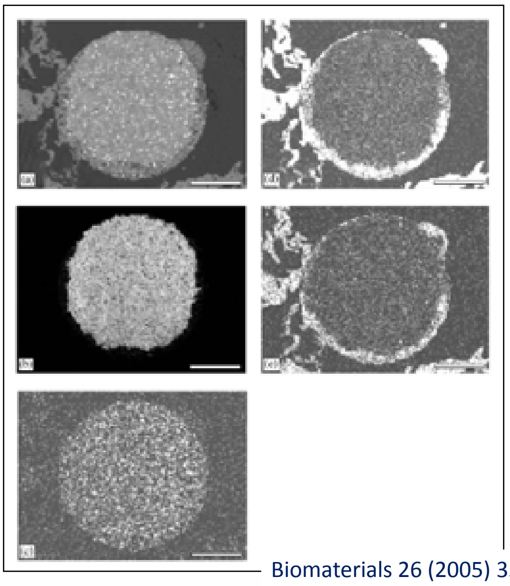
Magnesium – corrosion in the body?

Simulated body fluid

	1 Liter SBF/ ml
KCl	5.63
NaCl	59
$NaHCO_3$	18
$MgSO_4*7H_2O$	5
CaH_2 bzw. $CaCl_2$	25
TRIS	50
NaN_3	10
K_2HPO_4	5.25

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Magnesium – corrosion in the body



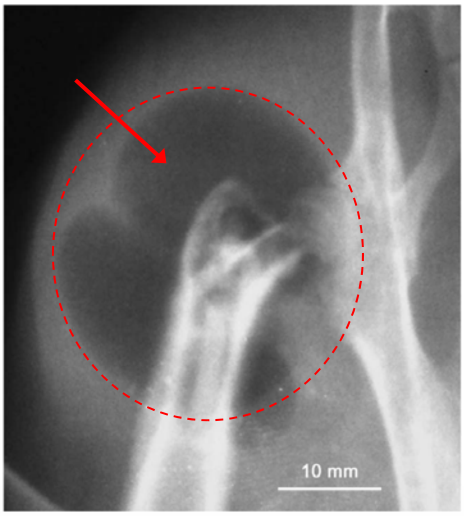
EDX analysis:

→ degraded implant: replaced by a conversion layer containing mainly Ca & P

→ rare earth elements were distributed homogeneously in the corrosion layer & in the remaining implant material but not in the surrounding bone

Biomaterials 26 (2005) 3557–3563

Magnesium – corrosion in the body



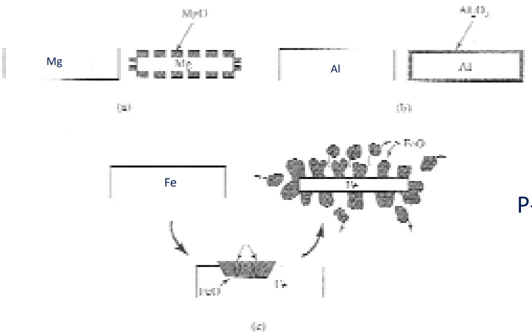
Subcutaneous gas bubbles observed on postoperative radiographs for 4 weeks during magnesium implant degradation

Biomaterials 26 (2005) 3557–3563

Oxide layers – specific volume

P-B-Ratio < 1

P-B-Ratio = 1-2



P-B-Ratio > 2

$n\,M + m\,O_2 = M_nO_{2m}$

$$Pilling-Bedworth-Ratio = \frac{oxide\ volume\ per\ metal\ atom}{metal\ volume\ per\ metal\ atom} = \frac{(M_{oxide})(\rho_{metal})}{n(M_{metal})(\rho\rho_{oxide})}$$

Stents

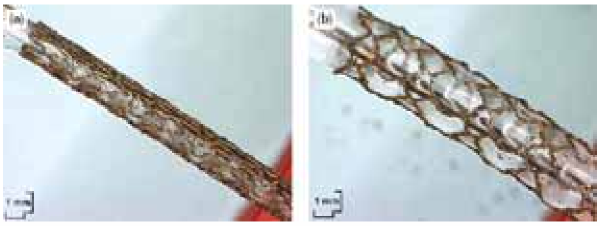
Bioabsorbable stents

Possible Materials??

Bioabsorbable iron stents

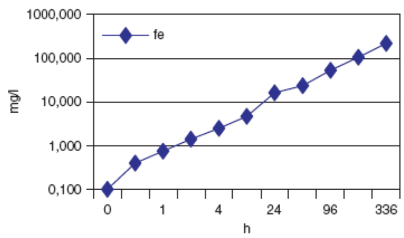
Bioabsorbable Iron Stent

- Iron is an essential element (daily need: 0,5-5 mg)
- stent weighs about 40 mg (coronary) or 250 mg (peripheral)
- low toxicity, because of the low rate of corrosion
- systemic toxicity is not to be anticipated even after implantation of multiple stents



Bioabsorbable Iron Stent

Studies with **pure iron** (less than 1 % contamination) foils (diameter 26 mm, thickness 0,91 mm) in **electrolyte**:



→ **Loss** of **15 % mass** after 1 week's incubation in human serum

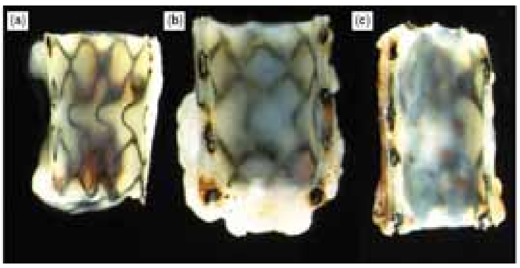
Bioabsorbable Iron Stent

In vivo studies

12 months after implantation: corrodible **iron stent** (left) and **316L stent** (right) in the descending aorto of a minipig

Bioabsorbable Iron Stent

Macroscopic aspect of corrosion process 3 (a), 6 (b) and 12 (c) months after implantation



(a) Struts of the stents are clearly visible, corrosion plagues limited to the intersections
(b) Progressive loss of structure, accumulation of corrosion products
(c) Loss of integrity

Max Schaldach - Stiftungsprofessur Biomedizinische Technik MSBT

Biodegradable magnesium stents

Reasons for favoring Mg as stent material

- Hypothrombotic properties
- Predictable tissue tolerance
- Mechanical properties: Outstanding stability-to-mass ratio
- Therapeutically used
- Vasodilating properties:

  As a physiologic calcium antagonist,
  magnesium inhibits the muscle contraction
  and thus the tone of vessels.

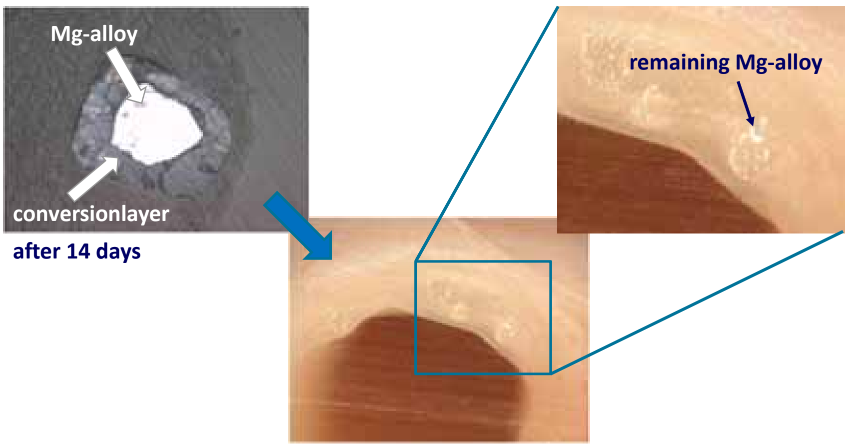
Bioabsorbable magnesium-stent

1 stent (1.1 mm × 10 mm):
≈ 4 mg magnesium

0.7 l drinking water:
≈ 110 mg magnesium

- **Mg → essential mineral:**
  - **20 g in human bodies**
  - **350 mg recommended ingestion per day**
- **Mg → relaxation of muscels**
- **Mg → very low allergen reactions**

Degradation of Mg-stents



after 14 days

after 56 days

Thank you for your attention!

Max Schaldach -
Stiftungsprofessur

Biomedizinische
Technik MSBT