Corrosion of metals

MB - JASS 09
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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
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*

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Corrosion

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

\[ M \rightarrow M^+ + e^- \] \text{(Oxidation)}

The produced electrons are **consumed** at the **cathodic side**:

- 2 possibilities in aqueous solution:
  
  I) \[ 2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2 \] \text{(Reduction)}
  
  II) \[ \text{O}_2 + 2 \text{H}_2\text{O} + 4e^- \rightarrow 4 \text{OH}^- \] \text{(Reduction)}
Corrosion of iron (Fe):

Anode: \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

Cathode: \[ \text{O}_2 + 4e^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^- \]

Formation of rust: \[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \]
Corrosion

Only noble metals are stable in aqueous environment

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

Other reason for stability:

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

Corrosion

↑: noble metals, cathode
↓: base metals, anode

\[ \Delta U = E_{\text{anode}} - E_{\text{cathode}} \]

< 0 → reaction possible!

→ Actually titanium is less noble, but: high O₂-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)*

**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)
Corrosion

**Corrosion – Pourbaix-diagram**

**Pourbaix-diagram:**
- Electrochemical equilibrium diagram
- Valid only for endless time!
- No information about reaction rate!
Corrosion – Pourbaix-diagram

\[ Fe \rightarrow Fe^{++} + 2e^- \]

\[ E_{Fe/Fe^{++}} = E_{Fe/Fe^{+}}^0 + \frac{0.059}{2} \cdot \lg c_{Fe^{++}} \]

\[ E_{Fe/Fe^{+}} = -0.62\text{Volt} \]

\[ \Rightarrow \text{No pH-value dependance: horizontal line I} \]

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

\[ E_{Fe/Fe_2O_3} = E_{Fe/Fe^{+}}^0 + \frac{0.059}{2} \cdot \lg \frac{c_{H^+}^6}{c_{Fe^{++}}^2} \]

\[ E_{Fe/Fe_2O_3} = 1.09 - 0.18pH \]

\[ \Rightarrow \text{pH-value-dependance: line II} \]
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
Corrosion – Pourbaix-diagram

Yellow: corrosion area

Corrosion – Pourbaix-diagram

Yellow: areas with stable oxides
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 PO₄³⁻ dissolved in water)

- More aggressive than seawater!

- Corrosion increased at areas with mechanical stress

- Can provoke an inflammation

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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:**

\[
Fe \rightarrow Fe^{++} + 2e^- \\
2H^+ + 2e^- \rightarrow H_2 \quad \text{(acid medium)} \\
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(alcaline medium)}
\]

**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 O₂-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 ↓O₂ concentration
**Pitting corrosion**

Initiation:
Oxide layer breakup

Processes in the pit

FeCl₂ + H₂O \rightarrow FeClOH + H⁺ + Cl⁻

Illuminations on corrosion

- pH \rightarrow Porbaix-diagram
- microstructure \rightarrow galvanic elements
- temperature \rightarrow ↑ diffusion constant
  \rightarrow ↓ O₂-conc. in open systems
- O₂-concentration \rightarrow drop-model
- velocity of flow
- salt-concentration
Corrosion of metals

Examples:
- titanium
- iron
- 316L
- magnesium

Titanium
### Implants

<table>
<thead>
<tr>
<th>properties</th>
<th>bone</th>
<th>magnesium</th>
<th>Ti-alloy</th>
<th>Co-Cr-alloy</th>
<th>316L</th>
</tr>
</thead>
<tbody>
<tr>
<td>density (g/cm³)</td>
<td>1,8-2,1</td>
<td>1,74-2,0</td>
<td>4,4-4,5</td>
<td>8,3-9,2</td>
<td>7,9-8,1</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>3-20</td>
<td>41-45</td>
<td>110-117</td>
<td>230</td>
<td>190</td>
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<td>fracture toughness (MPam¹/²)</td>
<td>3-6</td>
<td>15-40</td>
<td>55-115</td>
<td>0,7</td>
<td></td>
</tr>
</tbody>
</table>

### Titanium

- **rutil**
- **anatas**
- **brookit**

**structures**
- hex $\alpha$-Phase at 883°C
- kruz $\beta$-Phase at 1868°C
- melt
Titanium

Corrosion Resistance?

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

- \( Ti \rightarrow Ti^{2+} + 2e^- \quad -1.75V \)
- \( Ti^3+ + 3H_2O \rightarrow TiO^{2+} + 2H^+ + e^- \quad +0.10V \)

\( TiO_2 \)
- n-type semiconductor
- amorphous
- anodisation: crystalline
= under specific electrochemical conditions
Passivation of Titanium

→ titanium oxide layer TiO$_2$

→ highly stable surface oxide layer provides excellent corrosion resistance
Iron

- 4.7 wt.-% of earth crust
- **Resistant** in dry air, in dry Cl, concentrated sulforic acid and in alkaline medium (except NaOH) with \( \text{pH} > 9 \)
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)
- brasses
- copper
- bronzes
- nickel (active)
- naval brass
- tin
- lead
- AISI Type 310, 317 stainless steels (active)
- AISI Type 304 stainless steel (active)
- cast iron
- steel or iron
- aluminium alloy 2024
- cadmium
- aluminium alloy 1100
- zinc
- magnesium and magnesium alloys

Anodic (active)

316L
Surgical stainless steel is a specific type of stainless steel, used in medical applications.

### Elemental composition

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<th>Element</th>
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<tr>
<td>C</td>
<td>0.08</td>
</tr>
<tr>
<td>Cr</td>
<td>16.7</td>
</tr>
<tr>
<td>Ni</td>
<td>12.1</td>
</tr>
<tr>
<td>Mo</td>
<td>2.4</td>
</tr>
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- Low content of C
- High addition of Cr and Ni

Corrosion Resistance?
Formation of a **compact oxide layer** \((\text{Cr}_2\text{O}_3)\) → protection against corrosion

but...

Thermal treatments (welding, annealing) lead to \(\text{Cr}_2\text{C}_6\)-precipitations in the grain boundaries

\[ 23\text{ Cr} + 6\text{ C} \rightarrow \text{Cr}_2\text{C}_6 \]

→ Inside the grain decreased Cr-concentration

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

- Different concentrations near the grain boundaries and in the grain boundaries
  - Danger of contact corrosion
Current density potential diagram

- Current density: j
- Critical current density: j_{crit}
- Passive current density: j_{pass}
- Evolution of oxygen potential: E
- Measurement: electrochemical cell with 3 electrodes

Electrolyte: 0.14 M NaCl, pre-treatment: grinding (1200)
316L

→ mainly protection
  but
→ pitting caused by chloride-ions

Microscopic picture of 316L after electrochemical treatment

Titanium

→ Leveling of grinding grooves because of grown oxide layer

Microscopic image of Ti after electrochemical treatment
## Magnesium

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</tr>
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</table>
Magnesium

- **Atomic number**: 12
- **Atomic mass**: 24,305
- **Symbol**: Mg
- **Name**: Magnesium
- **Boiling temperature**: 1107 K
- **Melting point**: 651 K
- **Density**: 1.74 g/cm³

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

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**corrosion reactions of magnesium**

\[
\text{Mg(s)} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2(s) + \text{H}_2(g), \\
\text{Mg(s)} + 2\text{Cl}^- (aq) \rightarrow \text{MgCl}_2, \\
\text{Mg(OH)}_2 (s) + 2\text{Cl}^- \rightarrow \text{MgCl}_2. 
\]

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

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blut [mmol/l]</td>
<td>142,0</td>
<td>3,6-5,5</td>
<td>1,0</td>
<td>95,0-107,0</td>
</tr>
</tbody>
</table>

Pourbaix-diagram of Mg
Magnesium

Mg-corrosion in the body?

Simulated body fluid

<table>
<thead>
<tr>
<th></th>
<th>1 Liter SBF/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>5.63</td>
</tr>
<tr>
<td>NaCl</td>
<td>50</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>18</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>5</td>
</tr>
<tr>
<td>CaH₂ bzw. CuCl₂</td>
<td>25</td>
</tr>
<tr>
<td>TRIS</td>
<td>50</td>
</tr>
<tr>
<td>NaN₃</td>
<td>10</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>5.25</td>
</tr>
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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

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

\[ \text{P-B-Ratio} = \frac{\text{oxide volume per metal atom}}{\text{metal volume per metal atom}} = \frac{n(M_{\text{metal}} / \langle P_{\text{metal}} \rangle)}{n(M_{\text{metal}} / P_{\text{metal}})} \]

P-B-Ratio = 1·2

P-B-Ratio > 2

\[ n\text{M} + m\text{O}_2 = \text{M}_n\text{O}_{2m} \]

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

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: corrosible iron stent (left) and 316L stent (right) in the descending aorto of a minipig

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

(a) Struts of the stents are clearly visible, corrosion plaques limited to the intersections
(b) Progressive loss of structure, accumulation of corrosion products
(c) Loss of integrity
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 muscles
- Mg → very low allergen reactions

Degradation of Mg-stents

Mg-alloy
conversion layer
after 14 days

remaining Mg-alloy

after 56 days
Thank you for your attention!