

University Hospital Tübingen
Section „Medical Materials Science & Technology“

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Corrosion

Fundamentals of Corrosion and Corrosion Test Methods

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Metallic Biomaterials

Metals and its alloys widely used as biomaterial because:

- Strong material
- Ductile: Relatively easily formed into complex shape
- High modulus and yield point: make them suitable for bearing large load without leading to a large deformations and permanent dimensional change.



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Metals commonly used in Biomedical Application	
Metals	Applications
Cobalt-chromium alloys	Artificial heart valves, dental prosthesis, orthopedic fixation plates, artificial joint components, vascular stents
Gold and platinum	Dental fillings, electrodes for cochlear implants
Silver-tin-copper alloys	Dental amalgams
Stainless steel	Dental prosthesis, orthopedic fixation devices (such as plates and screw), vascular stents
Titanium alloys	Artificial heart valves, dental implants, artificial joint components, orthopedic screws, pacemaker cases, vascular stents

Metallic Biomaterials

Biocompatibility

↕

Corrosion Resistance

Biocompatibility is very important because of danger of toxicity, tissue and immune response.



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Corrosion

The destructive electrochemical attack of a material.



- Average cost in western countries:
4 to 5% of the Gross National Product (GNP)



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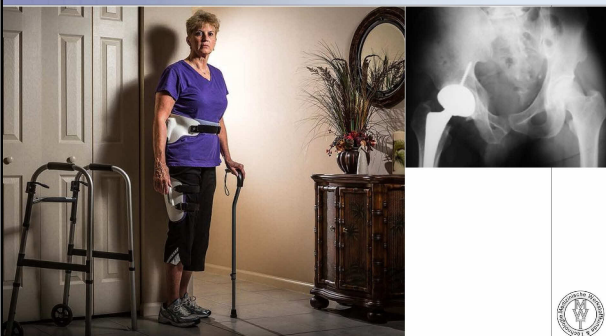
Why is corrosion control important?

Corrosion of implant materials may lead to penetration of released metal ions into the surrounding tissues and blood stream causing health problems.




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Corrosion induced implant problems



Dianne Pingel, 66: Five surgeries since hip replacement 18 months ago. Blood tests showed metal poisoning. Her thigh bone broke during surgery to remove the recalled hip. "Sitting is an impossibility. I have to lie on my back. I don't really get any sleep."

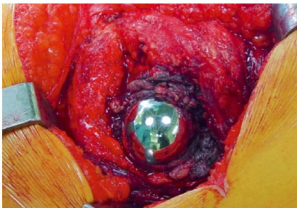


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Metallosis

When excessive metal builds up near the joint, the lymph nodes and surrounding joint fluid attempt to “clean” the body by absorbing the ions and transporting them to the kidneys, where they are removed from the body in the urine. However, sometimes the body is overwhelmed by the amount of metal, and this can cause a number of complications.

Metal ions released into the surrounding tissues and into the bloodstream and can create toxic levels in the body, leading to metallosis.




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CORROSION AND DEGRADATION

ISSUES TO ADDRESS ...

- Why does corrosion occur?
- What metals are most likely to corrode?
- How does environment affect corrosion rate?
- Which forms of corrosion do we know?
- How do we suppress corrosion?
- How can we measure corrosion?




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Basic Definitions

Current is the flow of electrons through a medium. A metal conducts electricity without changing its properties. This is called metallic conduction.

Ionization is the process of adding electrons to or removing electrons from atoms or molecules, creating ions. High temperatures, electrical discharges, and nuclear radiation can cause ionization.

- Current can be conducted by the movement of these ions.

The compounds that conduct electric current by ion movement are called **electrolytes**, and this ionic motion is called **electrolytic conduction**.

Conductivity is a measure of the ability of a substance to allow electron flow.

- Conductivity indicates the amount of ions in solution, which relates directly to the potential of corrosion taking place.

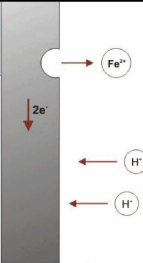


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What is Corrosion

The chemical environment to which a material is subjected in its life span may cause changes in the material properties. Corrosion is the reaction of the engineering material with its environment with a consequent deterioration in properties of the material.

Corrosion will include the reaction of metals, glasses, ionic solids, polymeric solids, composites and coating systems.




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Definition of Corrosion

Corrosion is the deterioration of a material due to interaction with its environment.

Electrolysis is the decomposition by electric current (in the context of corrosion the use of electrical current to bring about chemical change).

An *electrolyte* is defined as an electricity-conducting fluid; that is, it has positive and negative ions that can move and constitute an electrical current.

Pure water is a poor conductor (contains H^+ and OH^- ions only). When a salt is added it becomes a good conductor.

Corrosion is electrochemical in nature because the corrosive chemical reactions involve transfer of charge.



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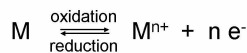
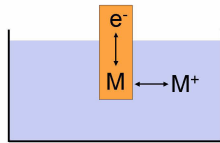
Why does corrosion occur?

- Basic considerations



One electrode

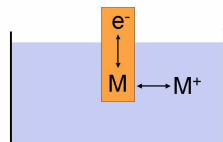
Whenever a metal is in contact with an aqueous solution such as blood or saliva there is a spontaneous tendency for metal ions to go into solution, leaving electrons behind.



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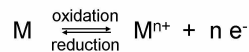


One electrode



electrode potential*,
equilibrium of metal ion concentration

*) there is no way to measure Voltage directly



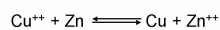
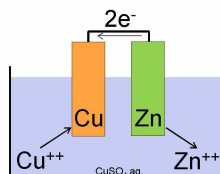
Notice that the reaction moving to the right involves the removal of electrons, the **oxidation** of metal atoms to the positive ions (cations), while the converse reaction is a **reduction** of the cation to metal, the addition of electrons.

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Galvanic couple

The metal with the higher tendency to dissolve (Zn) unbalances the equilibrium. The higher electron concentration forces reduction of Cu.



The electrode associated with the metal ion reduction process is the **cathode**, that associated with the oxidation process is the **anode**.

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What metals are most likely to corrode?

- Electro motive force (EMF) series
- Passivation



Electrochemical Cells

The ability of a metal to corrode will depend on the potential difference between the metal and the electrolyte.

- For example, magnesium and zinc go into solution to a greater extent than iron, and these metals will be more negative with respect to the electrolyte than iron.
- Nickel, lead, and copper go into solution less readily and produce a smaller potential difference.
- The potential difference depends on the ability of the metal to gain or loose electrons.



Electro Motive Force Series (EMF)

Electromotive Series		Electromotive Series	
Metal	Normal electrode potential* (Volts)	Metal	Normal electrode potential*
Gold	+1.4	Antimony	+0.1
Platinum	+1.2	Tungsten	+0.05
Iridium	+1.0	Hydrogen	+0.000
Palladium	+0.83	Lead	-0.126
Silver	+0.8	Tin	-0.136
Mercury	+0.799	Molybdenum	-0.2
Osmium	+0.7	Nickel	-0.25
Ruthenium	+0.45	Cobalt	-0.28
Copper	+0.344	Indium	-0.3
Bismuth	+0.20	Cadmium	-0.402
		Iron	-0.440
		Chromium	-0.56
		Zinc	-0.762
		Niobium	-1.1
		Manganese	-1.05
		Vanadium	-1.5
		Aluminum	-1.67
		Beryllium	-1.70
		Titanium	-1.75
		Magnesium	-2.38
		Calcium	-2.8
		Strontium	-2.89
		Barium	-2.90
		Potassium	-2.92

Metals with a more negative Standard Electrode Potential are more likely to corrode relative to other metals.

increase in ease of oxidation



Thermodynamics

Nernst equation

$$E = E^0 - \frac{R \cdot T}{n_e \cdot F} \ln \frac{[\text{Red}]}{[\text{Ox}]}$$

E: Potential
 E^0 : Normalpotential (298K, 1-molare Lsg.)
 R: allg. Gaskonstante, $R = 8,32 \text{ Jmol}^{-1} \text{K}^{-1}$
 T: (absolute) Temperatur in K
 n_e : Zahl der bei der Reaktion übertragenen e^-
 F: Faraday-Konstante, $F = 96485 \text{ Cmol}^{-1}$

Source: www.Elektrochemie-Uni-Marburg.de



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Thermodynamics

Nernst Equation:

$$E = E^o - \frac{RT}{nF} \ln(Q)$$

THE Basic equation which describes ALL corrosion reactions

For example:

$$E = E^o - \frac{RT}{nF} \ln \left(\frac{[Fe^{2+}]}{[H^+]^2} \right)$$


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Passivity and Polarization of a Metal

Metals that normally fall victim to corrosion will sometimes exhibit a passivity to corrosion.

Passivity is the characteristic of a metal exhibited when that metal does not become active in the corrosion reaction.

Passivity is caused by the buildup of a stable, tenacious layer of metal oxide on the surface of the metal.

Once the layer, or film, is formed, it acts as a barrier separating the metal surface from the environment.

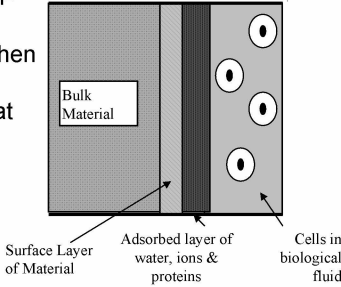


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Passivation

Metals such as titanium, zirconium, chromium, aluminum, and the stainless steels form thin, tenacious oxide films when exposed to the atmosphere or to pure water at room temperature.

- Very effective in minimizing further corrosion.

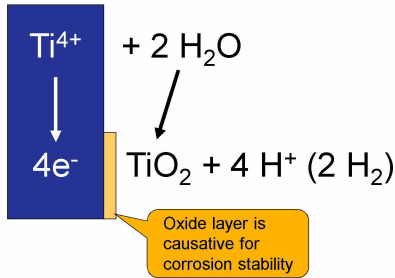


Labels in diagram: Bulk Material, Surface Layer of Material, Adsorbed layer of water, ions & proteins, Cells in biological fluid

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Passivation of titanium

EMF of Ti = -1.75 V (indicating low corrosion stability)



Oxide layer is causative for corrosion stability

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Purpose of biomaterial application

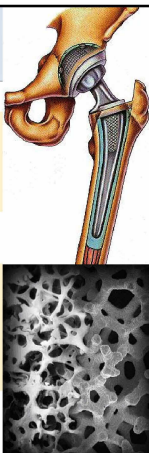
Long term functionality

→ **high corrosion resistance**
(Ti, Ti alloys)

versus

Short time stability (biodegradable materials)

→ **low corrosion resistance**
(Mg alloys, Fe alloys)



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How does environment affect corrosion rate?

- Electrolyte / Biological surrounding
 - Chemical composition of the solution
- Flow rate (velocity of the fluid)
- Temperature
- Mechanical impact
- Radiation



Electrolyte / Biological surrounding

Kind of body liquid

- Chemical composition
- pH value
- oxygen concentration

Chloride ions attack steel, fluoride attacks zirconium, and zinc causes damage to iniconel.

In-vitro: use of SBF (simulated body fluid)



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Flow rate

At high velocity, the corrosion layer will be relatively thin.

- The film in contact with the metal is mechanically scrubbed by the passing fluid.

Important for implants in blood vessels (e.g. stents, heart valves, etc)




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Temperature

As temperature increases corrosion rate also increases.

Increasing T speeds up oxidation/reduction reactions.



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Mechanical impact

Tribocorrosion: Destruction of the passive layer (re-passivation kinetics)

- Formation of debris during wear

Stress corrosion

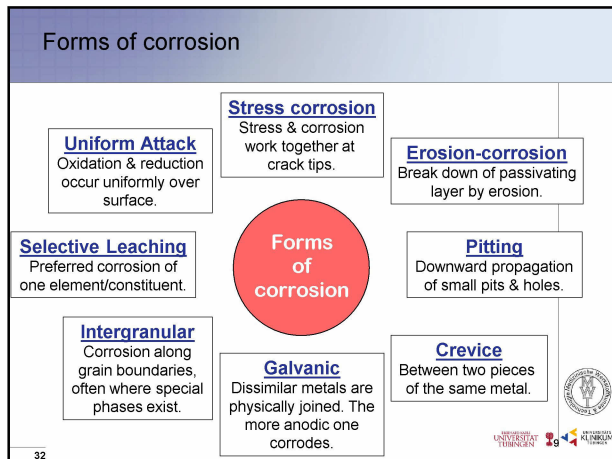


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Which forms of corrosion do we know?





Galvanic corrosion

Causes:
Dissimilar metals
Electrolyte
Current Path

Described by Galvanic Series

Solutions:
Choose metals close in galvanic series
Have large anode/cathode ratios
Insulate dissimilar metals
Use "Cathodic protection"

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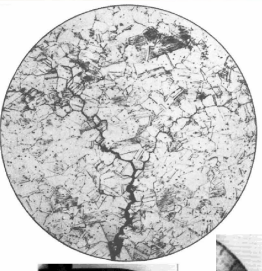
Intergranular corrosion

Occurs in specific alloys – precipitation of corrosive specimens along grain boundaries and in particular environments.
e.g. : Chromium carbide forming in SS, leaving adjacent areas depleted in Cr.

Solutions:
High temp heat treat to re-dissolve carbides.
Lower carbon content (in SS) to minimize carbide formation.
Alloy with a material that has stronger carbide formation (e.g., Ti or Nb).

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Stress corrosion



Aka: stress corrosion cracking

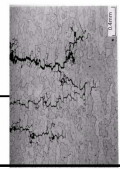
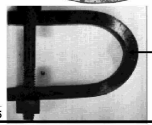
Cracks grow along grain boundaries as a result of residual or applied stress or trapped solid corrosion products

Stress levels may be very low

Solutions:

Reduce stress levels

Heat treatment



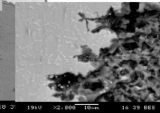
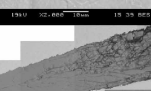
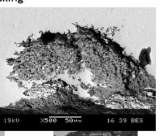
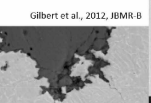
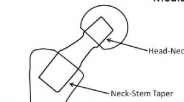
Stress Corrosion Cracking (SCC)

Modular Neck Corrosion: 2012

In-Vivo Oxide-Induced Stress Corrosion Cracking in Ti-6Al-4V Modular Neck-stem Tapers

Medial proximal neck-stem taper cracking

Gilbert et al., 2012, JBMR-B



Fretting corrosion

Example for fretting corrosion



Mastication: ca. 1400 cycles per day

Force during mastication: 60-260 N

Bite force: 500-700N

Bruxism forces: > 800N



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Fretting Corrosion

Hip Prosthesis Corrosion Sources

Examples of Current Modular Designs

Modularity, articulating surfaces and other interfaces are where mechanically assisted corrosion can occur.

Most severe corrosion observed at modular tapers
Corrosion at one location affects all others (e.g., voltage drops)

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Tribocorrosion/wear induced implant problems

Reduction reactions at metal surfaces may kill osteoblast-like cells

Extracellular metal debris

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Fretting Corrosion

Electrochemistry of Fretting Interfaces

Metal ions, phosphate, chloride, hydrogen ions accumulate in crevice

Fretting currents consist of dissolution and repassivation reactions

Oxidation debris accumulates in crevice

Crevice Solution Oxide Metal

Debris

To external surface

- $M \rightarrow M^{n+} + ne^{-}$
- $M + H_2O \rightarrow MO + 2H^{+} + 2e^{-}$ Excess electrons decrease voltage of implant

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Fretting / Crevice Corrosion

Crevices and Spatially Separated Half-Cell Reactions

- Crevice and fretting localize oxidation
 - Oxide film repassivation
 - Metal ion dissolution
- Outside Crevice
 - Reduction (multiple, biologically based species available)
- Note: in crevice
 - Oxygen depletion
 - pH drops
 - Cl^- , PO_4^{3-} increases to balance M^{n+}
- Note: Fretting disrupts oxide in crevice and accelerates oxidation by 6 orders of magnitude.
- Build up of electrons drops voltage of surface

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Crevice corrosion

Causes: Concentration gradients in electrolyte cause some areas high in ion concentrations that accelerate oxidation.

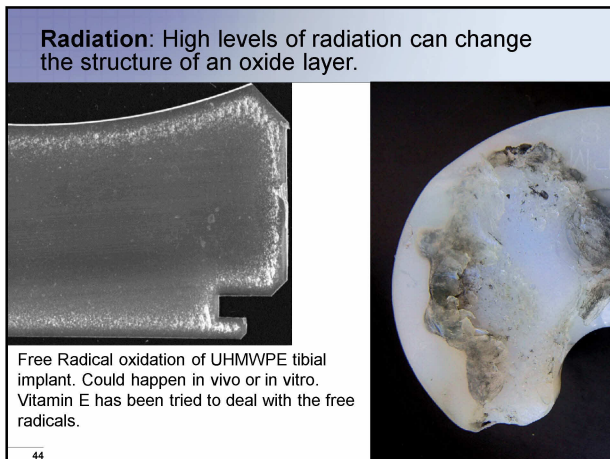
Prevention:
Weld – don't rivet
Polish surfaces
Adjust composition; e.g., add Mo to SS

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Crevice corrosion

Example

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How do we suppress corrosion?

- Self-protecting alloys
- Coatings
- Anodising
- Chemical conversion
- Avoiding of galvanic couples

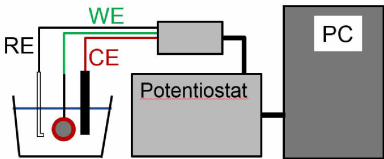




Corrosion test methods

- Electrochemical Analysis
- Ion release analysis

Corrosion test methods
Electrochemical



RE = Reference Electrode
WE = Working Electrode
CE = Counter Electrode

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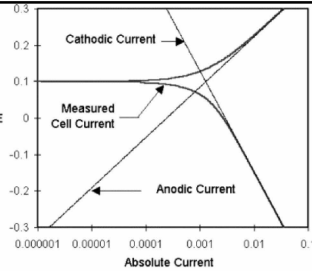
Electrochemical work station

Electrochemical cell

Corrosion test methods

When a metal is immersed in a corrosive medium, both anodic and cathodic currents occur on the specimen surface. Any corrosion processes that occur are usually a result of anodic currents.

At equilibrium a specimen has both anodic and cathodic currents present on its surface which are exactly equal in magnitude, termed the corrosion potential, E_{CORR} .

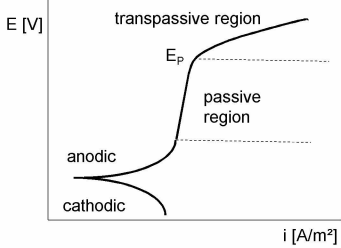


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Corrosion test methods

Potentiodynamic anodic polarization is the characterization of a metal specimen by its current potential relationship. The specimen potential is scanned slowly in the positive going direction and therefore acts as an anode such that it corrodes or forms an oxide coating.

These measurements are used to determine corrosion characteristics of metal specimens in aqueous environments.



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Corrosion test methods

- Counter Electrode (CE) - Graphite rod
- Platinum electrode
- Reference Electrode (RE) - Calomel electrode
- Ag/AgCl
- Working Electrode (WE) - Sample

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Corrosion test methods

Embedding sample in resin

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Sample holder

Corrosion test methods

ISO and ASTM standards

ASTM	
G 1-88	Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens
G 3-89	Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing
G 5-87	Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements
G 16-88	Practice for Applying Statistics to Analysis of Corrosion Data
G 31-72	Practice for Laboratory Immersion Corrosion Testing of Metals
G 46-76	Practice for Examination and Evaluation of Pitting Corrosion
F746-87	Test Method for Pitting or Crevice Corrosion of Metallic Surgical Implant Materials

Source: Annual Book of ASTM Standards, Vol. 3.02, 1989

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Corrosion test methods

Corrosion measurement	
Open-circuit-potential	Immersion of a metal in an electrolyte for a period of time Recording the potential over time Determination of the open-circuit-potential (=E_{corr}) as a function of time
Anodic polarization/ cyclic polarization	Dynamic corrosion measurement at a defined speed Starting in the cathodic region at a potential -E _{corr} , end potential in the anodic part Calculation of parameters see slide
Cyclic voltammetry	Dynamic corrosion measurement at a defined speed (by ex. v=5,10, 20, 50, 100 mV/sec) Starting in the cathodic region until potential in the anodic region and back to the starting potential (by ex. -1V to +1V, back to -1V) Calculation of oxidation and redox peaks

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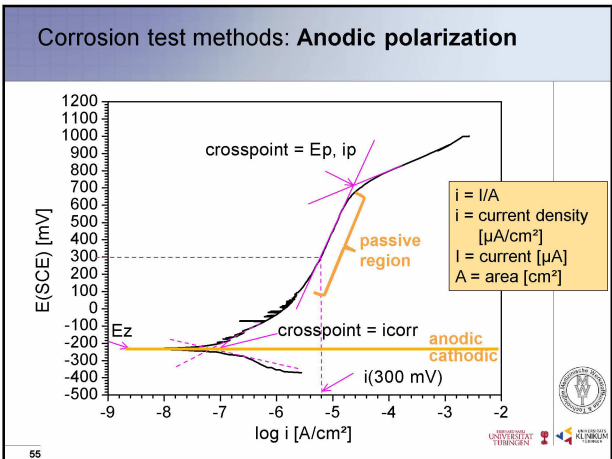


Corrosion test methods

Corrosion measurement	
Potentiostatic polarization	Static corrosion measurement Recording the current over time at a applied potential Determination of the current density after a period of time Calculation of the electrical charge (Q) by integration or $Q=i \cdot t$
Galvanostatic polarization	Static corrosion measurement Recording the potential over time at a applied current density (positive/negative) Determination of the potential after a period of time
Linear polarization (Rp)	Dynamic corrosion measurement at low speed Recording the current density during a potential range of $\pm 20 \text{ mV} \sim E_{\text{corr}}$ Calculation of R_p by linear regression

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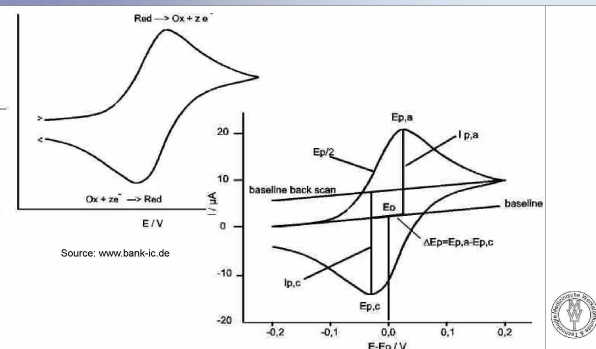
Corrosion test methods: Anodic polarization

Parameter	
Ep [mV]	= pitting potential / breakdown potential crosspoint of passive region and transpassive region by linear regression
ip [μA/cm²]	= corresponding current density at Ep
Ez [mV] or E(i=0) [mV]	= zero potential potential between cathodic and anodic region, the current density = 0
i(300 mV) [μA/cm²]	current density at a potential of 300 mV
E(-6) [mV]	Potential at a current density of 1 μA/cm²
E(-5) [mV]	Potential at a current density of 10 μA/cm²
Ecorr after 2 h [mV]	Potential after 2 h taken from open-circuit-potential measurements



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Corrosion test methods: Cyclic voltammetry





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Corrosion test methods: ISO standards

ISO 10271: Dentistry – Corrosion Test Methods

ISO 10271

Static immersion Test over 42 days in artificial saliva (0.1 M sodium chloride + 0.1 M lactic acid).

Analyzing of the elements by ICP-OES or AAS after 1, 4, 7, 14, 21, 28, 35 and 42 days.

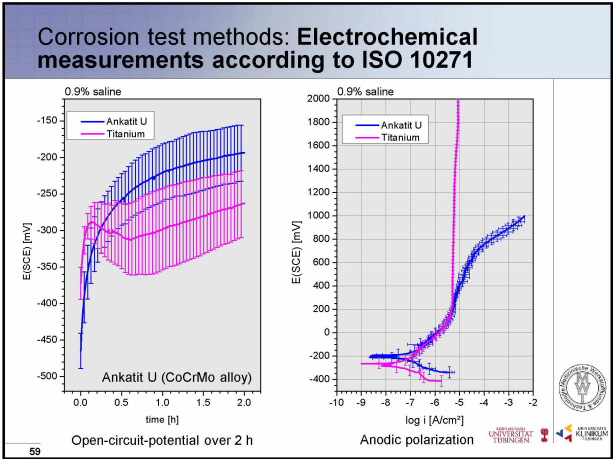
Determination of mass loss rate [μg/cm² 7d]

Electrochemical corrosion measurements consisting of open-circuit-potential measurements over 2 hours followed by anodic polarization starting from -150 mV~Ecorr to 1 V (Ref) with a speed of 1mV/sec in 0.9% saline at 37°C.

The parameters Ecorr after 2 h, Ez, Ep, ip, icorr, i(300mV+Ez) must be determined.



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Corrosion test methods: **Electrochemical measurements according to ISO 10271**

Parameter	Ankattit U	Titanium
E _{corr} after 2h [mV]	-190 ± 48	-263 ± 46
E _z [mV]	-215 ± 37	-273 ± 38
E _p [mV]	708 ± 27	-
i _p [μA/cm ²]	31 ± 16	-
i _{corr} [nA/cm ²]	87 ± 3	56 ± 10
i ₃₀₀ [μA/cm ²]	7 ± 1	5 ± 0
i(300mV+E _z) [μA/cm ²]	3 ± 0	2 ± 1
Additional parameters		
E(-6) [mV]	-272 ± 39	-8 ± 50
E(-5) [mV]	-	-
β _a [mV/dec]	190 ± 7	200 ± 21
β _c [mV/dec]	115 ± 35	131 ± 15

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Corrosion test methods: **Measurements according to ISO 10271**

Static Immersion Test

- 3 samples with a size of 30 x 10 x 1.5 mm
- Wet-grinding of the samples up to SiC1200.
- Ultrasonically cleaning with ethanol for 3-5 minutes.
- Each sample is put into a 15 ml PP-tube and filled with 10 ml 0.1 M sodium chloride/0.1 M lactic acid.
- The samples are stored in a climate chamber at 37°C.
- Change of the electrolyts after 1, 3, 7, 14, 21, 28, 35 and 42 days.
- Analysis of the electrolytes with ICP-OES
- Calculation of mass loss for each sample and day
- Limit of total mass loss rate : < 200 μg/cm² after 7 days

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Corrosion test methods: **Measurements**
according to ISO 10271



Sampes in climate chamber (37°C)



Analysis of ion release (ICP-OES)

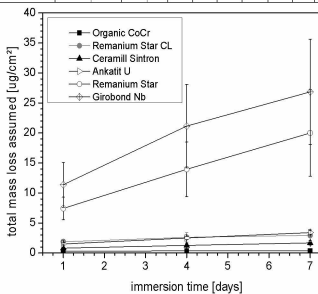


Auto sampler

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Corrosion of dental alloys / biomedical alloys
Static immersion test according to ISO 10271

Name	Co	Cr	Mo	W	Fe	Nb	Si	Mn	Ce	N	Ni	C	PRE
Remanium Star	61	28	-	9	-	x	1.5	-	-	x	-	-	42.85
Organic CoCr	63.55	28.4	6	-	0.5	0.5	0.6	-	-	-	0.05	0.002	48.2
Ceramill Sintiron	66	28	5	-	<1	-	<1	<1	-	-	-	-	44.5
Girobond Nb	62	25	5	5	<1	1.2	-	0.3	<1	-	-	-	49.75
Ankafit U	62.3	25.2	6	5	-	-	-	-	-	-	-	<0.02	53.25



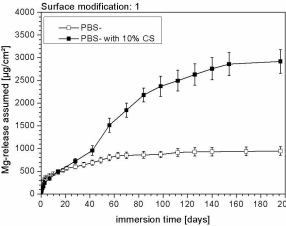
total mass loss assumed [µg/cm²]

immersion time [days]

PRE=
Pitting Resistant Equivalent
PRE=Cr+3.3(Mo+0.5W)

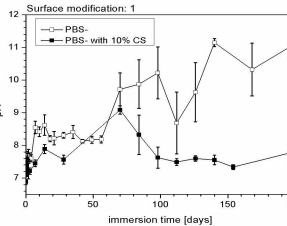
63

Static Immersion test according to ISO 10271 with
magnesium alloy WE43



Mg-release assumed [µg/cm²]

immersion time [days]



pH

immersion time [days]

Mg-release of WE43 (grinded) and electrolyte pH change

64

