New insights into chemical passivation of stainless surgical steel: Corrosion prevention and beyond

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Corrosion of surgical instruments – a persistant problem

Surgical instruments are constantly exposed to corrosive conditions.

Costs

- → **time for visual inspection**
  (is it blood or corrosion?)
- → **repairs**
- → **replacement items**

Chemical passivation methods

a) No passivation

Moisuring foam (*optionally*) → Manual Prewash (*optionally*) → Cold automated Prewash → Automated Wash → Rinse → Thermal disinfection

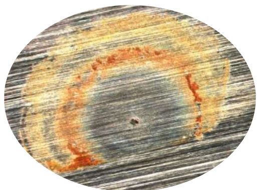
b) Periodic <u>separate</u> «service» cycle (not validated according to ISO 15883)

Alkaline Wash → Rinse → **Phosphoric /nitric acid product** → Rinse → **Returned to validated process**

c) Routine in-cycle passivation with citric acid-containing product

Moisuring foam (*optionally*) → Manual Prewash (*optionally*) → Cold automated Prewash → Automated Wash → Rinse → **In-process passivation** → Rinse → Thermal Dis-infection

Corrosion damage – what is the root cause?

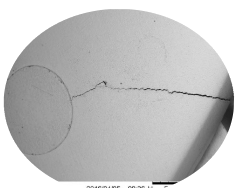


Pitting corrosion

Friction corrosion

Crevice corrosion

Galvanic corrosion



Stress corrosion

Laser marking

Corrosion of surgical instruments is associated with damage to the protective oxide layer („*passive layer*“)

- Mechanical stress
- Thermal stress (e.g. laser marking)
- Chemical stress:
  - Blood, skin disinfectant

Recommendation: «Red Brochure, 11th edition, AKI» https://www.a-k-i.org

Iron oxidises in an electrochemical redox-reaction to iron oxide („rust“)

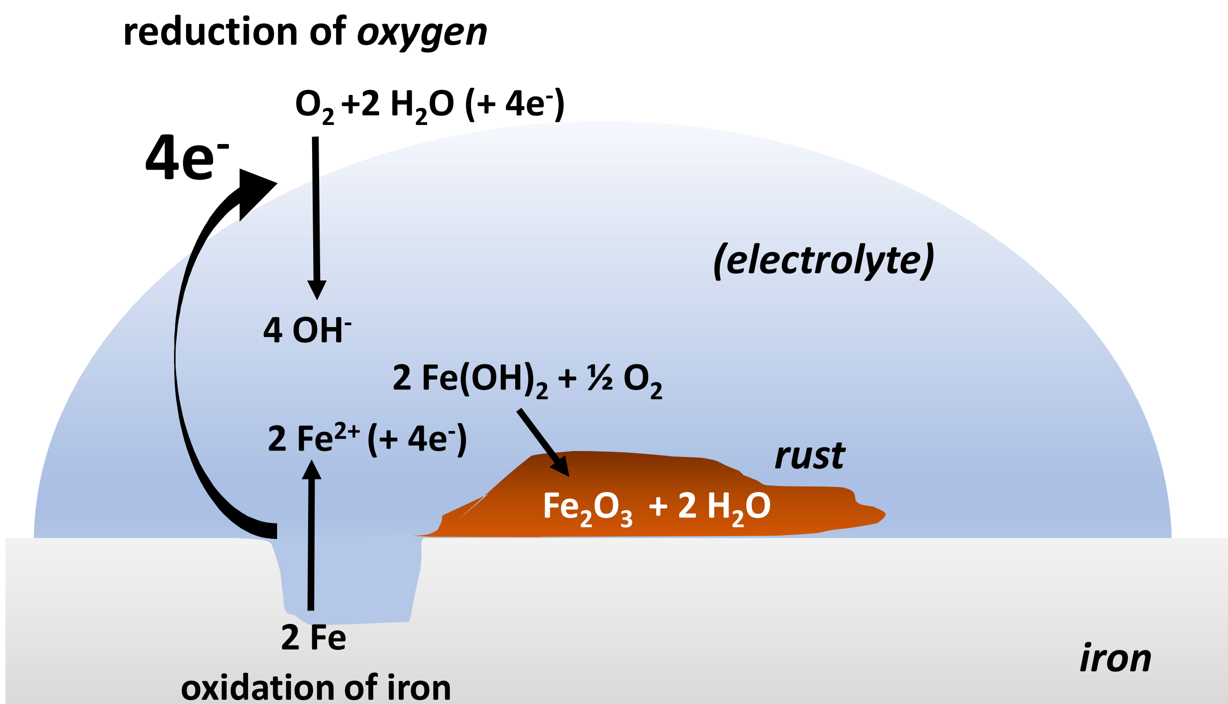
cathode

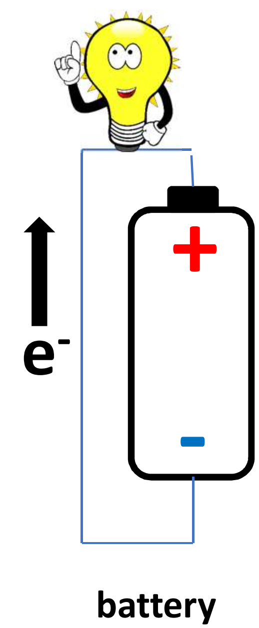
(+)

flow of electric current (electrons e^-)

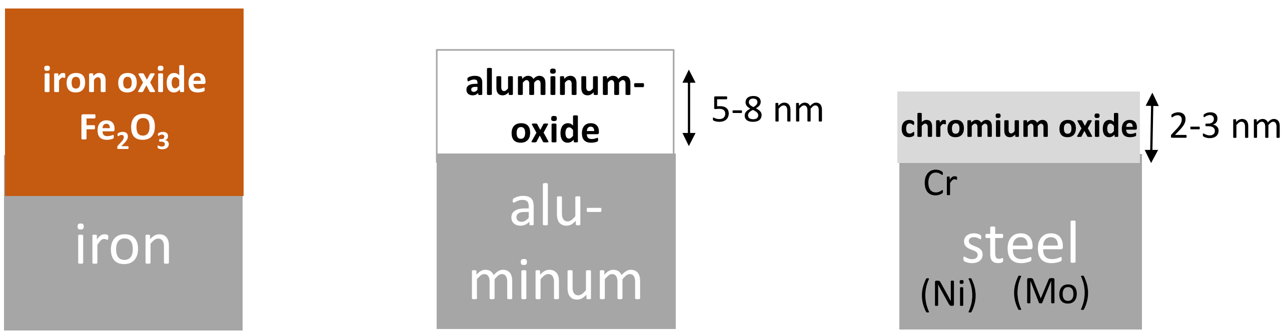
anode

(-)





A superficial oxide layer (passive layer) protects metal from corrosion



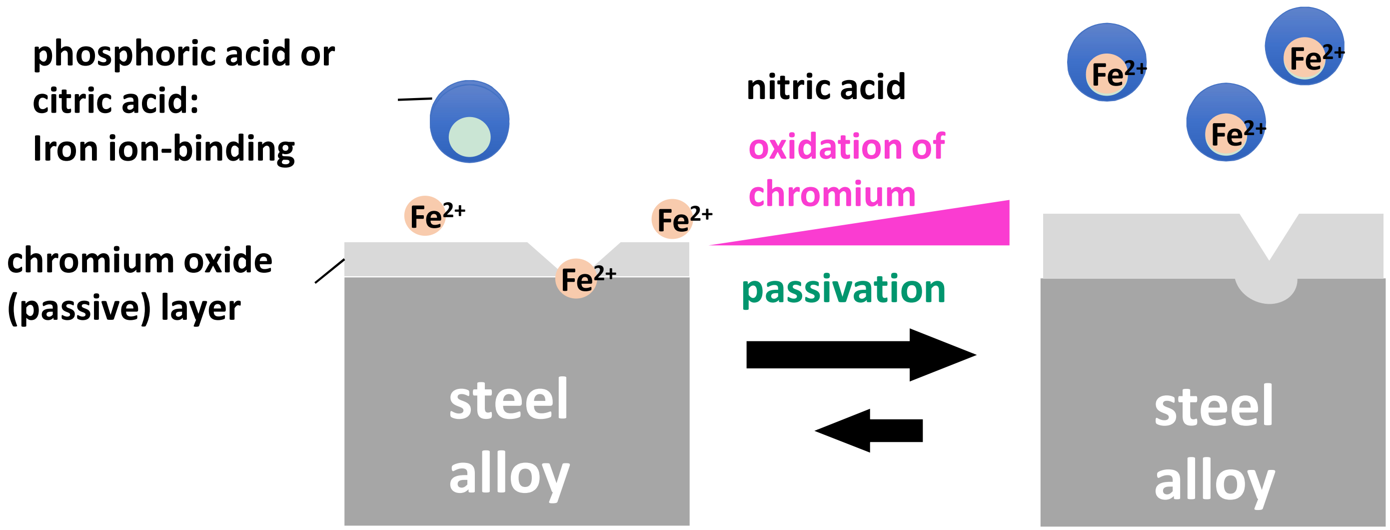
A chromium content of at least 12% allows for the formation of a protective oxide layer

Not self-passivating

Self-passivating

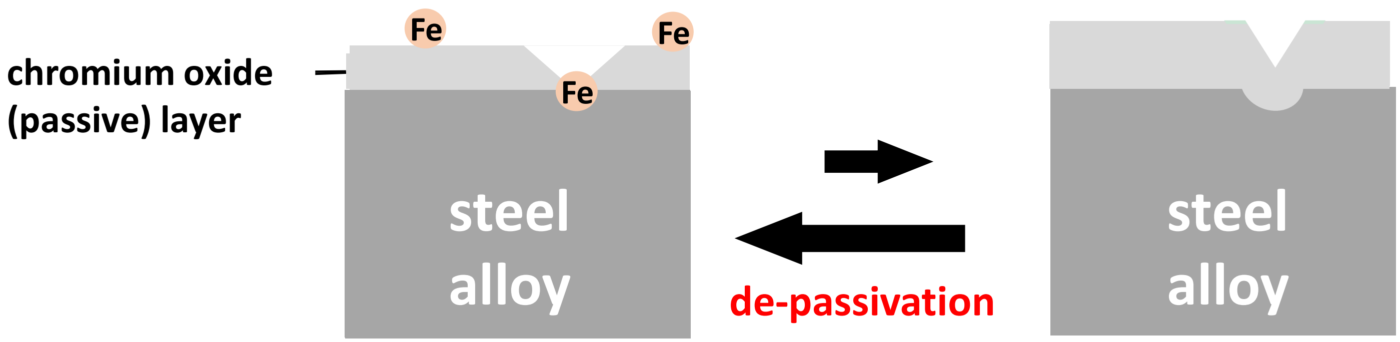
Can be passivated by a adding a blend of specific elements to the alloy

Better passivation through chemistry…



- Removal of free iron by phosphoric acid or citric acid
- Support of chromium oxidation by oxidizing chemistry, e.g. nitric acid

Daily use degrades the passive layer: de-passiation

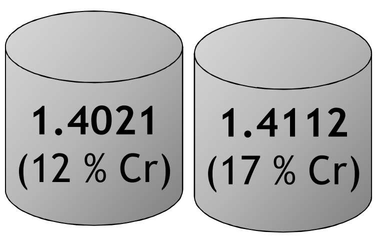


- Removal of chromium by chlorid ions (blood …), de-ionized water (sterilisation)
- Breach of the passive layer by mechanical damage

Intended purpose and manufacturability influence the choice of alloy and corrosion resistance

Alloy no. EN 10088-1	Chrom-ium content	Short name EN 10088-1	Hardness In Rockwell ISO 6508-1	usage ISO 7153-1	Corrosion resistance
1.4021	12-13 %	X20Cr13	44 - 48	Diverse (Foreceps, tongs… no scissors)	Minimum of chromium for forming a passive layer
1.4112	17-18 %	X90CrMoV18	52 - 60	Chisel, etc.	Good, relatively high chromium content

Design of the study



steel coupons
14 x 8 mm
polished surfaces (1 µm)

alkaline wash

70 °C, 10 min
1 % detergent

passivation

85 °C, 30 min

a) **no passivation**
b) **phosphoric-/nitric acid** (2 % deconex® 34 GR)
c) **citric acid** (0.5 %)

(equal amounts of acid)

analyses

1. **Passivation properties**
   Accelerated corrosions tests
   Electro-chemical tests
2. **Chemical properties**
   XPS, HAXPES
3. **Surface properties**
   Water contact angle
   Protein adhesion

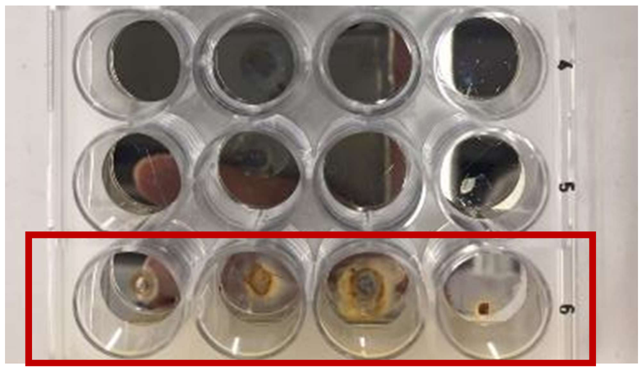
Accelerated corrosion tests

Salt spray test

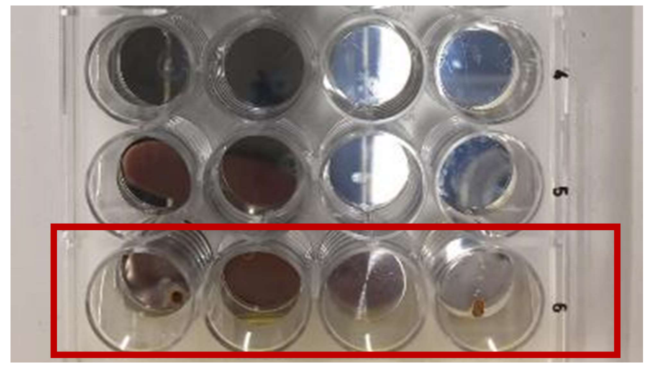
(ISO 9227:2017)

Awaiting report
(ca. 1000 h)

1.4021 (12 % Cr)



1.4112 (17 % Cr)



Passivated

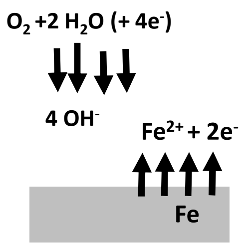
Not passivated

Not passivated test bodies corroded already after 1 h in physiological saline solution (0.9 % NaCl)

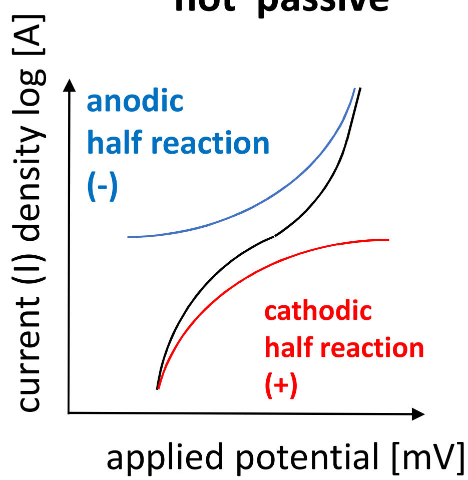
Assessment of corrosion resistance by electrochemical measurements

cathodic
half reaction
(+)

anodic
half reaction
(-)

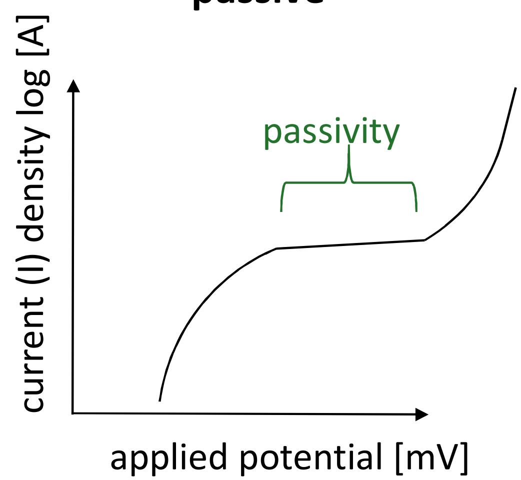


not passive

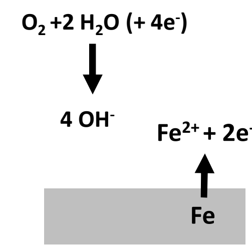


current increases rapidly

passive

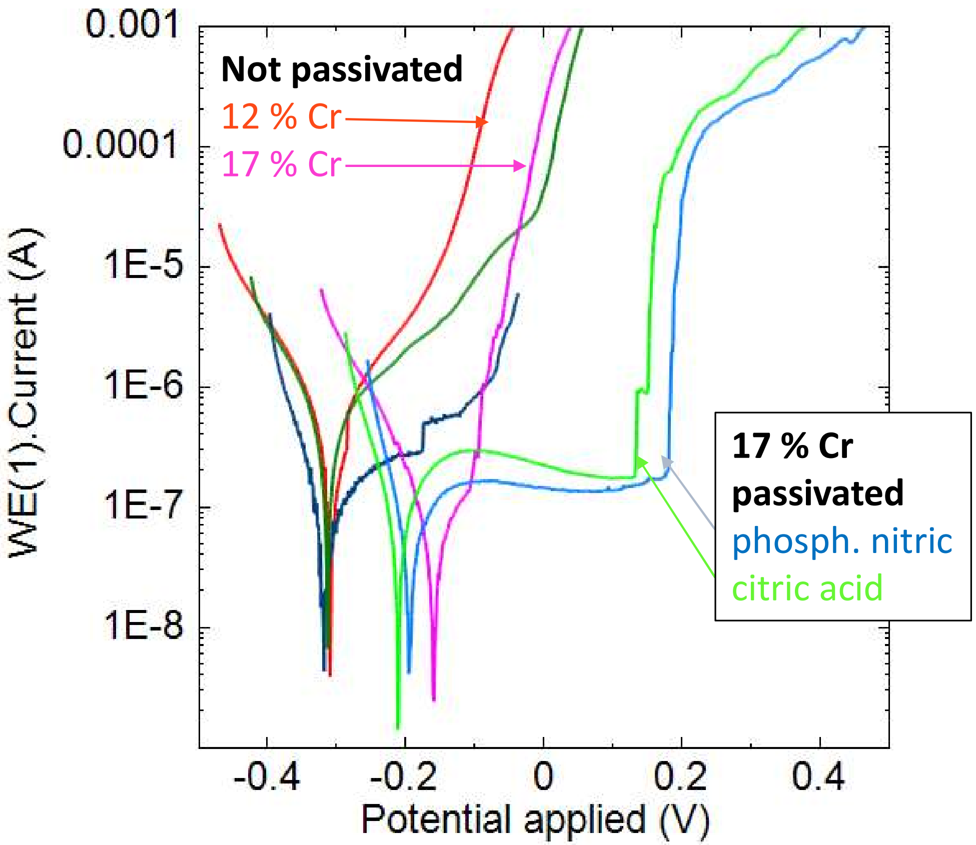


current (i.e., the redox-reaction) increase is delayed



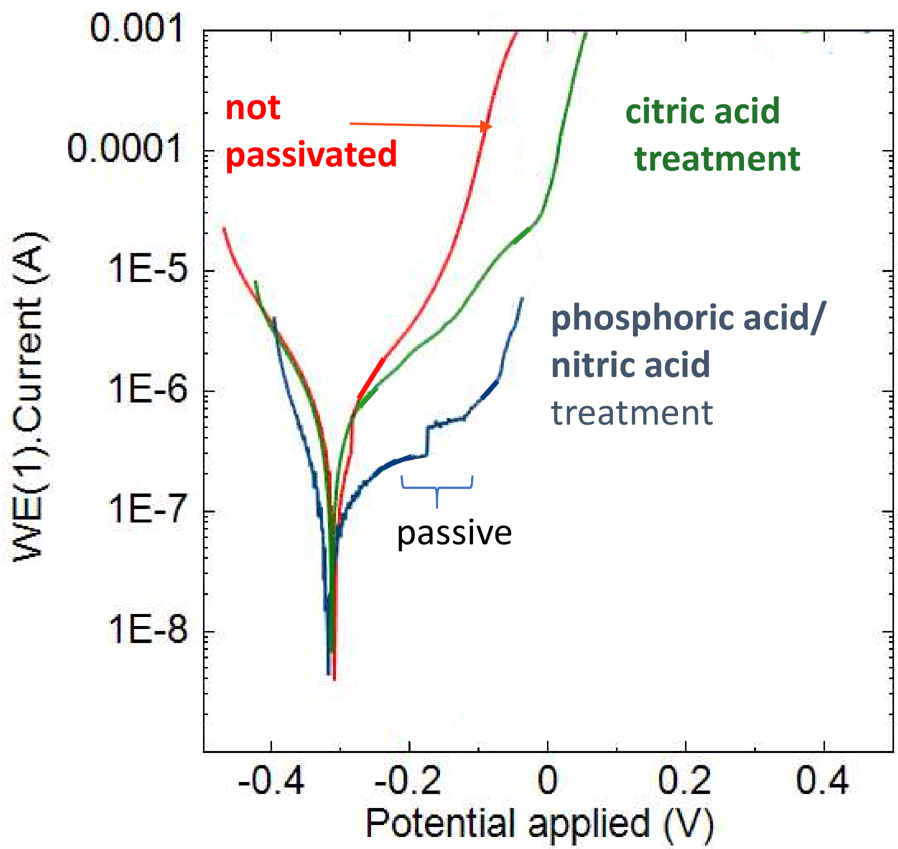
Measuring the dissolution of the iron metal via measuring the flow of electrical current «*potential* measurements»

Measurement of passivity by potential measurements



- **Not passivated test bodies** (both alloys, 12 % Cr, 17m % Cr) showed no corrosion protection
- **Alloy 1.4112 (17 % chromium):** both treatments achieved similar, good results

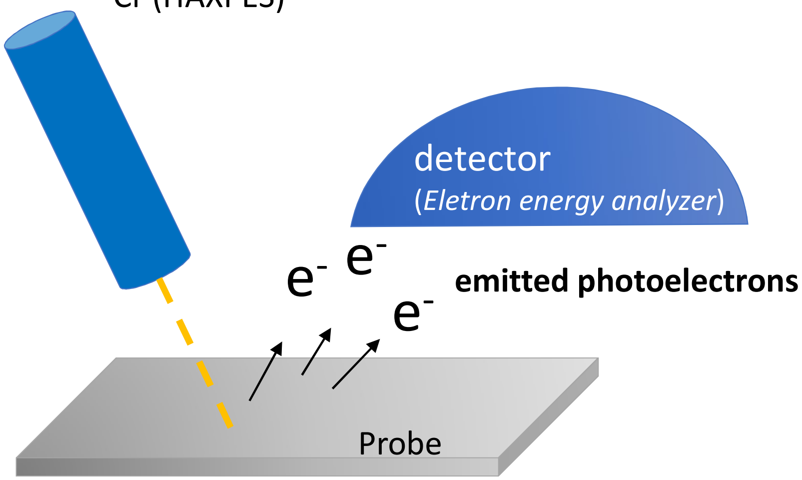
Measurement of passivity by potential measurements



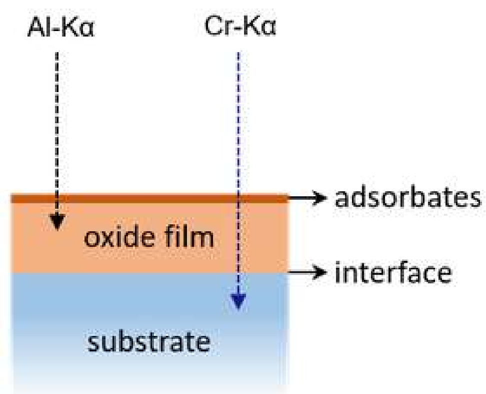
- **Alloy 1.4021 (12 % chromium)**: significantly better passivation with phosphoric acid/ nitric acid

X-ray Photoelectron Spectroscopy (XPS) and Hard X-ray Photoelectron Spectroscopy (HAXPES)

X-ray source
Al (XPS)
Cr (HAXPES)



alloy 1.4021



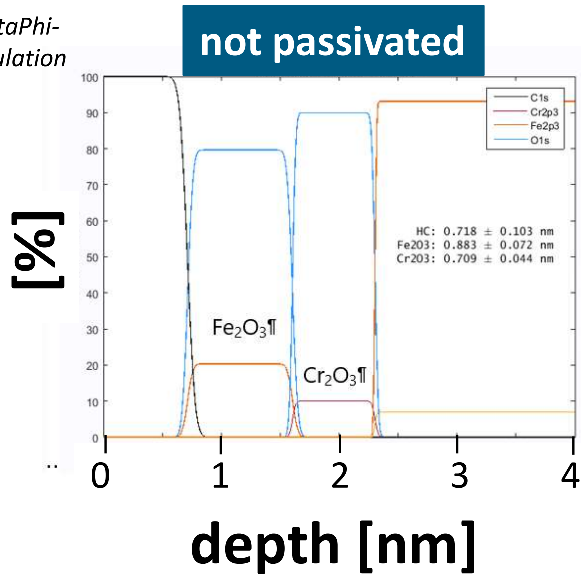
sketch: Empa

XPS:
Al-Kα x-ray source: **Analysis of the upper 4 nm**

HAXPES:
Cr-Kα (high energy) x-ray source: **Analysis of the upper 20 nm**

Assessment of passive layer architecture via HAXPES

StrataPhi-Simulation



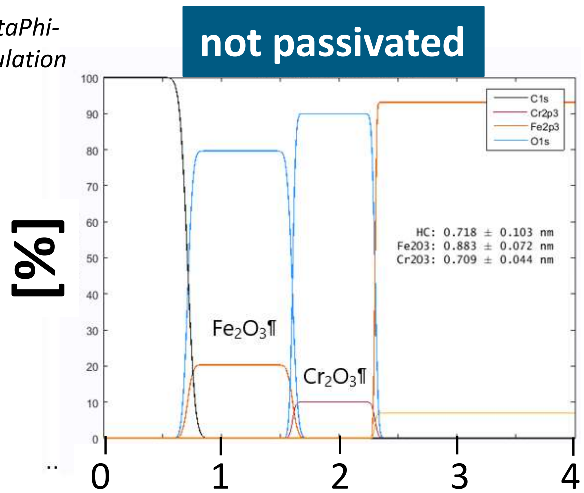
Iron oxide ca. 1 nm

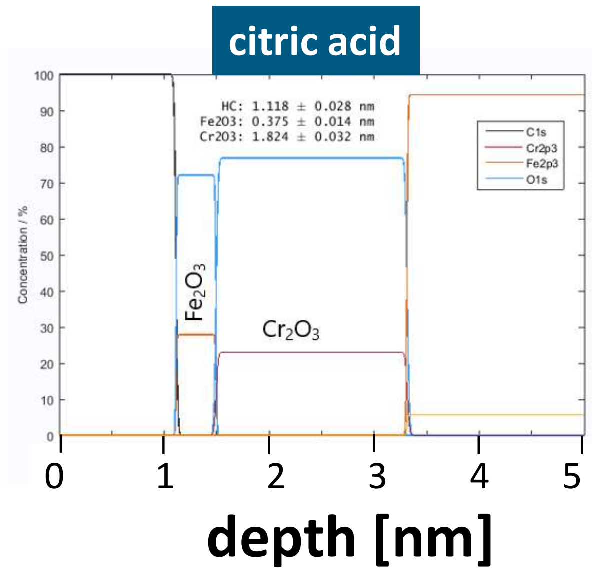
chromium oxide ca. 0.6 nm

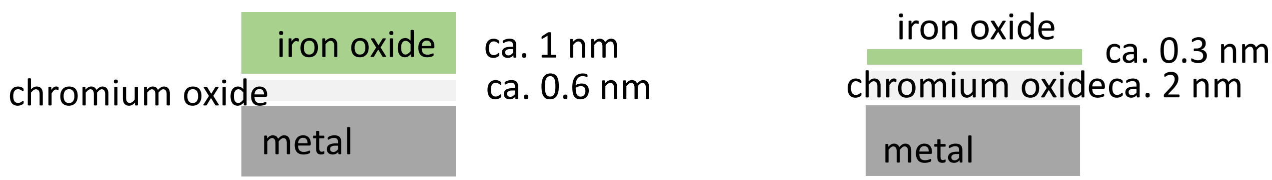
metal

Assessment of passive layer architecture via HAXPES

StrataPhi-Simulation



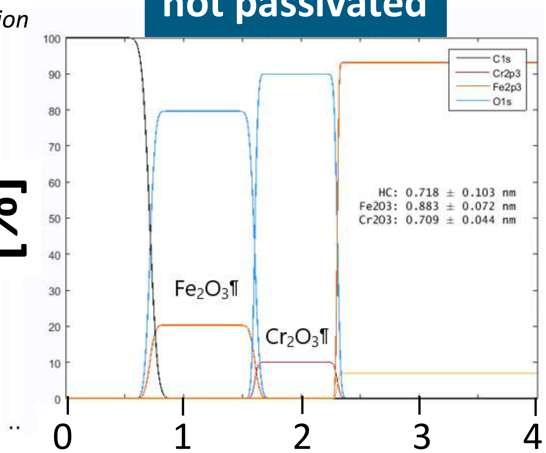




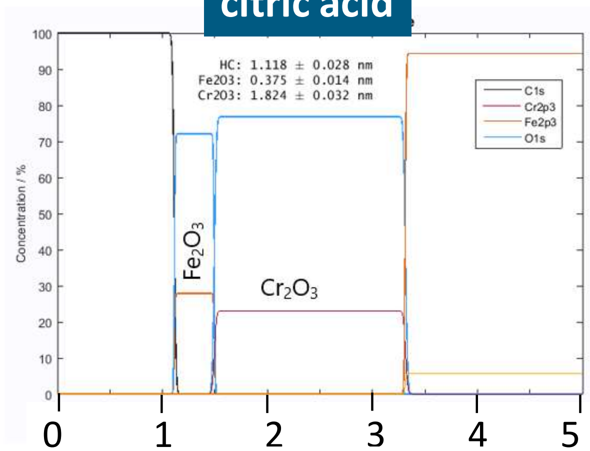
Phosphoric/nitric acid of 1.4021 steel yielded a 5 × thicker passive layer than citric acid

StrataPhi-Simulation

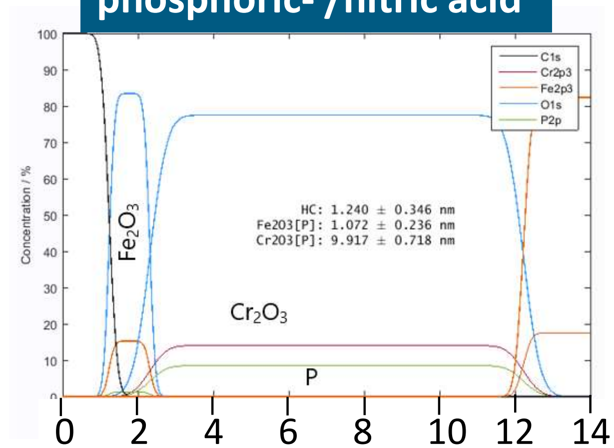
not passivated



citric acid



phosphoric- /nitric acid



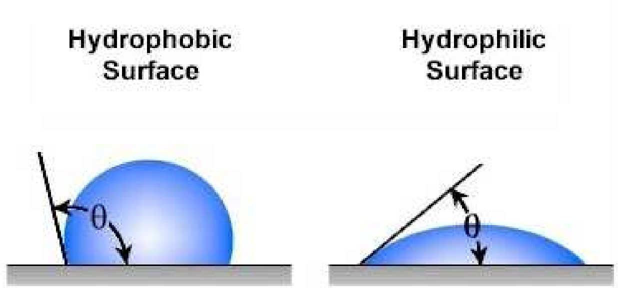
depth [nm]

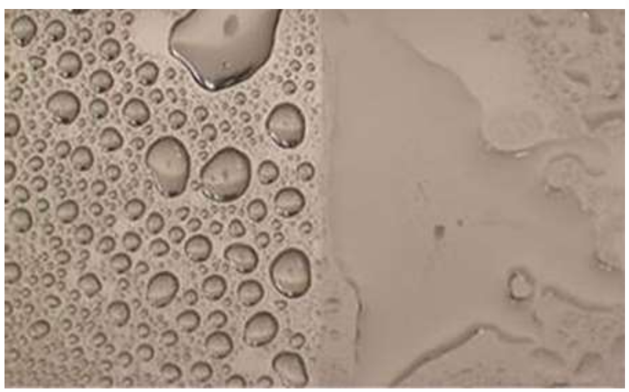
iron oxide ca. 1 nm
chromium oxide ca. 0.6 nm
metal

iron oxide ca. 0.3 nm
chromium oxide ca. 2 nm
metal

iron oxide ca. 0.3 nm
ca. 10 nm **chromium oxide/ chromium phosphate**
metal

Passivation alters steel surface properties: Water contact angle measurements





sample	Passi-vation	Fresh (°)	After 14d (°)
12% Cr	none	57.5	69.1
	Ph/Nitr	37.4	49.7
	citric	34.5	55.2

deviation ≤ ± 0.4°; n = 3

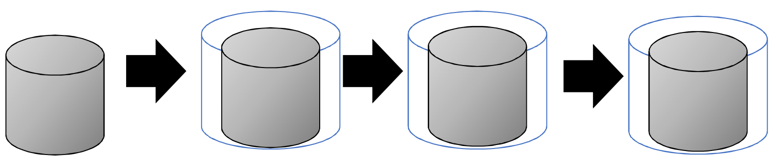
Freshly passivated samples

➔ Better drying performance in the washer disinfector?

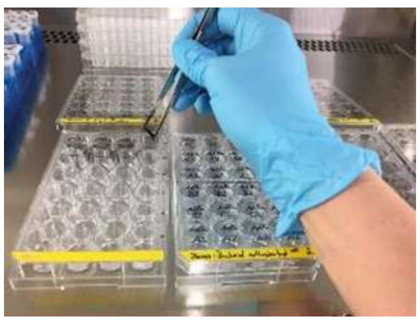
Assessment of adhesion of blood protein (BSA, bovine serum albumin)

Protein adhesion assay

2X



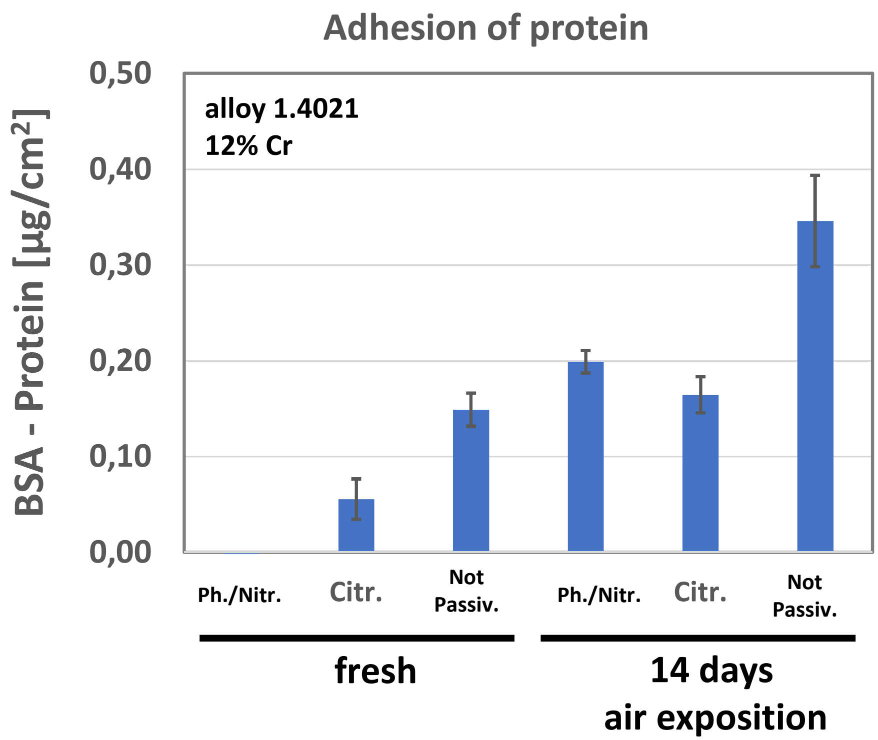
1.4021 12 % Cr → **200 µg/mL BSA** → **wash (water)** → **1 % SDS extraction**



Micro BCA protein assay

A_{562nm}, *(working range 0.5 – 20 µg/mL)*

n = 3 technical replicates



Conclusions

- **Passivation increases corrosion resistance**
- Passivation **renders stainless steel surfaces hydrophilic**, which **may have an influence of adhesion of soil and the drying process**
- Passivation with **phosphoric acid/ nitric acid**
  - was **significantly more effective on 1.4021 stainless steel** (12 % chromium) than citric acid passivation
  - yielded on 1.4021 steel a **5-fold thicker and differently composed** (chromium oxide/ chromium phosphate-containing) passive layer, when compared with citric acid passivation

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