Micro-arc anodized magnesium AZ31 alloy: towards application in veterinary implants

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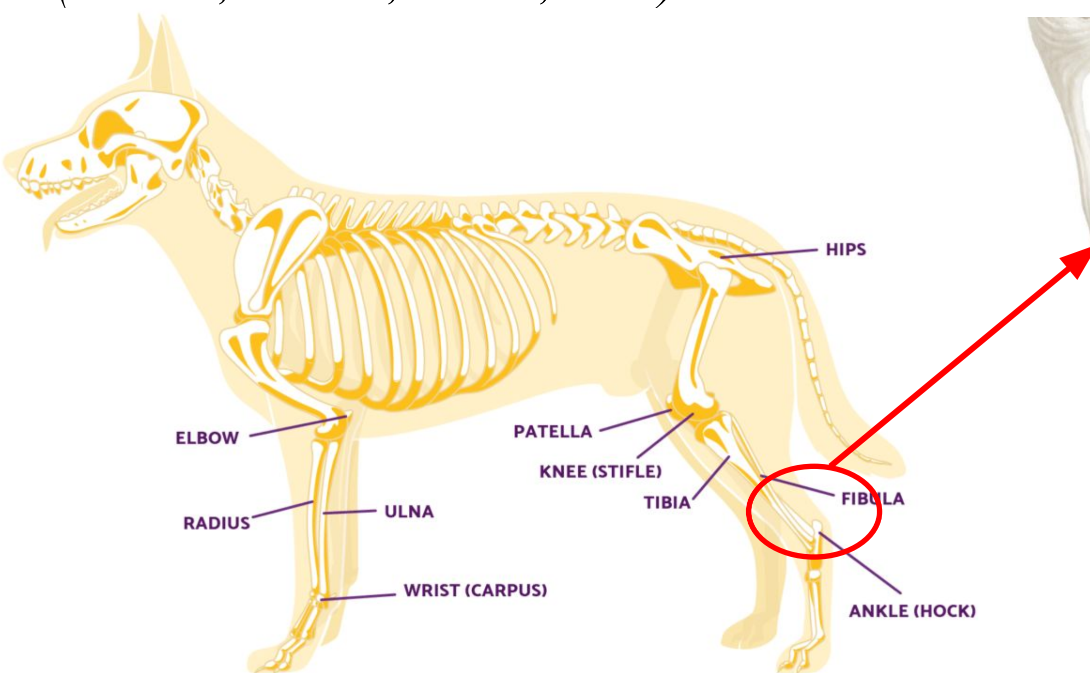
[MEET THE EXPERT] IMPLANTS

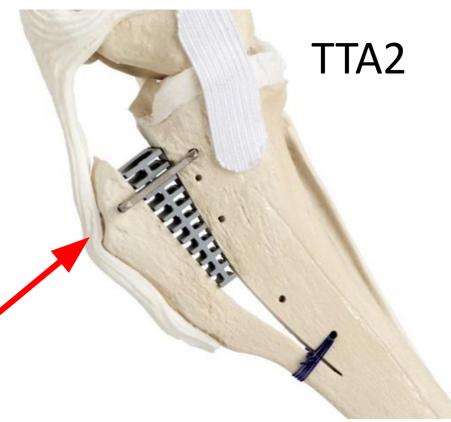
8th September, 2022

Introduction

KYON is leading Swiss provider of orthopedic implants and instruments to the veterinary market.
In 2004, KYON launched TTA (Tibial Tuberosity Advancement) for Cranial Cruciate deficiency in dogs

*Rupture of the Cranial Cruciate Ligament is the most common cause of lameness in dogs. US dog owners spent **$1.3 billion** on Cranial Cruciate treatment in the US in 2003 (JAVMA, Vol 227, No. 10, 2005)*





TTA2

TTA

www.kyon.ch/products-solutions/tta_tibial-tuberosity-advancement

Motivation

1st generation of KYON TTA is in **CP-4 Titanium**.

Advantages of using a Mg-alloy (MgAl3Zn1 or AZ31):

- bioresorbable (dissappears after several months)
- non-toxic;
- mechanical strength (290 MPa), ductility (elongation at break 15%), Young's modulus (45 GPa), machinability;
- economically affordable;
- in vivo biocompatibility*

* *N. Kawamura et al., Degradation and Biocompatibility of AZ31 Magnesium Alloy Implants In Vitro and In Vivo: A Micro-Computed Tomography Study in Rats, Materials. 2020 13(2):473.*

F. Witte et al., In vivo corrosion of four magnesium alloys and the associated bone response, Biomaterials, 2005, 26(17):3557-63.

Motivation

Magmaris® *stent from Biotronik*

Magnezix® *screw from Syntelllix*

www.biotronik.com/en-de/products/coronary/magmaris

www.syntellix.de

Problem

However, Mg degrades too fast in biological medium □

$$Mg_{(implant)} + 2H_2O \rightarrow Mg(OH)_2 + H_{2\,(gas)}$$

- Release of hydrogen gas around the implant (rejection)
- Loss of mechanical stability

The corrosion of a Mg implant must be carefully controlled (5 weeks)!

Solution

Micro-Arc Oxidation, MAO (also called **Plasma Electrolytic Oxidation, PEO**)

- PEO is well-established industrial anodizing process for Ti, Al, Mg;

Titanschrauben mit *Biocer* versehen (REM-Aufnahme der porösen Oberflächenmorphologie).

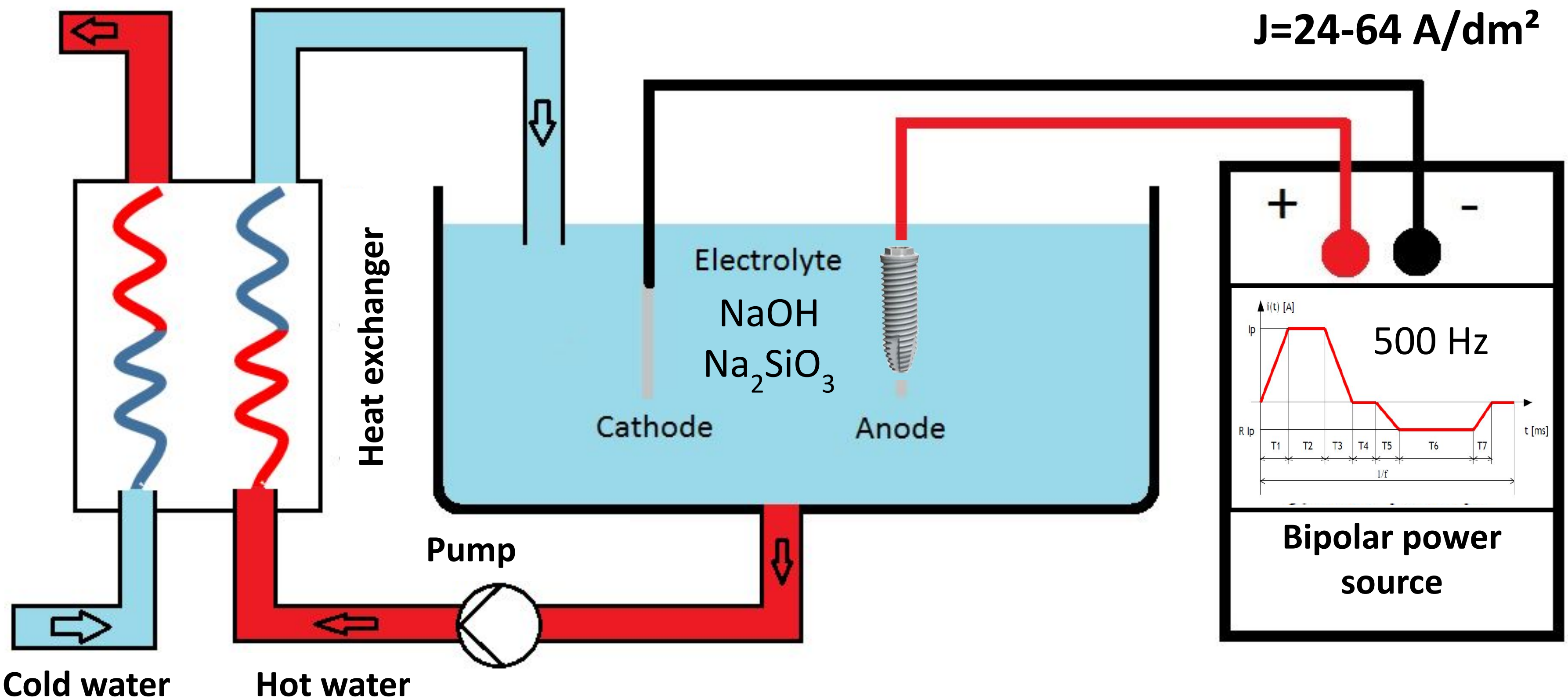
- PEO is fast and efficient (thick oxide layers in a few minutes);
- PEO uses “safe” chemicals;
- High number of publications and patents on PEO for Mg-alloys suggests its potential for implants

Plasma Electrolytic Oxidation (PEO)

PEO is similar to conventional anodizing, but at much higher voltages (>500 V)

□ Thicker (up to 200 µm) oxide layer (a breakdown threshold is overcome)

Mg^{2+} + O^{2-} □ MgO (surface layer)

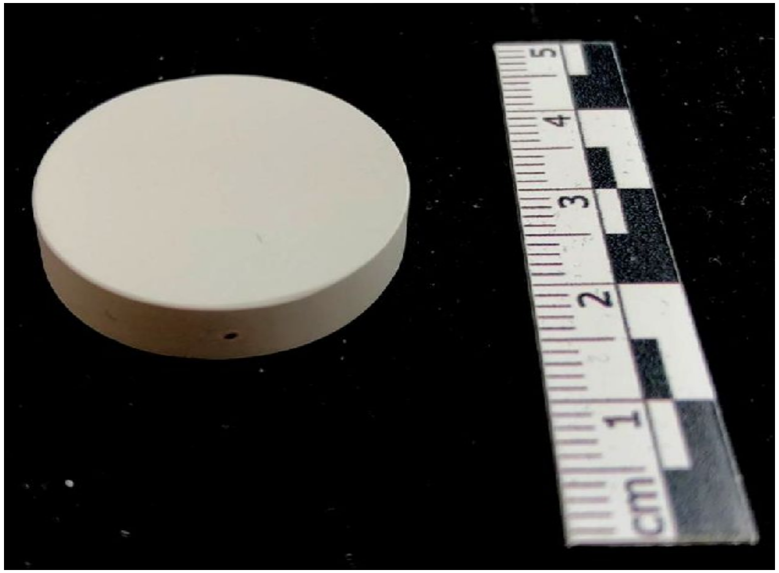


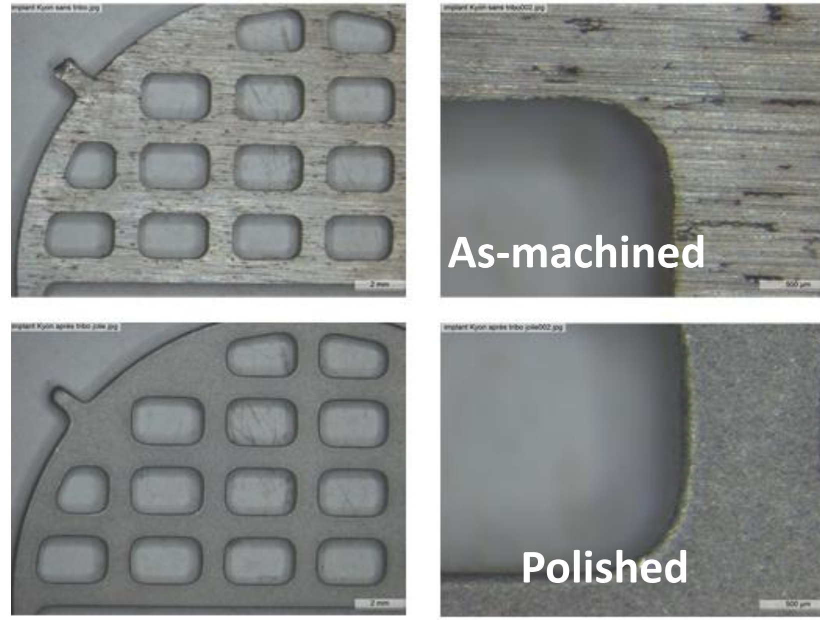
Plasma Electrolytic Oxidation (PEO)

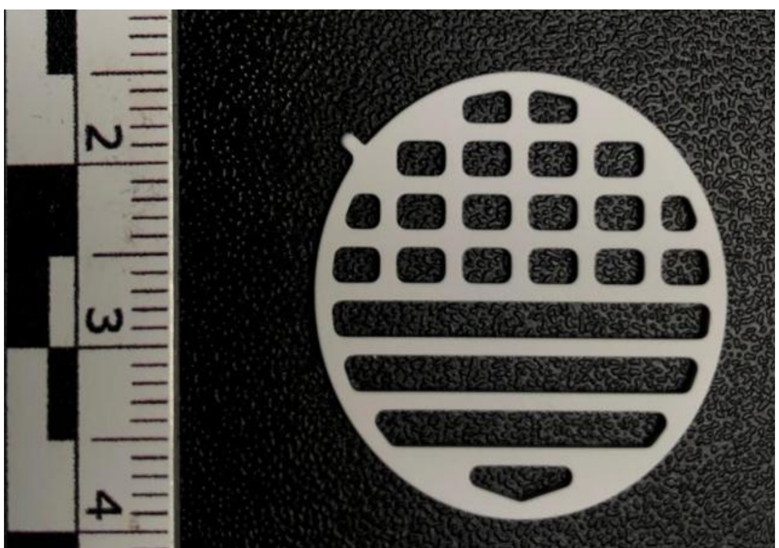
PEO is similar to conventional anodizing, but at much higher voltages (>500 V)

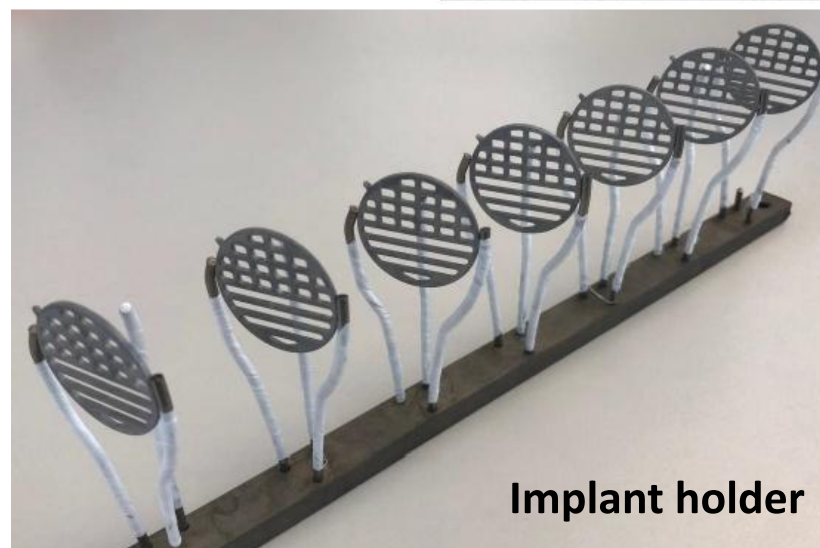
- Numerous electric arcs
- Local melting of the growing oxide layer
- Re-solidification and densification

Test samples



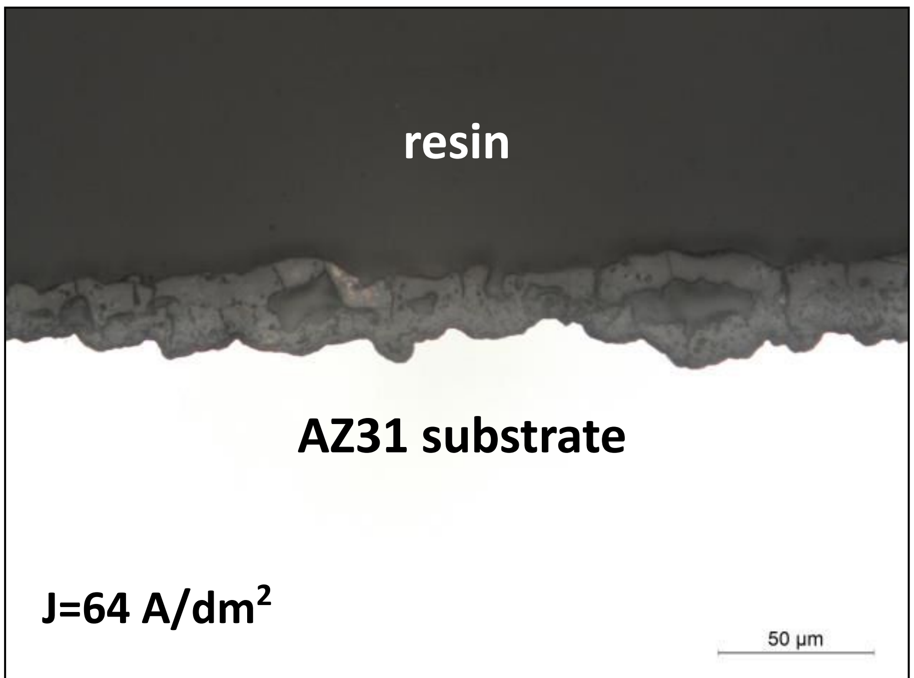




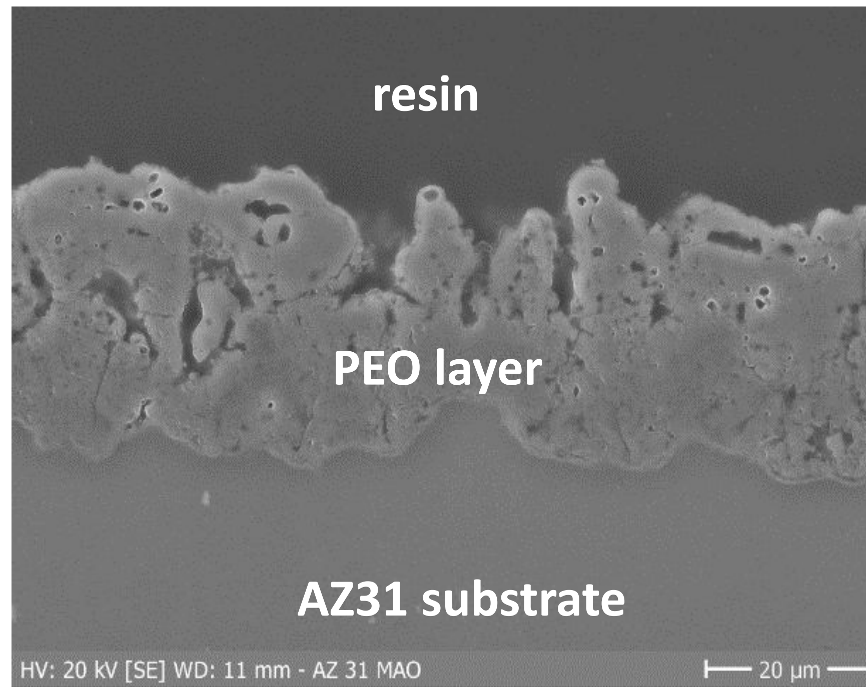


Cross-section morphology

- High surface roughness (a few μm)
- Morphology presents internal pores
- Layer coverage is OK over 3D implant geometry (inside the holes)
- Thickness increases linearly with the current density **(J)** from **7**±2 μm at J=**24** A/dm^2 to **25** ±12 μm at J=**64** A/dm^2 (treatment time **5 min**)



Optical Microscopy image

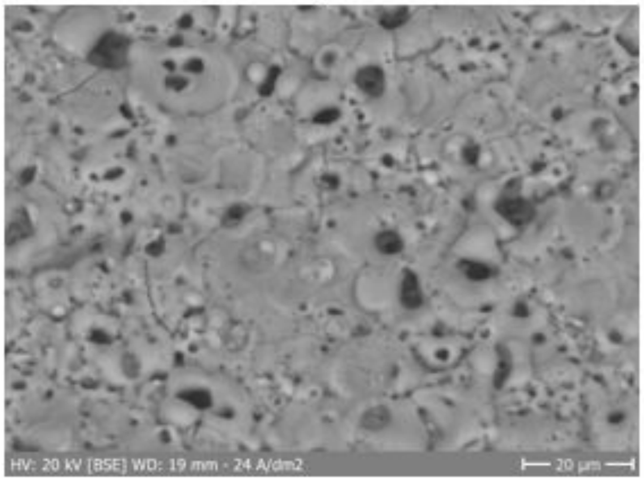


Scanning Electron Microscopy (SEM) image

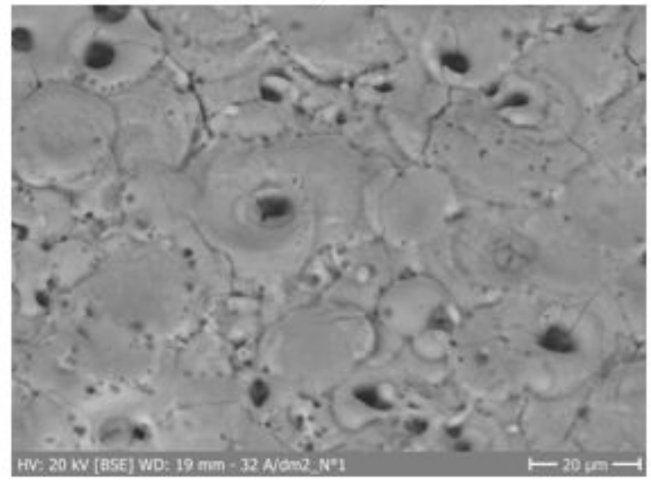
Surface morphology

Surface morphology presents open pores. Cracks appear at higher energies

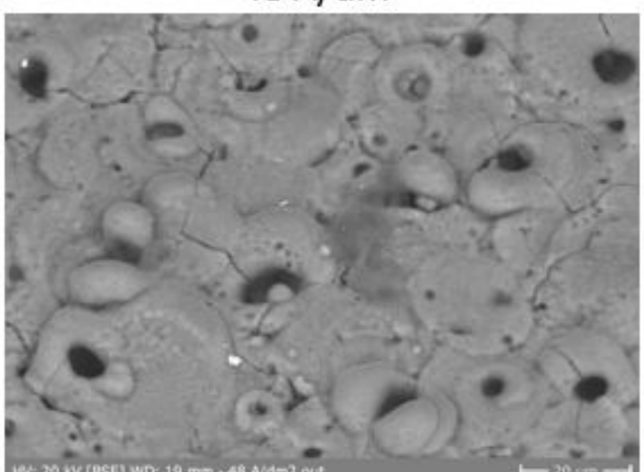
24 A/dm²



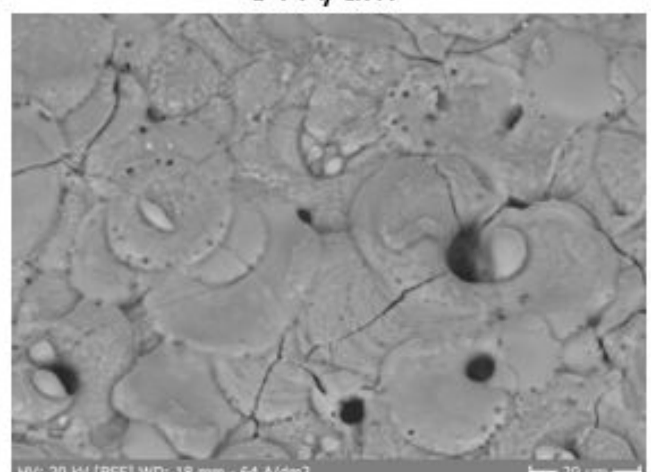
32 A/dm²



48 A/dm²



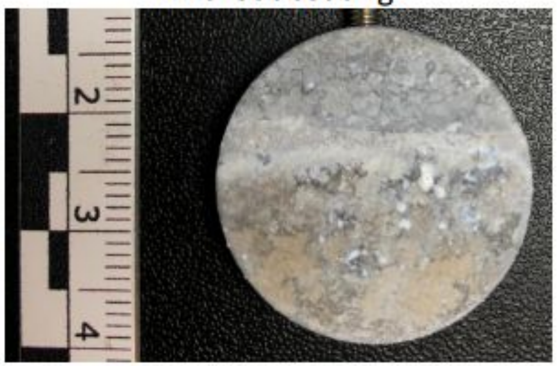
64 A/dm²



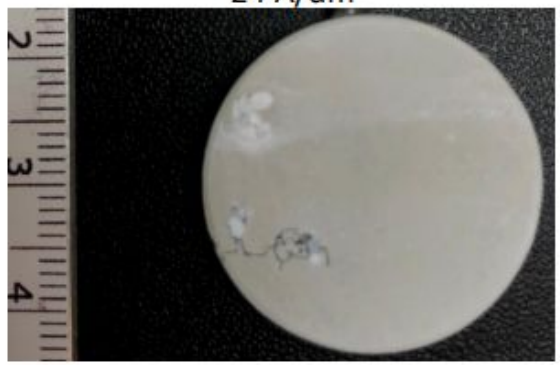
Immersion tests of the discs

After **21 days** of immersion in Simulated Body Fluid (Ringer's solution) @37°C

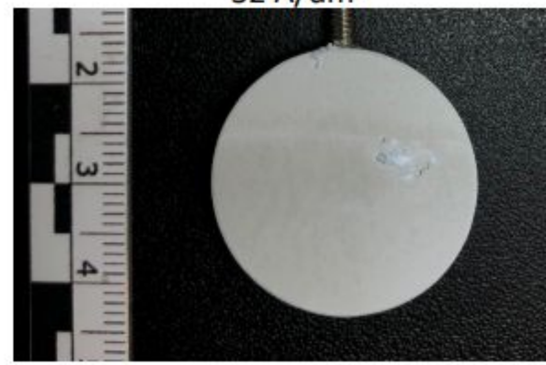
Without coating



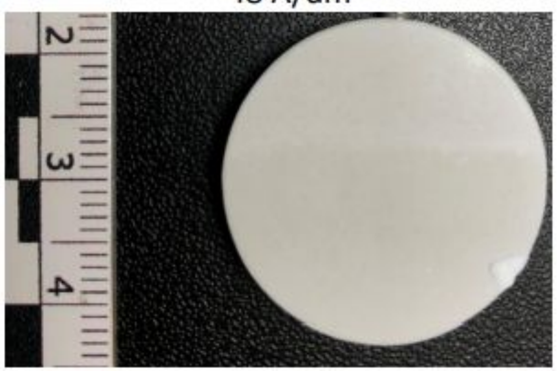
24 A/dm^2



32 A/dm^2



48 A/dm^2



64 A/dm^2

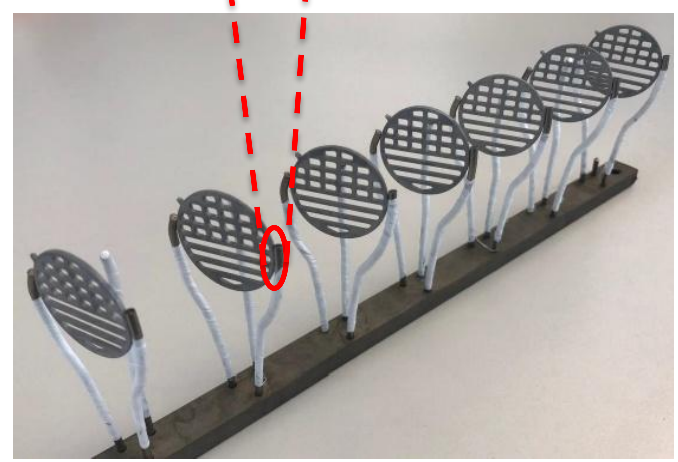
- Current density (***J***) does not have much influence on the corrosion resistance
- Corrosion spots occur randomly, esp. at edges

Immersion tests of the implants

7 days **14 days** **21 days**

PEO parameters:

- Current density: **J=32 A/dm^2**
- Time: 5 min
- Layer thickness: ~10 µm

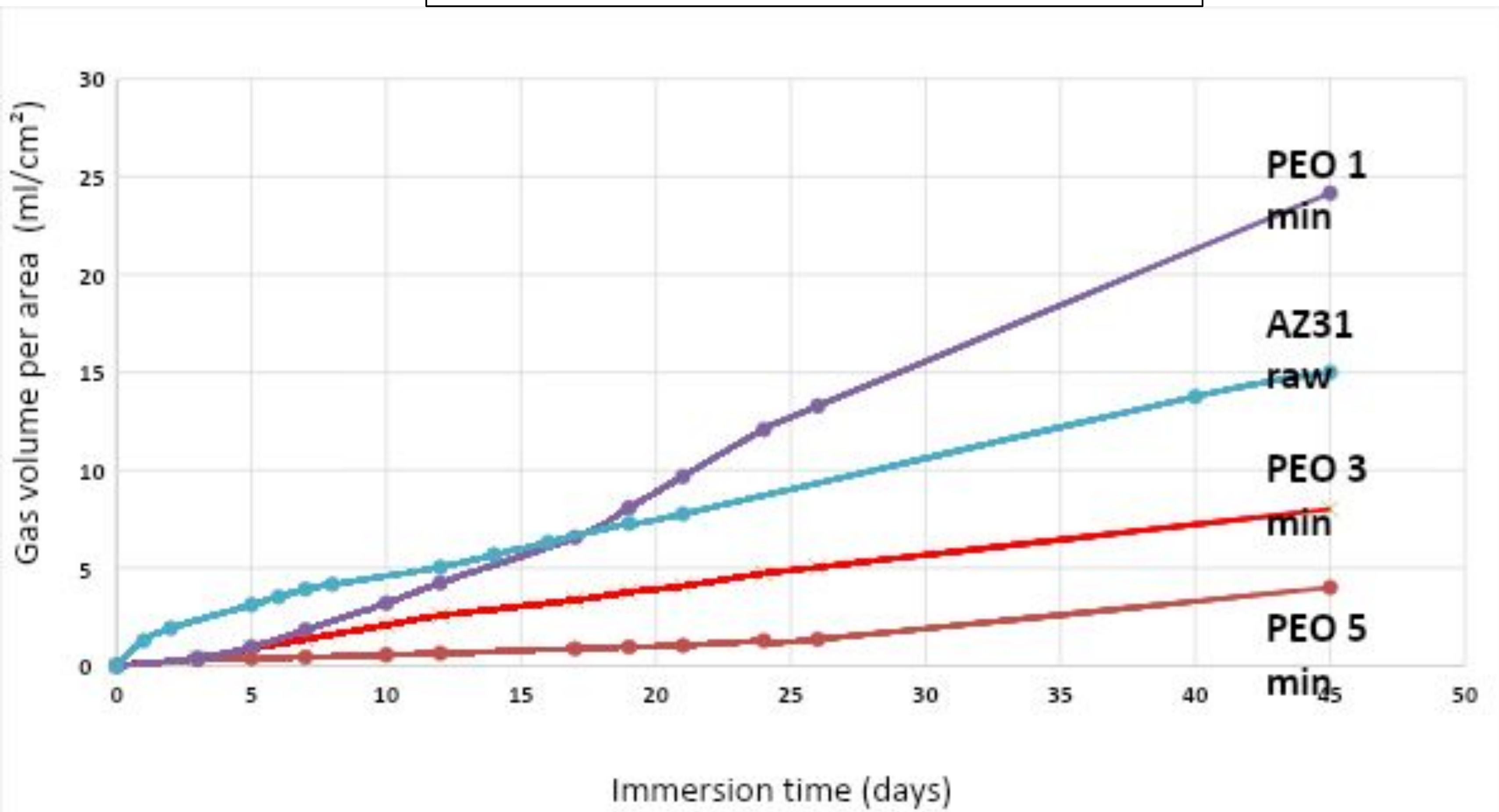


Corrosion starts at the points of contact with the sample holder

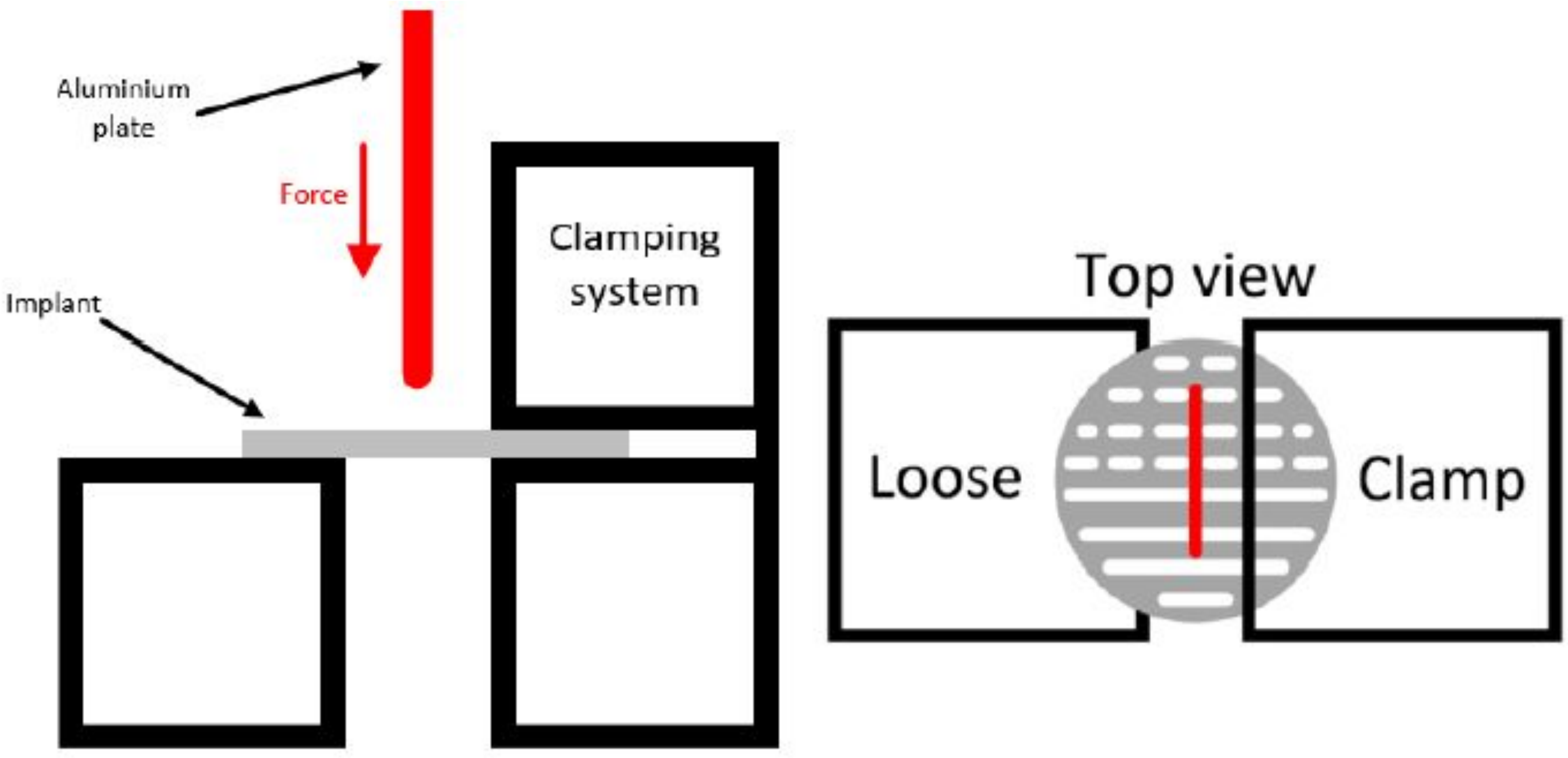
Hydrogen gas release

PEO parameters:

- J=32 A/dm^2
- **Time: 1, 3, 5 min**
- Layer thickness: 2, 4, 10 µm

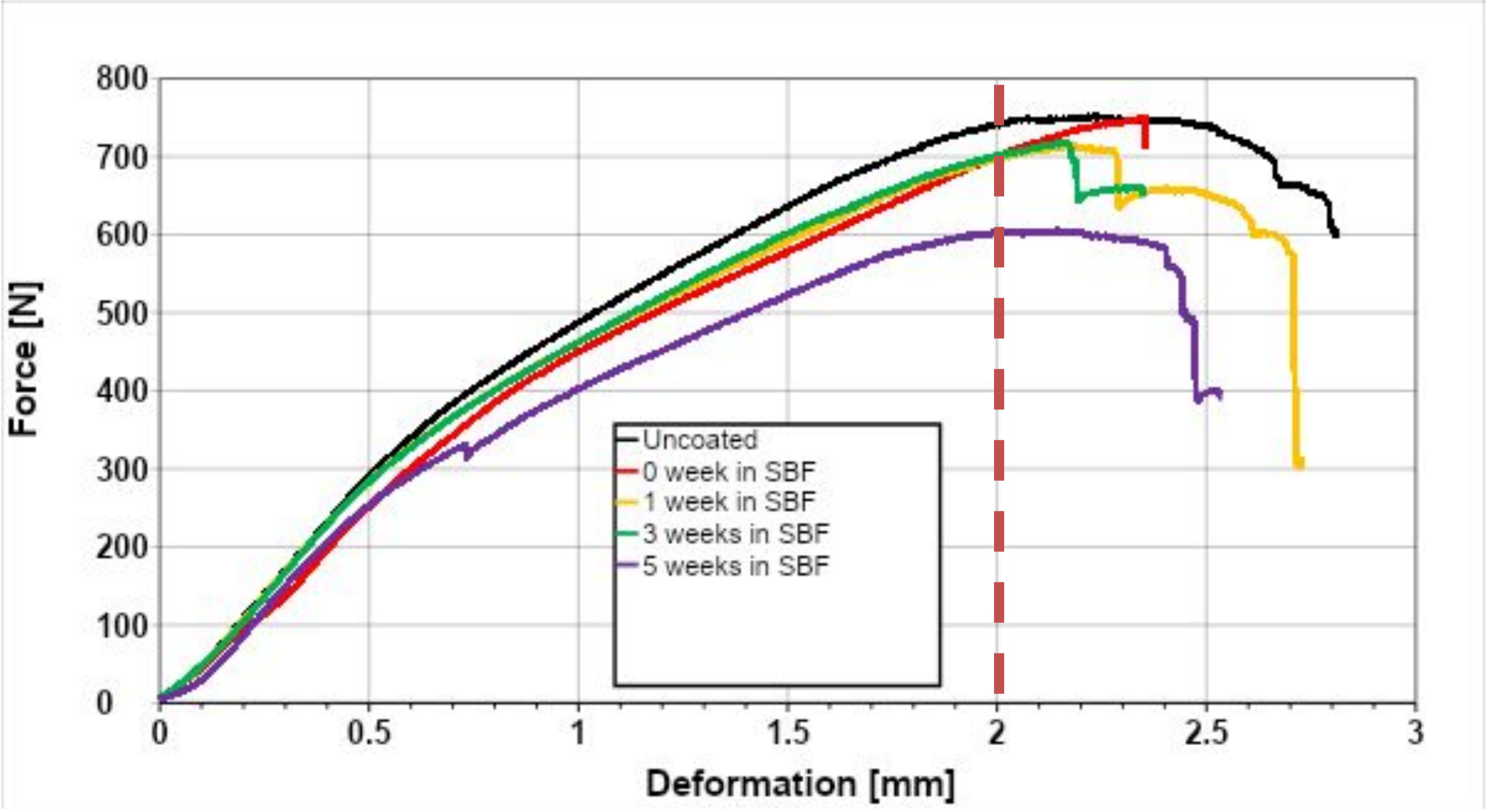


Mechanical bending test



Mechanical bending test results

- **No PEO :** the force (F) to bend implants 2mm **F = 740 N**
- **PEO** (5 min, J=32 A/dm^2) + **immersion** in SBF for **0-3 weeks** **F = 700 N**
- **PEO** + **immersion** in SBF for **5 weeks** **F = 600 N**



Conclusions & Perspectives

- ✔ Layer thickness increases with current density (***J***) and treatment time.

- ✔ Current density (***J***) does not have much influence on the corrosion resistance. Corrosion spots occur randomly. Sharp edges and contact points with the sample holder are critical for corosion

- ✔ Gas release from the implants anodized 5 min and immersed in SBF is low and predictable (at least for 5 weeks). Treatment time allows to control the corrosion rate.

- ✔ PEO-implants immersed in SBF possess good mechanical resistance, at least up to 5 weeks

- ✔ PEO is a fast and efficient method to control corrosion rate of the AZ31 implants

- ✔ **Clinical studies are necessary to validate the use of AZ31 in veterinary implants**

The END

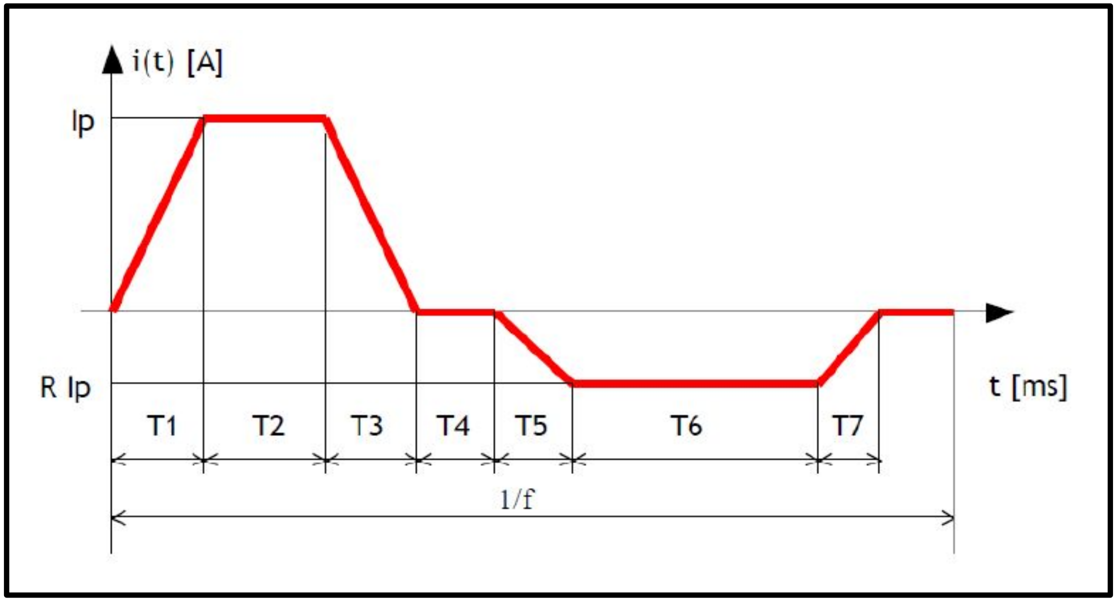
PEO process parameters

PEO Experiments:

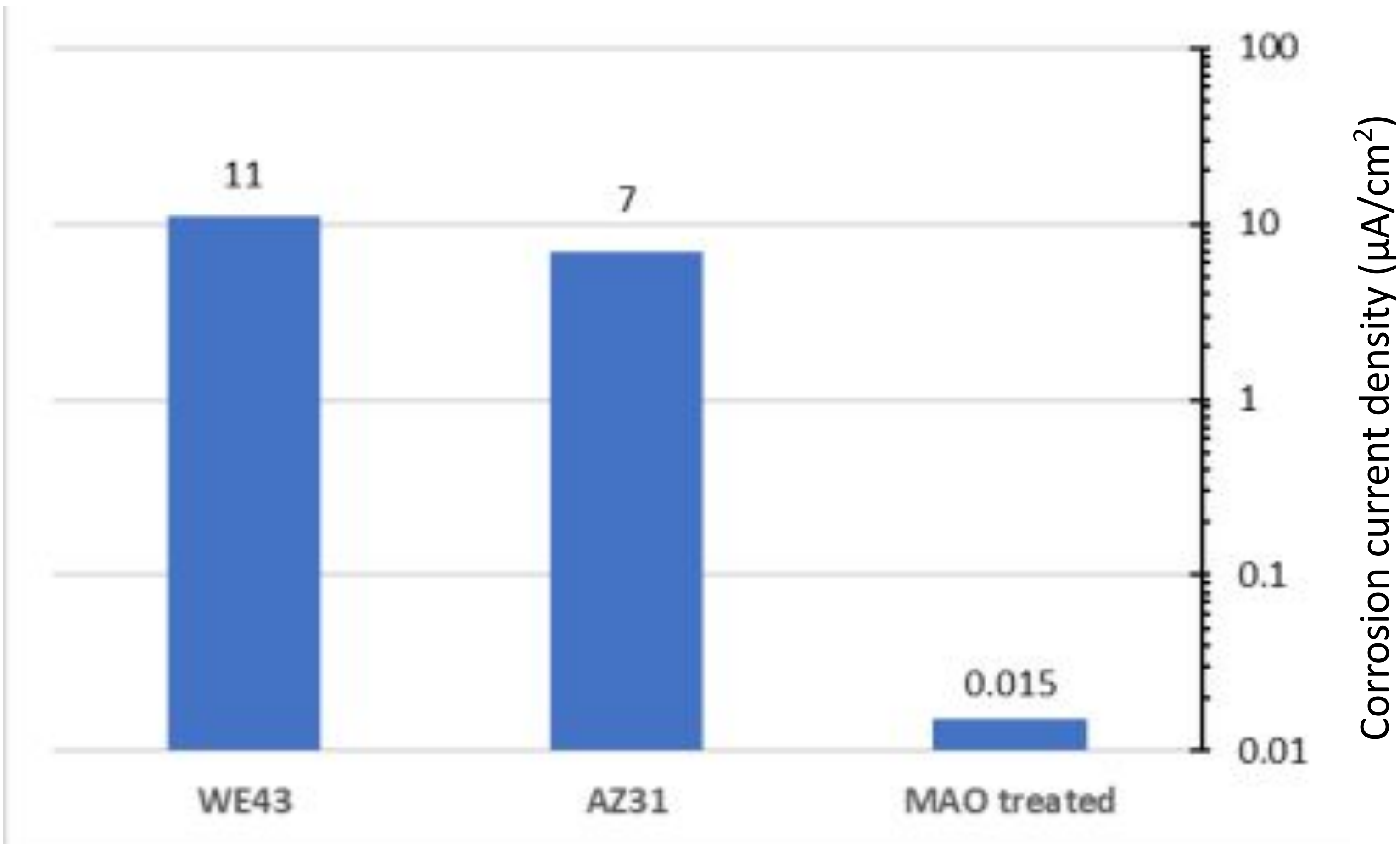
- CIRTEM® bipolar pulsed current source
  - Current density **24-64 A/dm²**
  - Maximum voltage 560 V
  - Frequency 500 Hz
  - Anode-cathode distance 18.5 cm
  - Treatment time 5 min

Electrolyte composition:

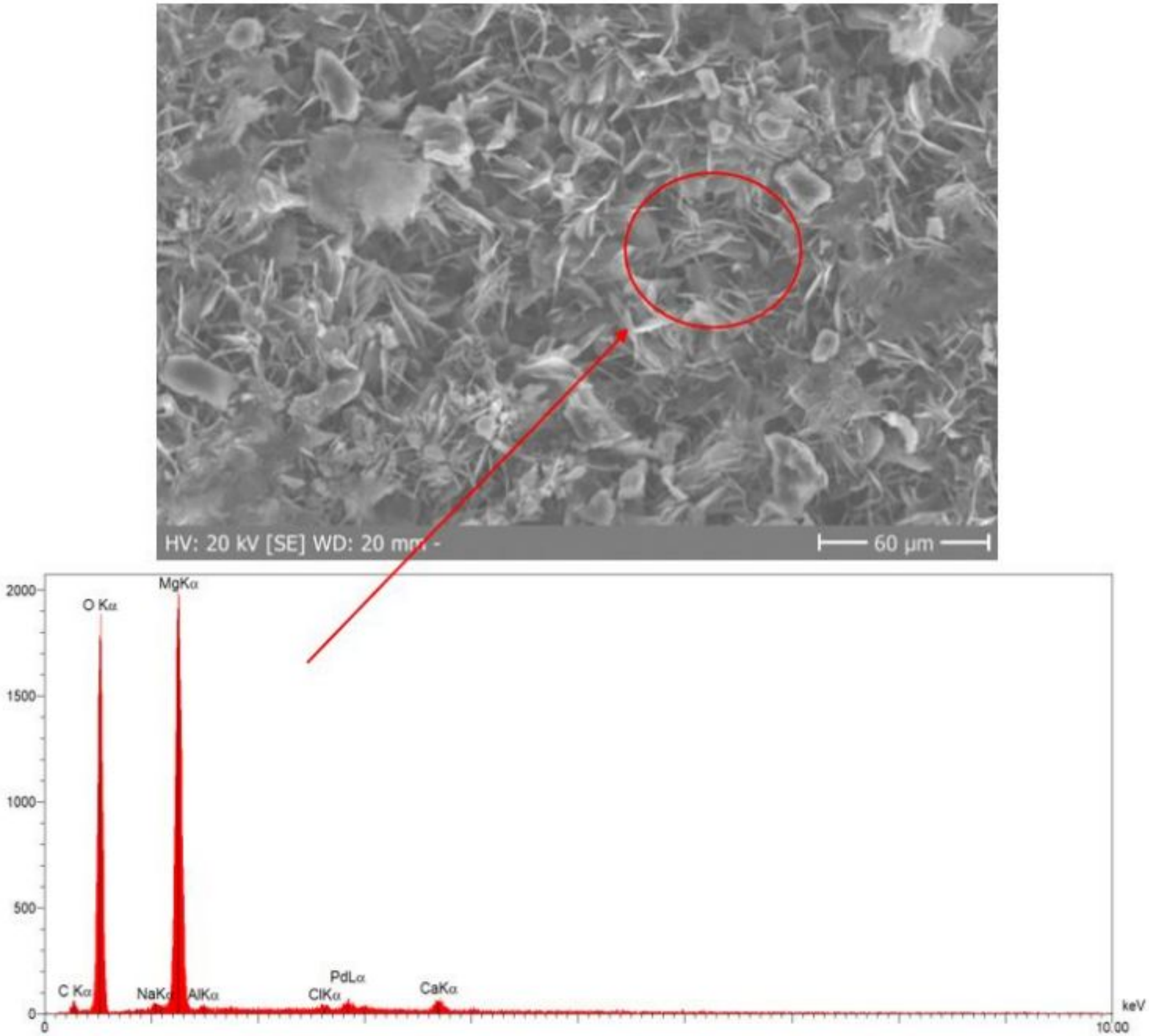
- Deionised water
- 2.8 g/l NaOH
- 7.5 ml/l of Na_2SiO_3
  - pH=12.5
  - Conductivity 8-13 mS/cm



Corrosion current comparison



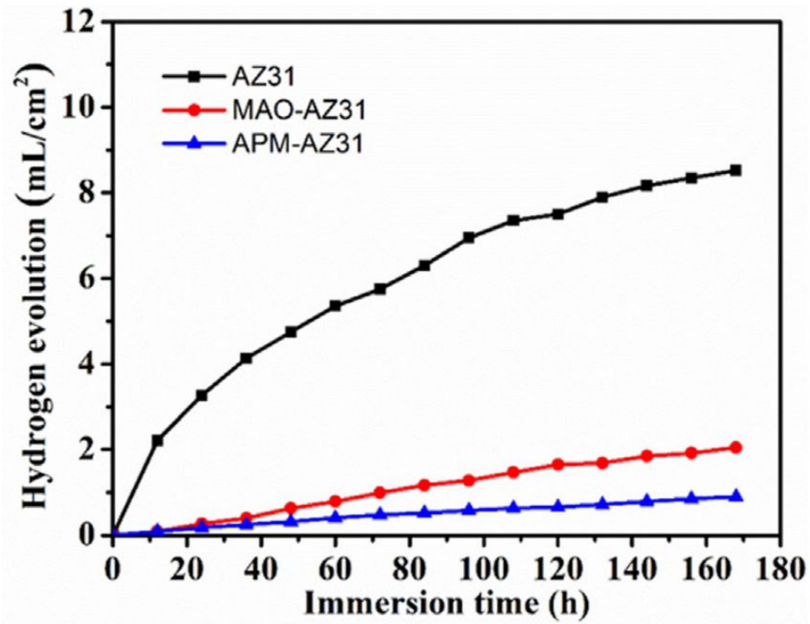
Surface SEM-EDX analysis (after immersion in SBF)



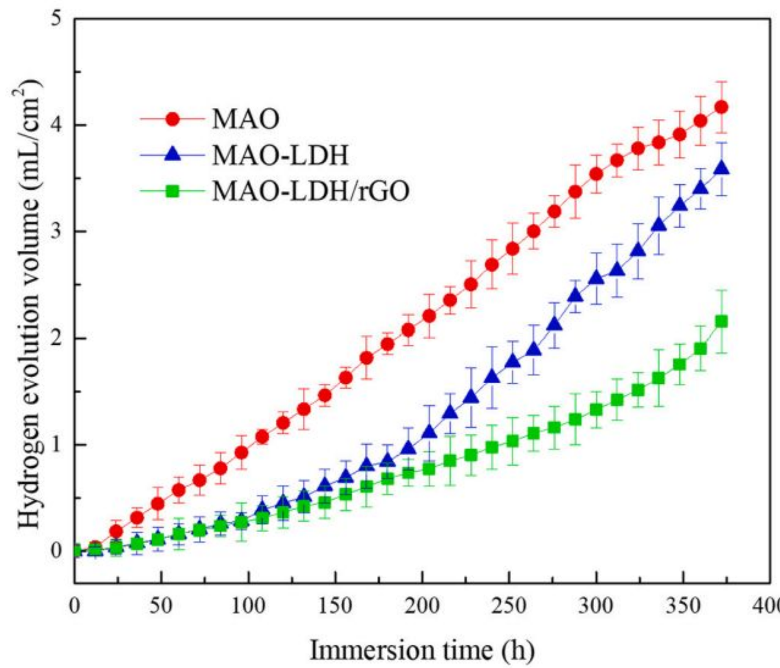
Hydrogen gas release test

Implants immersed in SBF (Ringer's solution) @37°C up to 45 days

Hydrogen gas release results (literature data)



Hydrogen evolution vs. immersion time for AZ31 and MAO-AZ31 (red) in PBS at 37° C.



AZ31 immersion in 3.5 wt% NaCl solution

X.Wang et al, « Enhanced anticorrosive and antibacterial performances of silver nanoparticles/ polyethyleneimine/MAO composite coating on magnesium alloys», Journal of Materials Research and Technology, Vol. 11, March–April 2021, pp 2354-2364

V. Zahedi Asl et al. « Corrosion properties and surface free energy of the Zn–Al LDH/rGO coating on MAO pretreated AZ31 magnesium alloy » Surface & Coatings Technology 426 (2021) 127764