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Investigation of electrochemically-induced repassivation of Al 7075-T6 and Al 2024-T3 as a function of applied stress and galvanic corrosion

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Investigation of Electrochemically - Induced Repassivation of Al 7075-T6 and Al 2024-T3 as a Function of Applied Load and Galvanic Corrosion

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Cork 2016

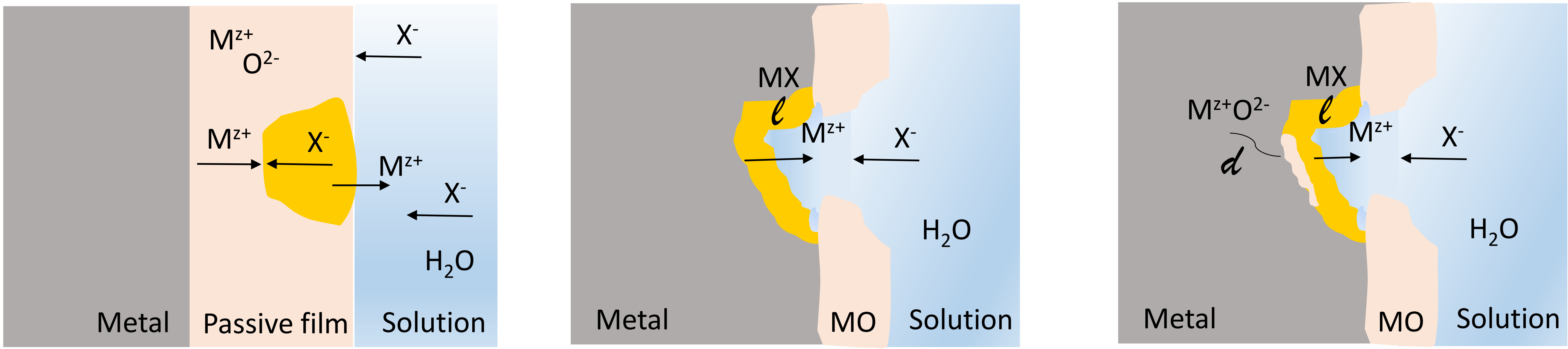
Talking points

- ❑ **Electrochemically-induced repassivation**
  - ✓ Halide film vs Oxide film
  - ✓ Active phase at grain boundaries: β phase (Al_3Mg_2) in Al-Mg alloys
- ❑ **Repassivation and bending load: Al 7075-T6 and Al 2024-T3**
  - ✓ Experimental variables: environment, electrochemical, mechanical
- ❑ **Galvanic corrosion and bending load**
  - ✓ Dissimilar metal CRES 304
- ❑ **Final remarks**

Electrochemically induced repassivation

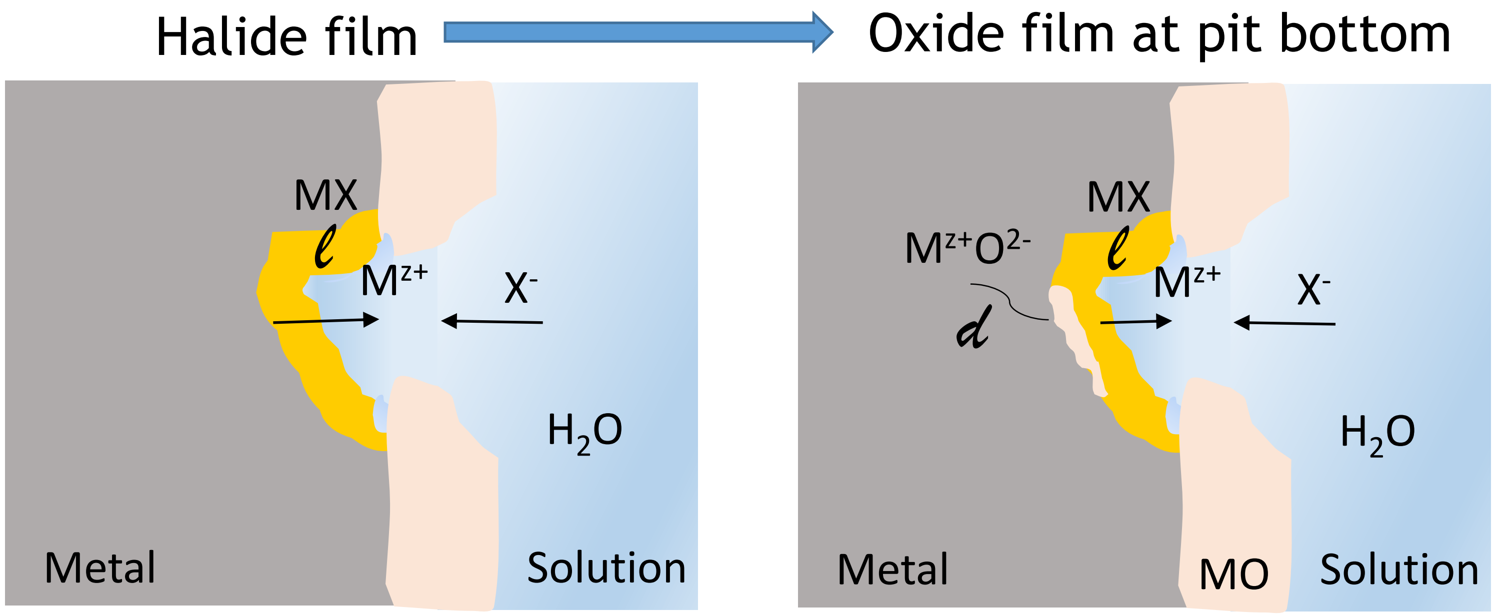
SCHEMATICS OF PIT INTIATION AND REPASSIVATION

Metal halide nucleation and growth | Halide film | Oxide film at the pit bottom

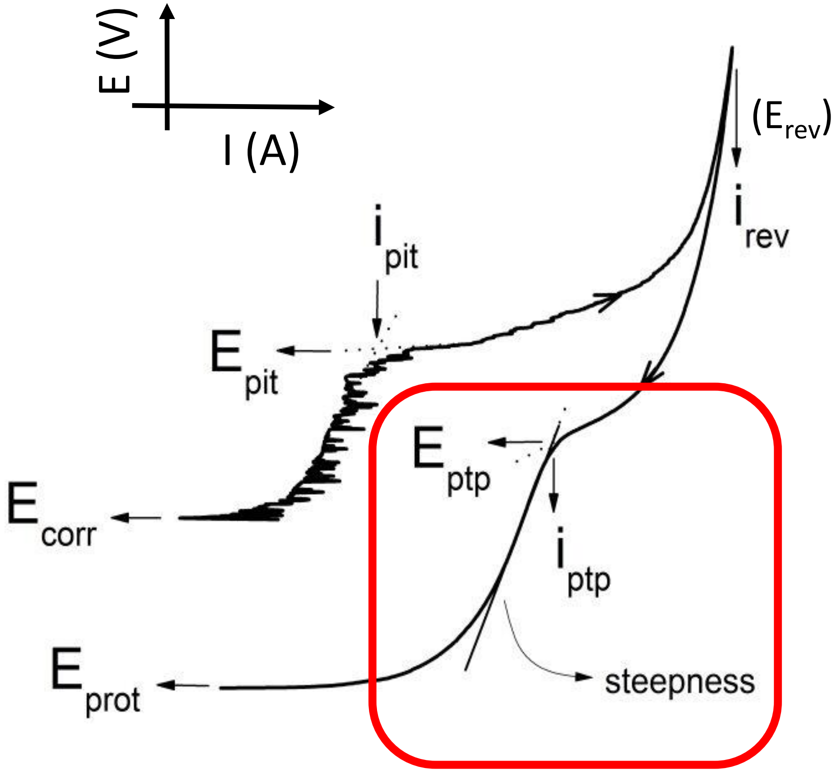


Very thin oxide film extends over the active surface on the pit bottom and then increases its thickness, resulting in complete repassivation.

Electrochemically induced repassivation



Pitting Scan (PS)



Eptp - thermodynamic driving force of Al dissolution

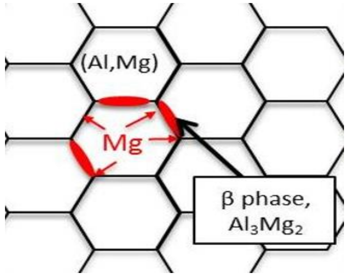
on freshly created (filmed) surface

iptp $\propto$ rate hydrolysis equilibrium at $[Al^{3+}]_{crit}$

$$2Al^{3+} + H_2O + OH^- \leftrightarrow 2Al(OH)^{2+} + H^+$$

steepness $\propto$ H^+ removal for full hydrolysis at Eprot (delayed repassivation constant ?!)

Active phase at grain boundaries: β phase precipitation



Al 5083-H111 as a function of sensitization time at 150 °C

✓ Commercial Al-Mg alloy, strain hardened by 20% of cold work, 10 years Lab. conditions

	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr
Al 5083-H111	**0.17**	**0.32**	0.04	**0.62**	4.32	0.03	0.02	0.02

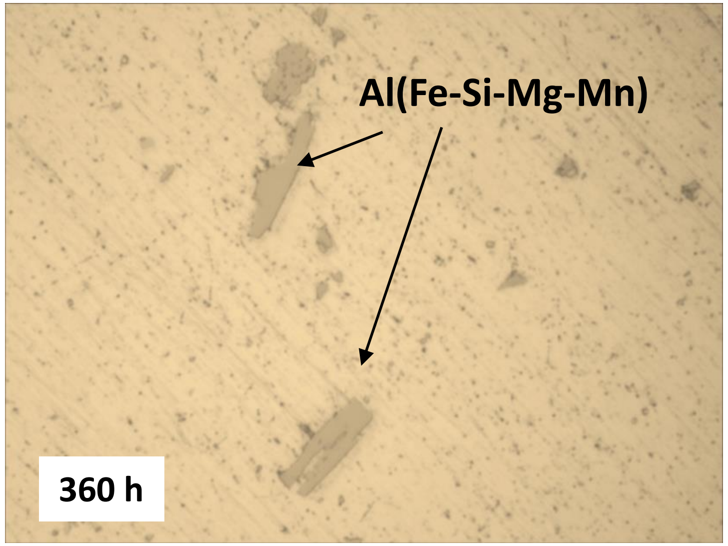
20 mm x 30 mm rectangular sheets, thickness 1.5 mm
Surfaces wet ground up to 1200 grit

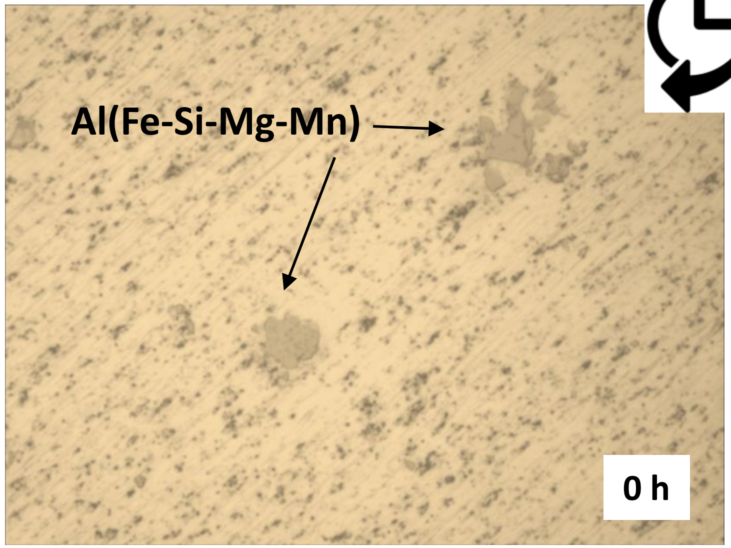
- Microstructure/composition (XRD, metallography*, SEM)
- Electrochemical properties (pitting scan, scan rate 0.1667 mV/s, 0.6 M NaCl, pH 6.5, room T)
- Mass loss test (NAMLT, 24-hours immersion HNO_3, ASTM G67)
- Mechanical properties (micro-hardness measurements 0.1 kgf/10 sec, diamond indenter, ISO 14577/DIN 50359)

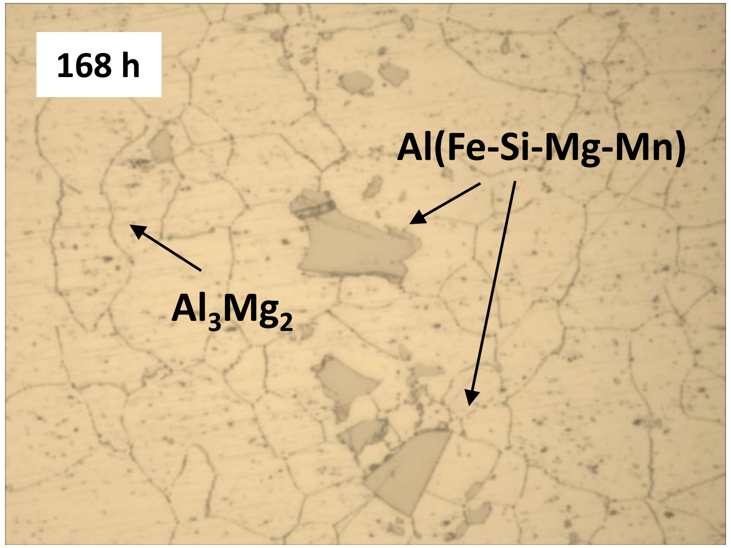
*Metallography
1) 0.05 μm colloidal Al_2O_3
2) chemical etching
$(NH_4)_2S_2O_8$ 1g/10 mL, 30 min, room T

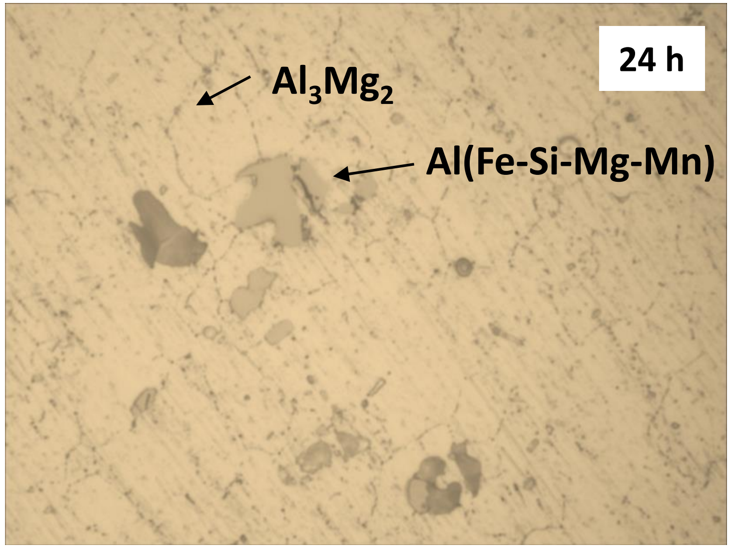
Active phase at grain boundaries: β phase precipitation

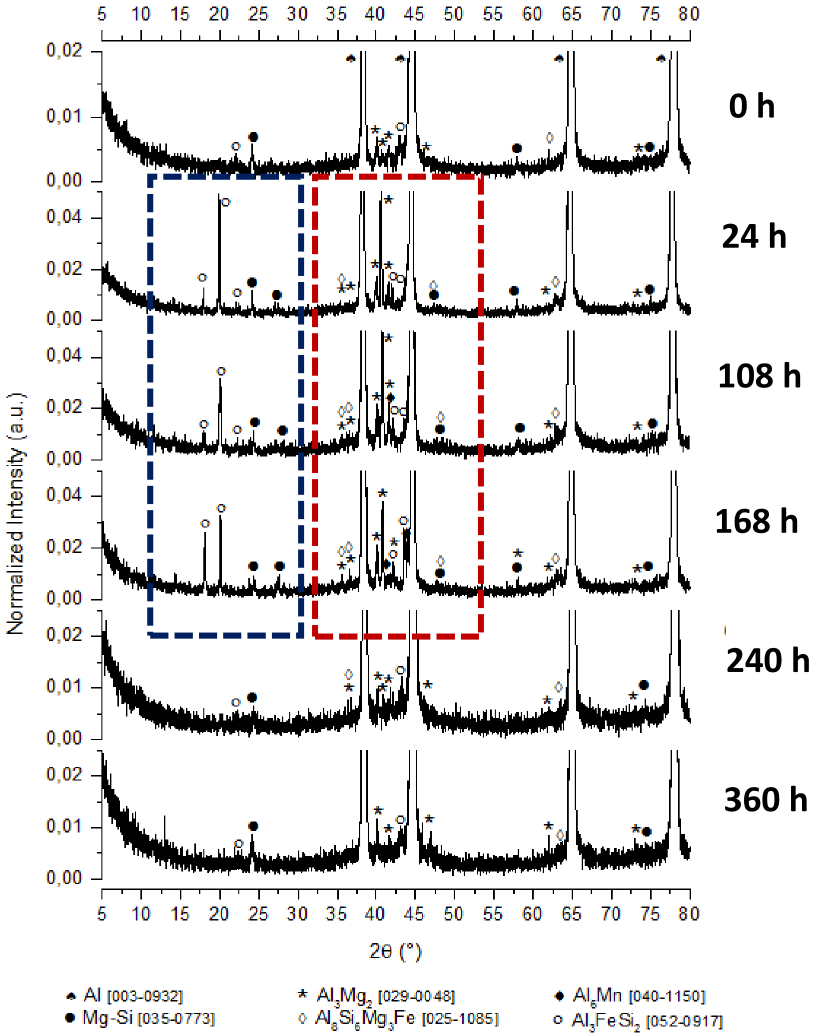
Al 5083-H111 as a function of sensitization time at 150 °C





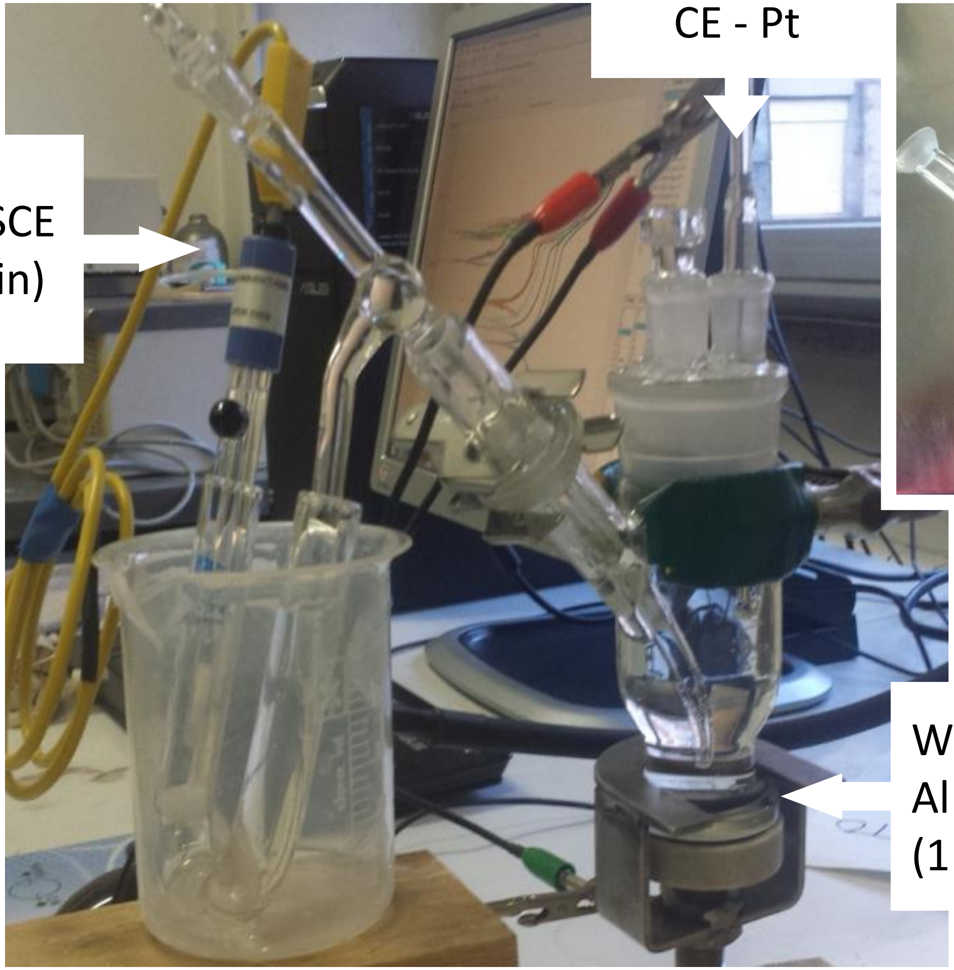






Active phase at grain boundaries: β phase precipitation at grain boundaries

Al 5083-H111 as a function of sensitization time at 150 °C



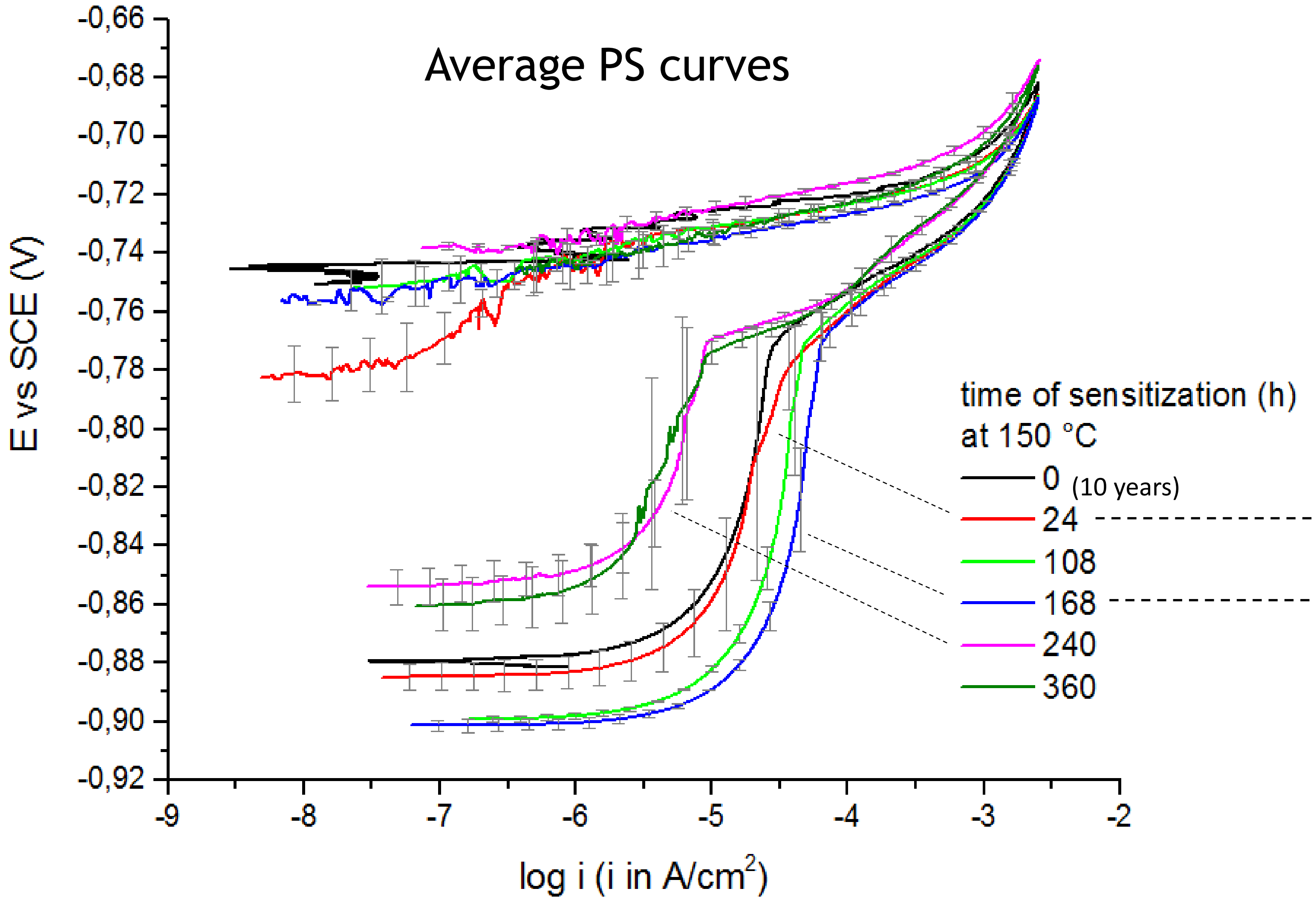
Pitting Scan (PS)

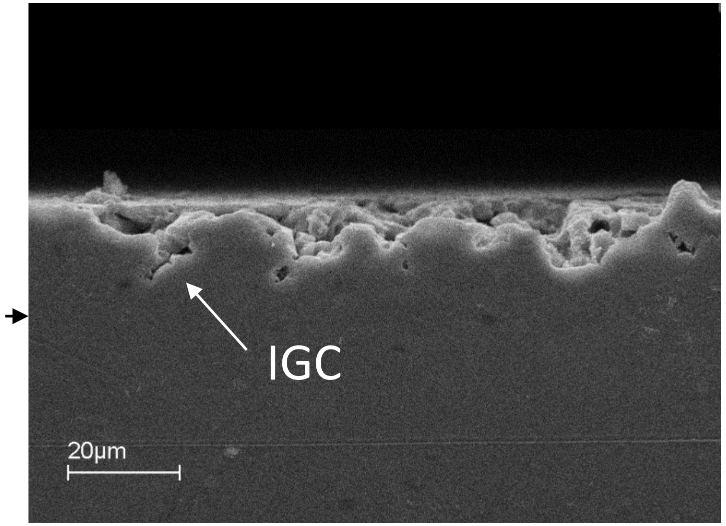
0.6 M NaCl (pH 6.5)

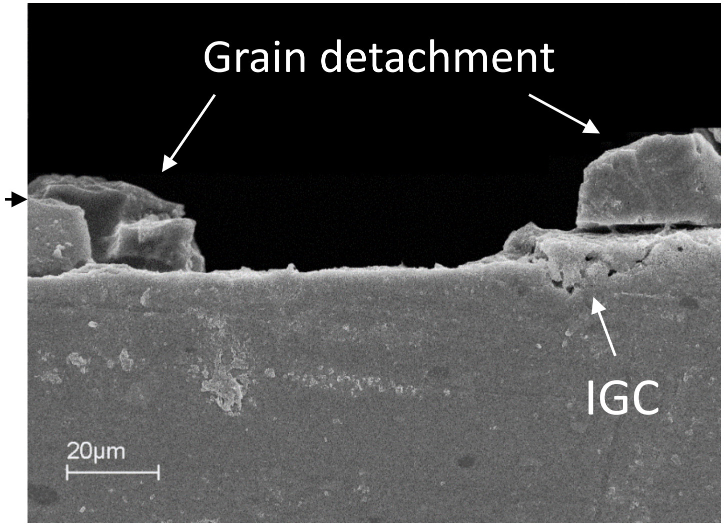
i_{rev} = 2.5 mA/cm^2
scan rate (ν) 0.1667 mV/s
(10 mV/min)

Active phase at grain boundaries: β phase precipitation at grain boundaries

Al 5083-H111 repassivation as a function of sensitization time at 150 °C

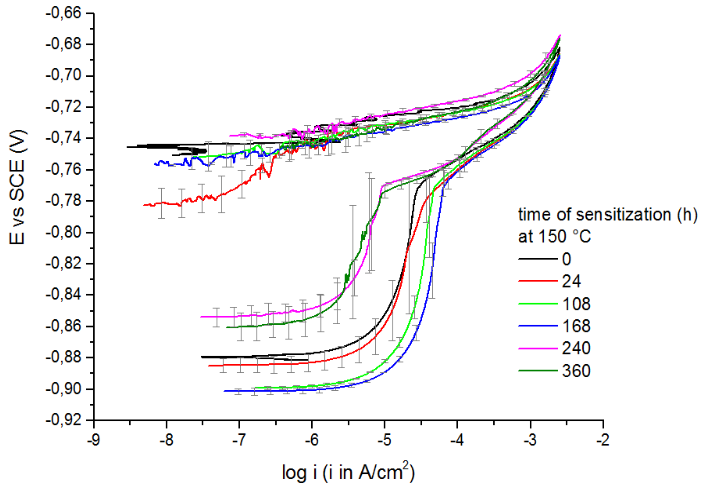


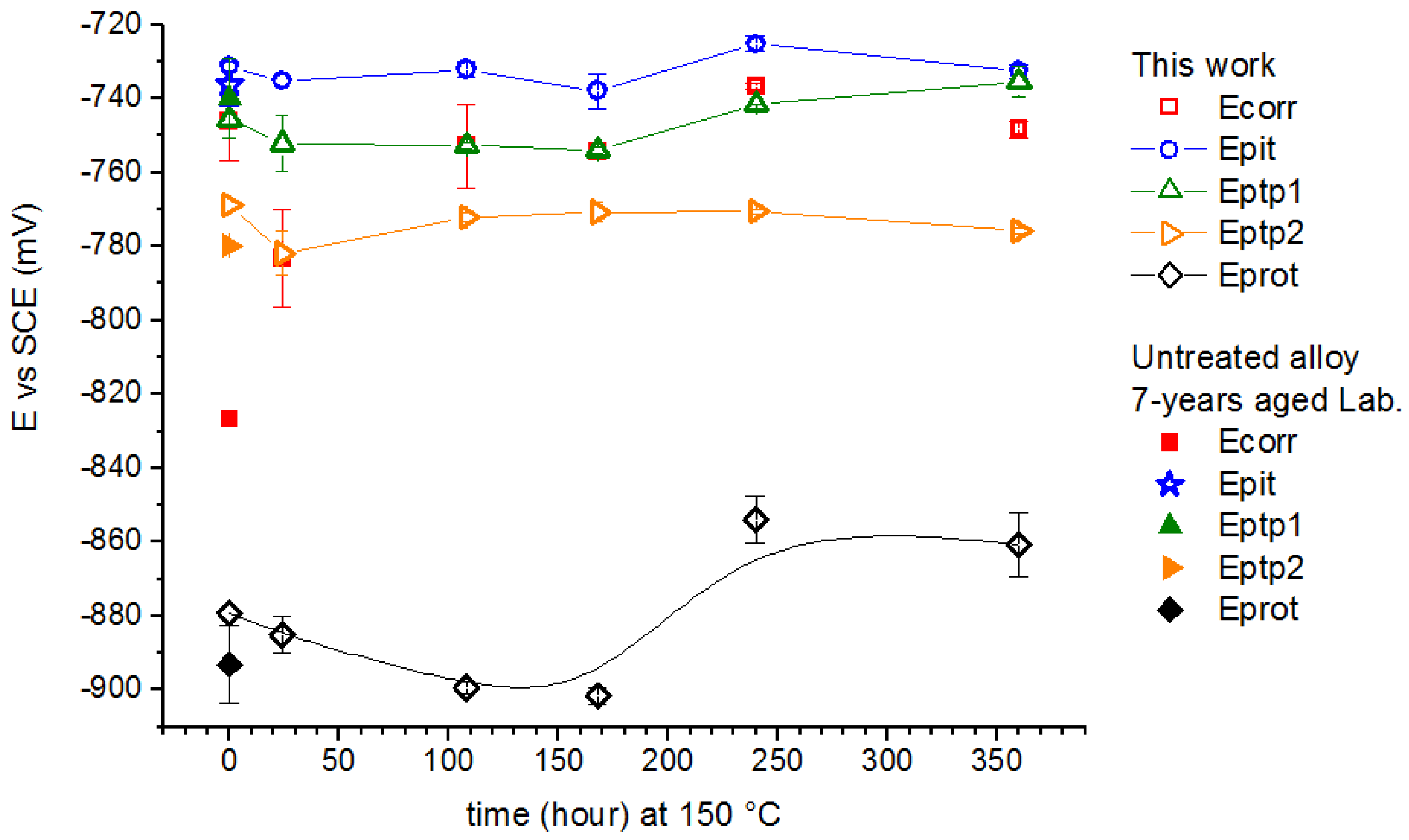




Active phase at grain boundaries: β phase precipitation at grain boundaries

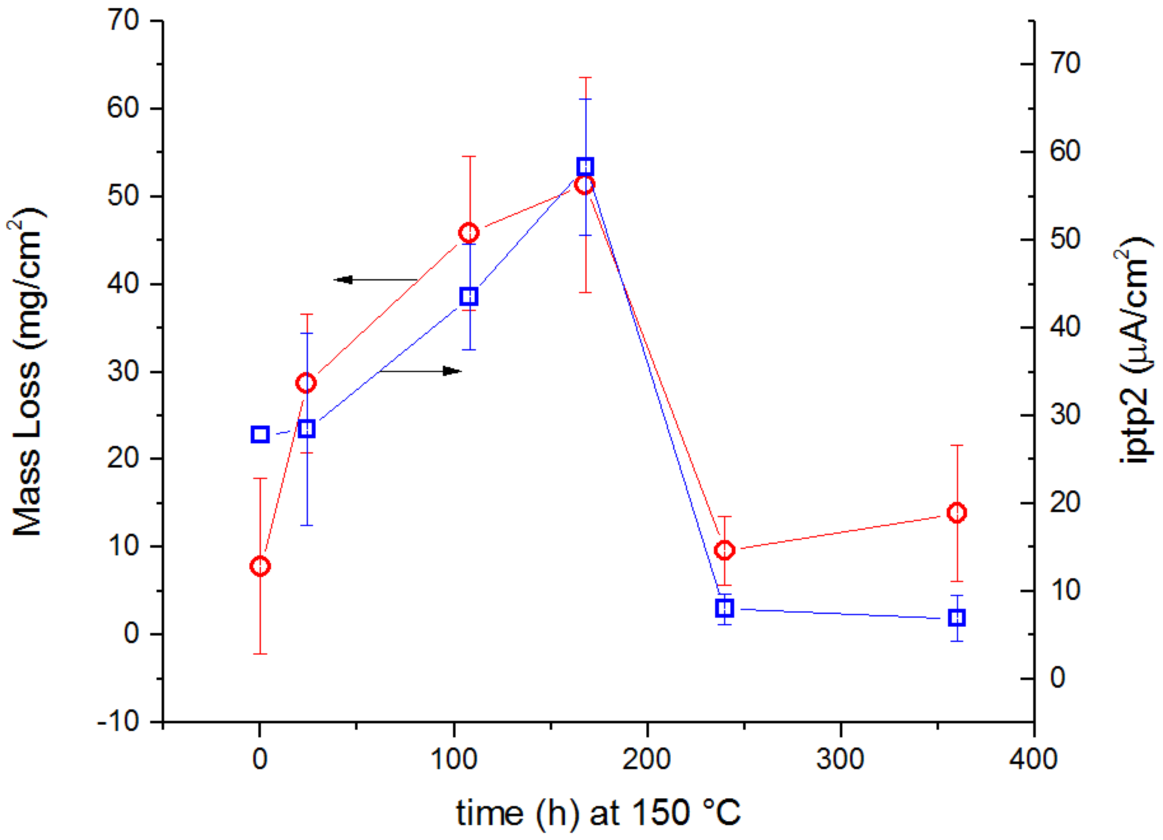
Al 5083-H111 repassivation as a function of sensitization time at 150 °C

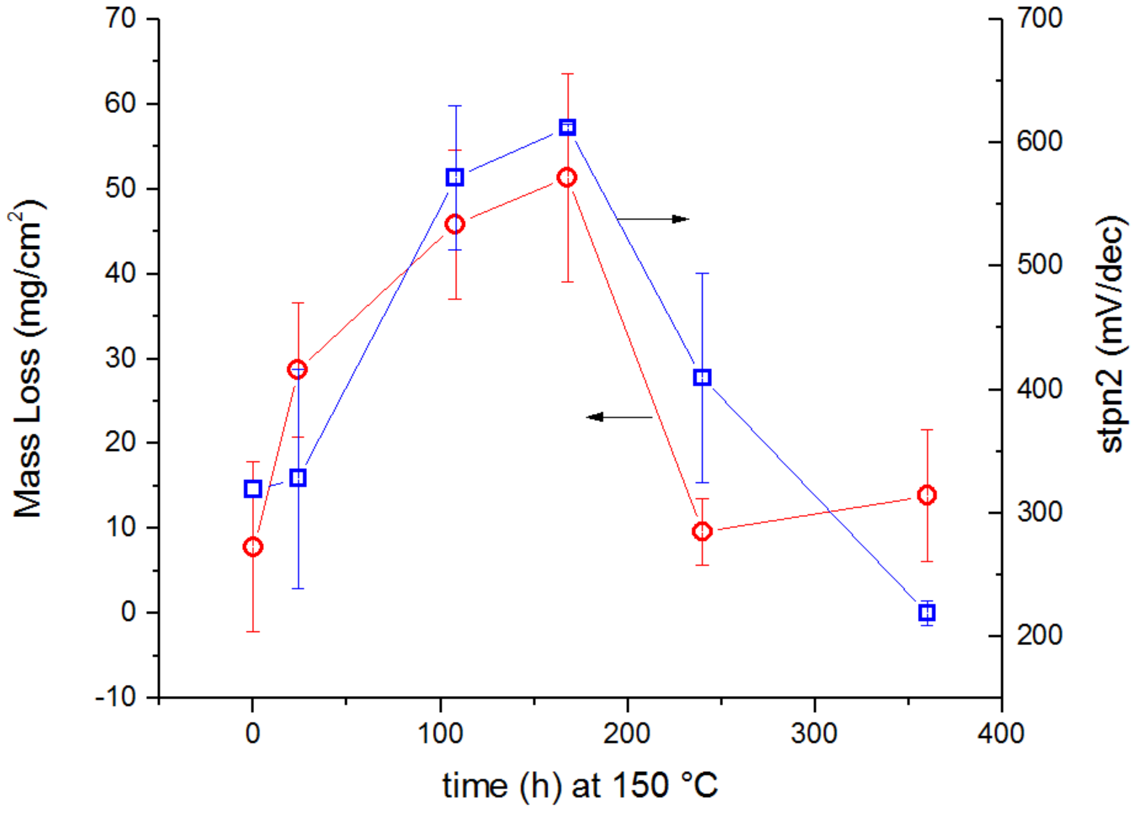




Active phase at grain boundaries: β phase precipitation at grain boundaries

Al 5083-H111 as a function of sensitization time at 150 °C





1) Combining in-situ generated by corrosion fresh surfaces and externally applied load?
2) Stress assisted galvanic corrosion?

Complex design requirements

Repassivation and bending load: Al 7075-T6 and Al 2024-T3

Experimental variables

- ✓ Environment - Test solution composition ($[Cl^-]$, pH, viscosity), pre-exposure time, temperature
- ✓ (Electro)chemical - electrochemical parameters (i_{rev}, E_{rev}, ν), galvanic coupling (joint with CRES 304)
- ✓ Mechanical - Static bending load (side in tension and compression), also followed by unload (residual tensile and compressive stress)

Materials, loaded specimens and electrochemical setup

Al 7075-T6 & Al 2024-T3 (Aviometal Spa, Italy)

Chemical composition (wt.%)

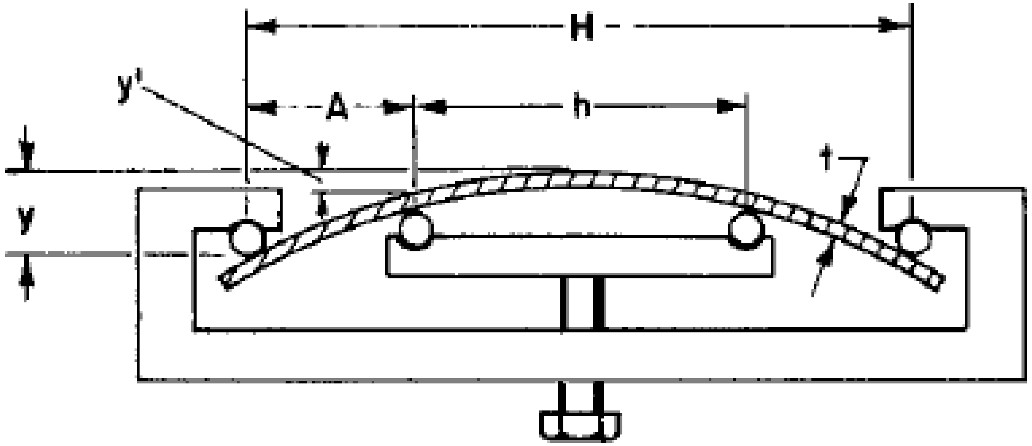
	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr
Al 7075-T6	0.06	0.13	**1.70**	0.02	**2.60**	**5.80**	0.04	0.20
Al 2024-T3	0.07	**0.12**	**4.40**	0.46	**1.50**	**0.08**	0.08	**0.03**

Mechanical properties (Stress – Strain curves)

	Al 7075-T6	Al 2024-T3
Thickness (mm)	2.0	1.5
Elastic Modulus E (GPa)	74.5	75.7
Yield strength YS, Rp02 (MPa)	**510**	**354**
Ultimate tensile strength UTS (MPa)	583	499

Materials, loaded specimens and electrochemical setup

Flat four-point bent-beam (4PPB) specimens (ASTM G39-99)

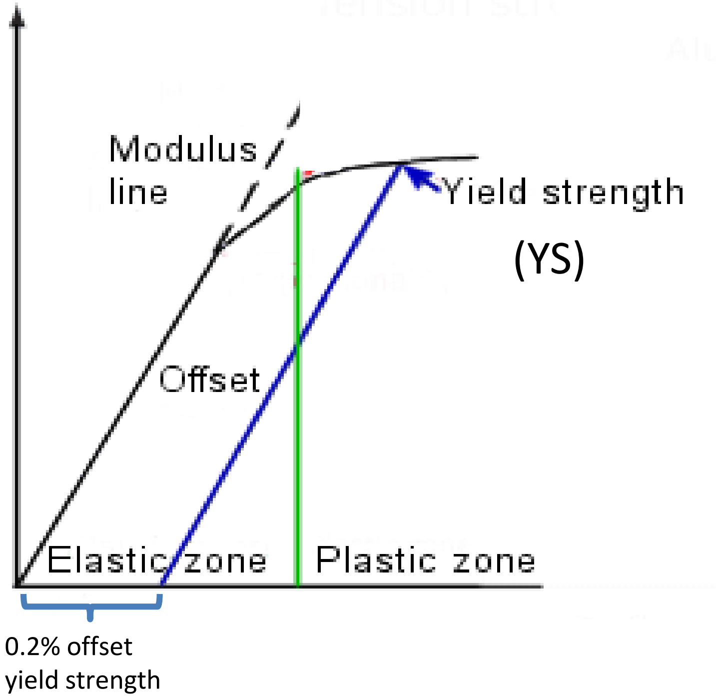


$$\sigma = \frac{12Ety}{(3H^2 - 4A^2)}$$

$$y = \frac{\sigma(3H^2 - 4A^2)}{12Et}$$

t – thickness of specimen
y – maximum deflection (between outer supports)
Y' – deflection between inner supports
h – distance between inner supports
H – distance between outer supports
A – distance between inner and outer supports

Constant load mostly below the elastic limit



Materials, loaded specimens and electrochemical setup

Flat four-point bent-beam (4PPB) specimens (ASTM G39-99)

side in tension

Laminae dimension: 165 x 25 x 2 mm (Al 7075)
165 x 25 x1.5 mm (Al 2024)

side in compression

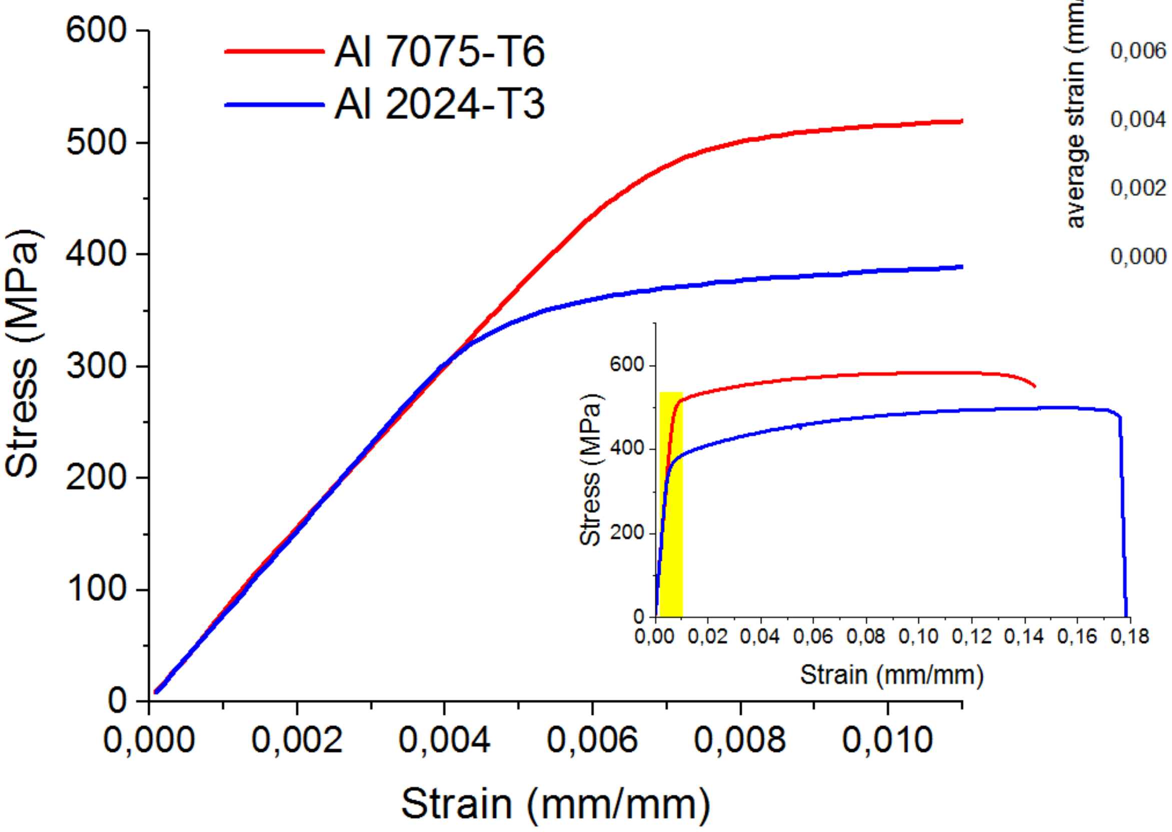
Laminae dimension: 248 x 38 x 2 mm (Al 7075)
248 x 38 x1.5 mm (Al 2024)

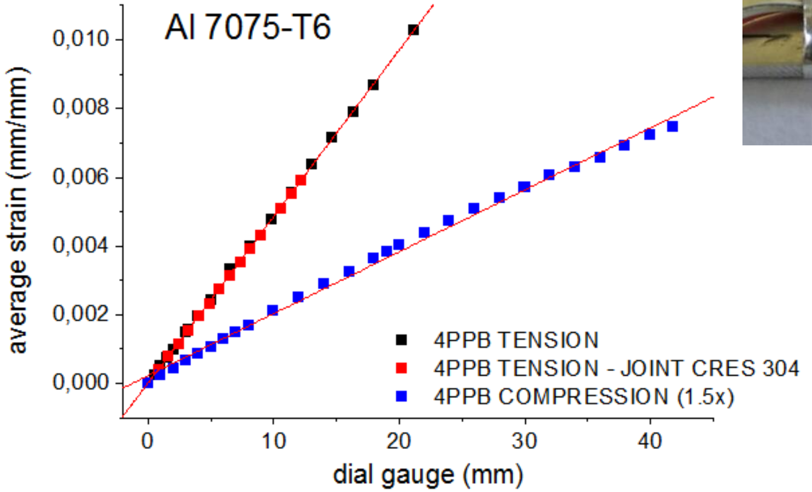
Glass or teflon spacers
Working surface - 3 μm finish

Materials, loaded specimens and electrochemical setup

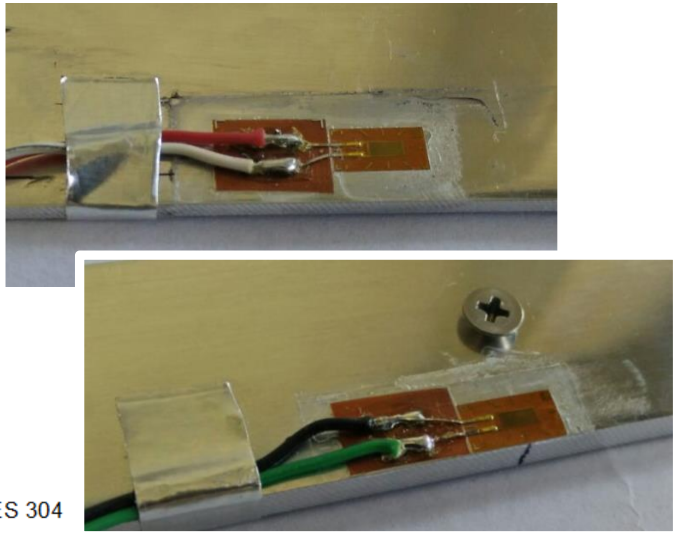
Flat four-point bent-beam (4PPB) specimens (ASTM G39-99)

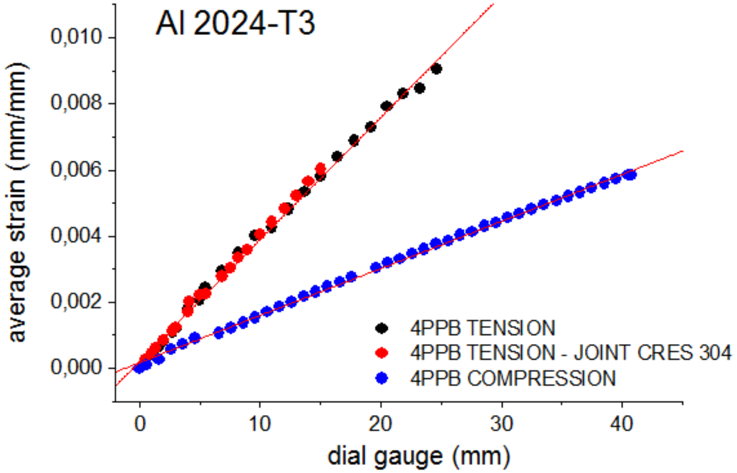
LOAD LEVELS





Strain gauges



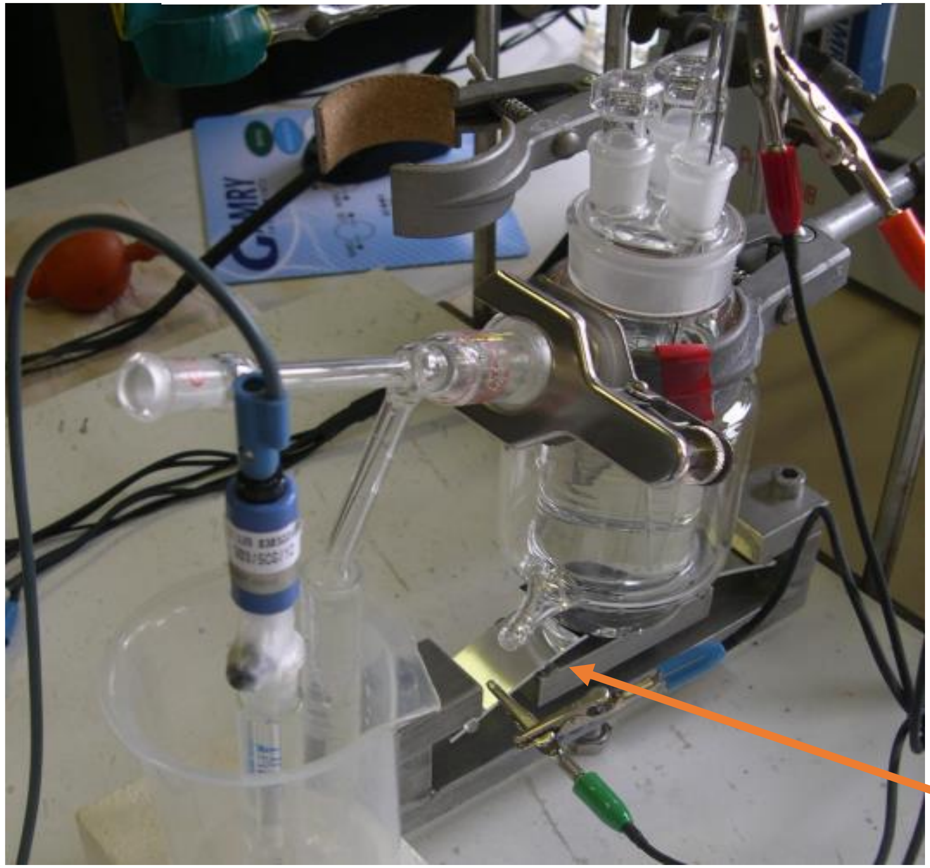


Materials, loaded specimens and electrochemical setup

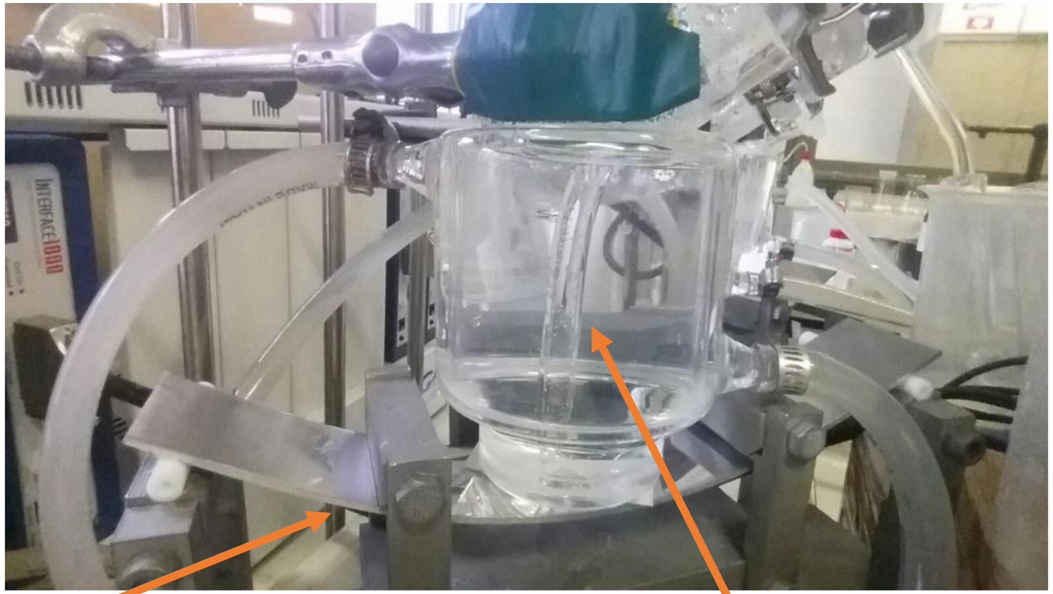
Electrochemical setup

Double walled Pyrex O-ring cell (bi-adhesive tape)
WE – Al alloy
CE – Pt
RE – SCE (Luggin)

4PPB SPECIMEN SIDE IN TENSION



4PPB SPECIMEN SIDE IN COMPRESSION



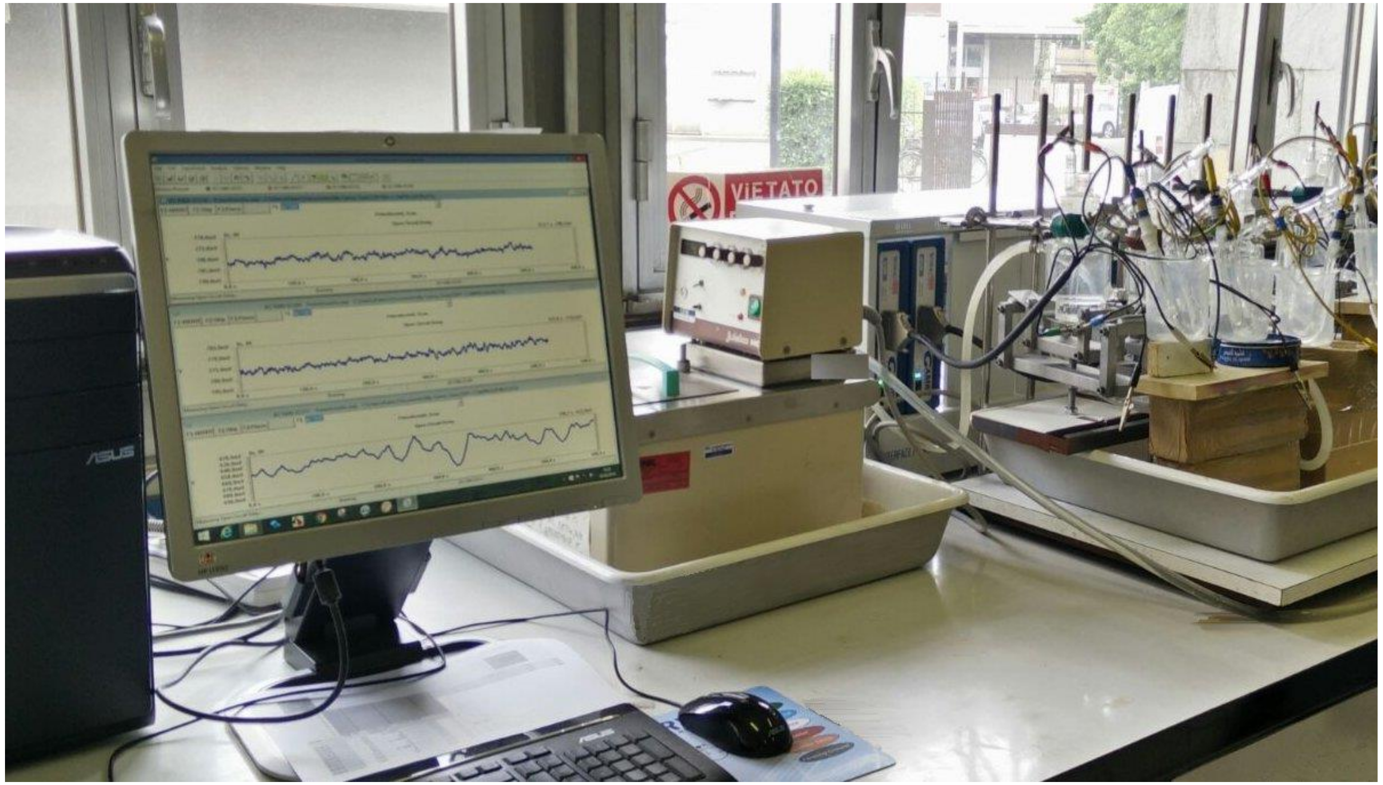
1 cm^2 exposed Al surface
3 μm finish

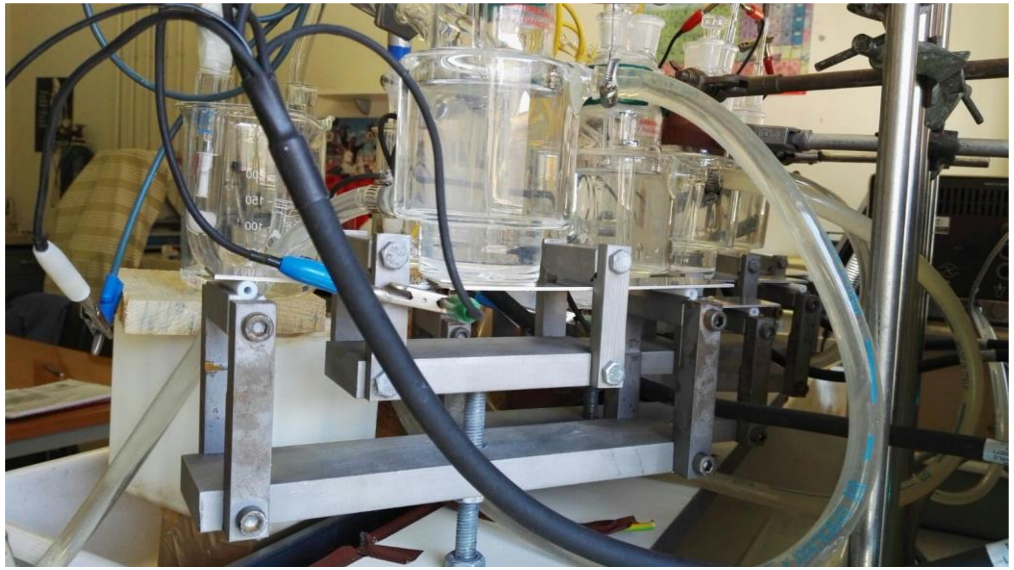
Luggin Probe

Materials, loaded specimens and electrochemical setup

Electrochemical setup

Computer-driven Gamry Multipotentiostat



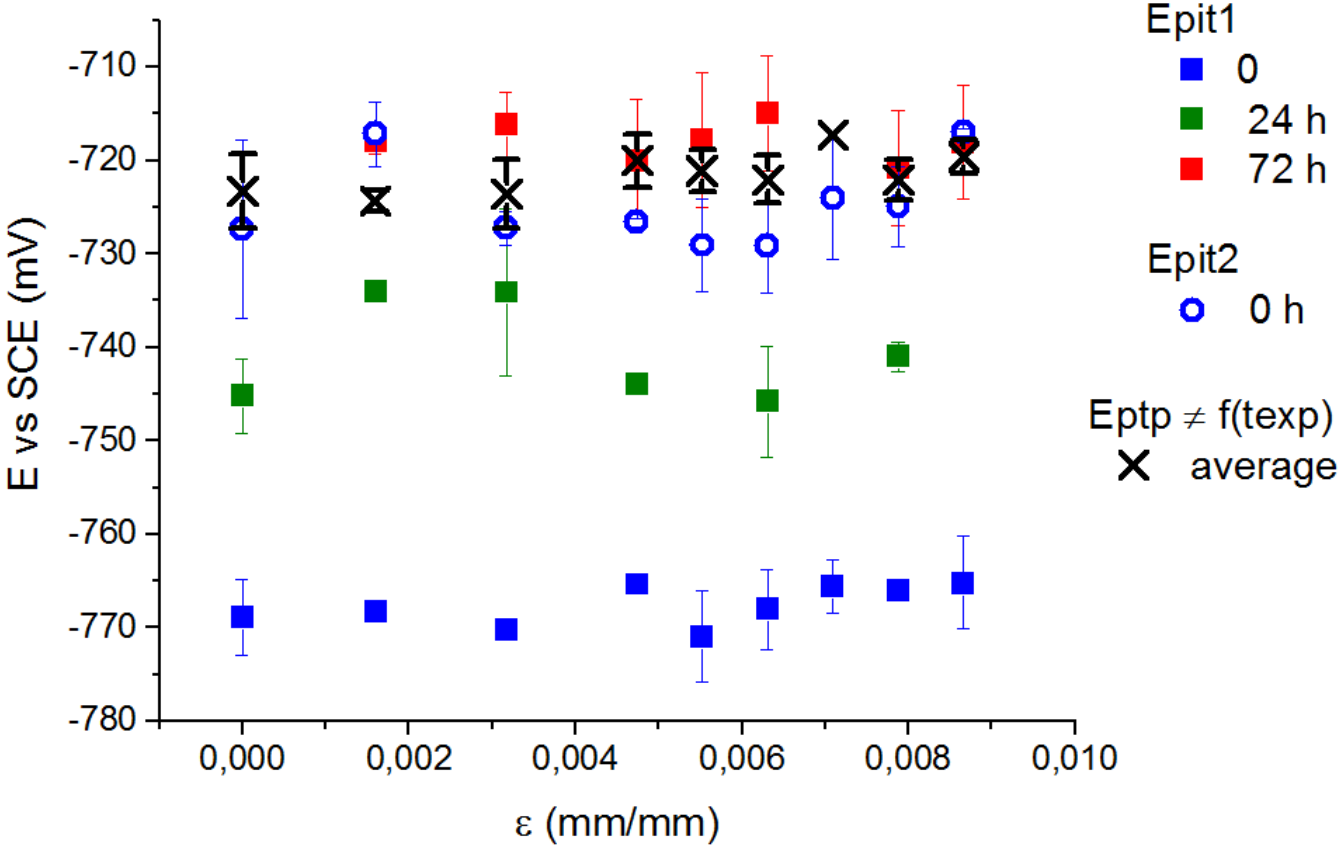


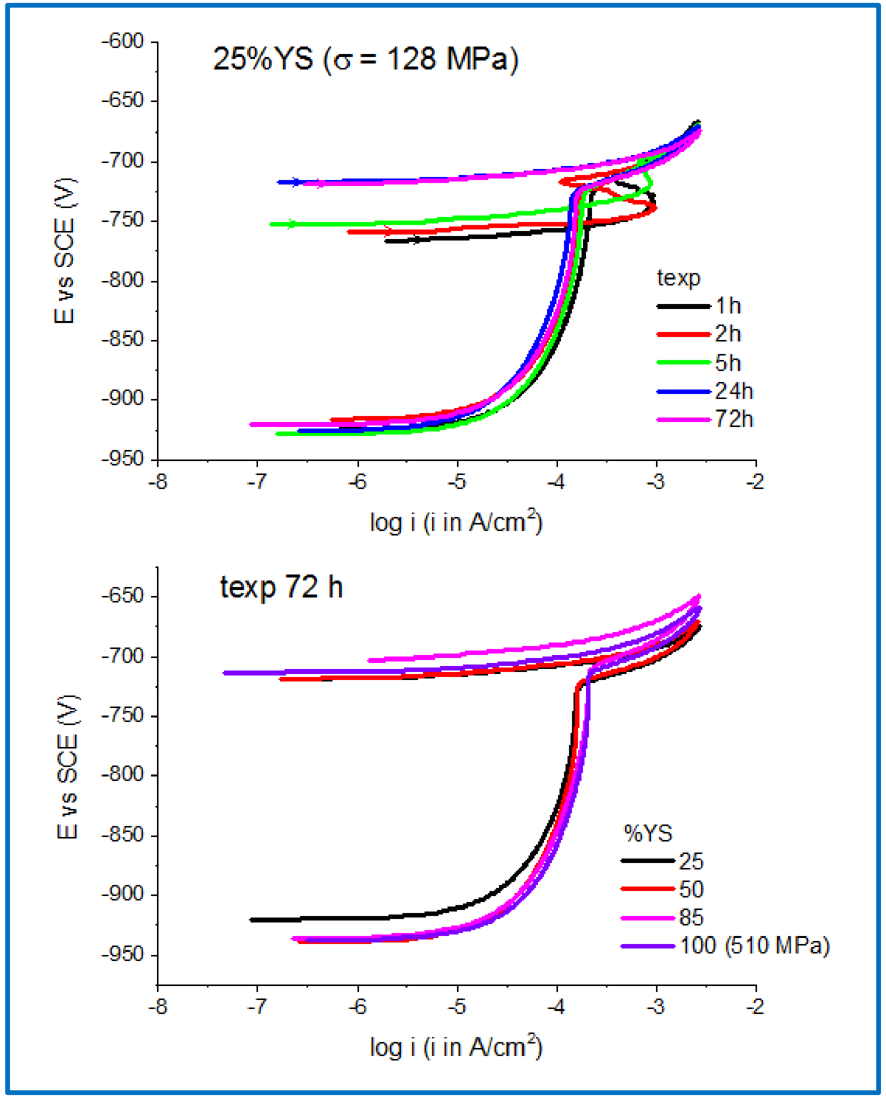
Parallel experimental runs in random order
At least 2 replications for each exp. condition

Repassivation and applied load   Al 7075-T6 Static bending load – side in tension

Pre-exposure time t_{exp}

0.6 M NaCl pH 6.5, room T, i_{rev} 2.5 mA/cm^2





Repassivation and applied load

Al 7075-T6 Static bending load – side in tension

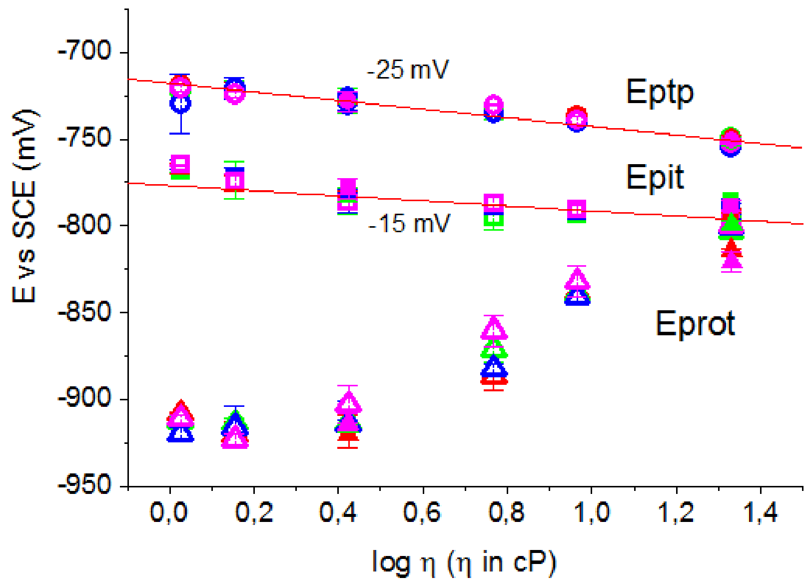
Test solution viscosity

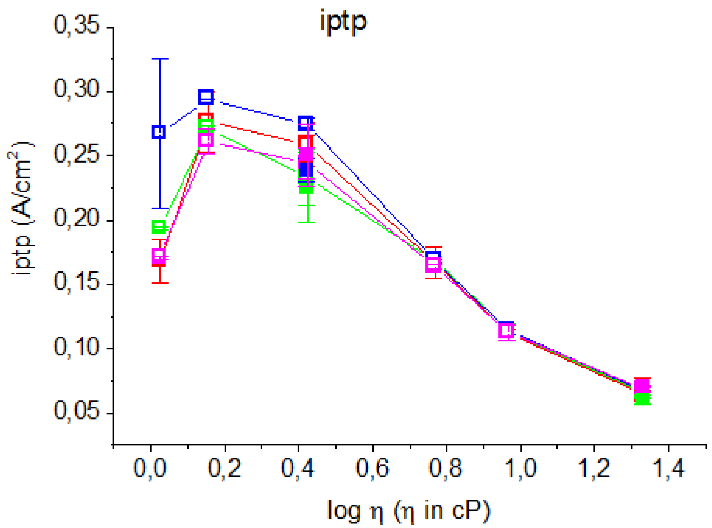
0.6 M NaCl pH 6.5/3.5, room T, i_{rev} 2.5 mA/cm^2

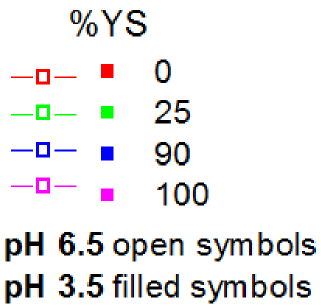
NaCl 0.6 M

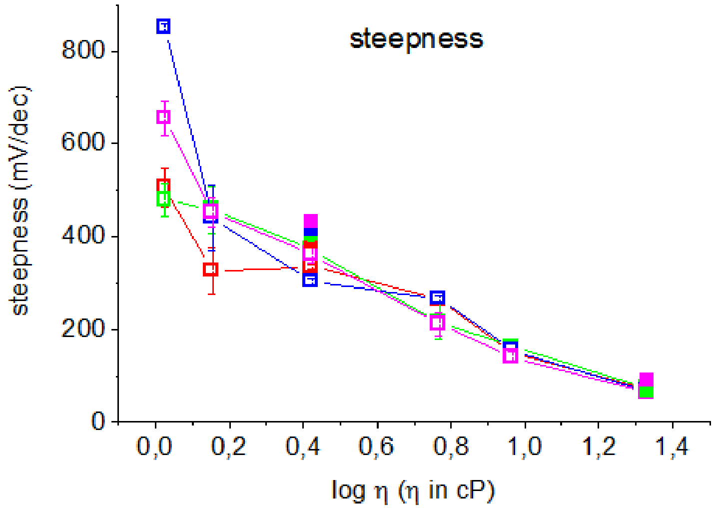
% Glycerol	η (cP)
0	1.06
10	1.43
20	2.65
30	5.87
40	9.25
50	20.0
60	21.5

Viscosity cup (2 mm)
ASTM D1200 Ford







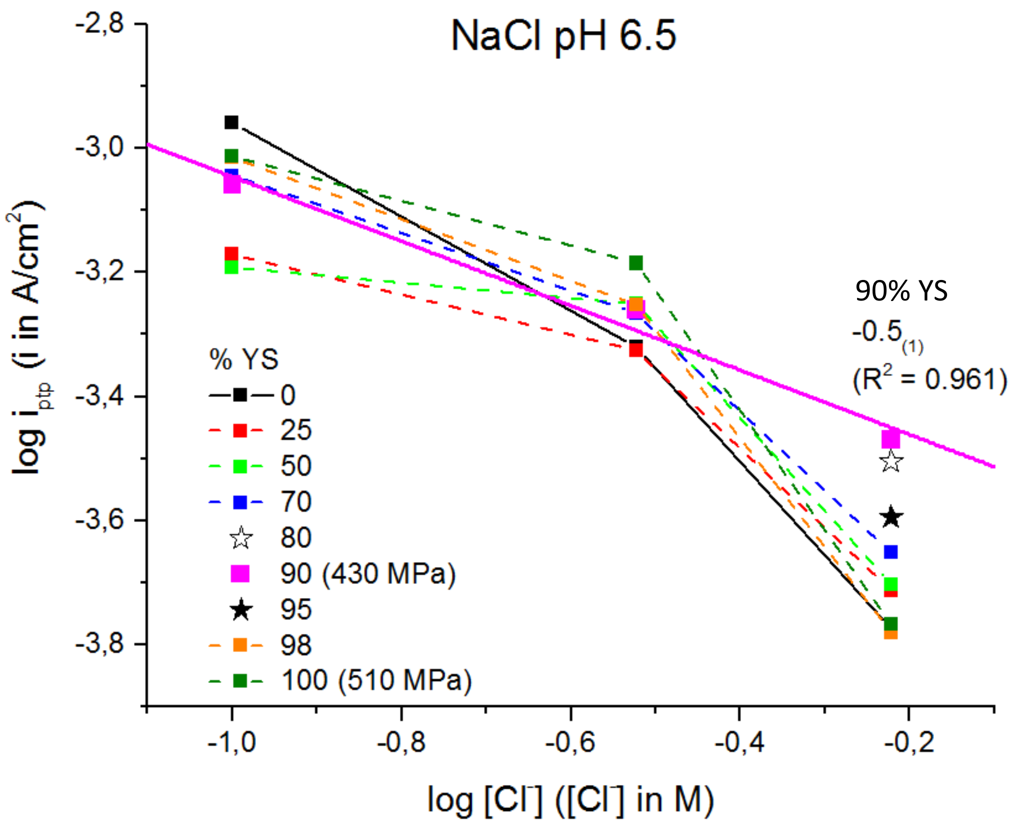


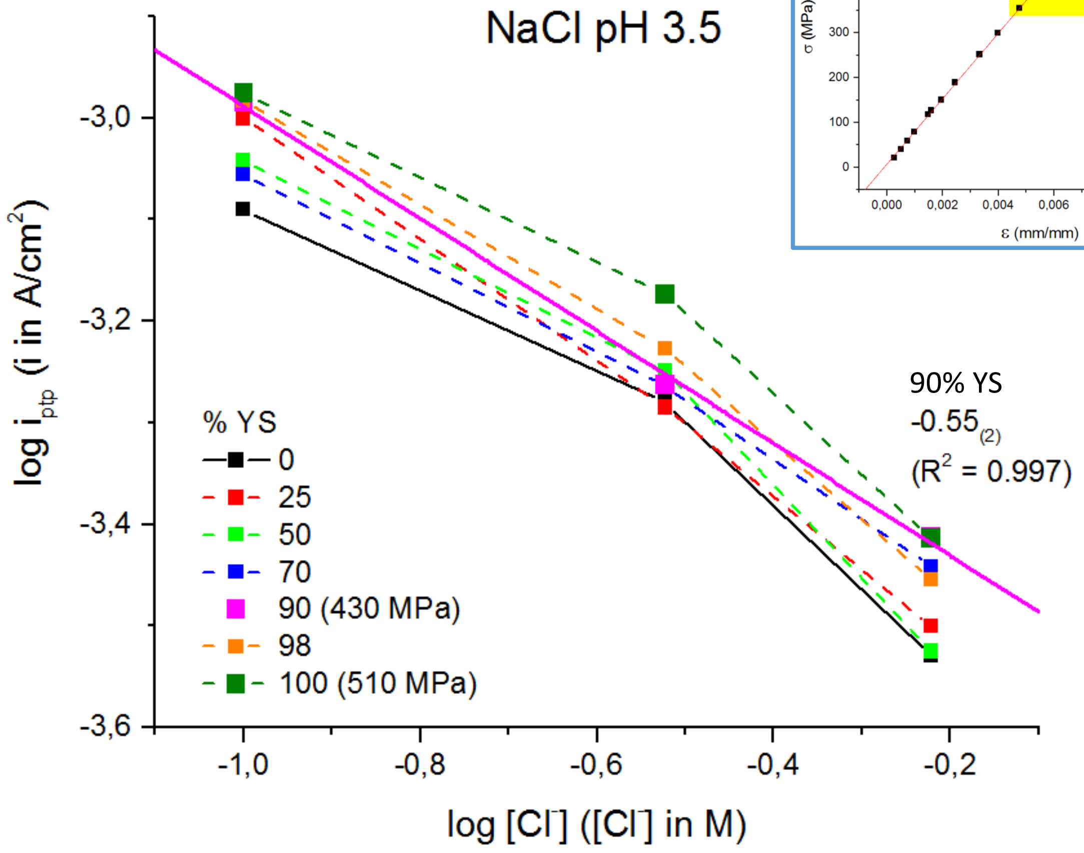
Repassivation and applied load

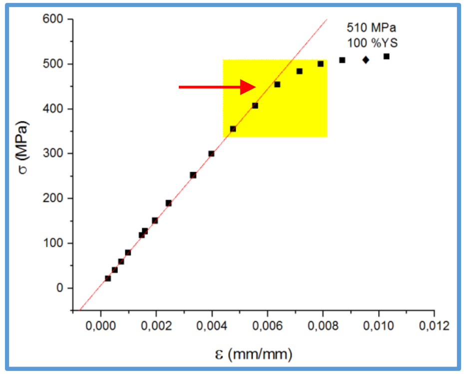
Al 7075-T6 Static bending load – side in tension

[Cl⁻] and pH

room T, i_{rev} 2.5 mA/cm²





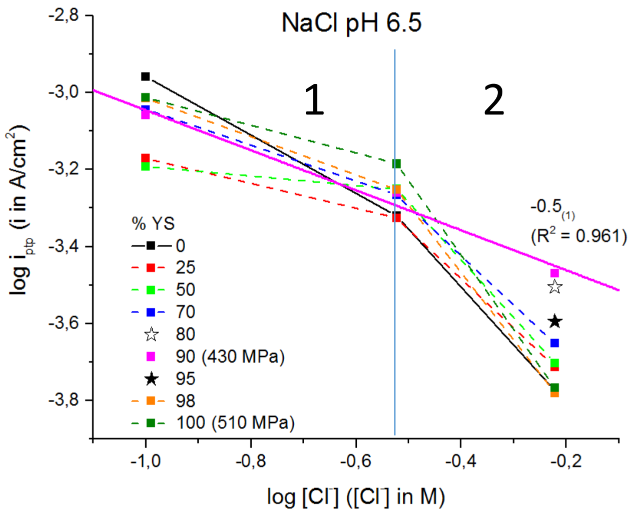


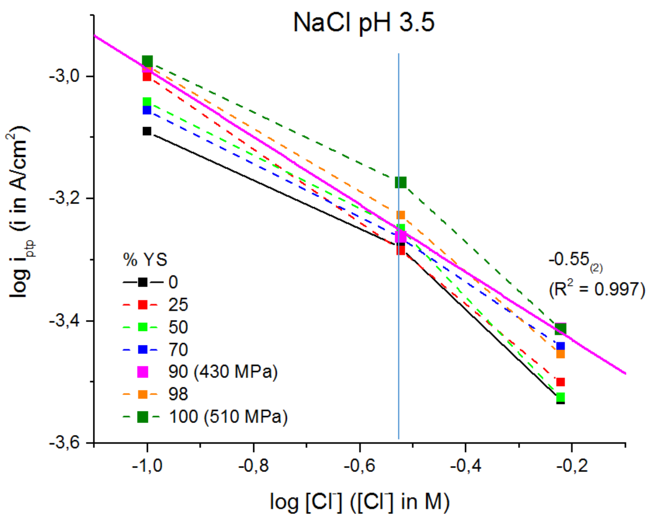
Repassivation and applied load

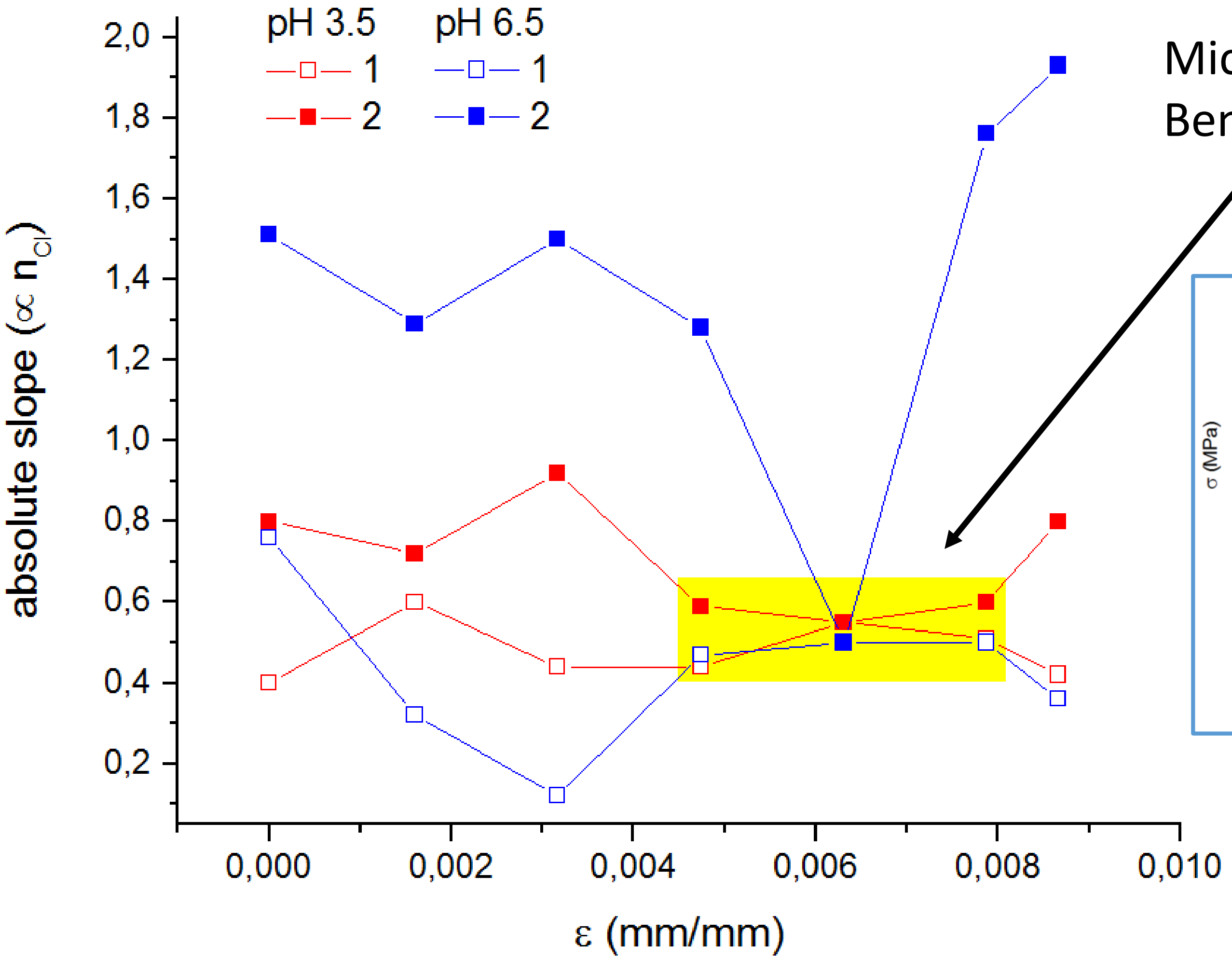
Al 7075-T6 Static bending load – side in tension

[Cl$^-$] and pH

room T, i_{rev} 2.5 mA/cm^2

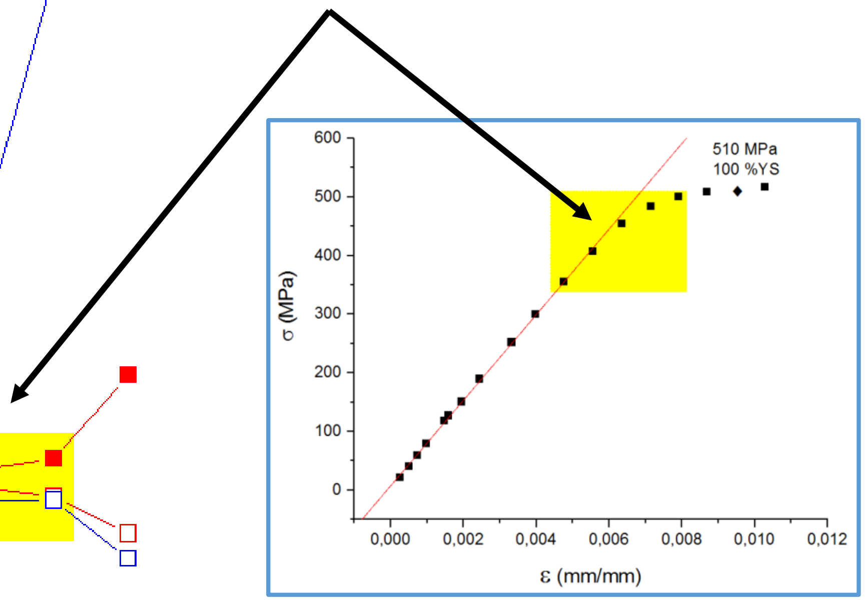






Microyielding?

Bending thin specimen

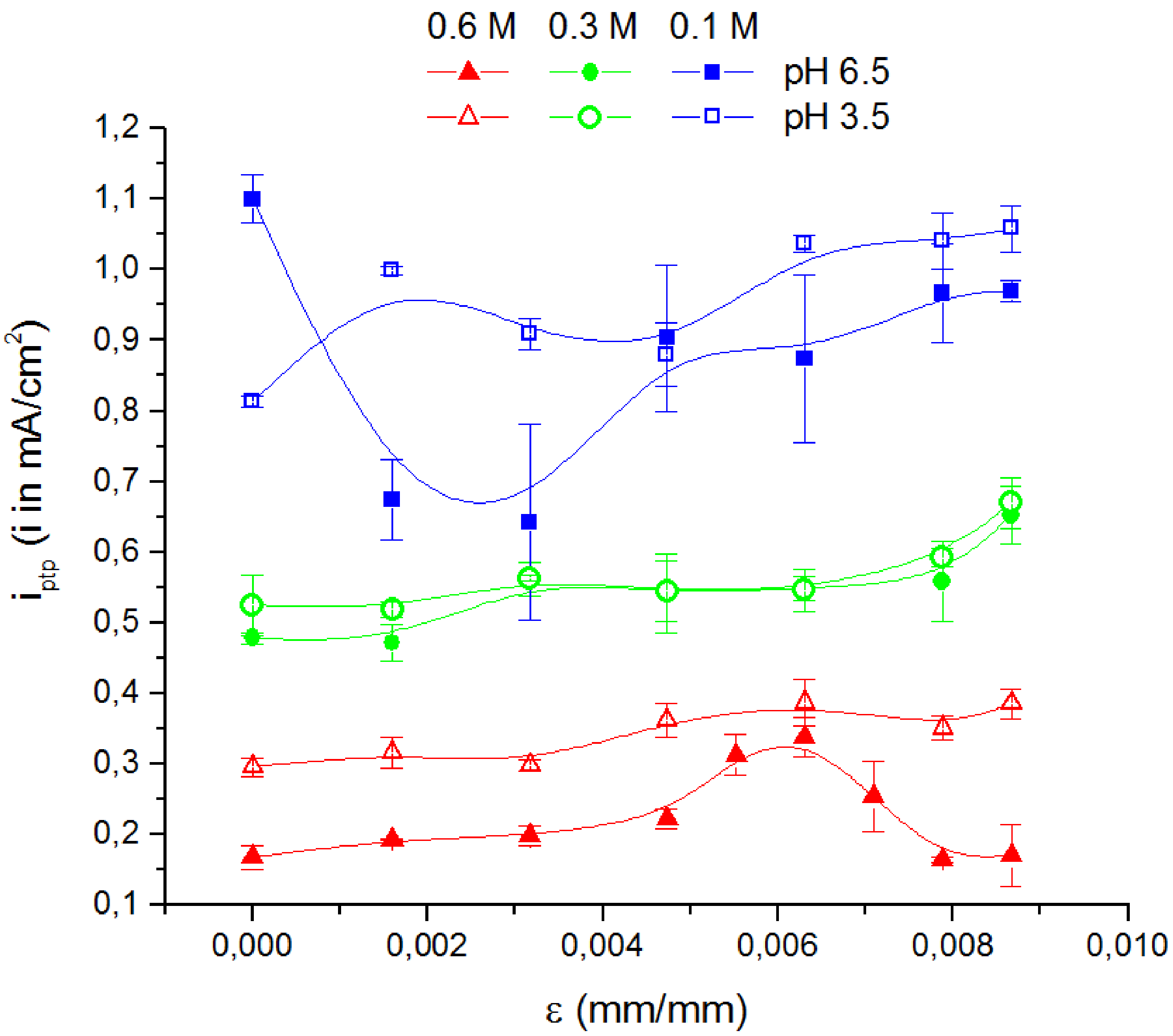


Repassivation and applied load

Al 7075-T6 Static bending load – side in tension

[Cl^-] and pH

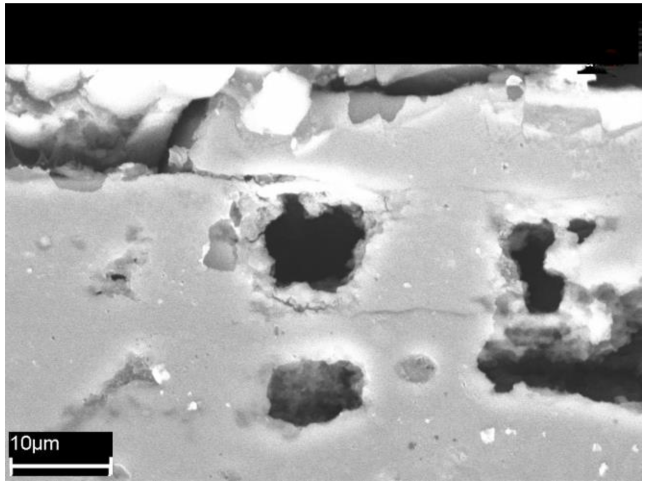
room T, i_{rev} 2.5 mA/cm^2

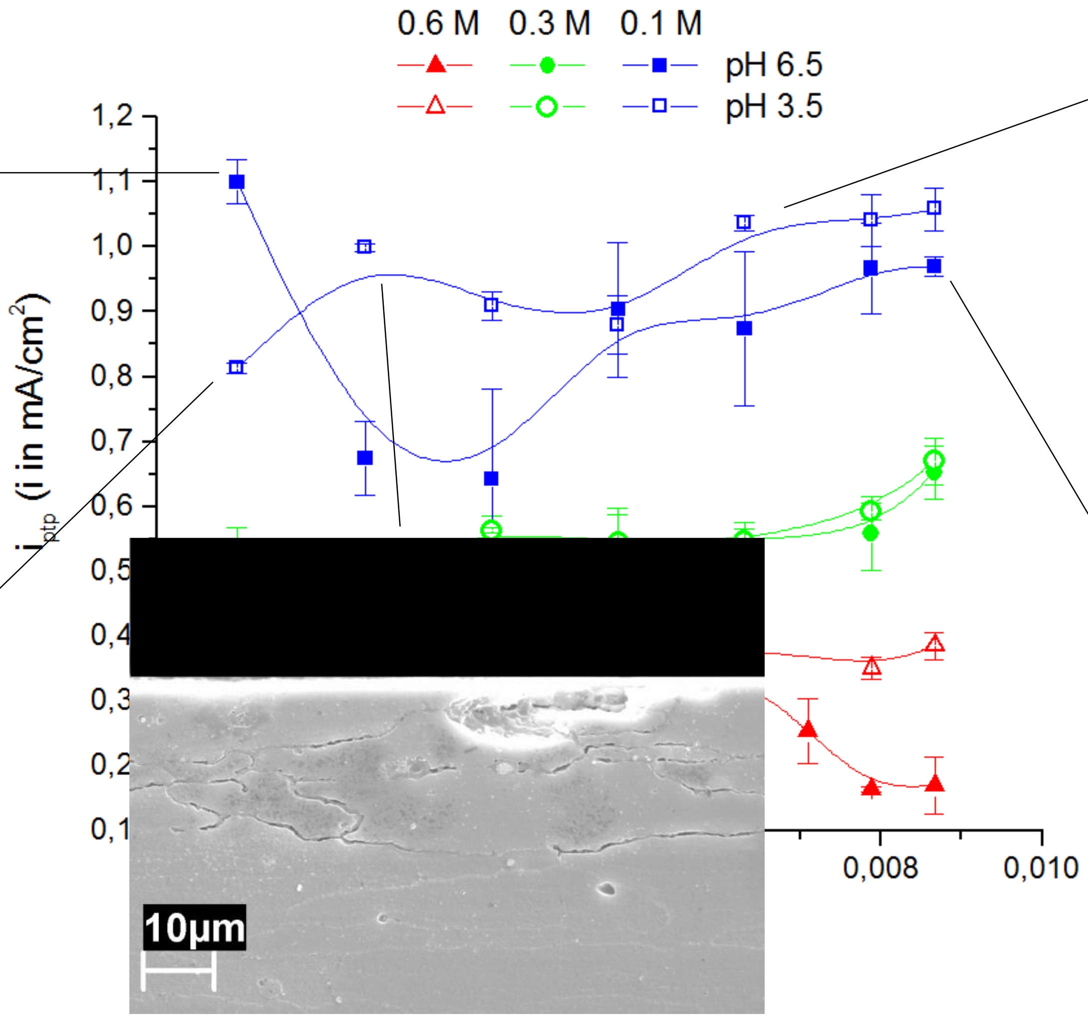


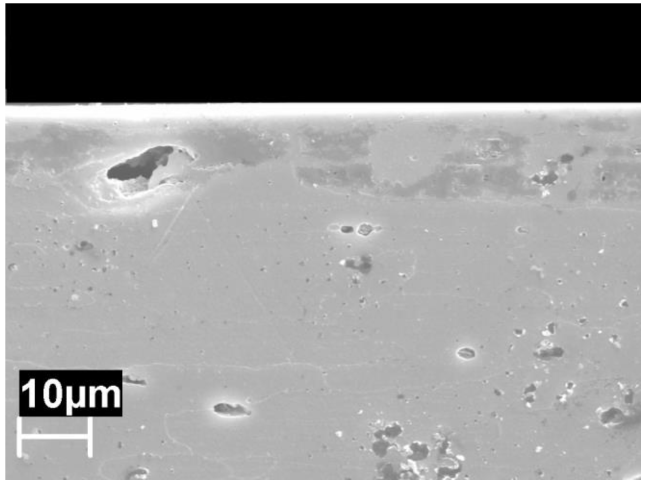
Repassivation and applied load   Al 7075-T6 Static bending load – side in tension

[Cl^-] and pH

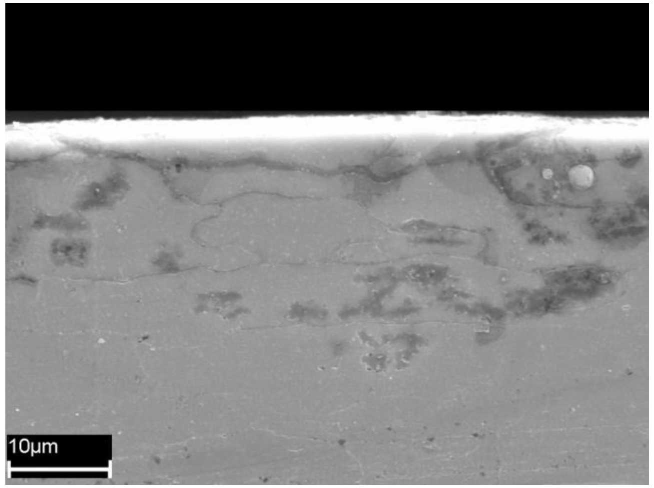
room T, i_{rev} 2.5 mA/cm²



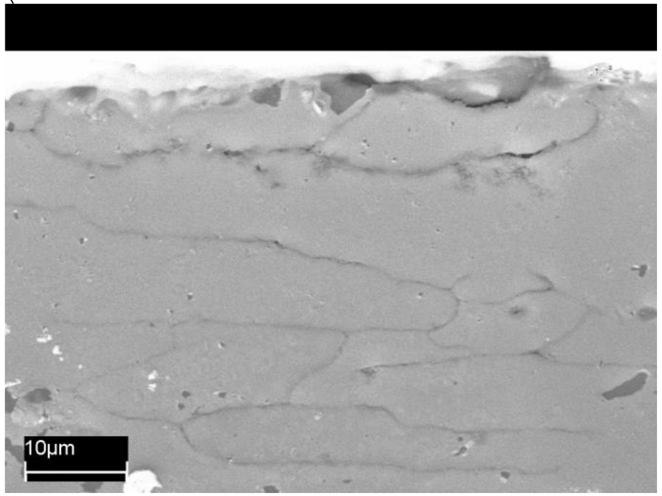




90% YS



100% YS

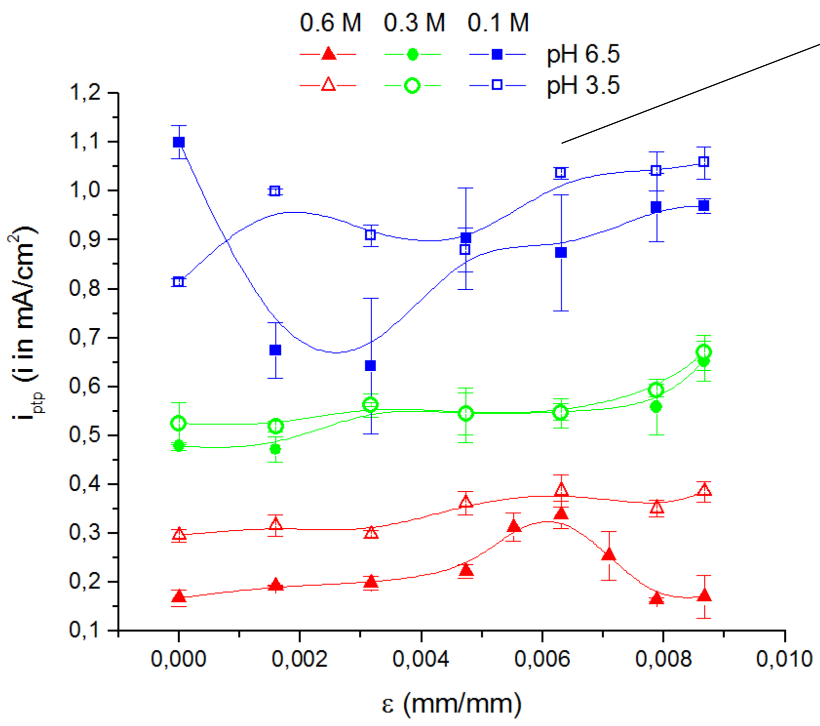


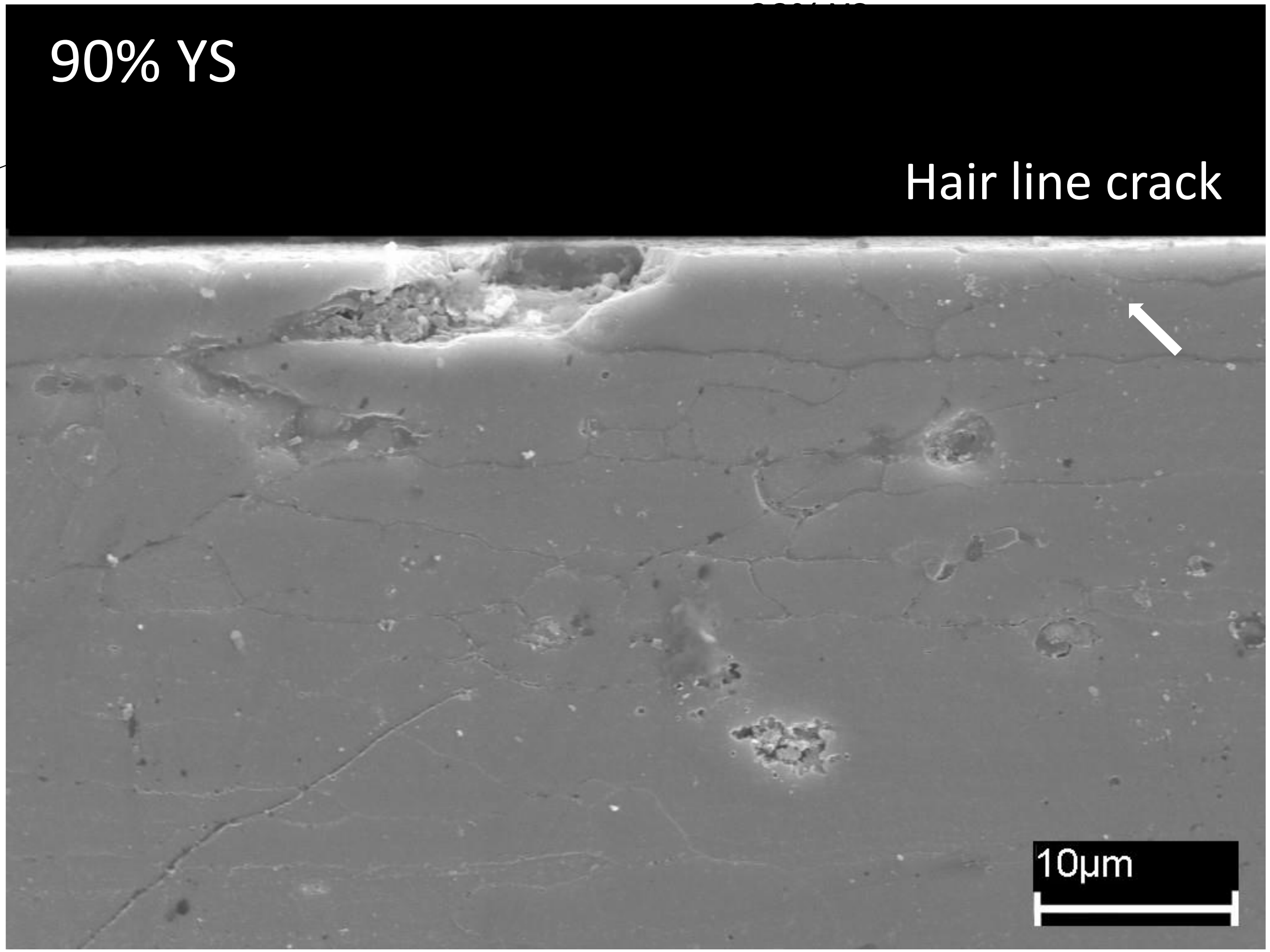
Repassivation and applied load

Al 7075-T6 Static bending load – side in tension

[Cl-] and pH

room T, i_{rev} 2.5 mA/cm^2





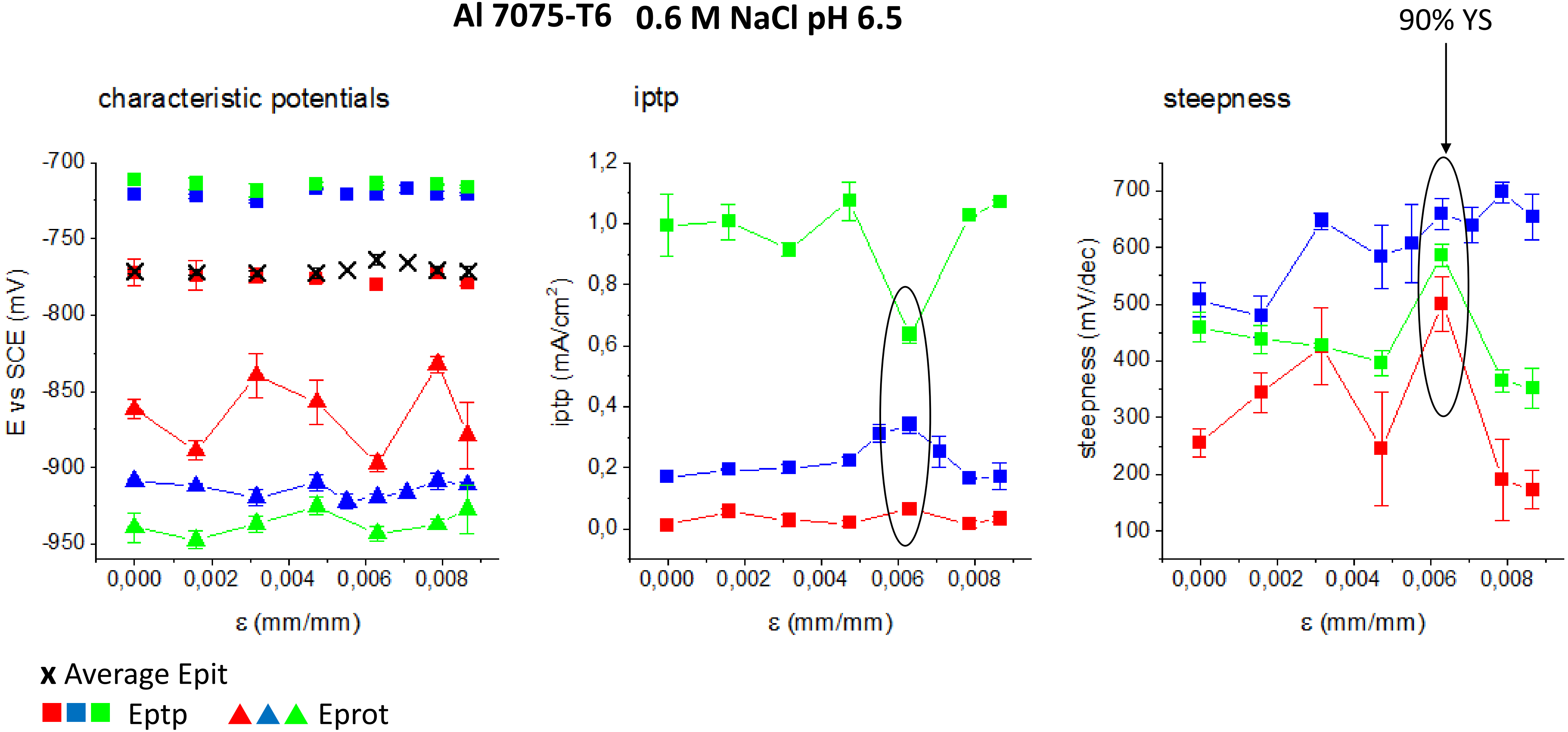
Repassivation and applied load Al 7075-T6 and Al 2024-T3

Static bending – side in tension

Amount of promoted corrosion i_{rev} (■) 1 (■) 2.5 (■) 5 mA/cm²

0.6 M NaCl pH 6.5/3.5, room T

Al 7075-T6 0.6 M NaCl pH 6.5



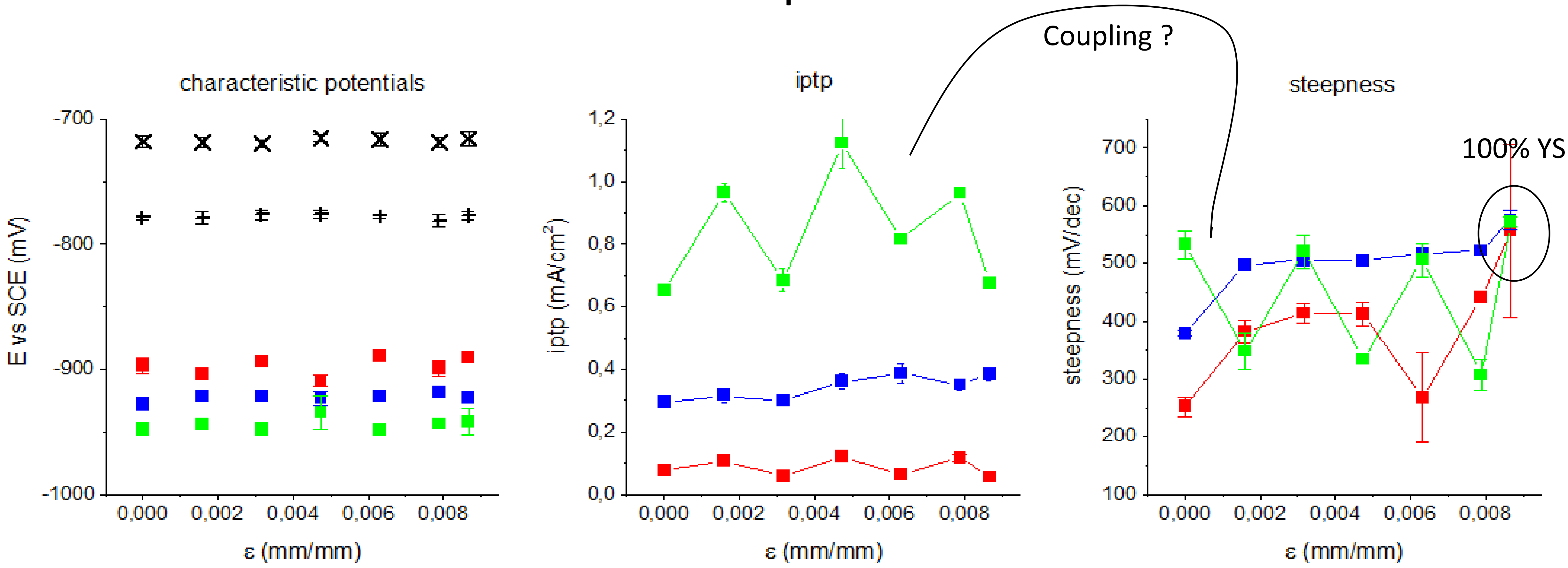
Repassivation and applied load Al 7075-T6 and Al 2024-T3

Static bending – side in tension

Amount of promoted corrosion i_{rev} (■) 1 (■) 2.5 (■) 5 mA/cm²

0.6 M NaCl pH 6.5/3.5, room T

Al 7075-T6 0.6 M NaCl pH 3.5



+ Average Epit **x** Average Eptp

■■■ Eprot

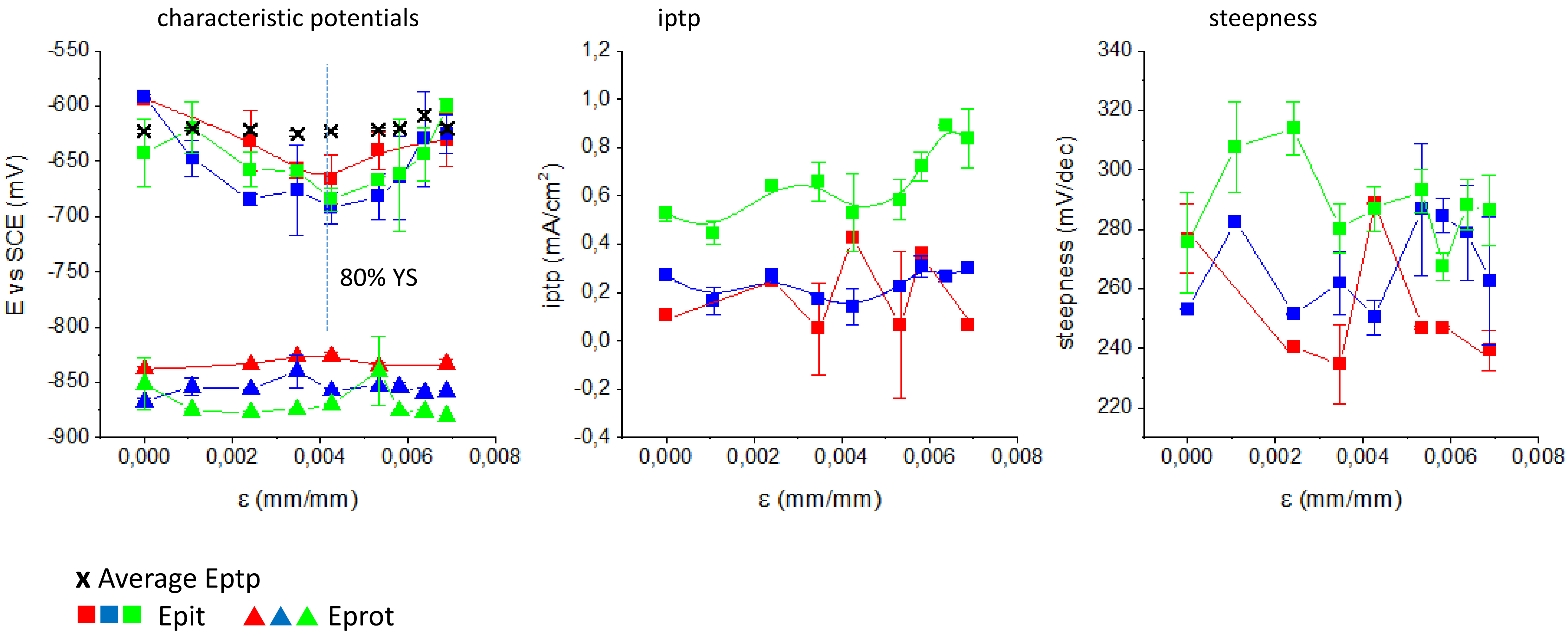
Repassivation and applied load Al 7075-T6 and Al 2024-T3

Static bending – side in tension

Amount of promoted corrosion i_{rev} (■) 1 (■) 2.5 (■) 5 mA/cm²

0.6 M NaCl pH 6.5/3.5, room T

Al 2024-T3 0.6 M NaCl pH 6.5



Repassivation and applied load Al 7075-T6 and Al 2024-T3

Static bending – side in tension

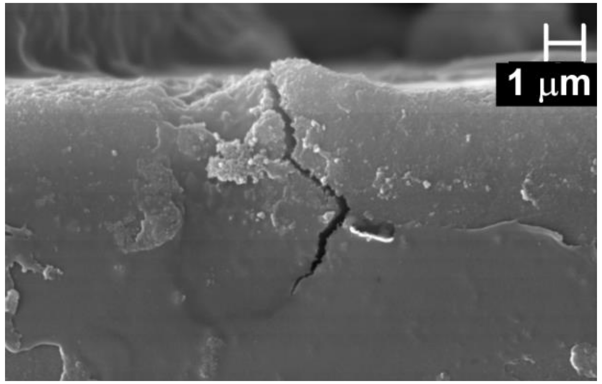
Amount of promoted corrosion i_{rev} (■) 1 (■) 2.5 (■) 5 mA/cm^2

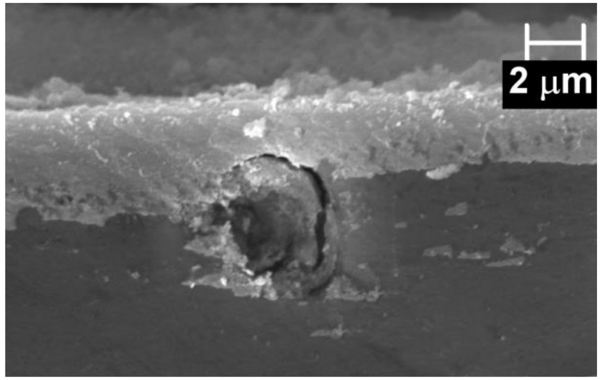
0.6 M NaCl pH 6.5/3.5, room T

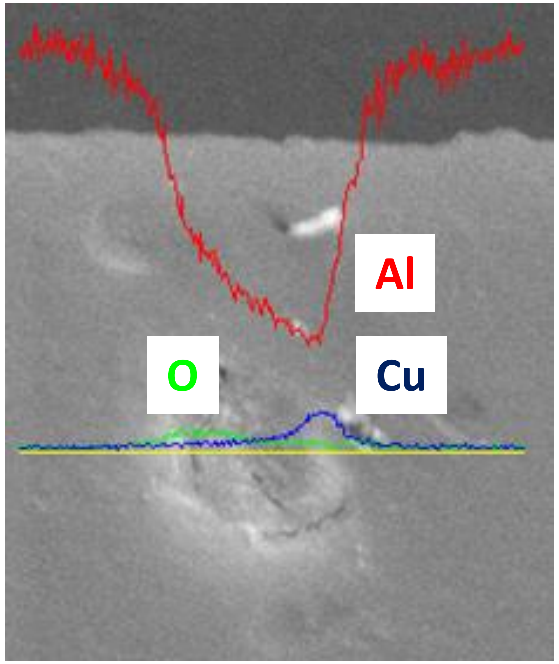
Al 2024-T3
pH 6.5

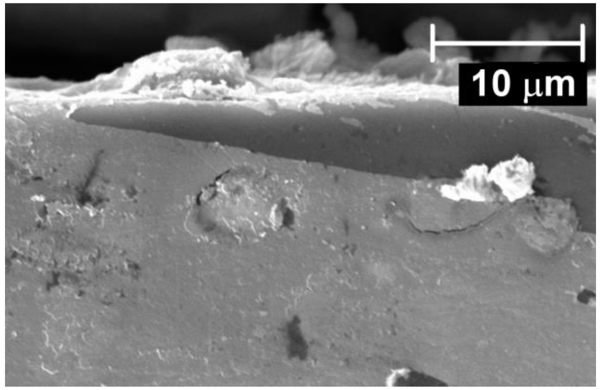
% YS

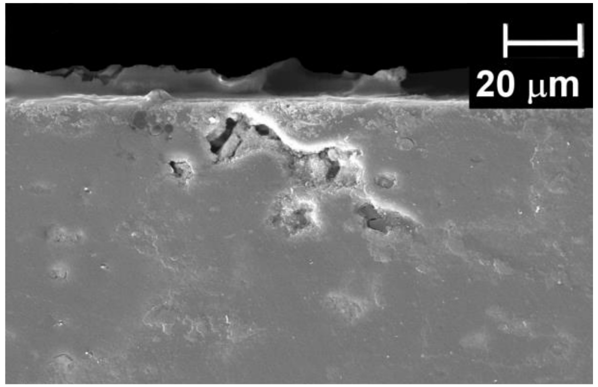
irev

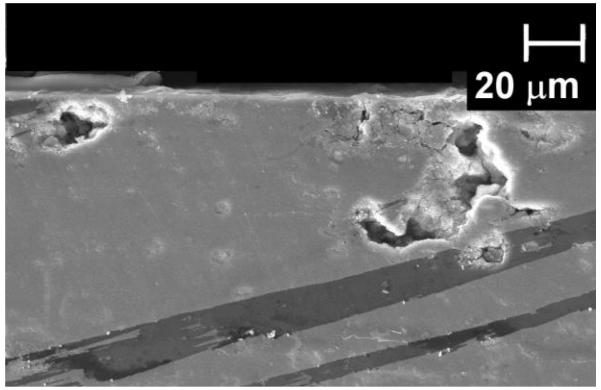












Repassivation and constant applied load: Al 7075-T6 & Al 2024-T3

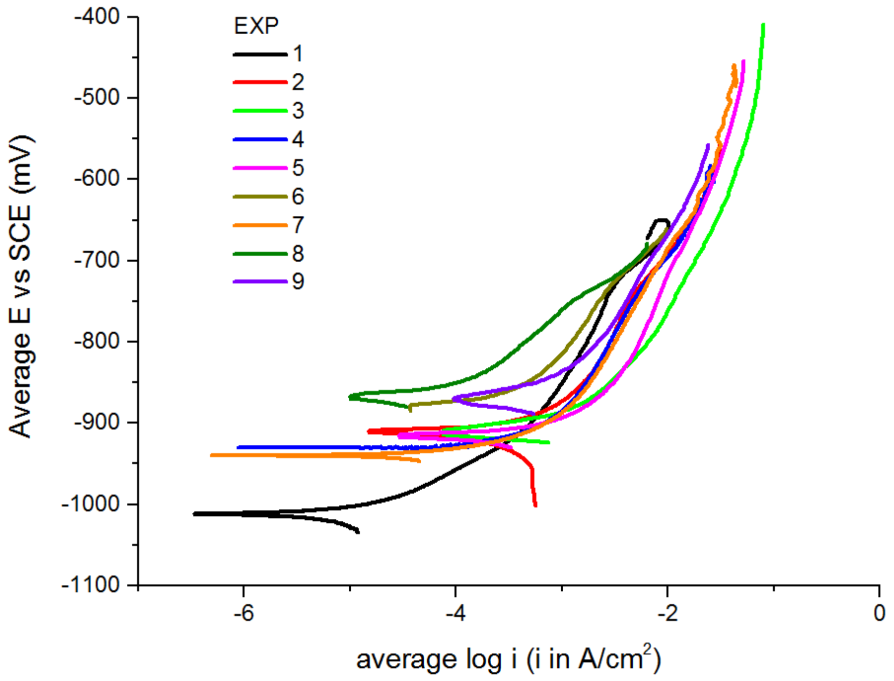
Bending load: sides in tension and compression

sides in tension and compression followed by unload

TAGUCHI ORTHOGONAL DESIGN L9

EXP	% YS	Scan rate (mV/s)	Erev vs SCE (mV)	T (°C)
1	50	0,1667	-550	40
2	50	5	-450	60
3	50	10	-350	80
4	80	0,1667	-450	80
5	80	5	-350	40
6	80	10	-550	60
7	100	0,1667	-350	60
8	100	5	-550	80
9	100	10	-450	40

Example: Al 7075-T6 (tension side, load)
Average reverse curves



Test solution: 0.6 M NaCl pH 6.5

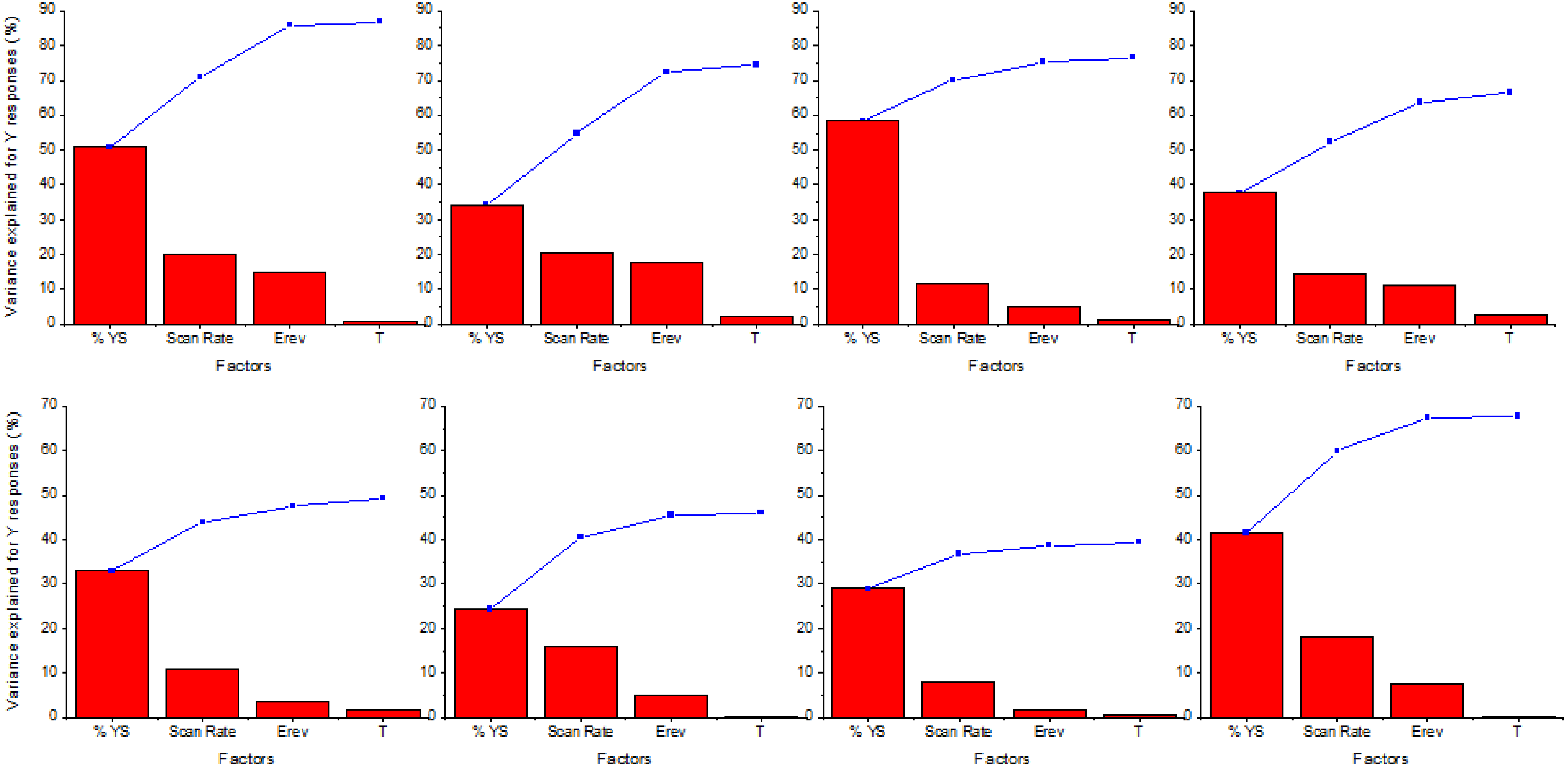
Potentiostatic polarization at Erev (10 min) followed by potential scan into the active region

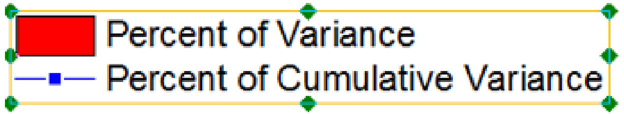
PARTIAL LEAST SQUARES ANALYSIS

Tension | Tension & Unload | Compression | Compression & Unload

Al 7075-T6

Al 2024-T3

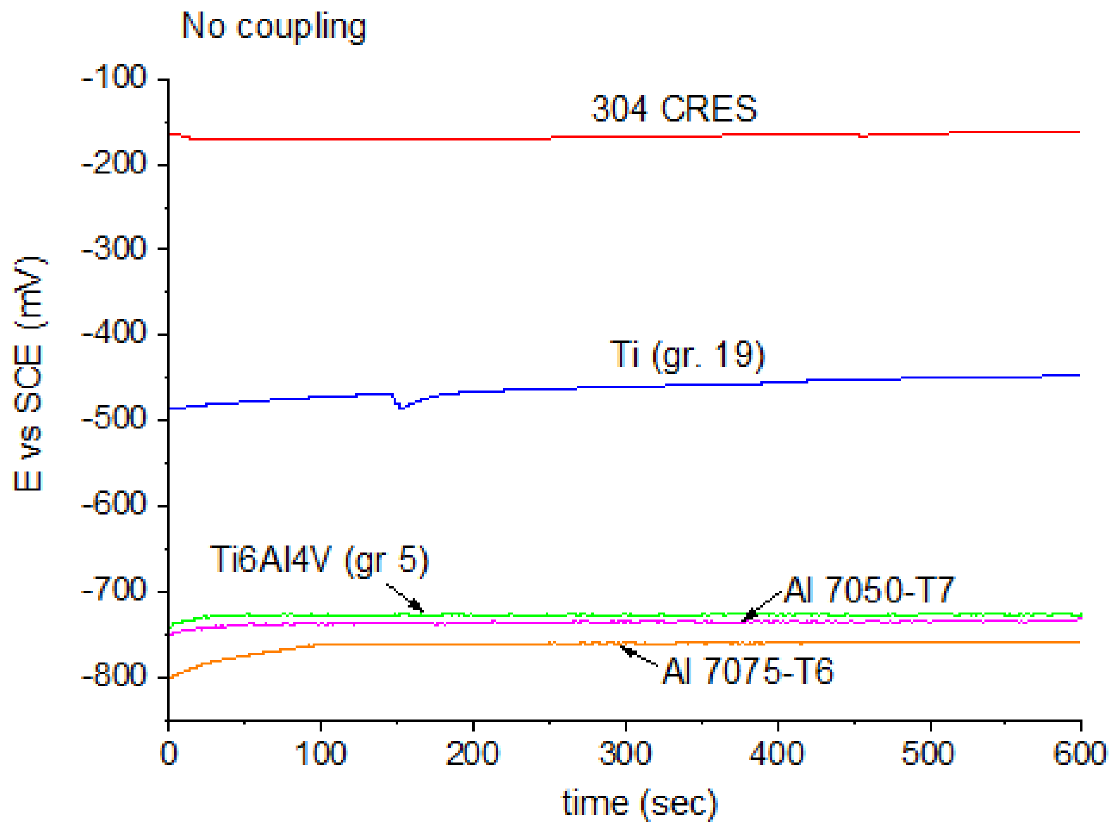


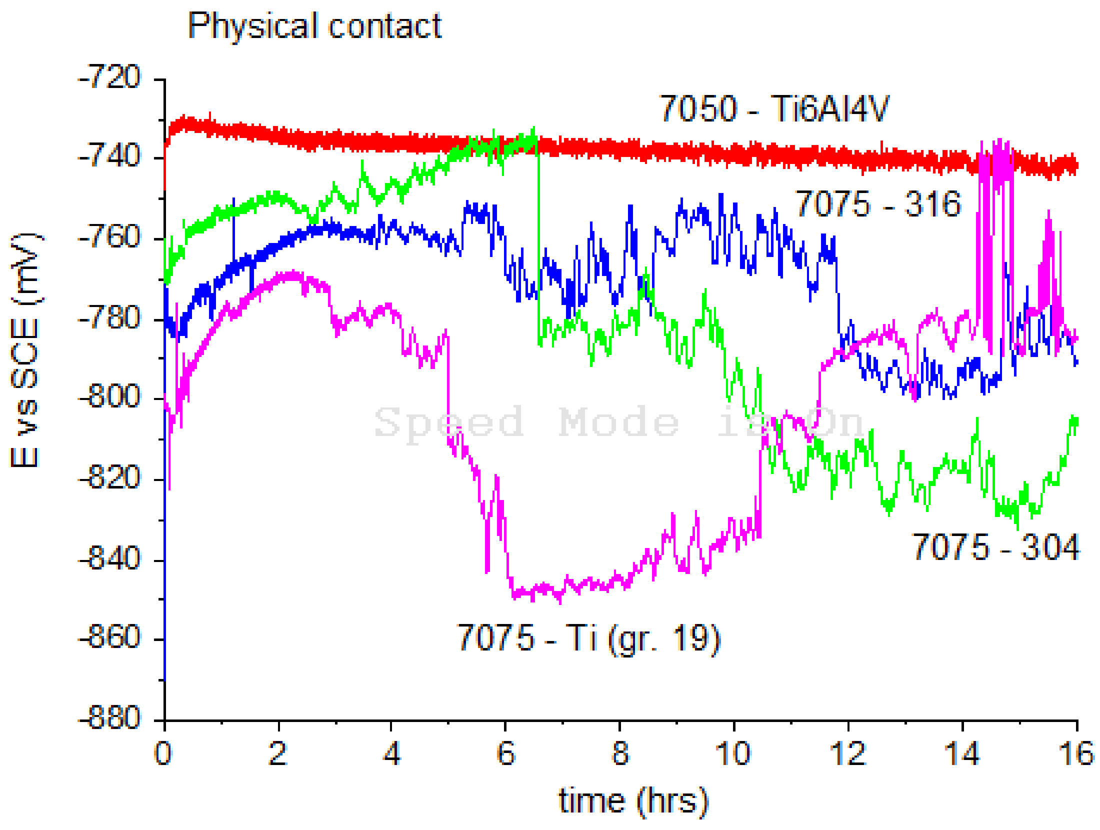


Y responses: Eptp, iptp, steepness, Eprot

Galvanic corrosion and load   Al 7075-T6 and Al 2024-T3

Preliminar experiments (0.6 M NaCl, pH 6.5, room T)





RATIO BETWEEN ANODE AND CATHODE AREAS (Aa/Ac) ≅10:1

Galvanic corrosion and load   Al 7075-T6 and Al 2024-T3

Static bending – side in tension

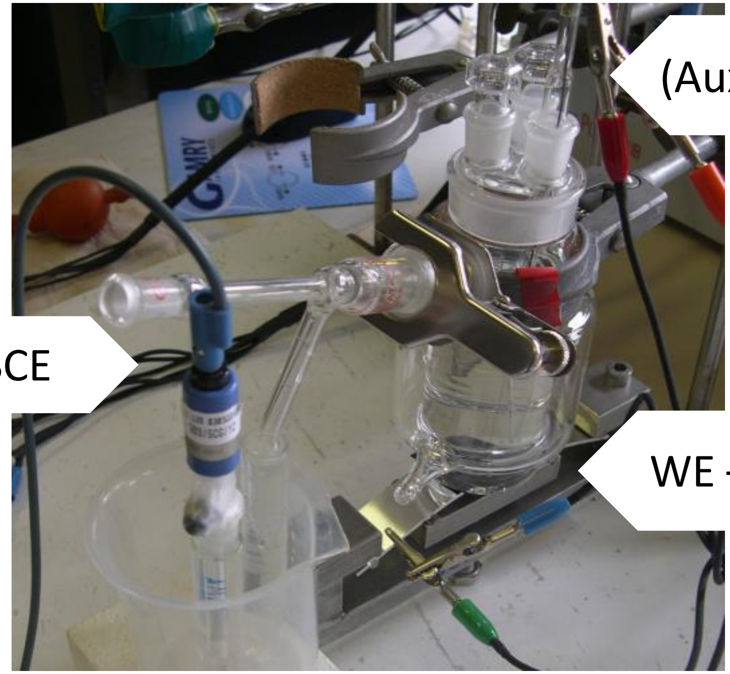
dissimilar metal: passing through CRES 304 screw

0.6 M NaCl pH 6.5, room T

Macrocouples

Al -- Pt
Al/Fe -- Pt

dissolved O_2 reduction
comparable contribution

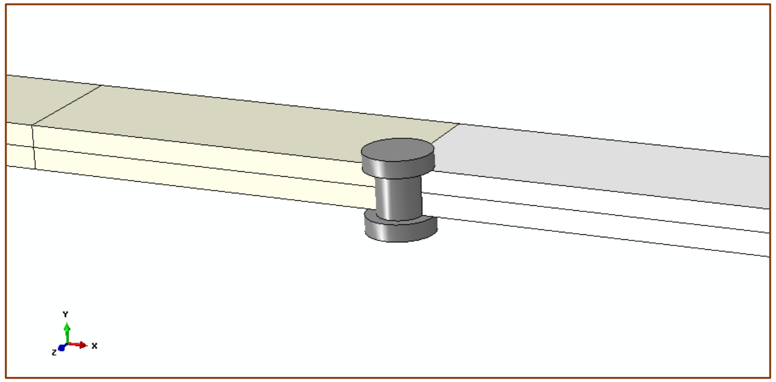


RE – SCE

(Auxiliary) Cathode Pt

WE – Al alloy (WE1) or Al alloy/CRES 304 (WE2)

Schematics of Al alloy/CRES 304



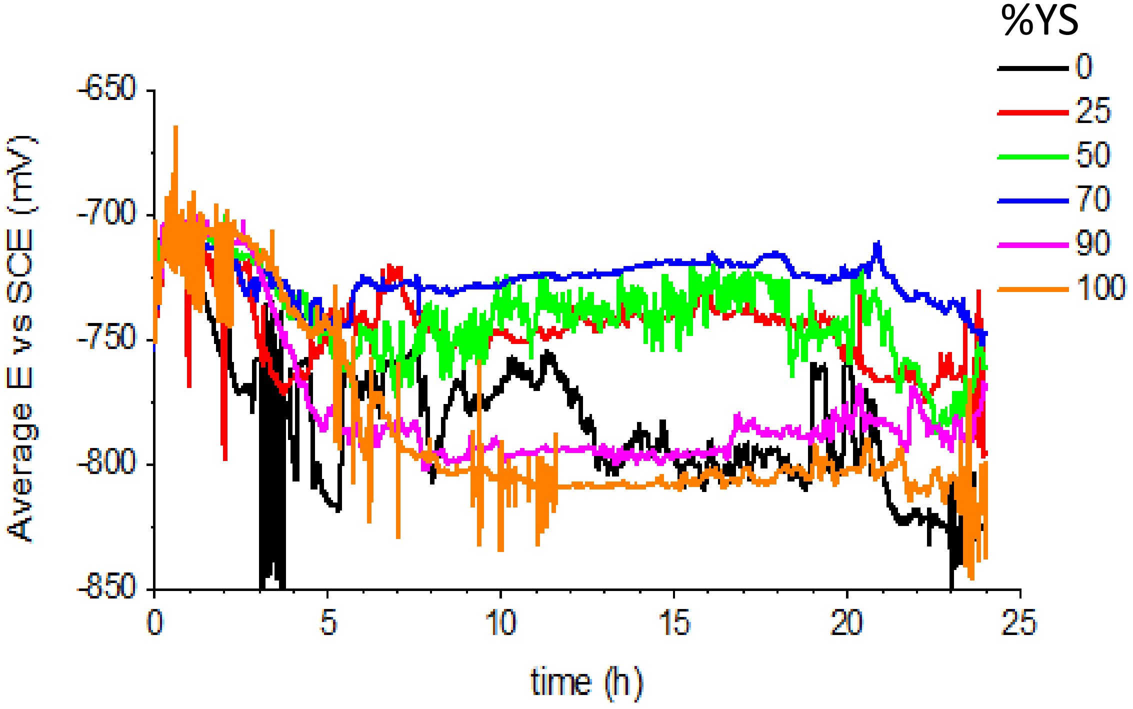
two laminae connected
with CRES 304 screw
tightening torque 3 Nm
Aa/Ac ≈ 2 : 1

Galvanic corrosion and load Al 7075-T6 and Al 2024-T3

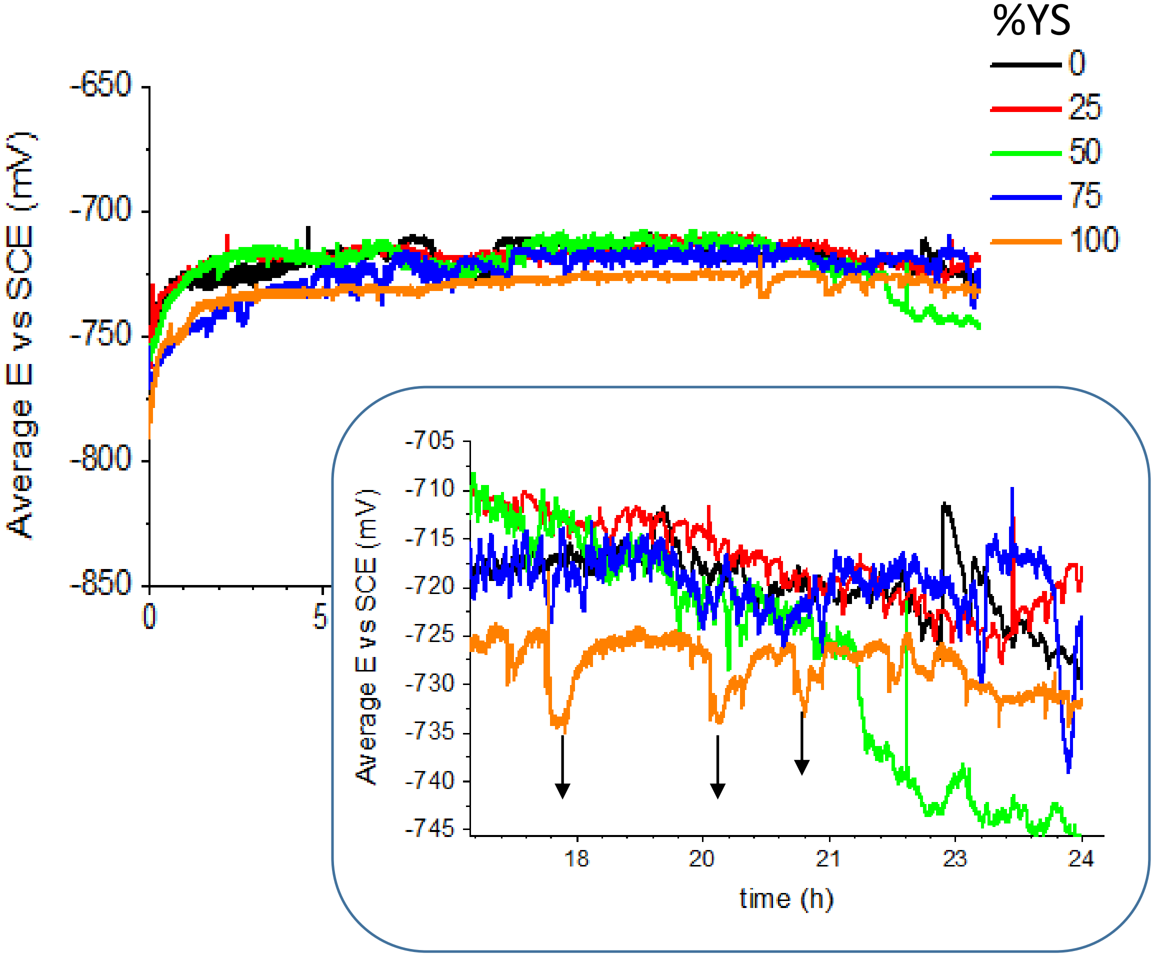
Static bending - side in tension

dissimilar metal passing through CRES 304 screw

WE1: Al 7075

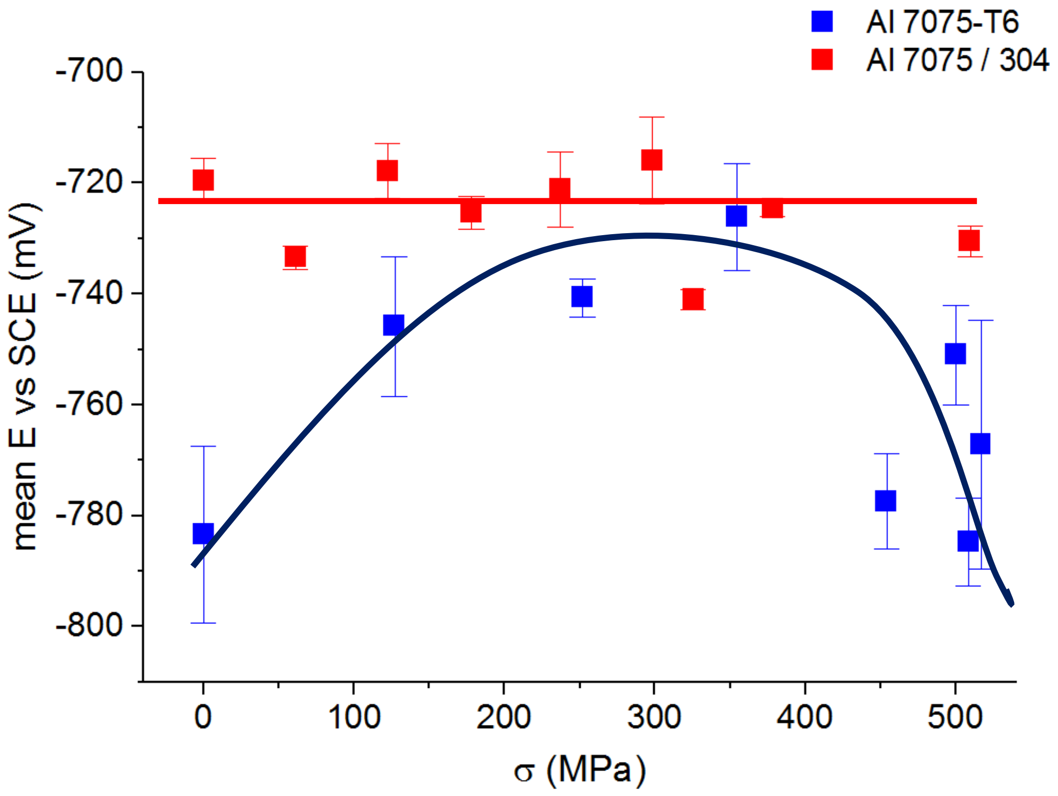


WE2: Al 7075 / CRES 304

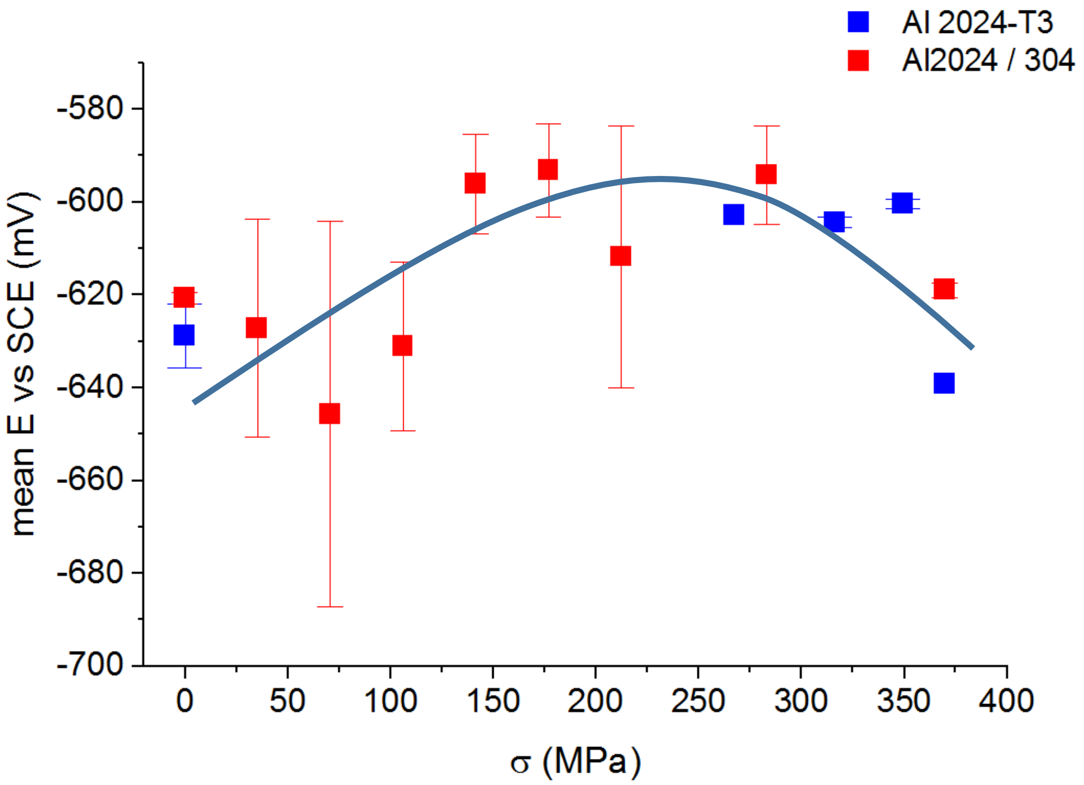


Galvanic corrosion and load   Al 7075-T6 and Al 2024-T3

Static bending - side in tension



dissimilar metal passing through CRES 304 screw



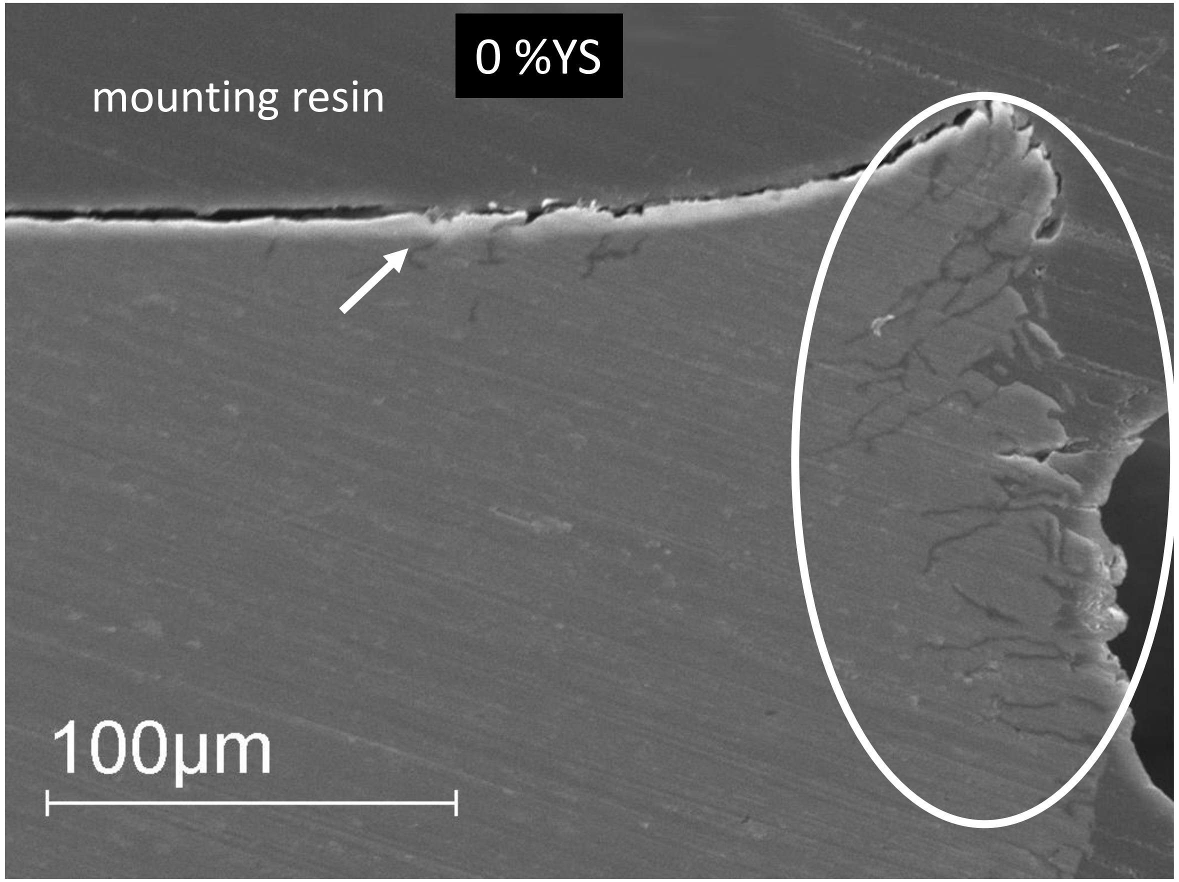
Galvanic corrosion and load   Al 7075-T6 and Al 2024-T3

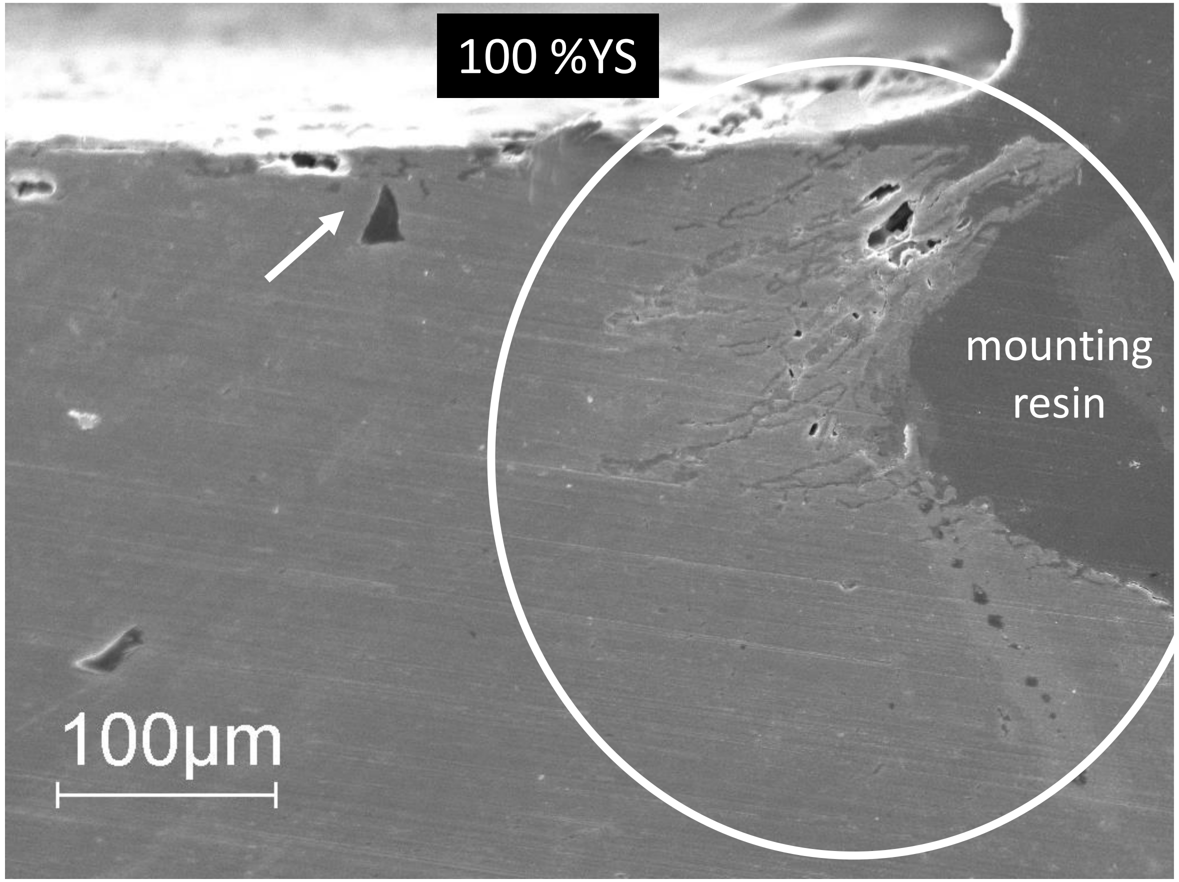
Static bending - side in tension   dissimilar metal passing through CRES 304 screw

WE2: Al 7075 / CRES 304

Higher maximum stress because bending stresses increased by the notch and thread effect

Stress-oriented dissolution enhanced with %YS





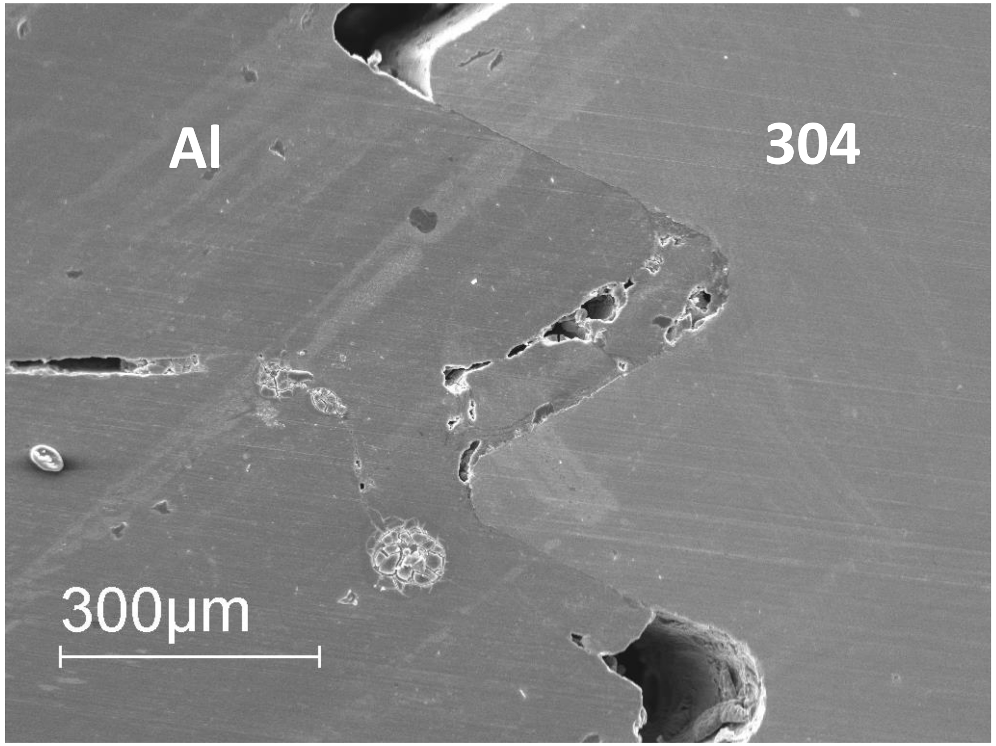
Galvanic corrosion and load Al 7075-T6 and Al 2024-T3

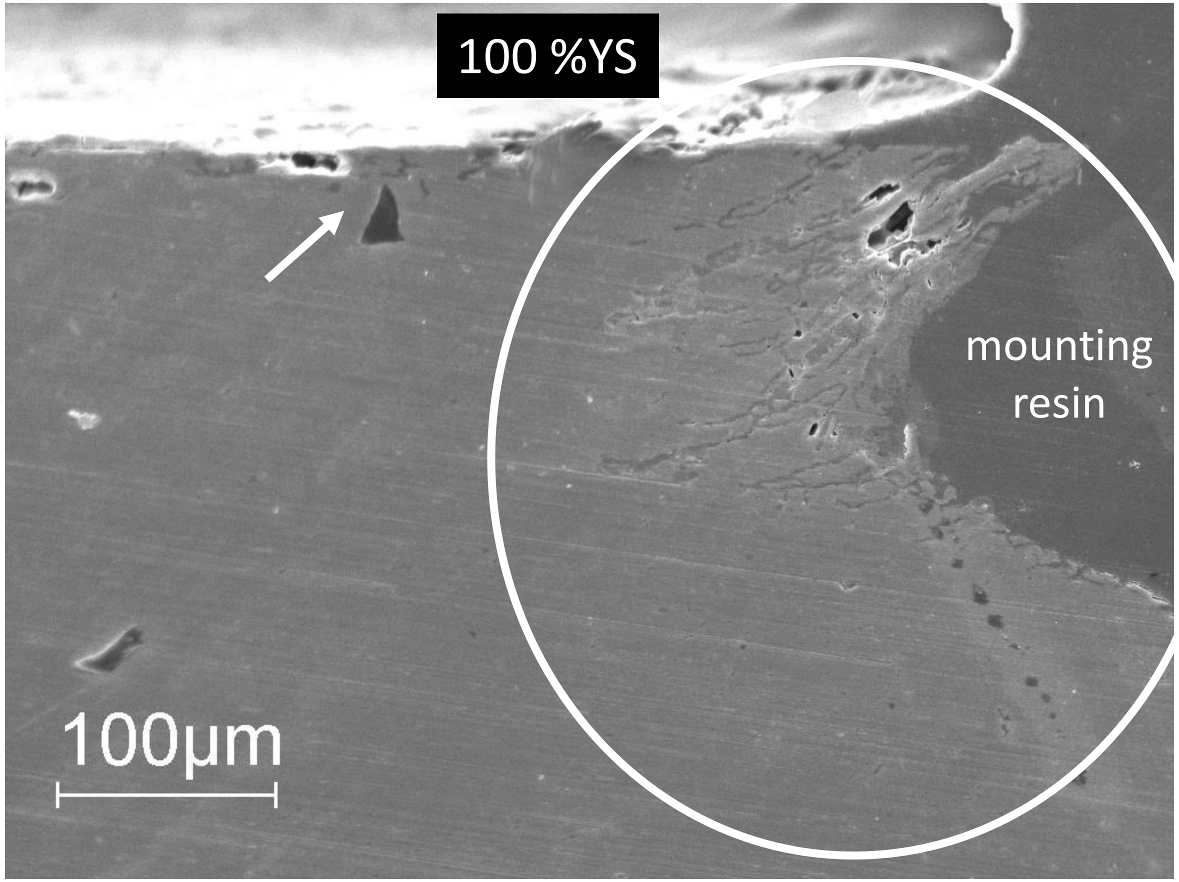
Static bending - side in tension dissimilar metal passing through CRES 304 screw

WE2: Al 7075 / CRES 304

Higher maximum stress because bending stresses increased by the notch and thread effect
Stress-oriented dissolution enhanced with %YS

contact between two laminae



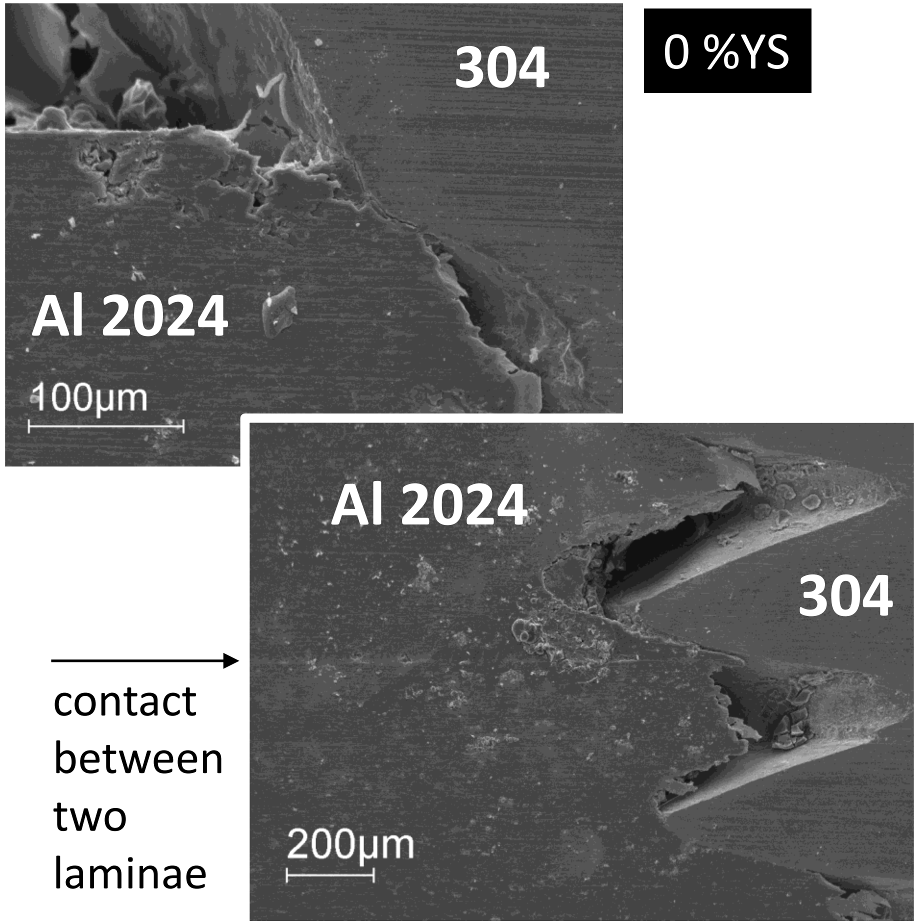


Galvanic corrosion and load Al 7075-T6 and Al 2024-T3

Static bending - side in tension

WE2: Al 2024 / CRES 304

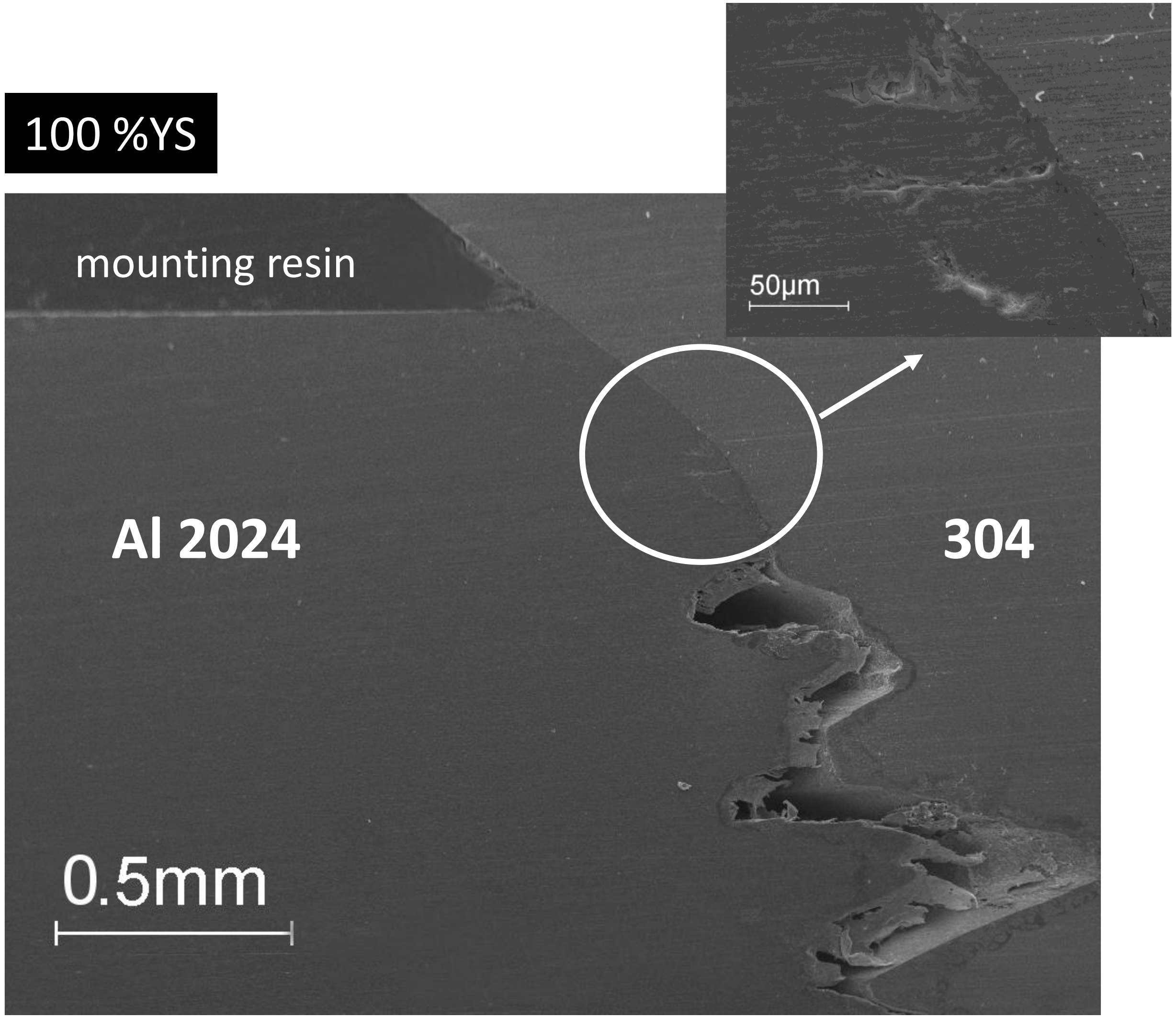
0 %YS



contact between two laminae

dissimilar metal passing through CRES 304 screw

100 %YS



Galvanic corrosion and load

Static bending - side in tension

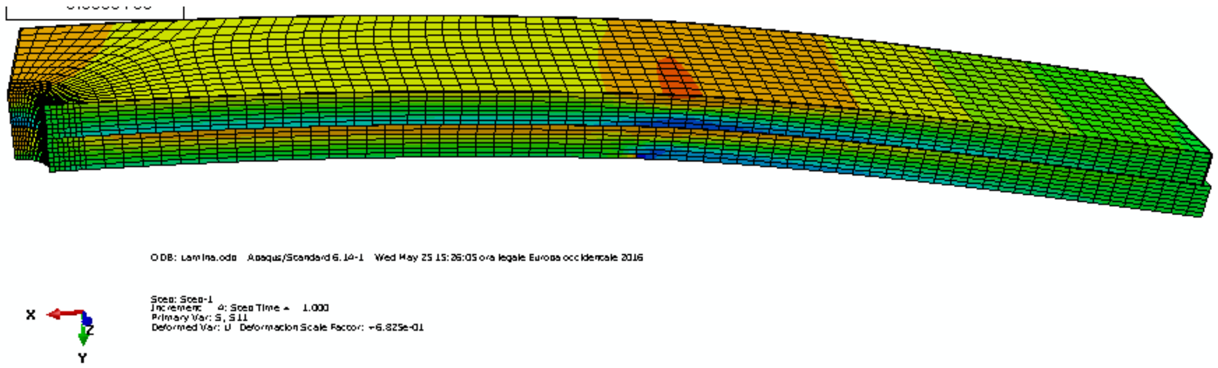
FEM ANALYSIS

- Stresses field in x direction (s11)
- von Mises stresses

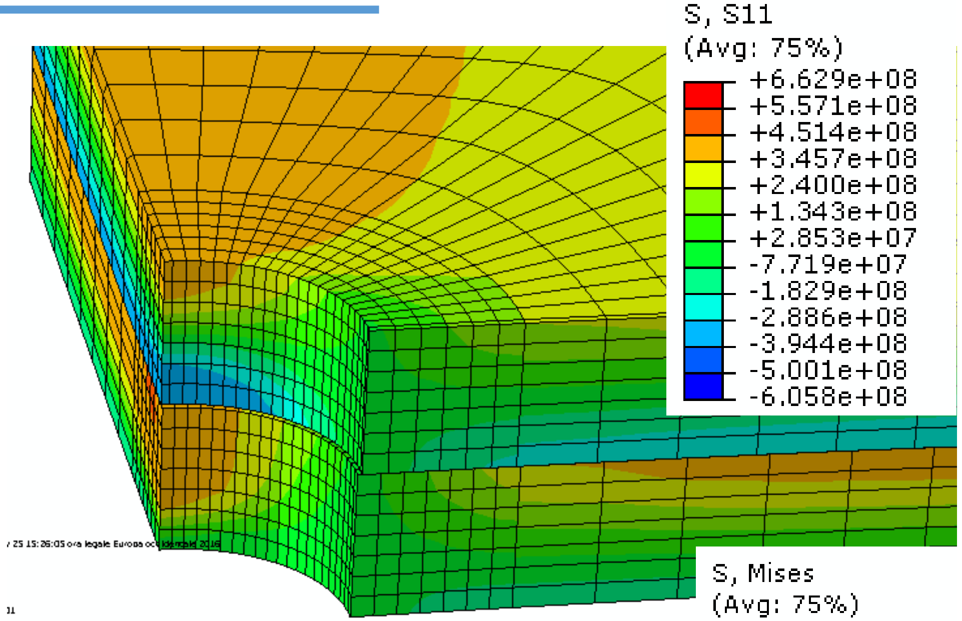
Applied displacement = 10 mm

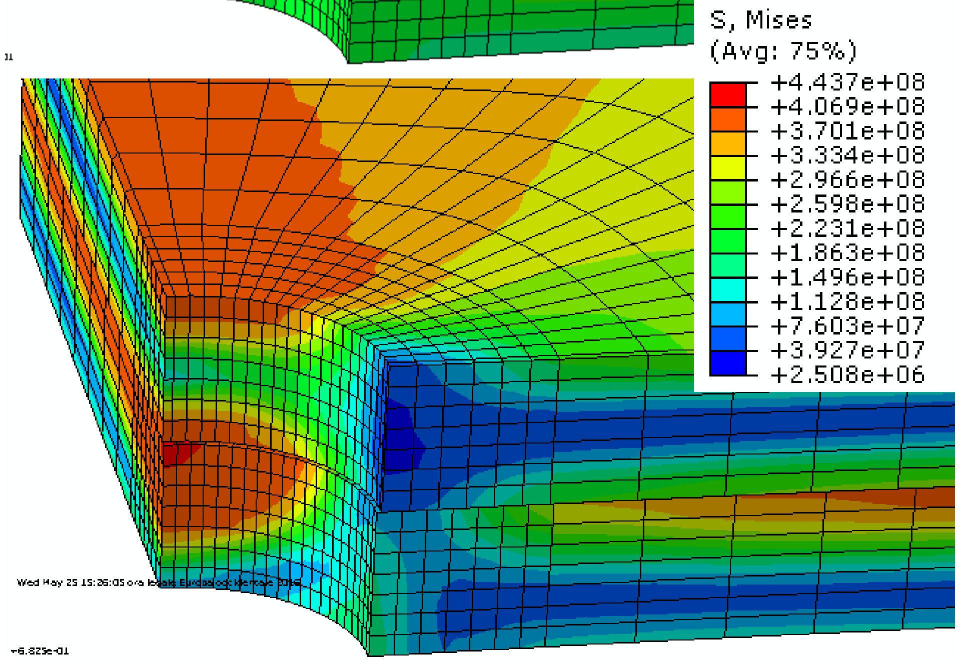
Static analysis with linear material behaviour

Contact with friction between the laminae



The stress concentration is higher on the top surface of both laminae due to the presence of the hole





Final remarks

- Electrochemically-induced repassivation in combination with bending load has indicated a critical condition for Al 7075-T6, suggesting inter-relation between local environment, electrochemical and mechanical states.
- Stress-oriented IG dissolution of Al 7075-T6 in contact with CRES 304 is enhanced with YS.
- Microstructural corrosion of Al 2024-T3, presenting less negative pitting potential than Al 7075-T6, could be responsible of the less evident effect of bending load on the repassivation and galvanic behaviors.
- Experiments under dynamic conditions (SSRT) and/or the use of lamina with stress concentration could help to understand better present findings.

Lamina with stress concentration (artificial notch)

Static bending - side in tension

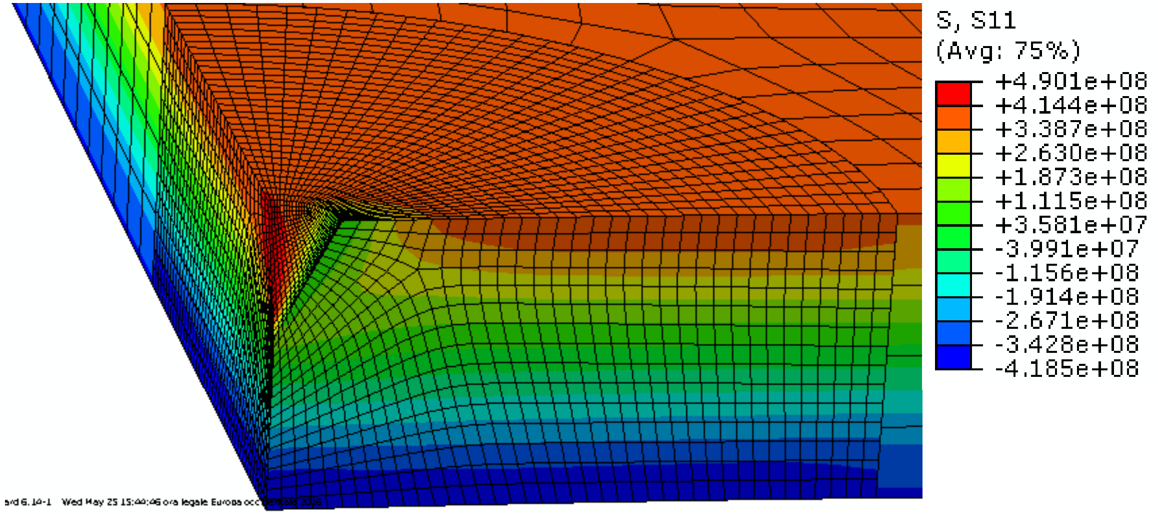
FEM ANALYSIS

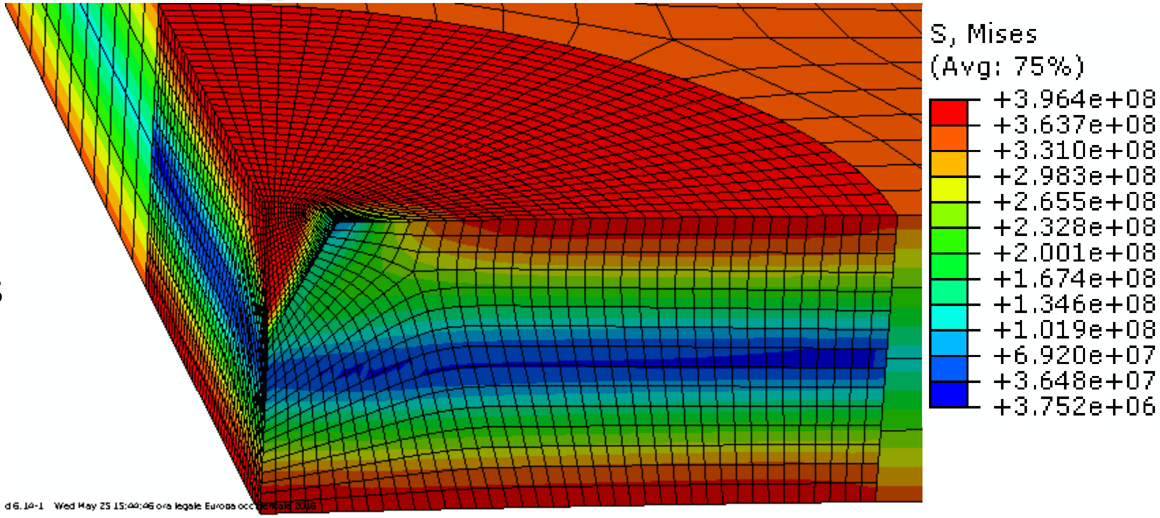
- **Stresses field in x direction (s11)**
- **von Mises stresses**

Depth of the notch = 0.4 mm
Diameter of the notch at the top surface = 0.2 mm

The notch allows to extend the high level of stress

from the top surface of the sheet along the lamina thickness





Thank you for the attention