Analysis of induced surface modifications effects on the electrochemical behaviour of LSP-treated metallic alloys

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1. **Motivation**
2. Experimental procedure
3. Experimental results
4. Concluding remarks
5. Ongoing work and future outlook

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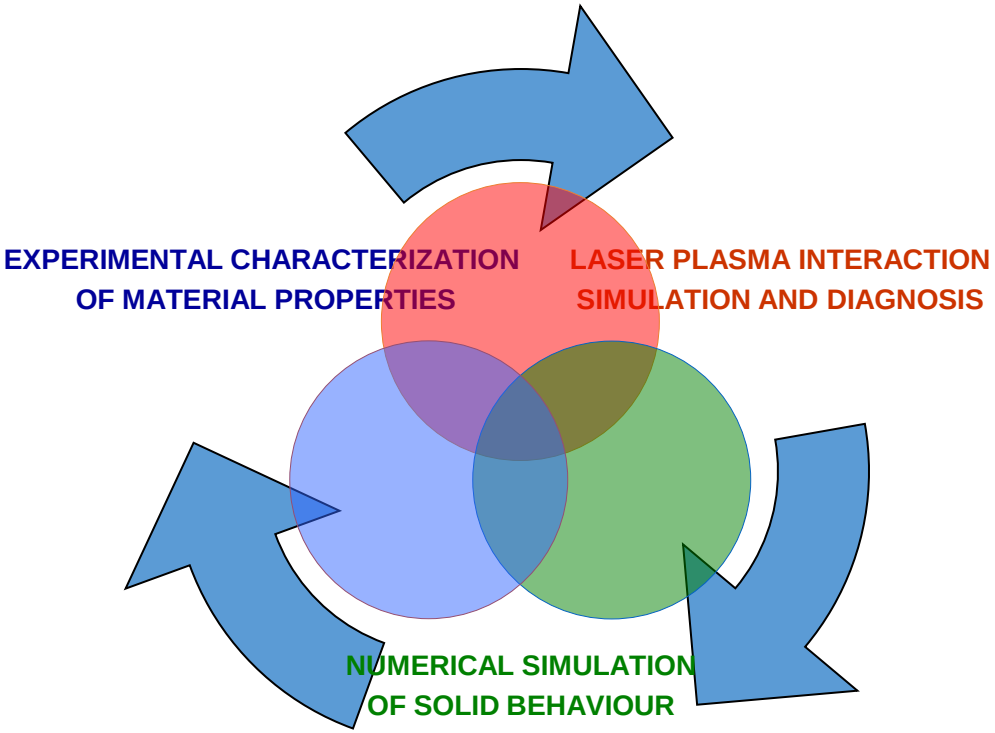
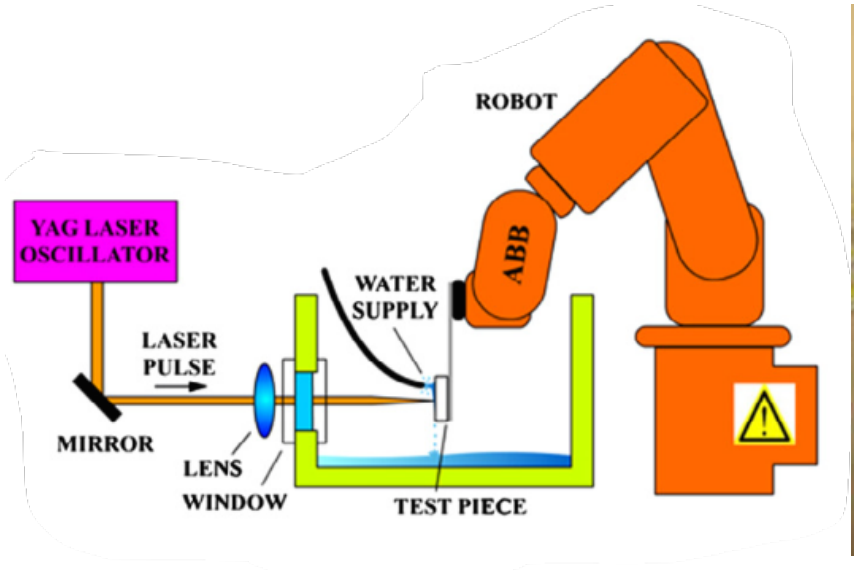
Metallic alloys

- Aluminum alloys: **AA2024-T3**
- Stainless steel: **AISI 316L**
- Titanium alloys: **Ti-6Al-4V**



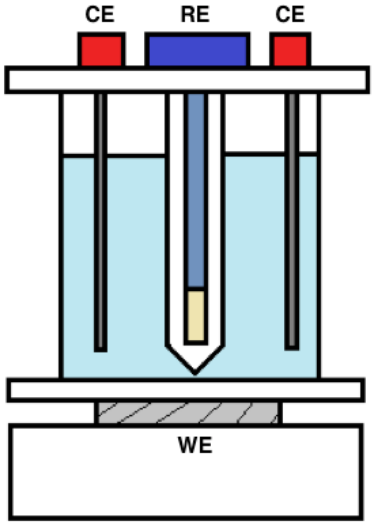


Process parameters

Wavelength (nm)	1064	**Pulse width (ns)**	9
Frequency (Hz)	10	**Spot diameter (mm)**	1.5
Energy (J/pulse)	2.8	**Overlapping (pulses/mm²)**	900 and 1600

Electrochemical techniques

- Open Circuit Potential evolution (**OCP**)
- Polarization curves
    a. Cyclic voltammetry
    b. Potentiostatic tests
- Electrochemical Impedance Spectroscopy (**EIS**)



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

Potentiostat PGSTAT 302N

Electrochemical techniques

- Open Circuit Potential evolution (**OCP**)
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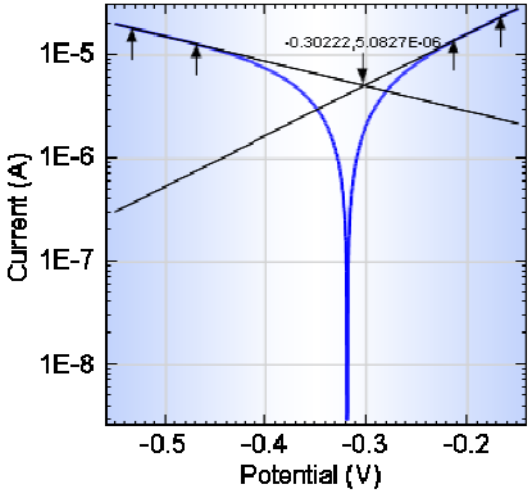


$$i = i_{corr}\left(e^{2.303\frac{\eta}{b_a}} - e^{2.303\frac{\eta}{b_c}}\right)$$

$$\eta = E - E_{corr}$$

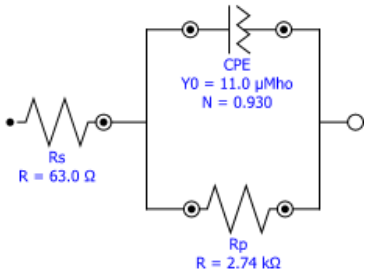
$$\eta = log(i_{corr}) + b_a \cdot log(i)$$

$$\eta = log(i_{corr}) - b_c \cdot log|i|$$

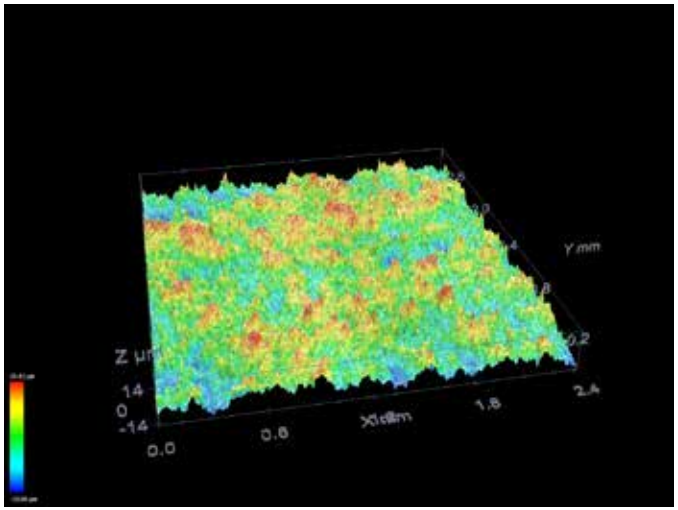
$$i_{corr} = 2.303\frac{b_a b_c}{b_a + b_c}\left(\frac{1}{R_p}\right)$$

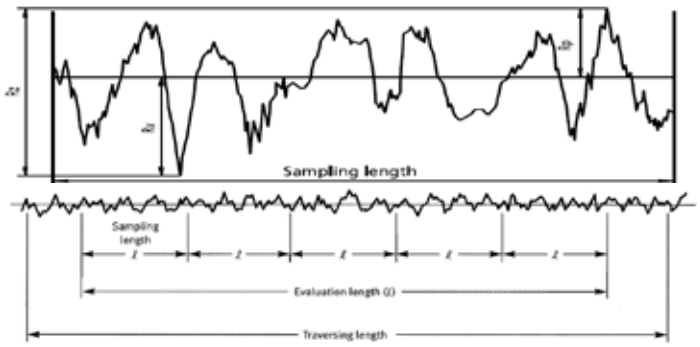
$$R_p = 2.303\frac{b_a b_c}{b_a + b_c}\left(\frac{1}{i_{corr}}\right)$$

$$R_M = \frac{M}{nF\rho} i_{corr}$$



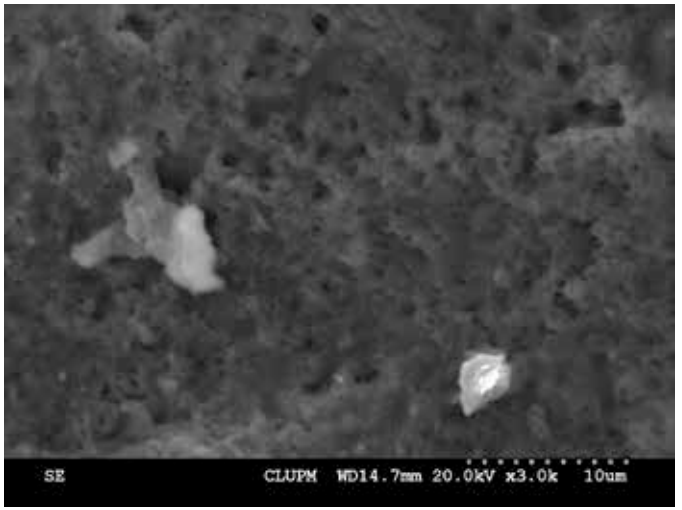
Confocal microscopy

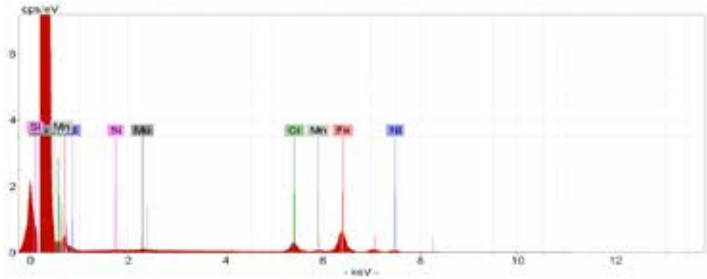




- **Roughness** measurements
- Morphology and size of **pits**

SEM / EDX

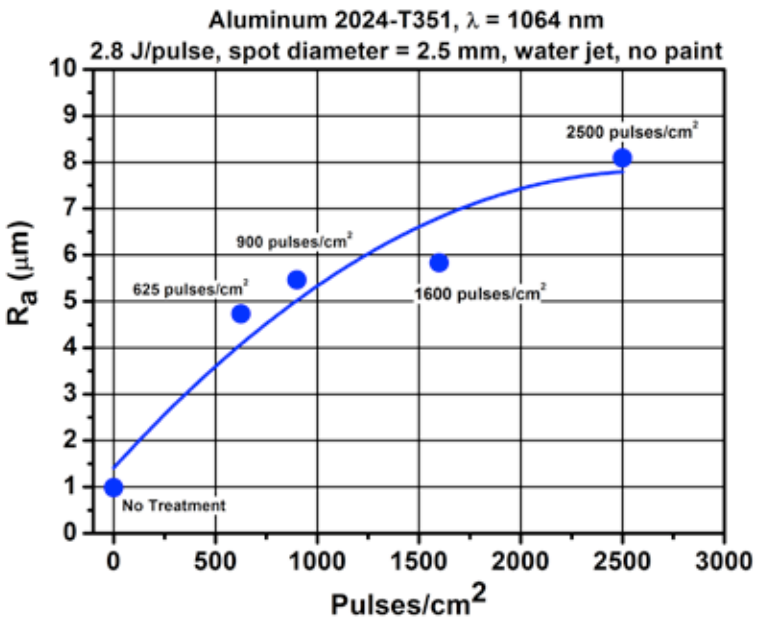




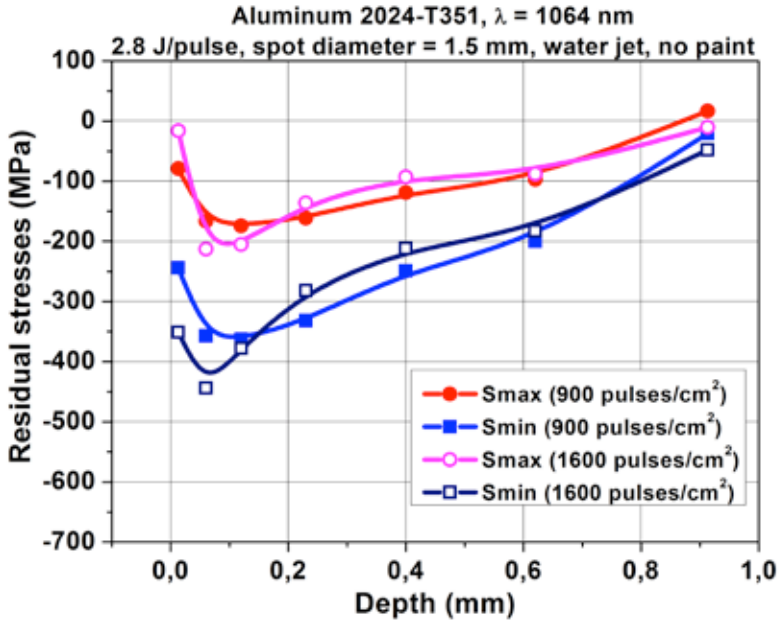
- **Composition** analysis
- Evolution of the **microstructure**

- **Untreated** material
- LSP **900** (pulses/cm^2)
- LSP **1600** (pulses/cm^2)

Roughness

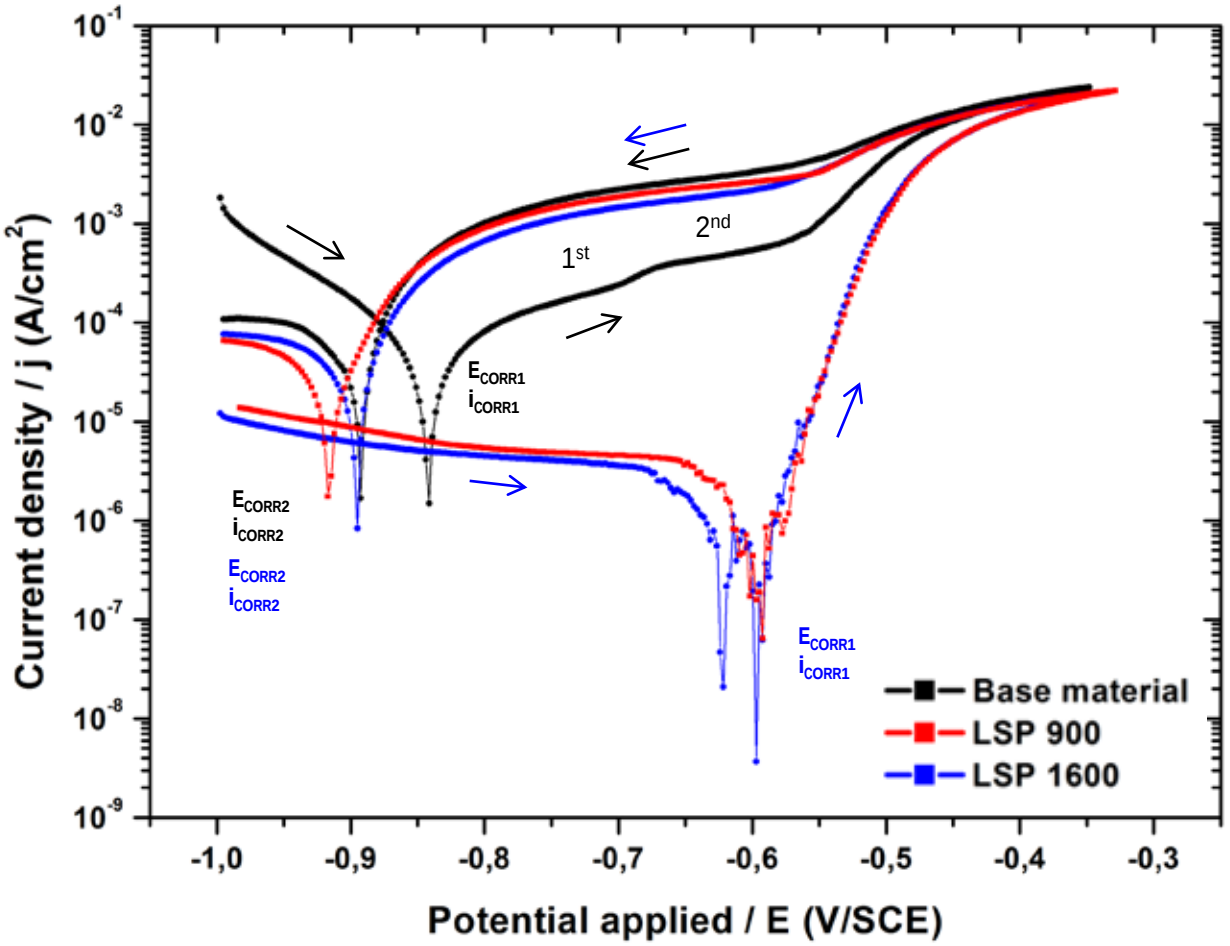


Residual stress



Polarization graph

Medium NaCl 0.5M T= 25ºC

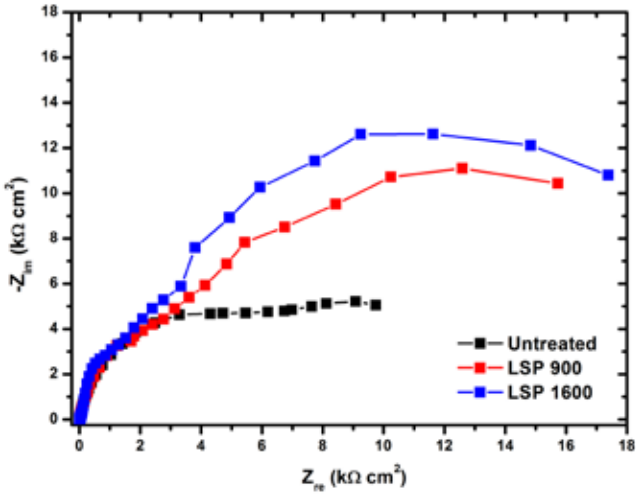


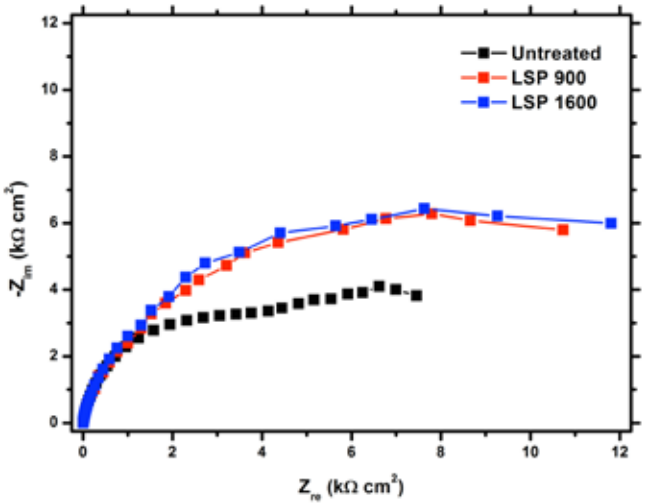
- Significant **improvement** compared to untreated samples
- **Negligible** differences on corrosion rates for **LSP-treated** samples
- **Localized attack** is clearly reduced on LSP specimens

	Untreated	LSP 900	LSP 1600
E_{corr}(mV)	-841	-595	-600
i_{corr}(μA/cm^2)	9.821	0.312	0.170
b_c(mV/dec)	2597.03	788.57	910.58
b_a(mV/dec)	191.38	145.82	148.54
C.R. (μm/year)	103.97	3.31	1.80

EIS

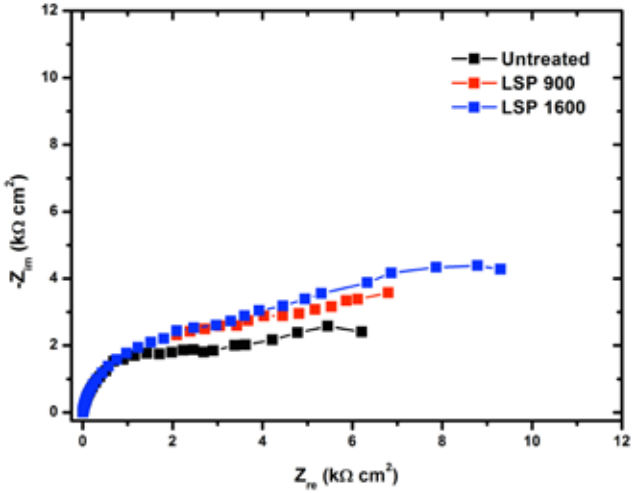
1 h

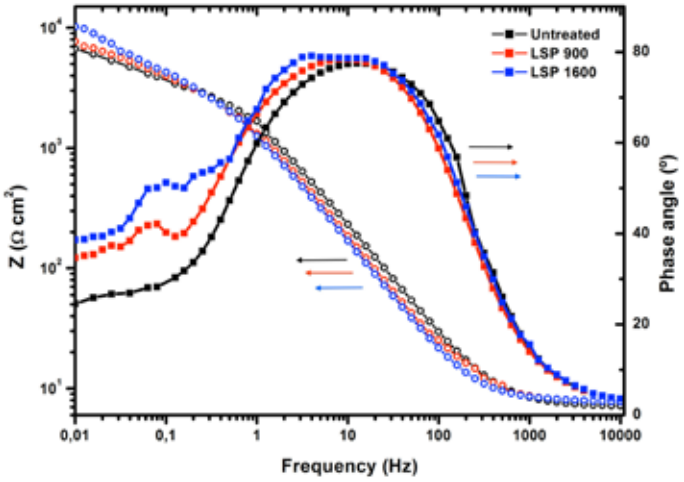




24 h

72 h

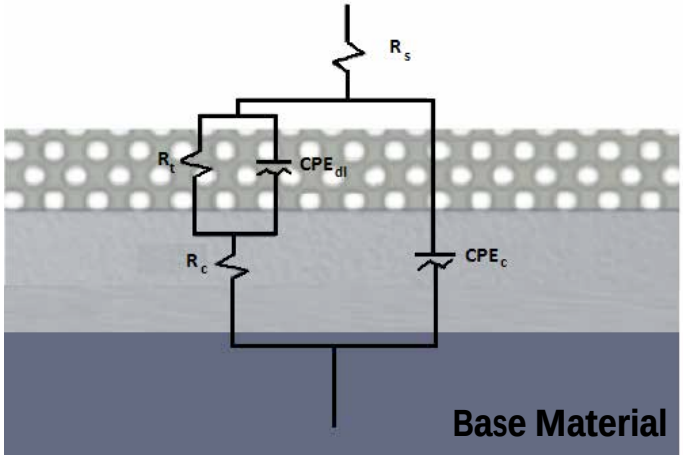




Bode

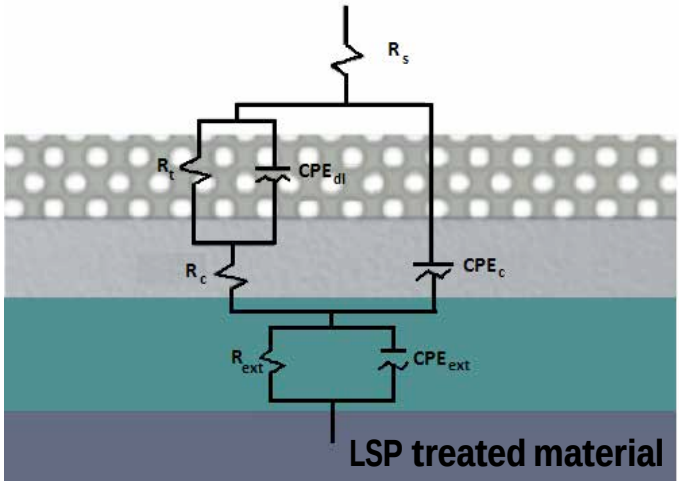
72 h

EIS



← Porous Layer (R_t, CPE_{dl})

← Compact Layer (R_c, CPE_c)



← Porous Layer (R_t, CPE_{dl})

← Compact Layer (R_c, CPE_c)

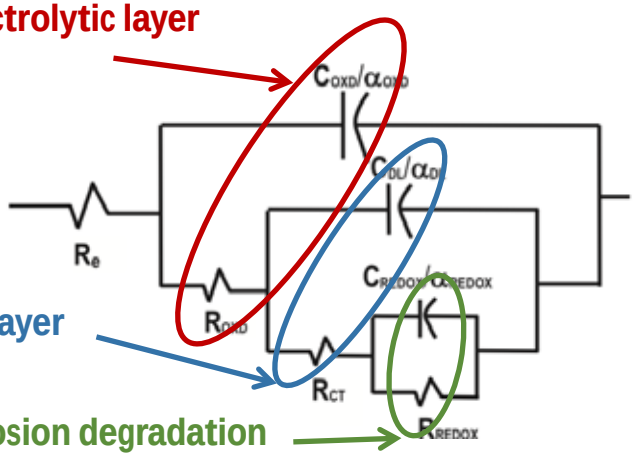
← Extra Layer (R_{ext}, CPE_{ext})

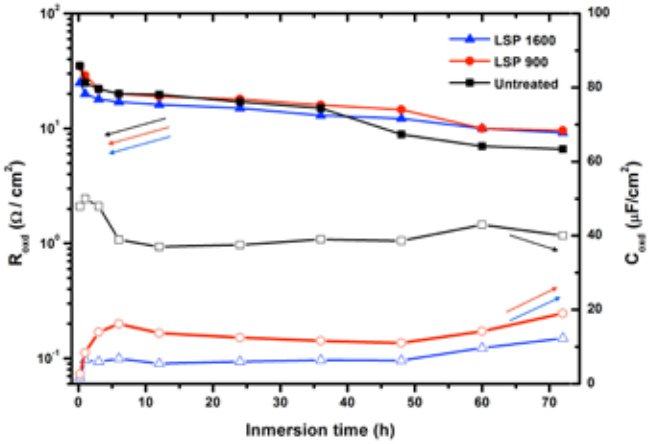
Electrical equivalent circuit

Protective electrolytic layer

Al Pasivation layer

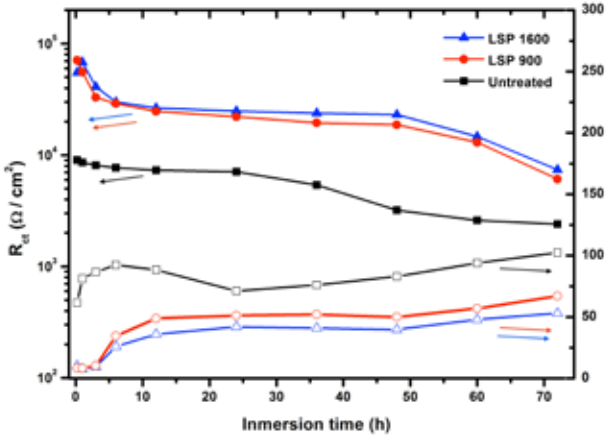
Localized corrosion degradation

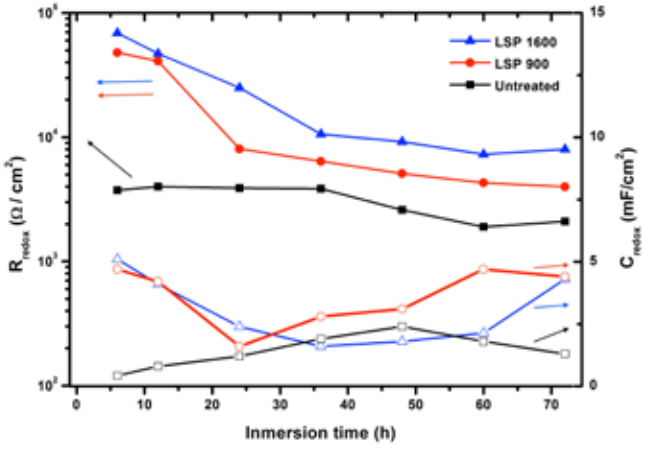




R_{oxd}
C_{oxd}

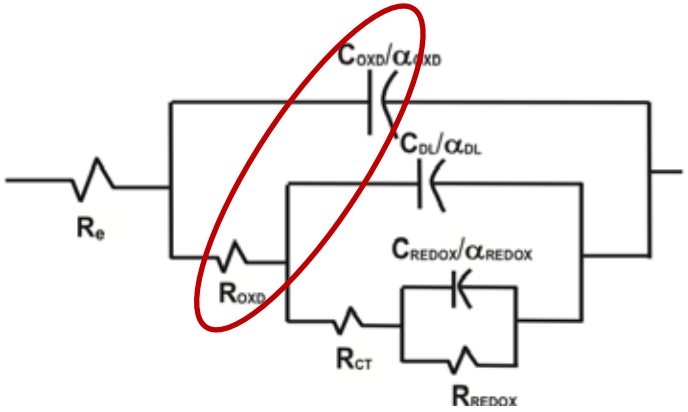
R_{ct}
C_{dl}

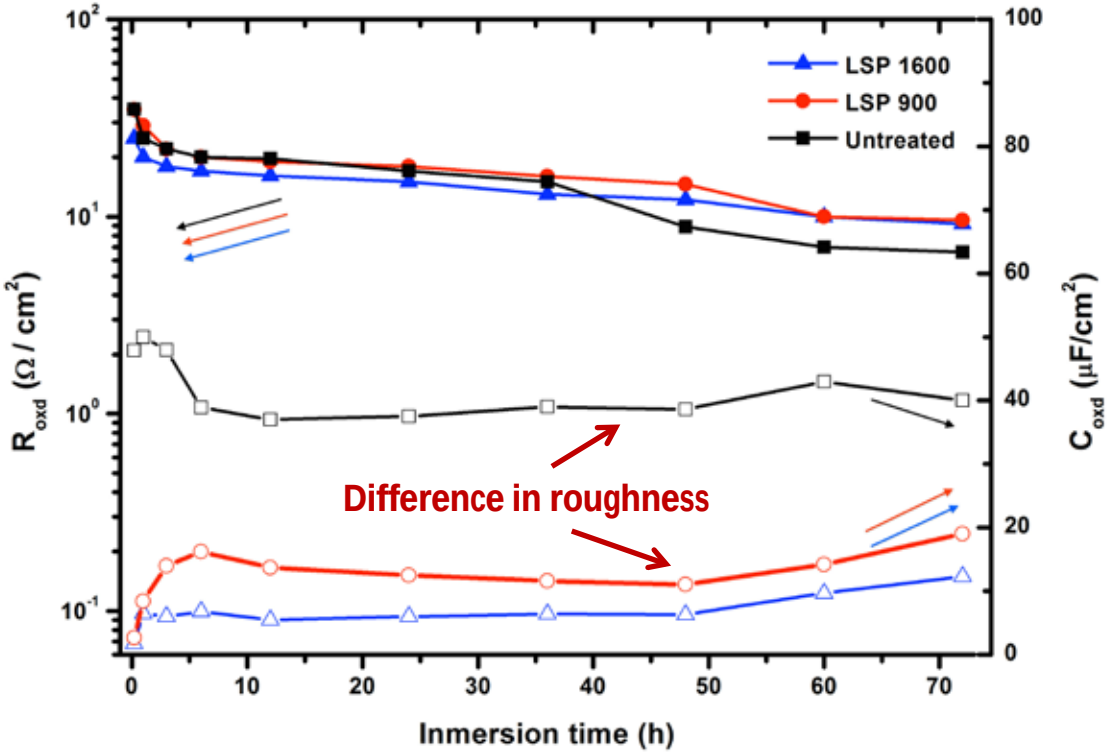




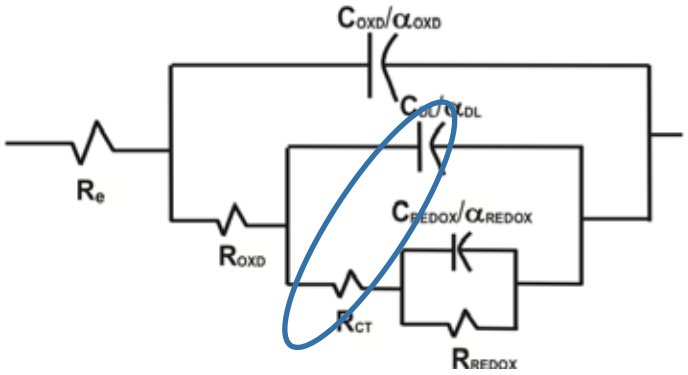
R_{redox}
C_{redox}

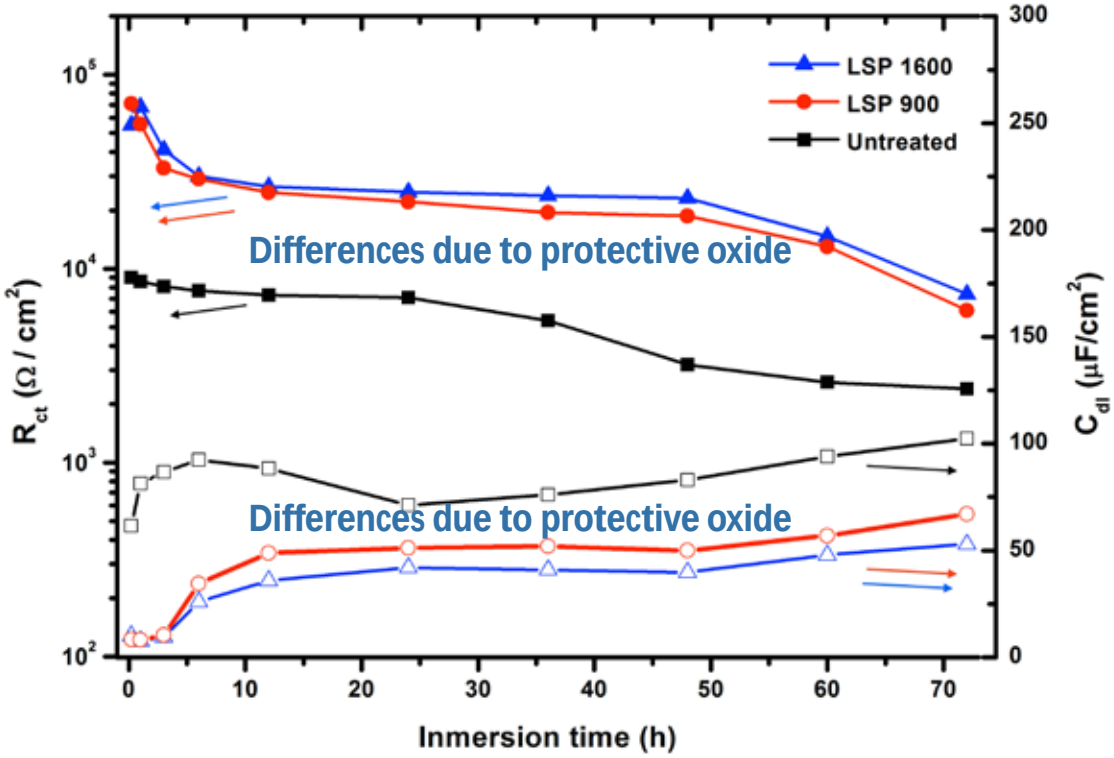
R_{oxd}
C_{oxd}


C_{OXD}/α_{OXD}
C_{DL}/α_{DL}
R_e
C_{REDOX}/α_{REDOX}
R_{OXD}
R_{CT}
R_{REDOX}

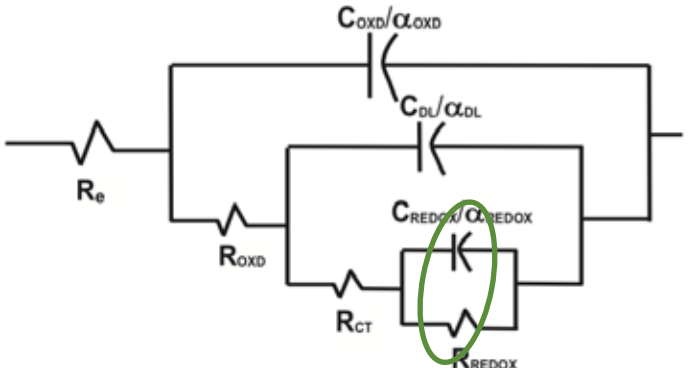

LSP 1600
LSP 900
Untreated
R_{oxd} (Ω / cm^2)
C_{oxd} (μF/cm^2)
Inmersion time (h)
Difference in roughness

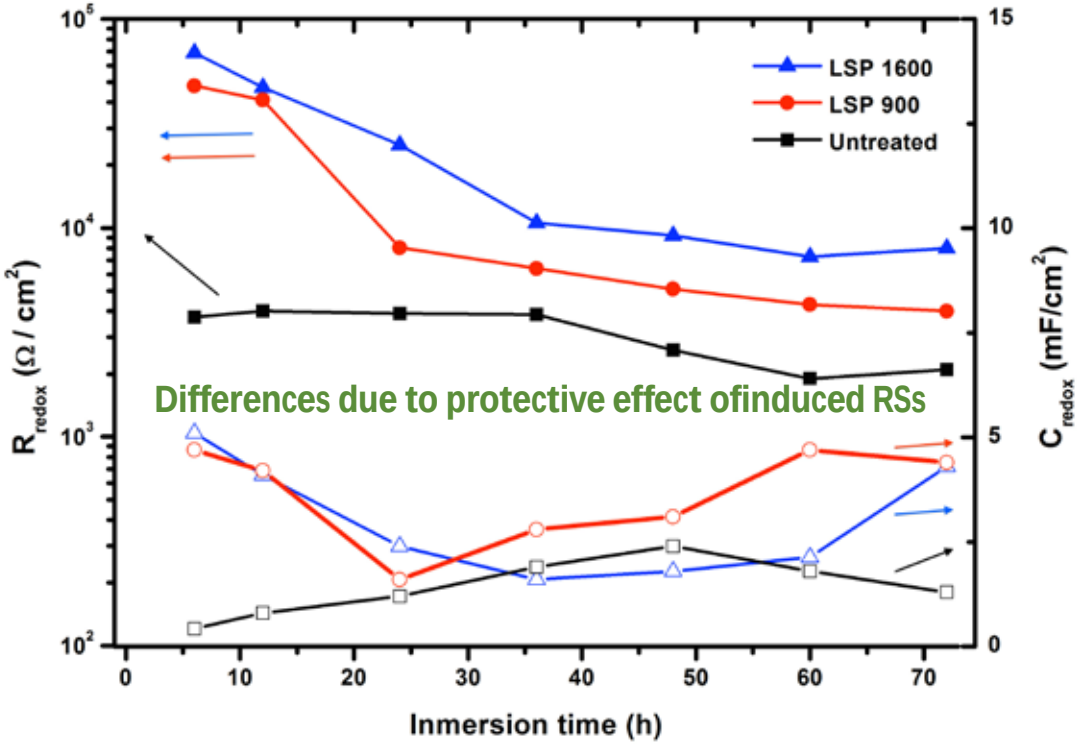
R_{ct}
C_{dl}


C_{OXD}/α_{OXD}
C_{DL}/α_{DL}
R_e
C_{REDOX}/α_{REDOX}
R_{OXD}
R_{CT}
R_{REDOX}


LSP 1600
LSP 900
Untreated
Differences due to protective oxide
Differences due to protective oxide
R_{ct} (Ω / cm^2)
C_{dl} (μF/cm^2)
Inmersion time (h)
10^5
10^4
10^3
10^2
0
10
20
30
40
50
60
70
300
250
200
150
100
50
0

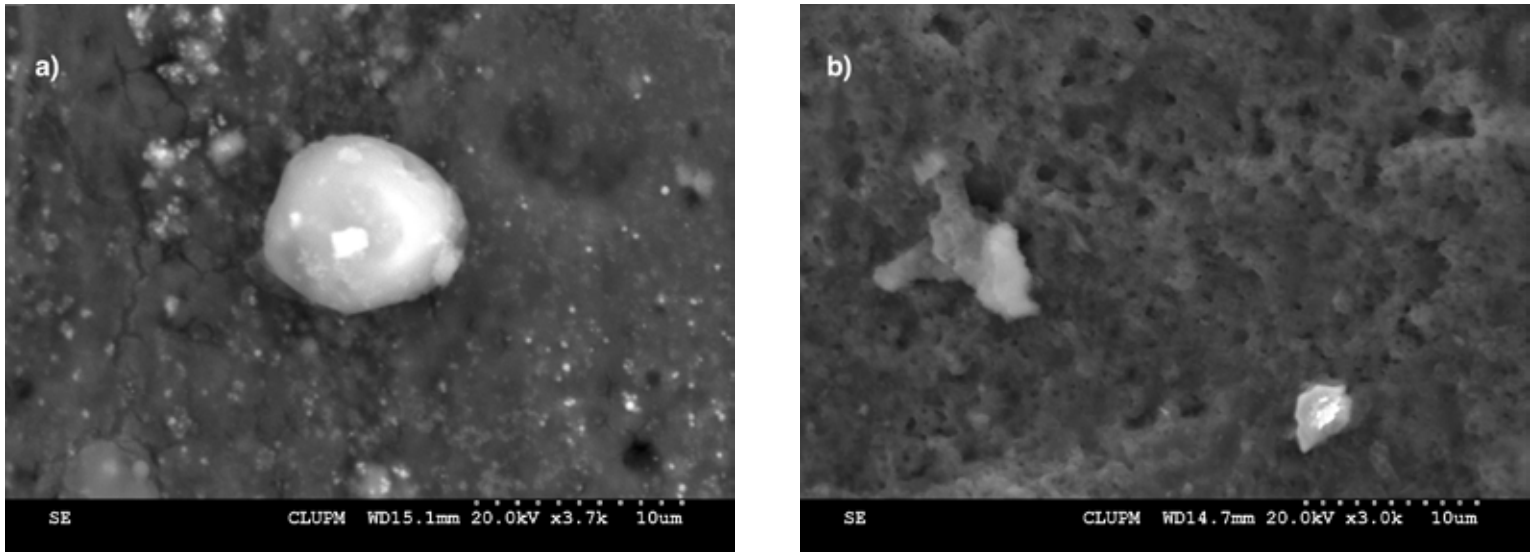
R_{redox}
C_{redox}





- Protective **oxide** layer in **LSP** treated samples
- Reduction of **IMCs**. Lower localized attack

Composition (wt%)	Al	O	Cu	Mg
Untreated	80,71	11,29	5,46	2,05
LSP 900	79,81	15,09	3,73	1,37
LSP 1600	78,64	15,15	3,68	1,57

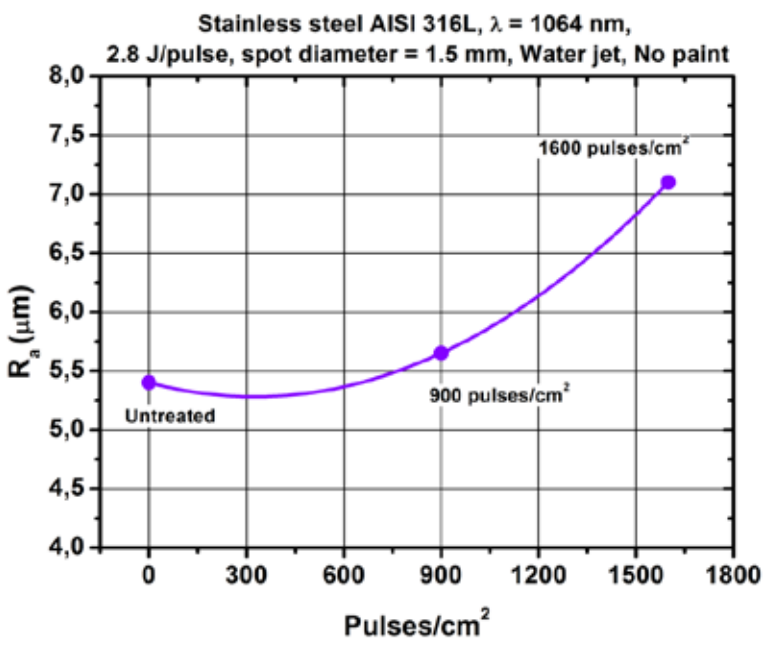


SEM images of S phase particles: a) Untreated AA2024 b) LSP-treated AA2024

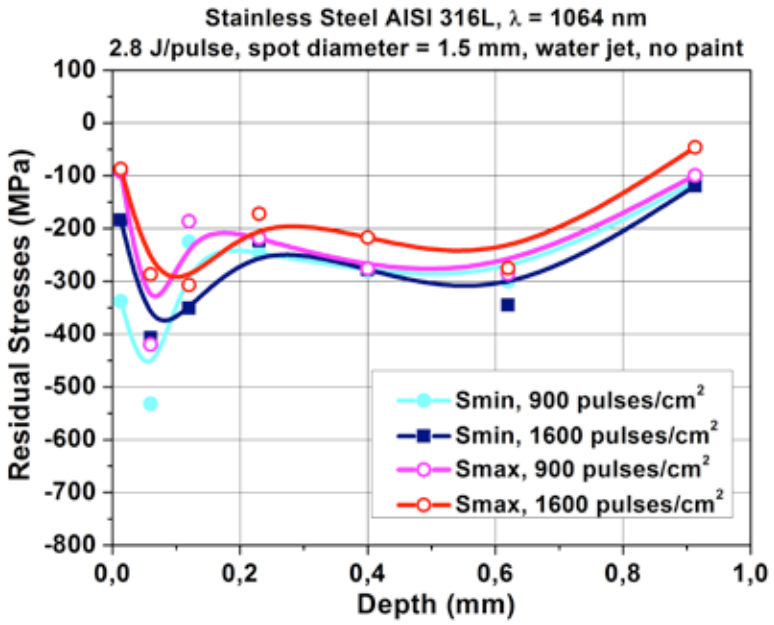
See J.A. DeRose et al.: Corrosion Science 55 (2012) 313–325

- **Untreated** material
- LSP **900** (pulses/cm^2)
- LSP **1600** (pulses/cm^2)

Roughness

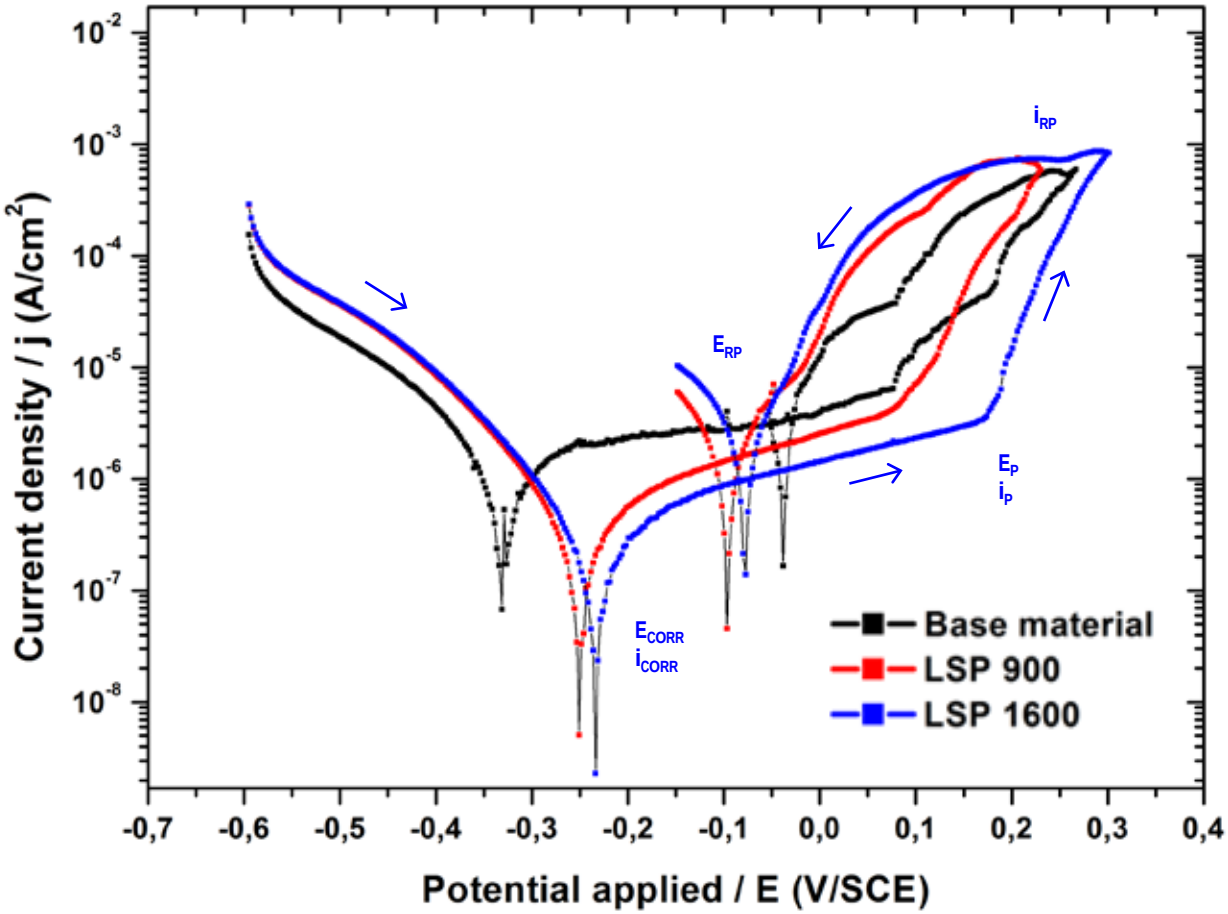


Residual stress



Polarization graph

Medium NaCl 0.5M T= 25ºC

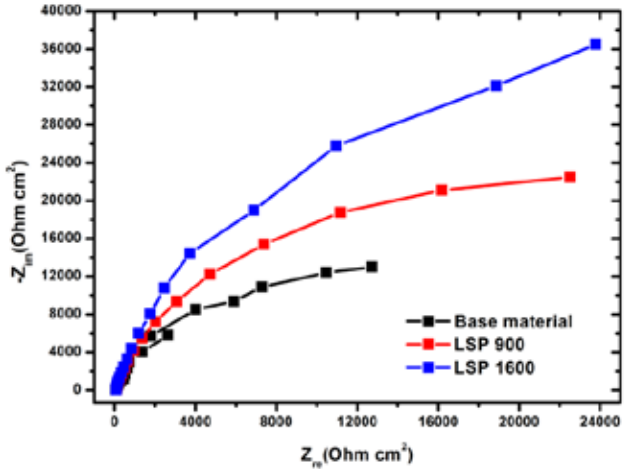


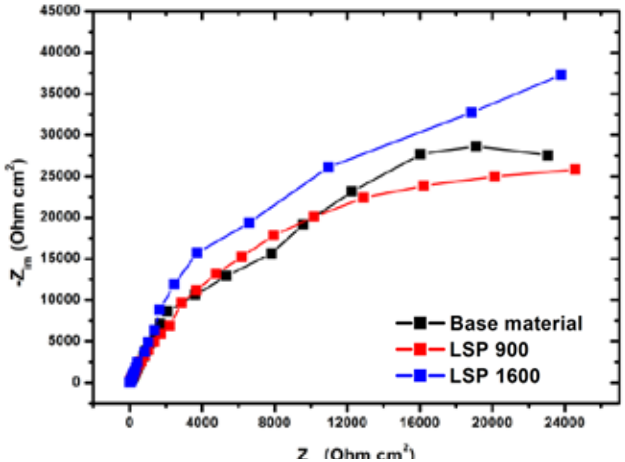
- **Improvement** compared to **untreated** samples
- Higher **stability** of the passive film with a **compressive** residual stress field
- **Repassivation** is related to **roughness** parameter

	Untreated	LSP 900	LSP 1600
E_{corr}(mV)	-328	-249	-236
i_{corr}(μA/cm^2)	0.298	0.077	0.064
E_p (mV)	161	151	234
i_p (μA/cm2)	3.241	2.156	1.253
E_{rp}(mV)	-21	-72	-54
i_{rp}(μA/cm^2)	715.103	801.306	924.582
C.R. (μm/year)	2.35	0.61	0.50

EIS

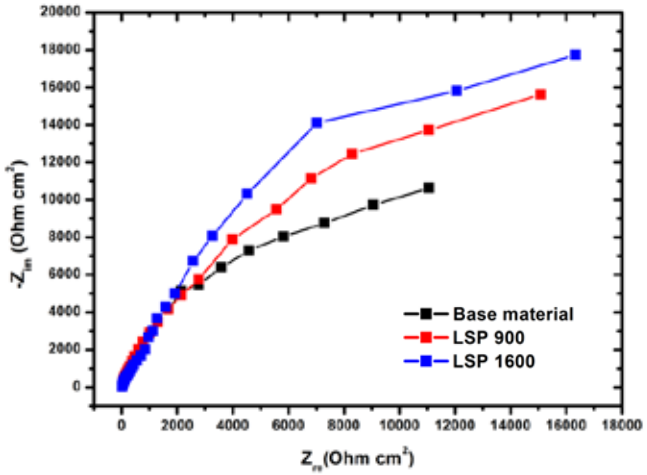
1 h





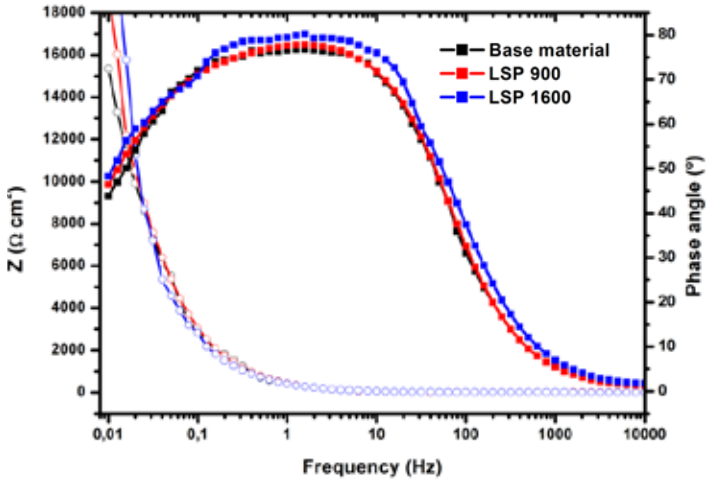
12 h

14 d

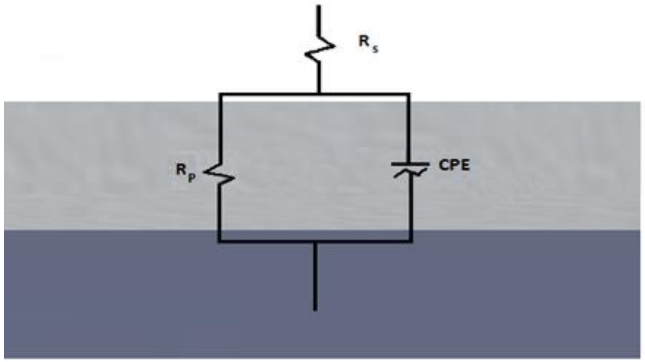


Bode

14 d



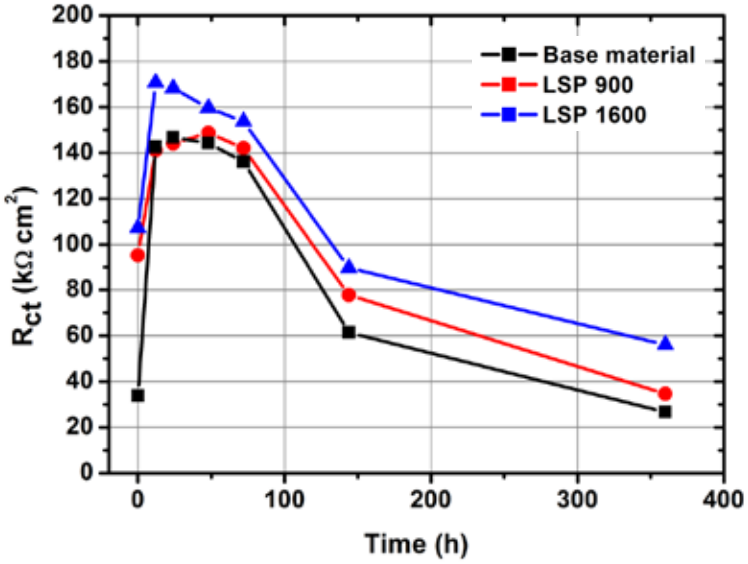
Electrical equivalent circuit

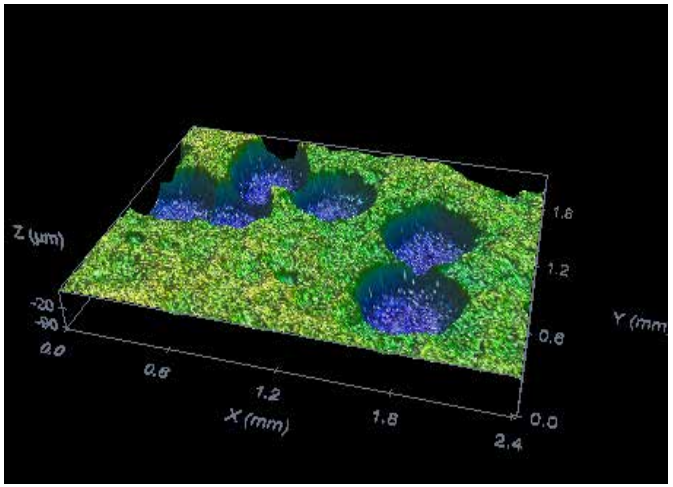


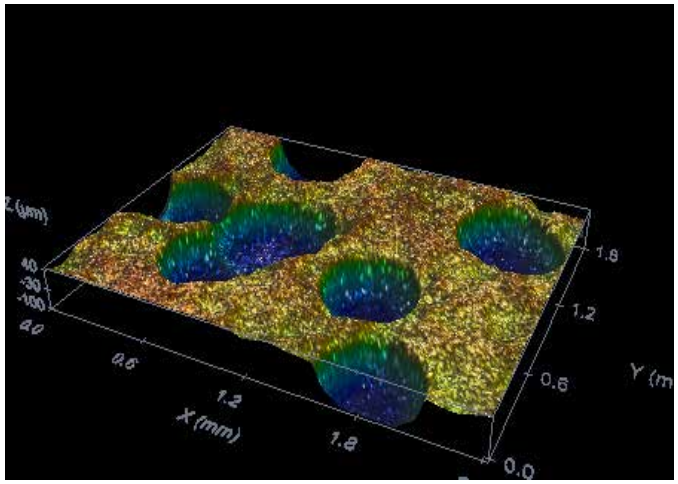
← Electrolyte (R_S)

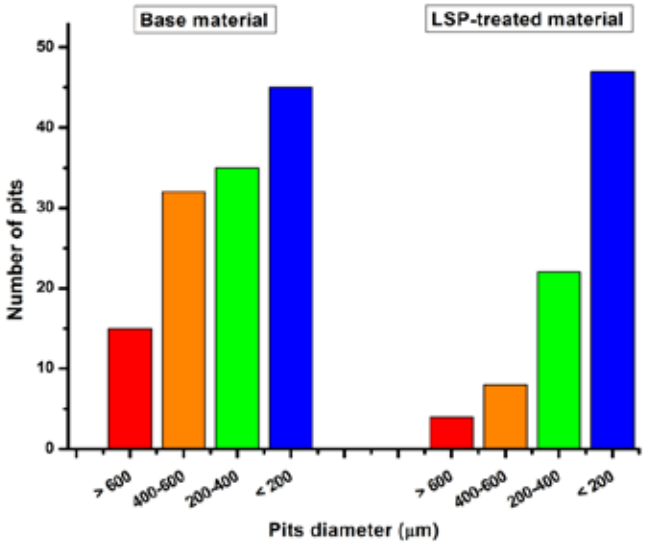
← Corrosion Barrier
Compact Layer (R_p, CPE)

← Substrate







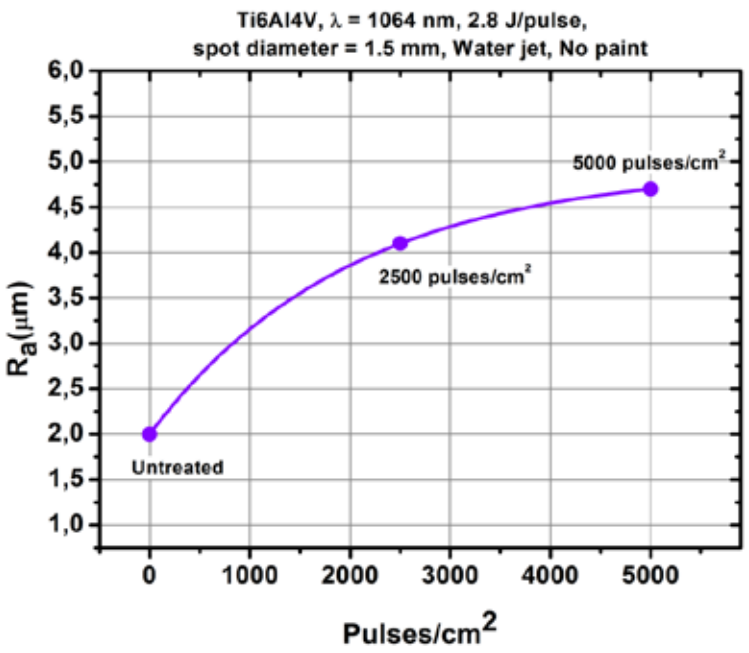


Analysis of pits

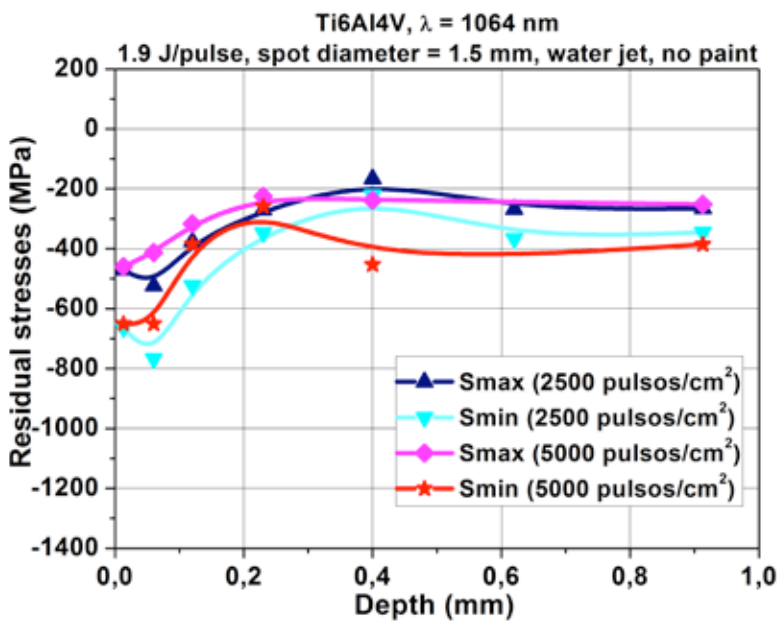
- Reduction in **number** and **size**
- Higher difference among pits larger than **200 µm**
- Benefitial effect of **compressive** residual stress field

- **Untreated** material
- LSP **2500** (pulses/cm^2)
- LSP **5000** (pulses/cm^2)

Roughness

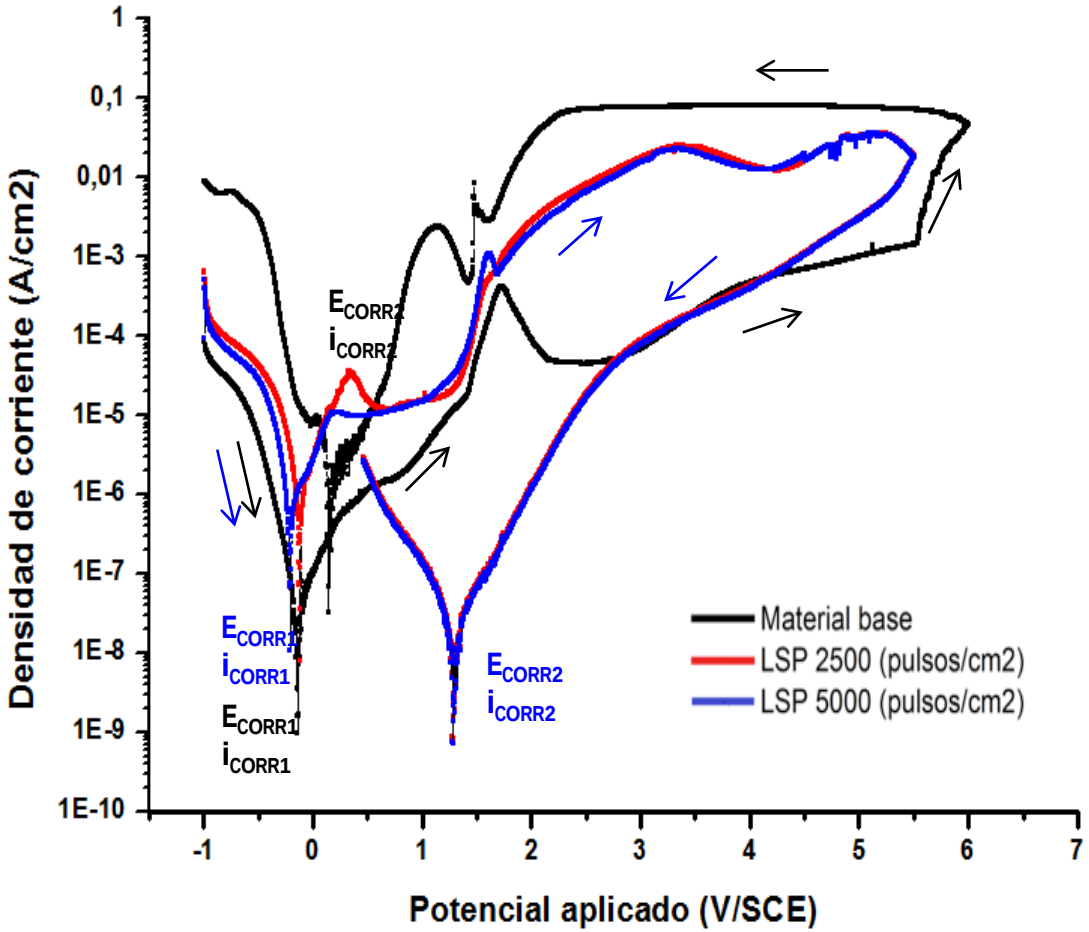


Residual stress

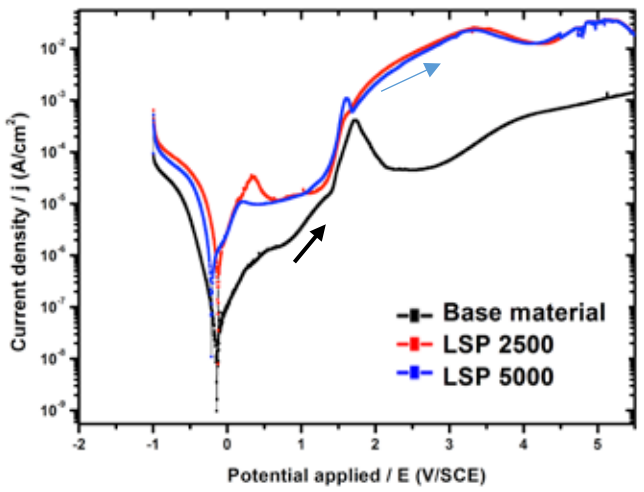


Polarization graph

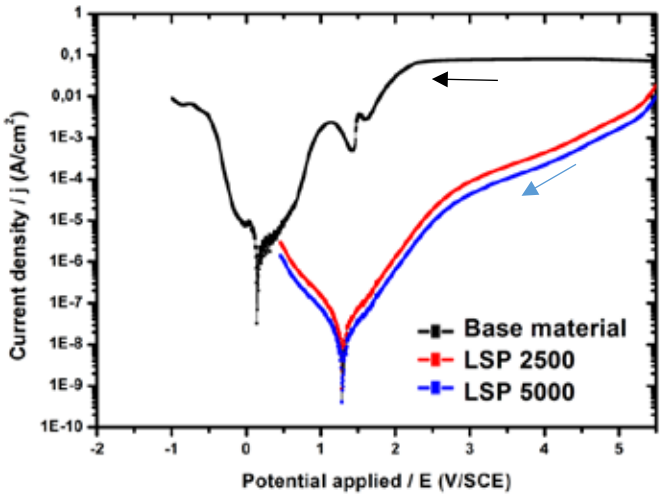
Medium NaCl 0.5M T= 25ºC



Direct scan

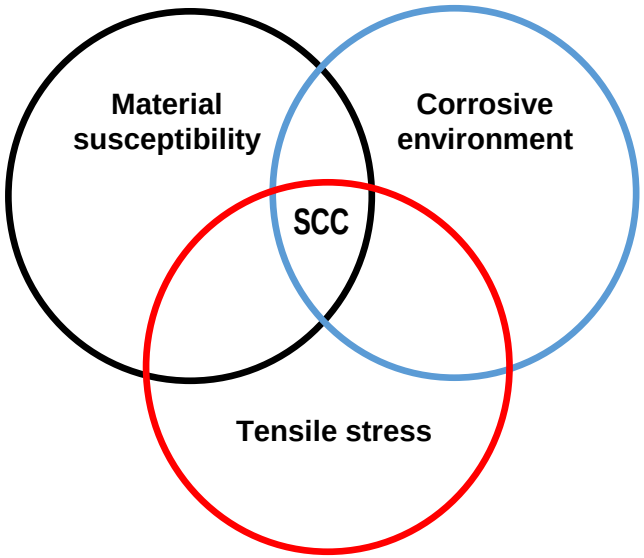


Reverse scan



	Untreated	LSP 2500	LSP 5000
E_{corr} (mV)	-144	-126	-196
I_{corr} (µA/cm²)	0.042	0.637	0.754
E_{corr2} (mV)	194	1285	1283
I_{corr2} (µA/cm²)	3.973	0.020	0.020

1. The systematic evaluation of the electrochemical changes induced in relevant materials by LSP treatment has been envisaged
2. Analysis of cyclic polarization curves with clear identification of corrosion parameters (Ecorr, Icorr, Mcorr, Ep, Ip) has been succesfully performed for Al2024-T351 and AISI 316L steel.
3. Electrochemical Impedance Spectroscopy (EIS) has been used in order to correlate the observed electrochemical behaviour (even at long timescales) with surface modifications induced by the LSP treatment, especially roughness and elemental chemical composition. A good physico-chemical process understanding has been gained in the case of Al2024-T351 and AISI 316L steel.
4. Work has been initiated for other key materials with a more complex behaviour (i.e. Ti6Al4V).
5. The development of a systematic assessment capability for the corrosion susceptibility modification effects of the LSP technique is under way.



Interaction stress-corrosion (SCC)

1. Stress corrosion cracking tests (**SSRT, CBT**)
2. Influence of Temperature on pitting (**CPT**)
3. Electrochemical noise analysis (**ECN**)

Thank you for your attention!

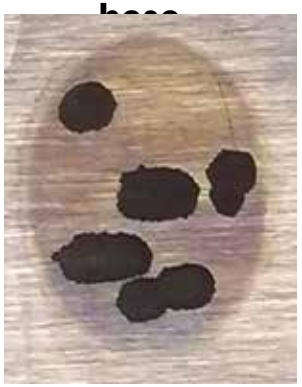
For further information, please contact:

jlocana@etsii.upm.es

Titanio Ti-6Al-4V

Ensayo potenciostático
(6 V, 0.1 A/cm^2, 80 min)

Material base



Cráteres

LSP 2500

Picaduras

LSP 5000

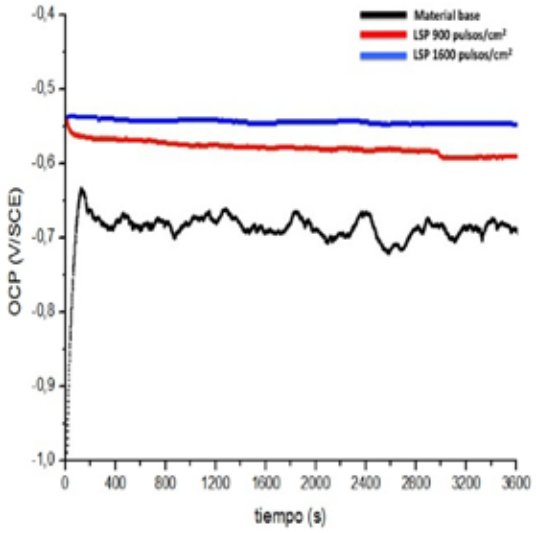
Poros

Condiciones de corrosión agresivas

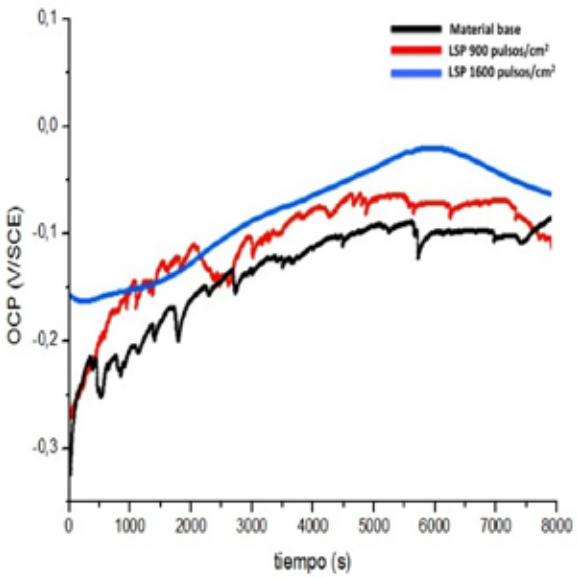
Mejora la respuesta a mayores **tensiones** residuales de **compresión**

OCP

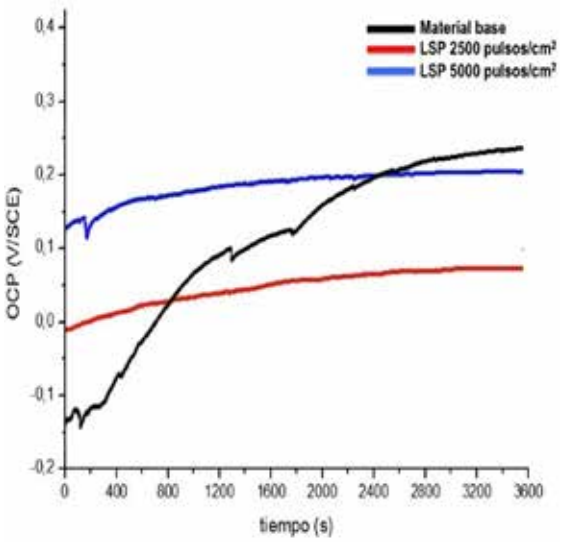
Aluminio



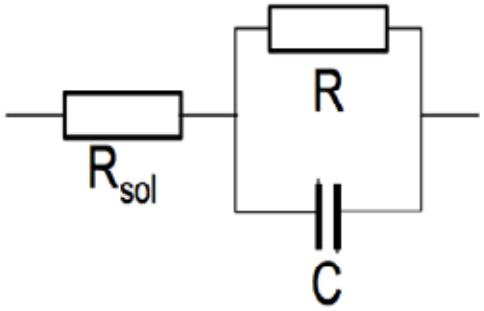
Acero



Titanio



EIS



$$Z' = R_{sol} + \frac{R_{ct}}{1 + \omega^2 C_{dl}^2 R_{ct}^2}$$

$$Z'' = \frac{C_{dl} R_{ct}^2 \omega}{1 + \omega^2 C_{dl}^2 R_{ct}^2}$$

$$\left(\frac{R_{ct}}{2}\right)^2 = \left(Z' - R_{sol} - \frac{R_{ct}}{2}\right)^2 + (Z'')^2$$

Ec. de circunferencia

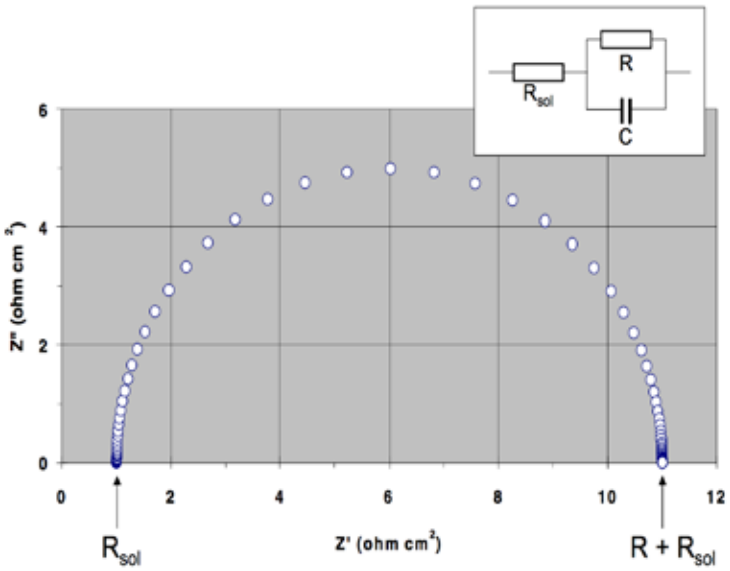
EIS

Ec. de circunferencia

$$\left(\frac{R_{ct}}{2}\right)^2 = \left(Z' - R_{sol} - \frac{R_{ct}}{2}\right)^2 + (Z'')^2$$

Centro $Z' = R_{sol} + \frac{R_{ct}}{2}$

Radio $\frac{R_{ct}}{2}$



Procesos de corrosión

Zona catódica

$$Me \leftarrow Me^{n+} + ne^{-}$$ **Reducción**

$$O_2 + 2H_2O + 4e^{-} \leftarrow 4OH^{-}$$ **Oxidación**

Zona anódica

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$ **Reducción**

$$Me \rightarrow Me^{n+} + ne^{-}$$ **Oxidación**