Application of local electrochemical probes for corrosion studies

13/01/15

Introduction

Usual electrochemical techniques used to study the corrosion behaviour of structural materials are linear polarization (LP) and electrochemical impedance spectroscopy (EIS).

LP gives the global behaviour of the material, and corrosion kinetic parameters such as corrosion parameters, corrosion rate, Tafel slopes.

EIS allows to model the electrochemical behaviour of metal/electrolyte interface, accounting for the presence of passivity layers, adsorption mechanisms...

These techniques give a global response of the sample but further insights may be needed to actually identify and understand the specific mechanism responsible for corrosion and its relationship with microstructural characteristics.

In this regard local probes give spatial insights at the microscale of the corrosion processes.

The following slides give some examples of results found in the literature and obtained using our instruments, M370/M470.

A general knowledge of each local technique is required.

Enjoy !

Outline

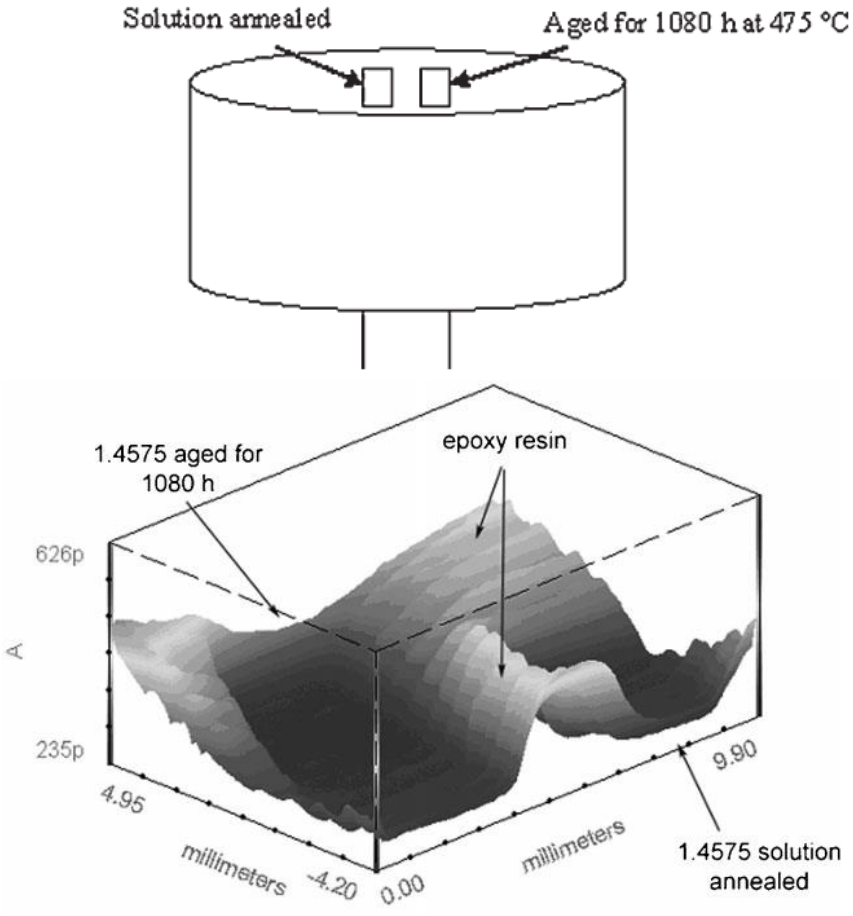
1. SECM
    a. dc-SECM
    b. ac-SECM
    c. ic-SECM
2. LEIS
3. SVP
4. SKP

Outline

1. SECM
   a. dc-SECM
   b. ac-SECM
   c. ic-SECM
2. LEIS
3. SVP
4. SKP

dc-SECM

Study of the electrochemical behavior of DIN 1.4575 superferritic stainless steel aged at 475° C



M. Terada, A. F. Padilha, A. M. P. Simoes, H. G. de Melo and I. Costa
Materials and Corrosion 2009, 60, No. 11

SECM is used in competition mode : the same reaction occurs on the sample and on the probe

The sample and the probe are polarized at -0.7 V/SCE.

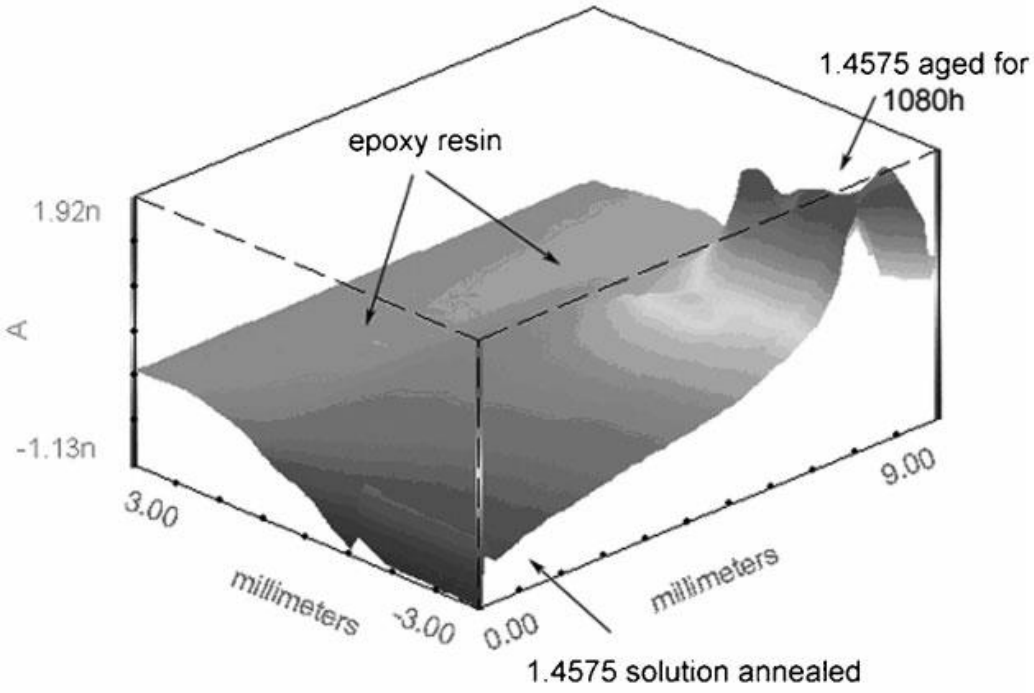
The reaction under study is O_2 reduction.

The current shown is the probe current.

Both materials are more prone to O_2 reduction than the resin.

dc-SECM

Study of the electrochemical behavior of DIN 1.4575 superferritic stainless steel aged at 475° C



The sample and the probe are polarized at 0.6 V/SCE.

The reaction under study is Fe dissolution.

The current shown is the probe current.

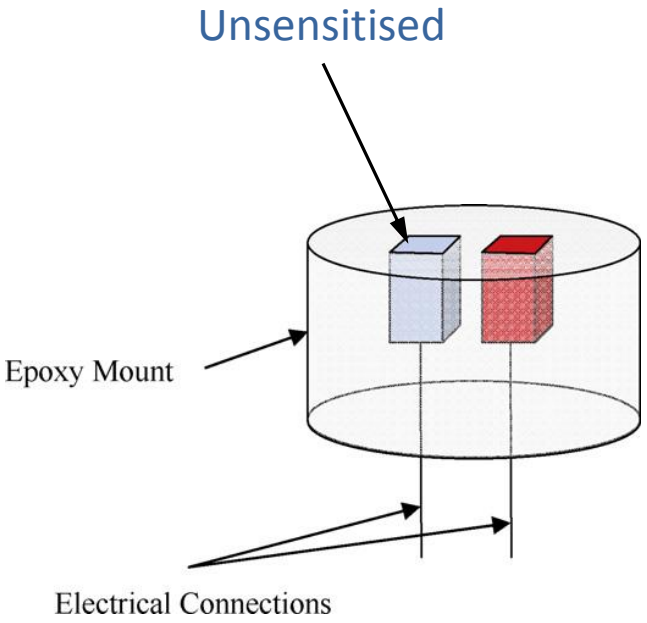
The aged steel is less prone to Fe dissolution, and hence more corrosion resistant.

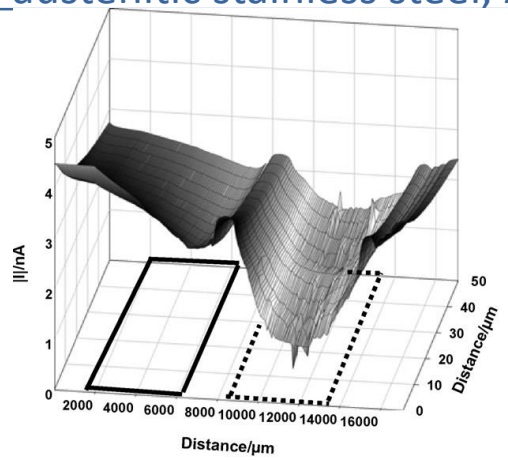
The decrease of corrosion is related to the presence of α' particles.

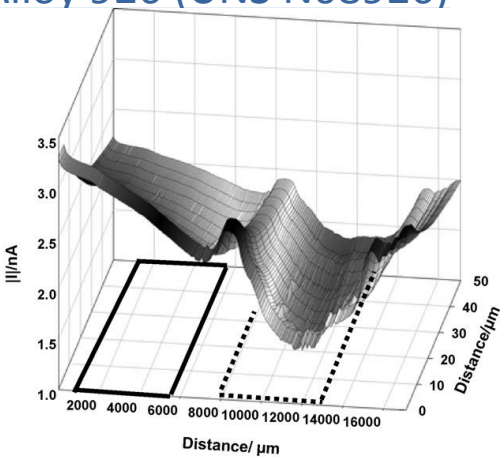
M. Terada, A. F. Padilha, A. M. P. Simoes, H. G. de Melo and I. Costa
Materials and Corrosion 2009, 60, No. 11

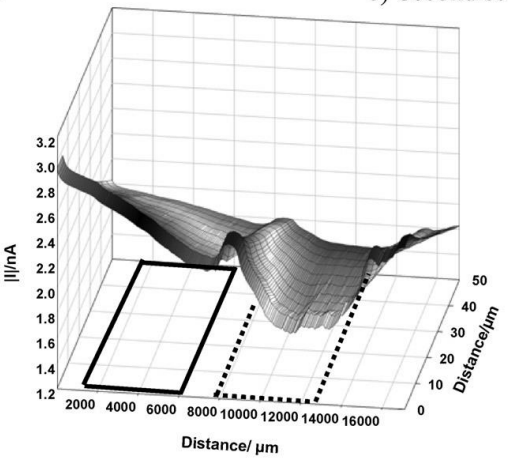
dc-SECM

Study of the sensitisation of a highly alloyed austenitic stainless steel, Alloy 926 (UNS N08926)









SECM polarized at -0.7 V/SCE to study O_2 reduction in aerated 35 g/L NaCl solution. Each scan took 2 hours to be performed.

Sensitised alloys show more reduction and consequently more corrosion due to a more conductive passive film.

Unsensitised Alloy 926 ▪▪▪▪▪ Sensitised Alloy 926

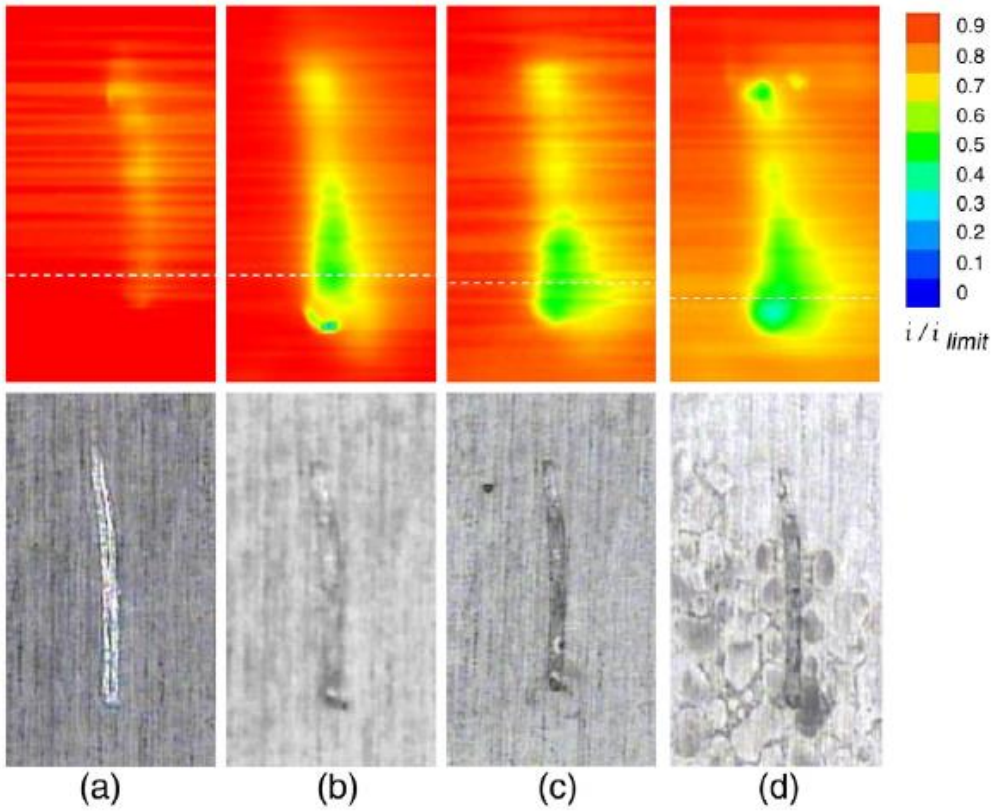
Electrochimica Acta 70 (2012) 105– 111
R. Leiva-García, R. Akid, D. Greenfield, J. Gittens, M.J. Munoz-Portero, J. García-Antón

dc-SECM

SECM study of defect repair in self-healing polymer coatings on metals

SECM used in feedback mode.
The tip is polarized at -0.6V/Ag/AgCl.
The studied reaction is O_2 reduction over a scratch in a sample with shape-memory polyurethane coating.

Corrosion activity in the defect increased as a function of immersion time in the solution (Fig. 2b–d), and cathodic processes were mainly located at the top and bottom of the scratch.



a) 4 h, b) 1 day, c) 2 days, d) 4 days of immersion in 0.05 M NaCl

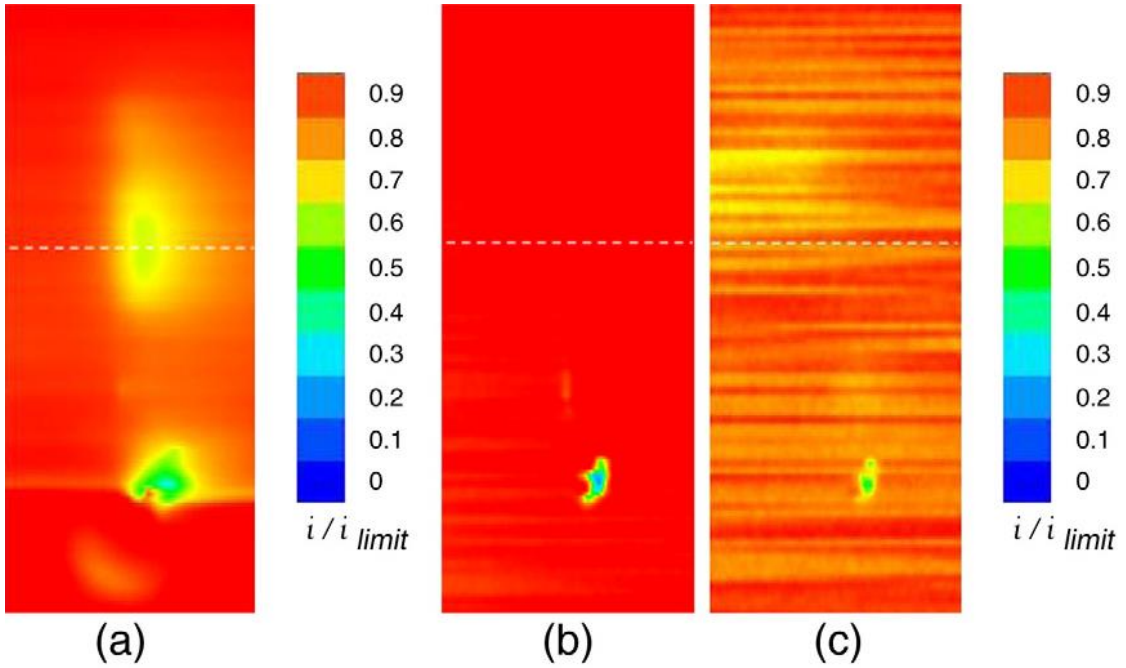
Electrochemistry Communications 13 (2011) 169–173
Y. González-García , J.M.C Mol, T. Muselle, I. De Graeve , G. Van Assche ,G. Scheltjens, B. Van Mele , H. Terryn

dc-SECM

SECM study of defect repair in self-healing polymer coatings on metals

SECM used in feedback mode.
The tip is polarized at -0.6V/Ag/AgCl.
The studied reaction is O_2 reduction over a scratch in a sample with shape-memory polyurethane coating.

One can see cathodic activity in the non-healed
sample.
In the non healed sample cathodic activity
only occurs at a defect in the polymer.
After 28 h no sign of corrosion on the heat-treated polymer coated sample.



Prior to thermal healing a) 1 day of immersion in 0.05 M NaCl
After thermal healing b) 4 h and c) 1 day of immersion in 0.05 M NaCl

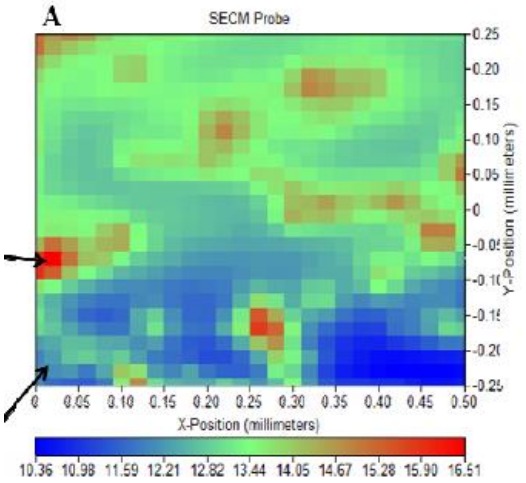
Electrochemistry Communications 13 (2011) 169–173
Y. González-García , J.M.C Mol, T. Muselle, I. De Graeve , G. Van Assche ,G. Scheltjens, B. Van Mele , H. Terryn

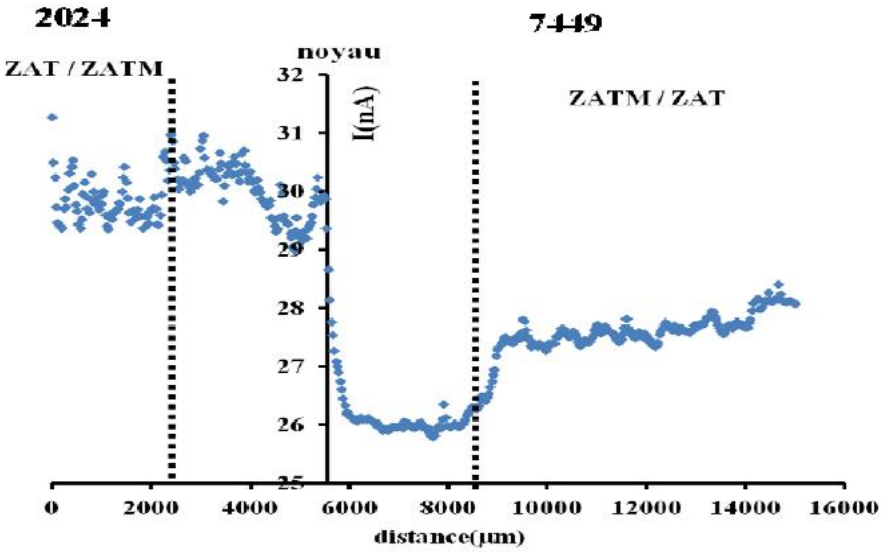
dc-SECM

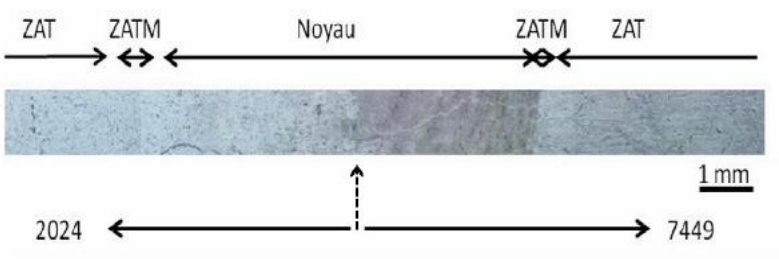
SECM study of Friction Stir Welded Al alloys

Fe^{2+} is used as a mediator and is oxidized at the probe.

Decrease of the current on the « nugget » means that the surface layer is more resistive and likely to be less prone to corrosion than the heat affected zones.







Ph.D. thesis, Djoudi Sidane, Université de Bordeaux, 2012

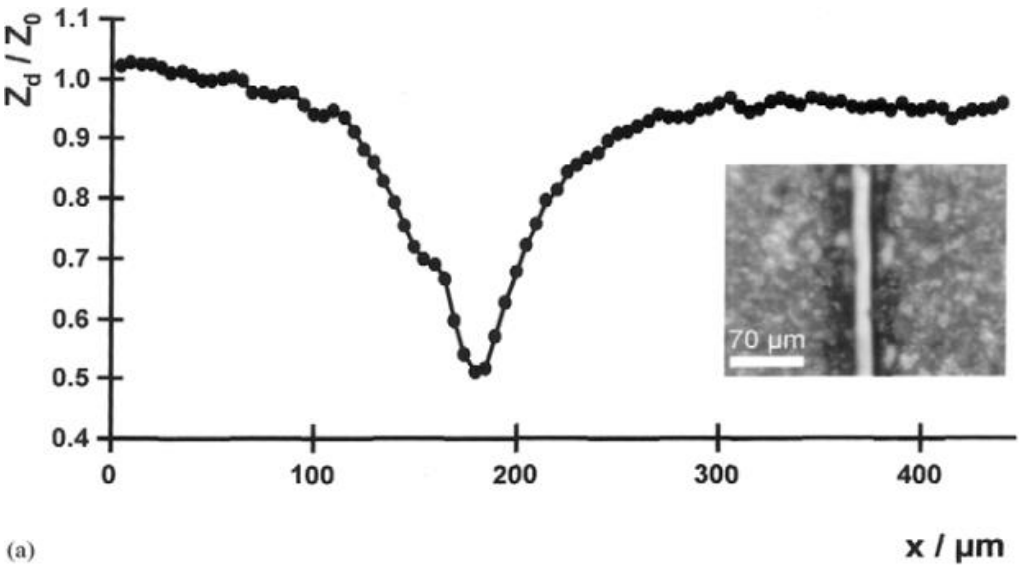
Outline

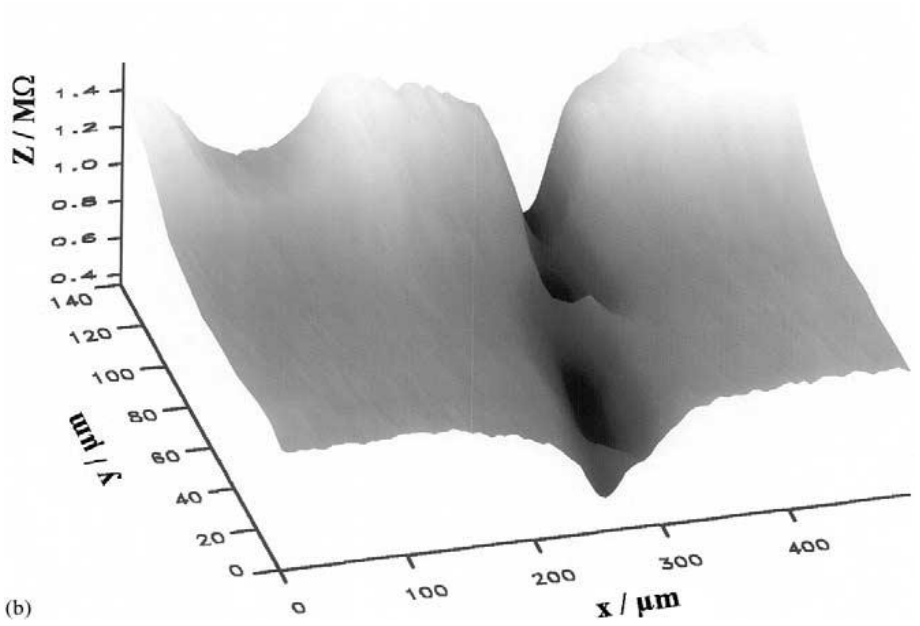
1. SECM
   a. dc-SECM
   b. ac-SECM
   c. ic-SECM
2. LEIS
3. SVP
4. SKP

ac-SECM

Investifgation of lacquered tin plates

Since ac-SECM is a mediator-free technique, it can be used to investigate freely corroding surfaces.
It was coined 4D-SECM by Schuhmann, the 4th dimension being the frequency.
It is used in constant-height mode to detect a scratch in the lacquer.





A) A single line-scan displaying the modulus |Z| as a function of the tip position in x-direction. Inset: optical image of the scratch.

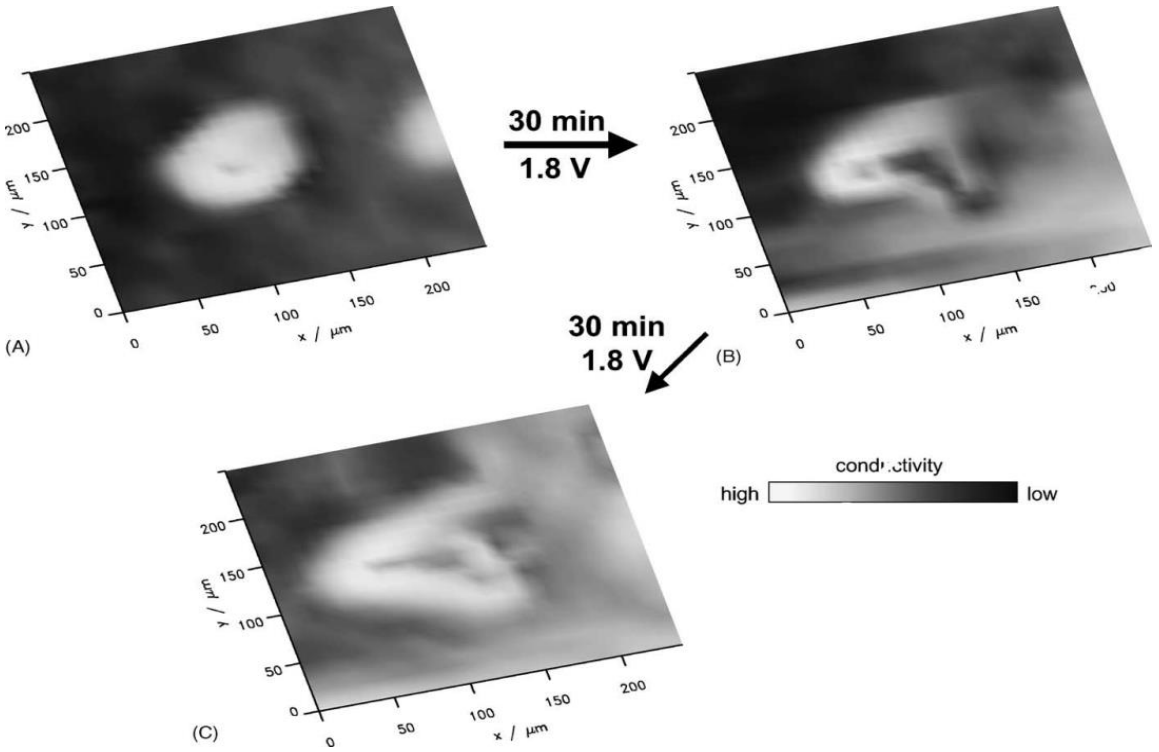
B) 3D-image of the scratch shown in (A) obtained with ac-SECM in a constant-height mode. The impedance of the probe is lower over the scratch.

Katemann et al., Electrochim. Acta 48 (2003) 1115-1121

ac-SECM

Oxide-covered Ni-Ti memory shape alloys

Heterogeneities are imaged using ac-SECM at 1 kHz.



The brighter regions correspond to areas of higher local surface conductivity. Very small heterogeneities can be imaged.

A. Schulte et al., Mat. Sci. and Eng. A 378 (2004) 523–526

Outline

1. SECM
    a. dc-SECM
    b. ac-SECM
    c. ic-SECM

2. LEIS

3. SVP

4. SKP

ic-SECM

- ic-SECM can be used in dc or ac mode. It allows to perform SECM experiments on large uneven samples, for example welded samples :

In ic-ac-SECM, there is no need to use mediator.
The local surface conductivity can give an idea of the local corrosion susceptibility of the different phases.

Outline

1. SECM
   a. dc-SECM
   b. ac-SECM
   c. ic-SECM

2. LEIS

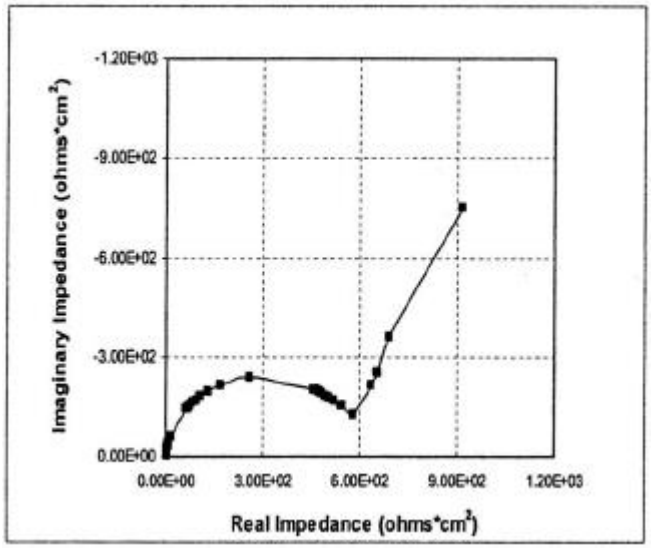
3. SVP

4. SKP

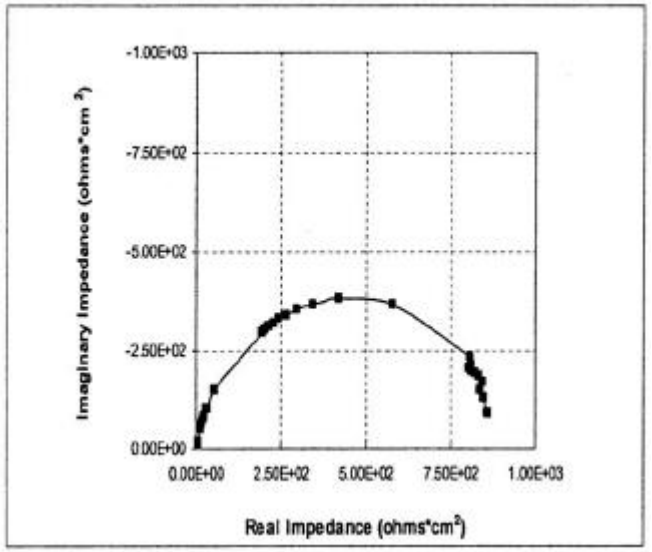
Investigating Localized Degradation of Organic Coatings

Two measurements modes are possible :
. Full local impedance spectrum at one single location (LEIS)
. Area maps of the local impedance of the sample at one frequency (LEIM)

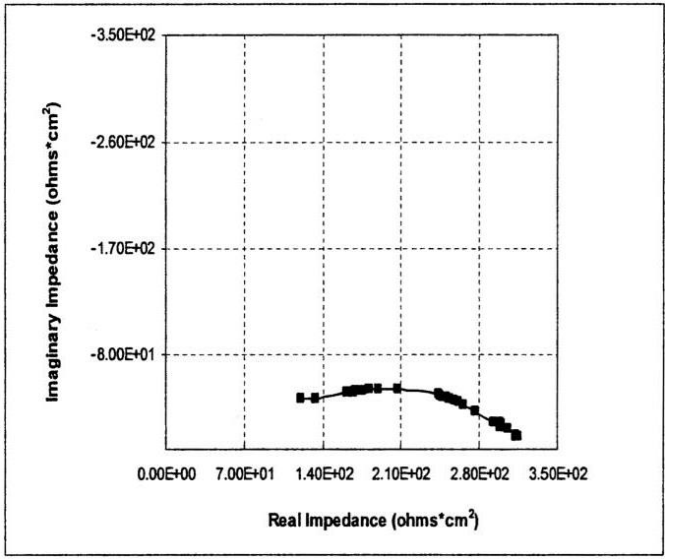
One can study the evolution of the LEIS over a coating defect with immersion time (in 10 mM NaCl) and identify the coating degradation mechanisms.



3 days



18 days



30 days

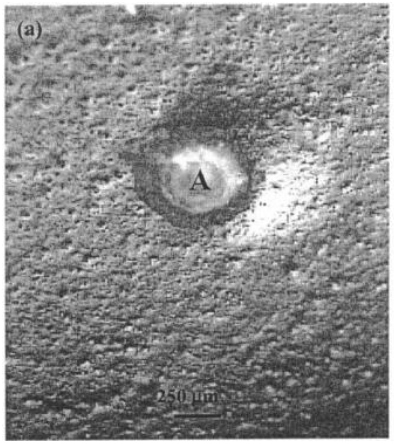
L. V. S. Philippe, G. W. Walter, S. B. Lyon, Journal of The Electrochemical Society, 150, 4, B111-B119 2003

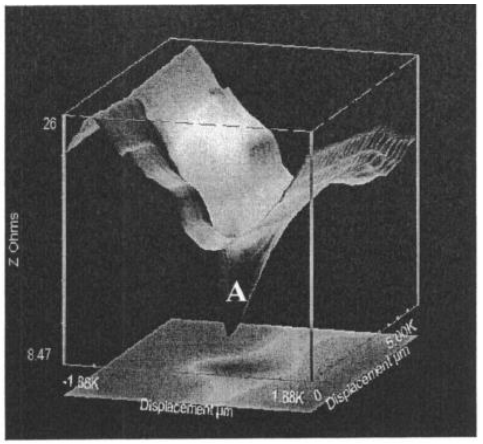
LEIS

Investigating Localized Degradation of Organic Coatings

One can study the local impedance map over a coating defect with immersion time (in 10 mM NaCl).

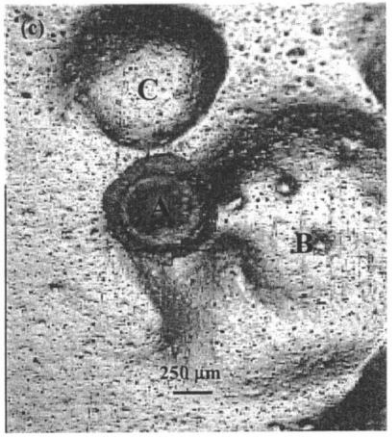
Optical image
after 18 days of immersion

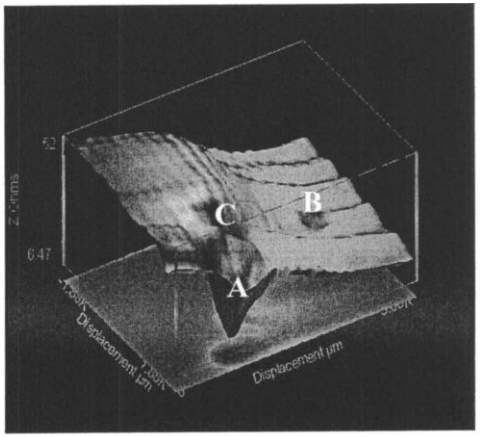




Impedance map at 1 kHz
after 3 days of immersion

Optical image
after 18 days of immersion



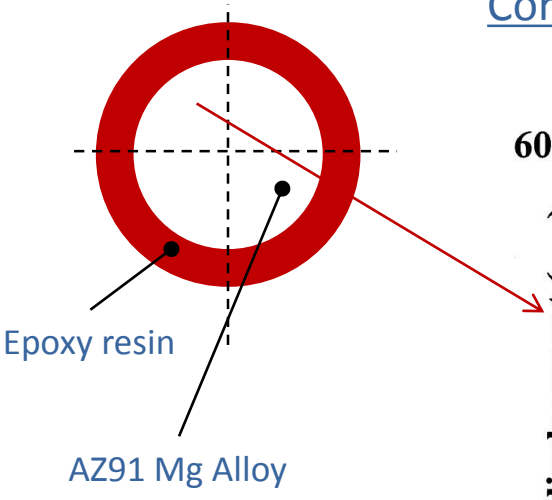


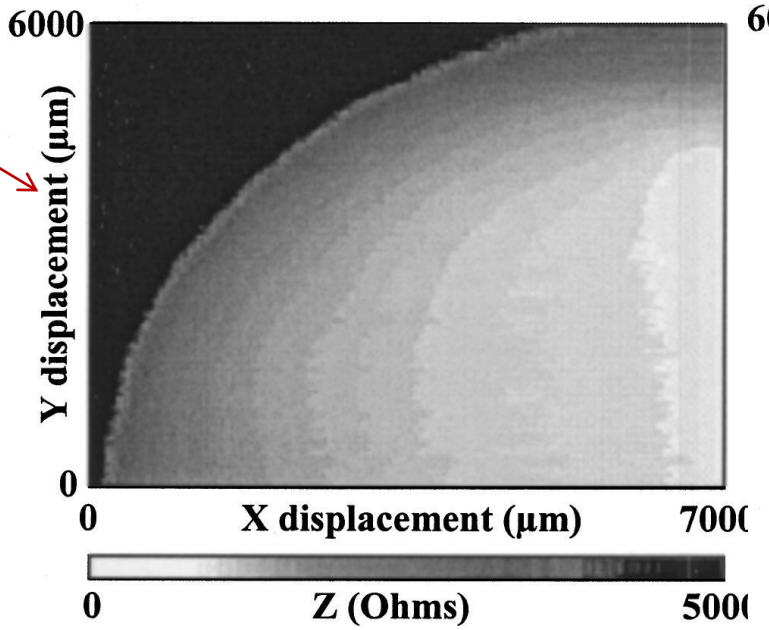
Impedance map at 1 kHz
after 18 days of immersion

L. V. S. Philippe, G. W. Walter, S. B. Lyon, Journal of The Electrochemical Society, 150, 4, B111-B119 2003

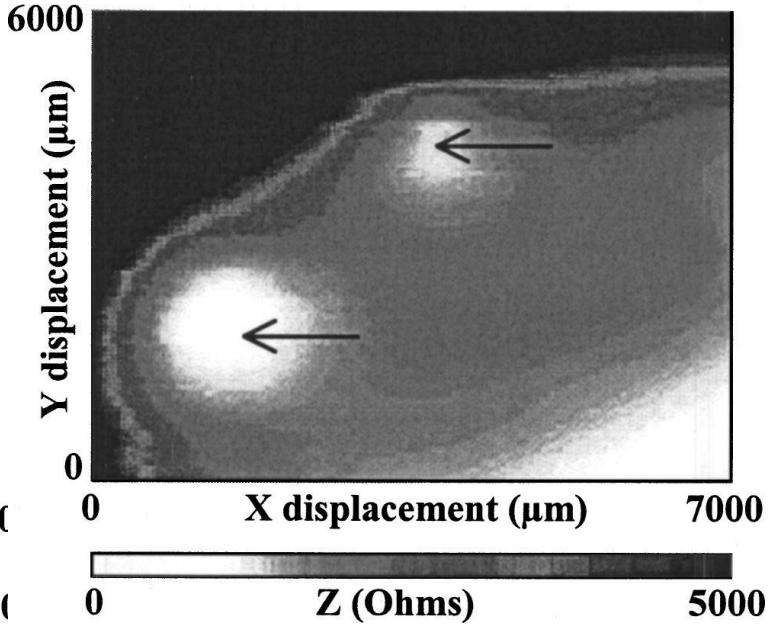
LEIS

Corrosion Behavior of an AZ91 Magnesium Alloy





LEIM at 10 Hz after 1 day immersion in 0.001 M Na_2SO_4



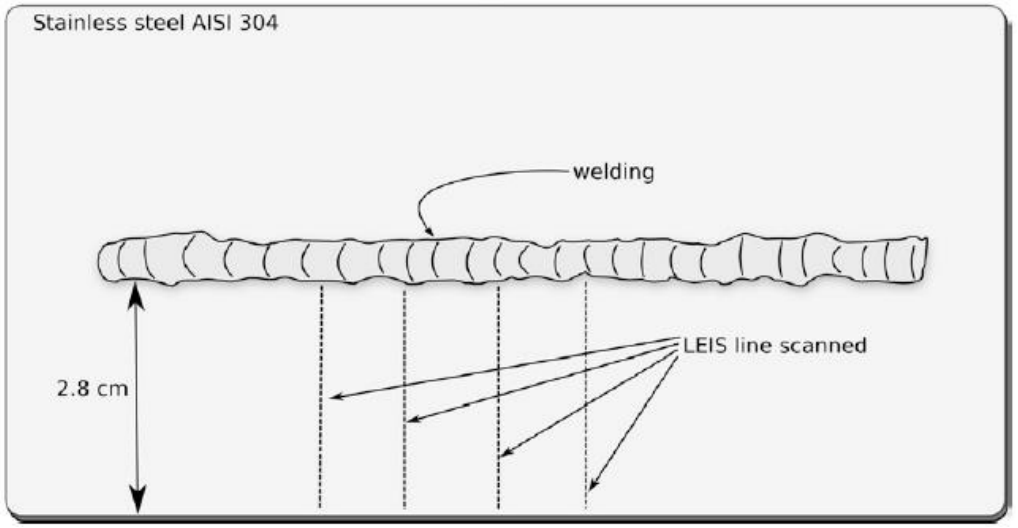
LEIM at 10 Hz after 4 days immersion in 0.001 M Na_2SO_4

The localization of the attack, related to morpholgical and compositional studies (SEM, EDS) allows to identify the metallic phases responsible for corrosion.

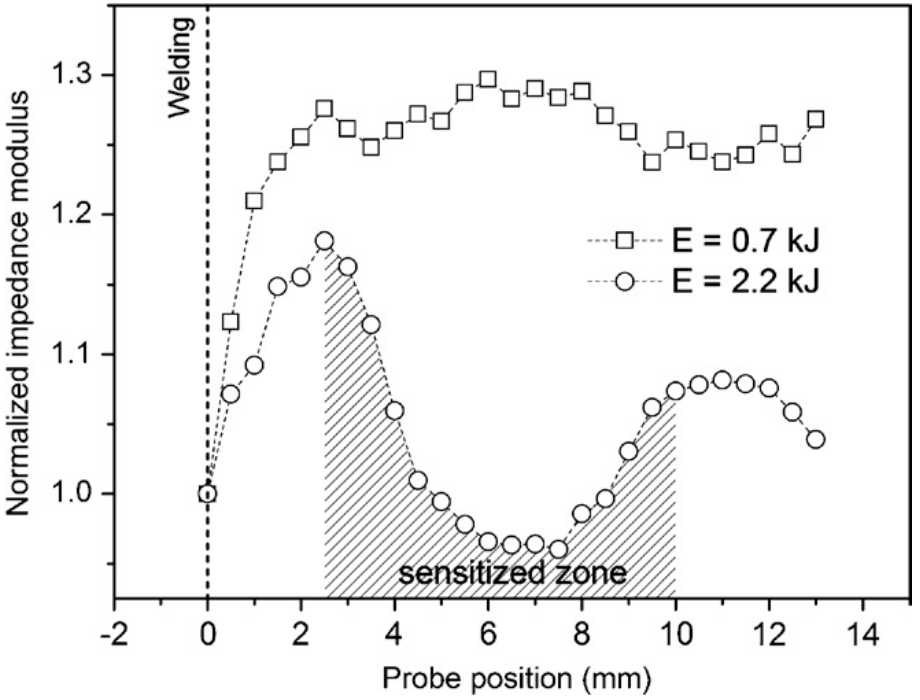
G. Baril, C. Blanc, M. Keddam and N. Pébère, Journal of The Electrochemical Society, 150 10 B488-B493 2003

LEIS

Determination of the sensitized zone extension in welded AISI 304 stainless steel



Schematics of the weld string



LEI line scan at 0.5 Hz 0.5 M H_2SO_4 + 0.01 M KSCN

The size of the sensitized zone can be determined as well as its corrosion susceptibility.

P. de Lima-Neto, J. P. Farias, L. F. G. Herculano, H. C. de Miranda, W. S. Araújo, J.-B. Jorcin, N. Pébère, Corrosion Science 50 (2008) 1149–1155

Outline

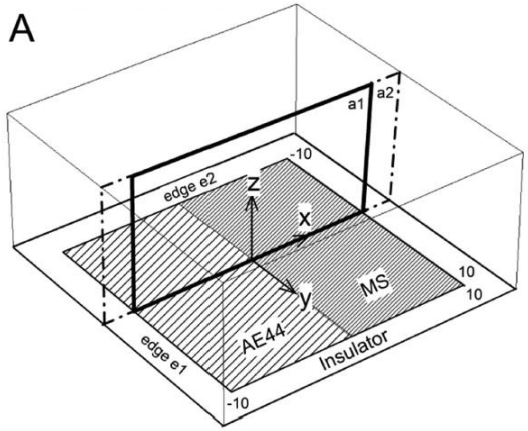
1. SECM
    a. dc-SECM
    b. ac-SECM
    c. ic-SECM

2. LEIS

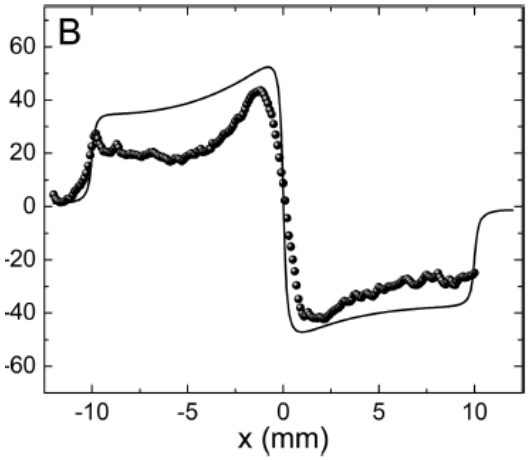
3. SVP

4. SKP

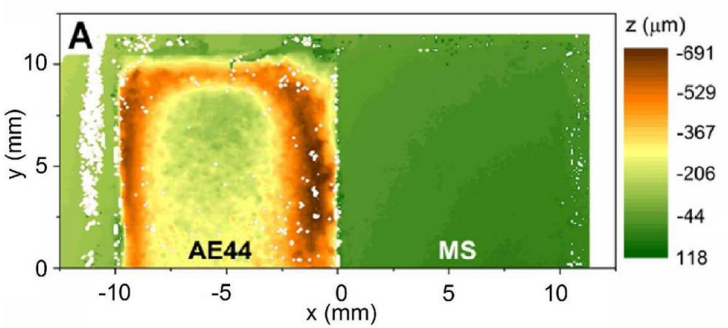
Influence of Edge Effects on Local Corrosion Rate of Magnesium Alloy/Mild Steel Galvanic Couple



System used : AE44/MS in 1.6 wt.% NaCl



Experimental SVET current density (dot) and current density calculated in 2D model with edge (line; z = 150 µm) when the SVET probe is located at 150 µm above the surface.



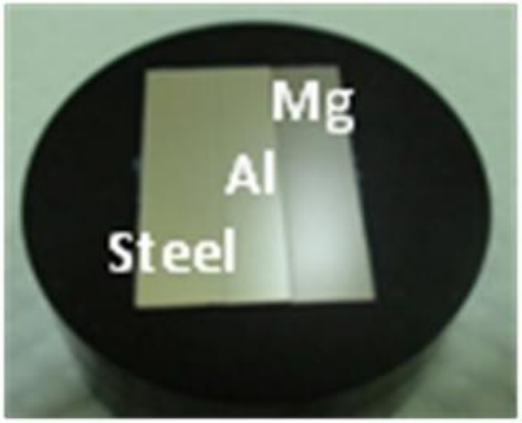
Contour of depth of anodic attack over a half area of the couple

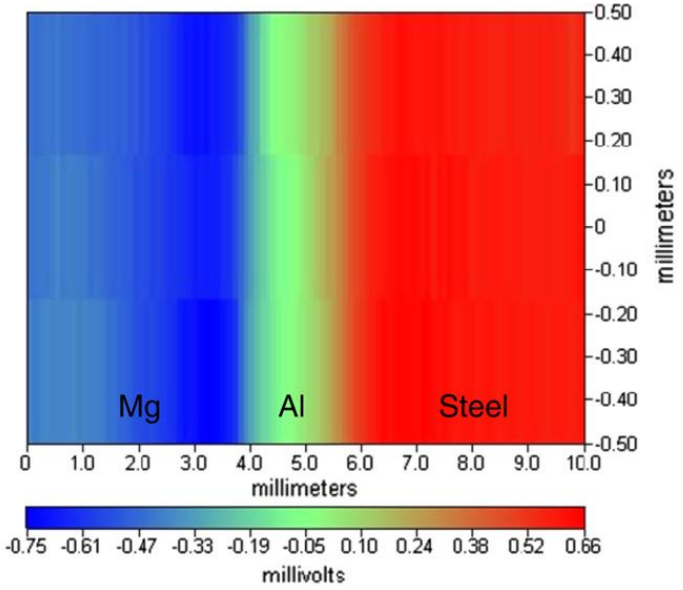
Calculated current densities are in agreement with experimental current and damage profile of the sample.

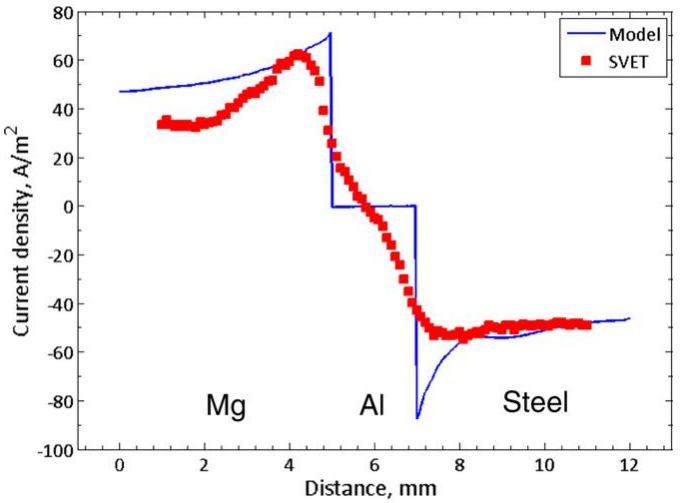
Dao Trinh, Philippe Dauphin Ducharme, Ushula Mengesha Tefashe, Joseph R. Kish and Janine Mauzeroll, Anal. Chem., 2012, 84 (22), pp 9899–9906

SVP

Galvanic corrosion between magnesium and mild steel





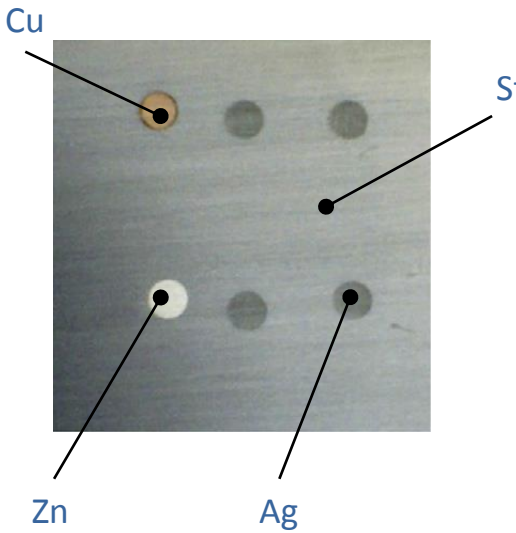


The influence of the size of the spacer on the galvanic coupling is modelled and validated by SVP experiments.
Optimum geometry for the reduction of galvanic coupling can be designed

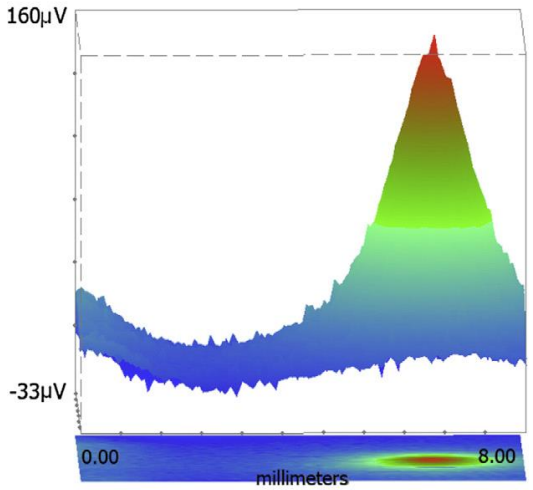
K. H. Deshpande, Corrosion Science 62 (2012) 184–191

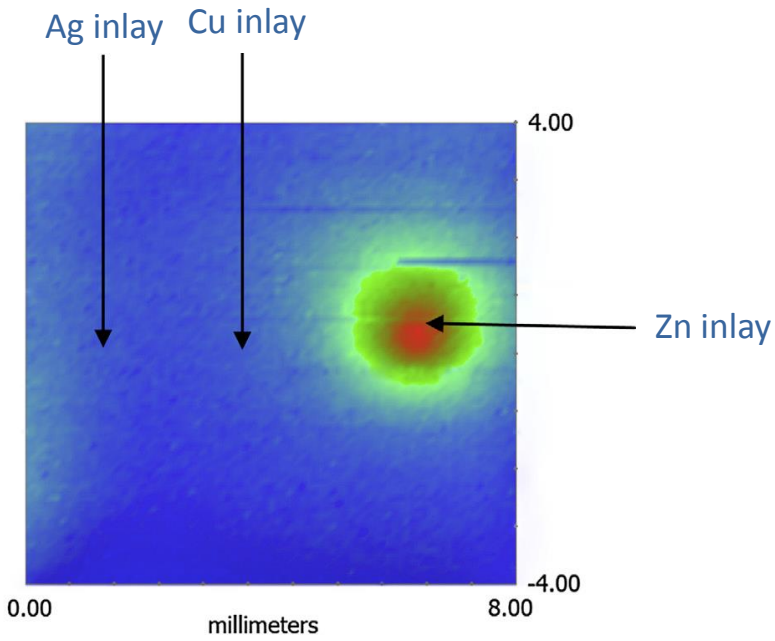
SVP

A cathodic delamination study of coatings with and without mechanical defects.



The sample is coated with transparent vinyl varnish.





SVP measurements when sample immersed in 0.06 M

Delamination starts on Zn particle.

R. Montoya et al. / Corrosion Science 82 (2014) 432–436

SVP

Investigating the self healing process on coated steel by SVET and EIS

Microencapsule was incorporated into an interpenetrating polymer network and applied over steel surface.

A scratch was made on the coated surface and its self healing ability was studied using scanning vibrating electrode technique (SVET) and electrochemical impedance spectroscopy (EIS).

Results of SVET studies show that the current density increases in the initial stage.

After 24 h, the current density decreases, which indicating the formation of passive polymer film due to the diffusion of core polymer present in the microcapsules through the holidays.

Increase in the resistance (10^7 Ω/cm^2) of the self healing coating was observed after 24 h in EIS studies confirming the formation of the passive film.

S. Neema, M. Selvaraj, J. Raguraman, S. Ramu,
Journal of Applied Polymer Science Volume 127, Issue 1, pages 740–747, 5 January 2013

Outline

1. SECM
    a. dc-SECM
    b. ac-SECM
    c. ic-SECM

2. LEIS

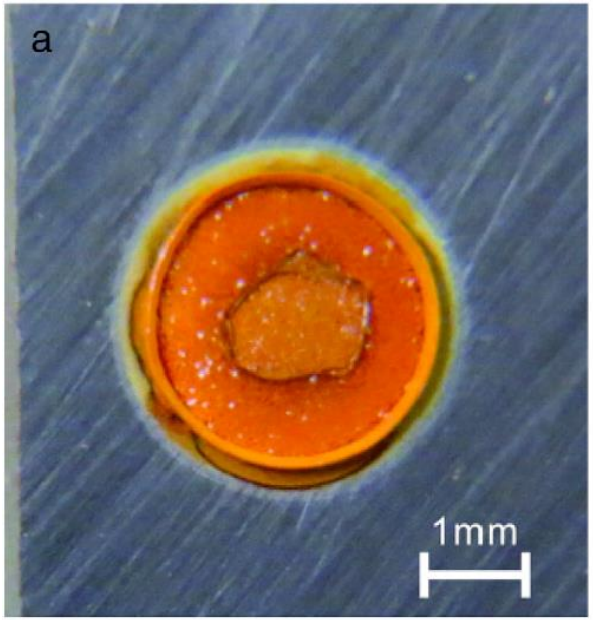
3. SVP

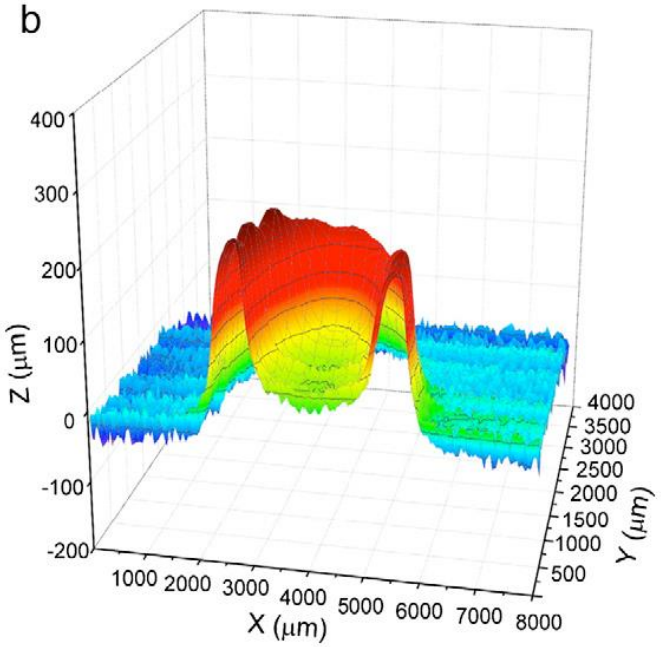
4. SKP

SKP

Mechanism of electrochemical corrosion of steel under water drop

SKP can be used as kelvin probe and capacitance probe for topography measurements.





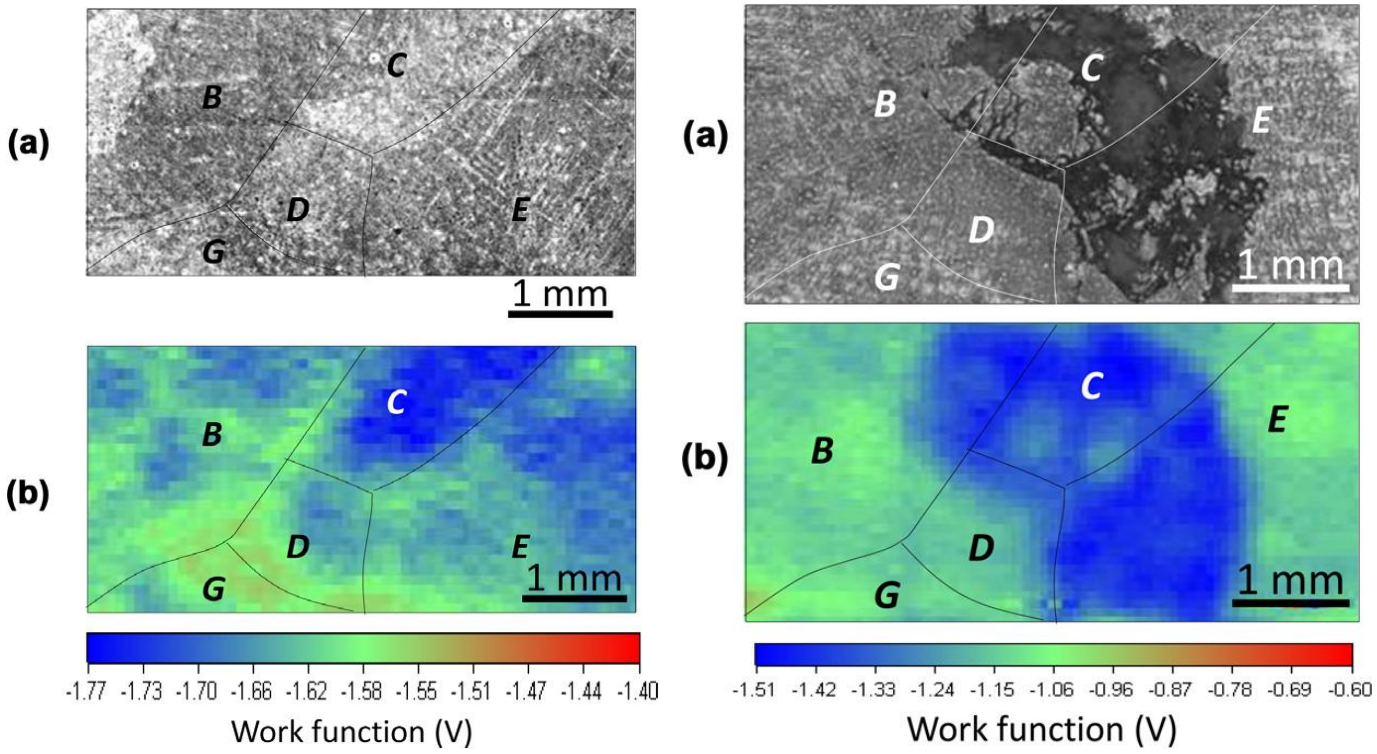
Localization of corrosion products on steel.

Electrochem. Comm. 35 (2013) 8–11

SKP

Crystal orientation and electrochemical corrosion of polycrystalline Mg

Optical image



SKP image

SKP allows to correlate corrosion morphology and work function differences

2 h immersion in the $Mg(OH)_2$ saturated solution

3 h immersion in 0.01 M NaCl

Guang-Ling Song, Zhenqing Xu, Corrosion Science 63 (2012) 100–112

Useful links

More references can be found here :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/references/coatings/

Please also find some application notes here :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/application-notes/

And the brochures here :
http://www.bio-logic.info/scanning-systems-scan-lab/downloads/brochures/

Requests can be placed here :
http://www.bio-logic.info/ask-for-a-quote-contact-us/

For more information on the techniques :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/tutorials/