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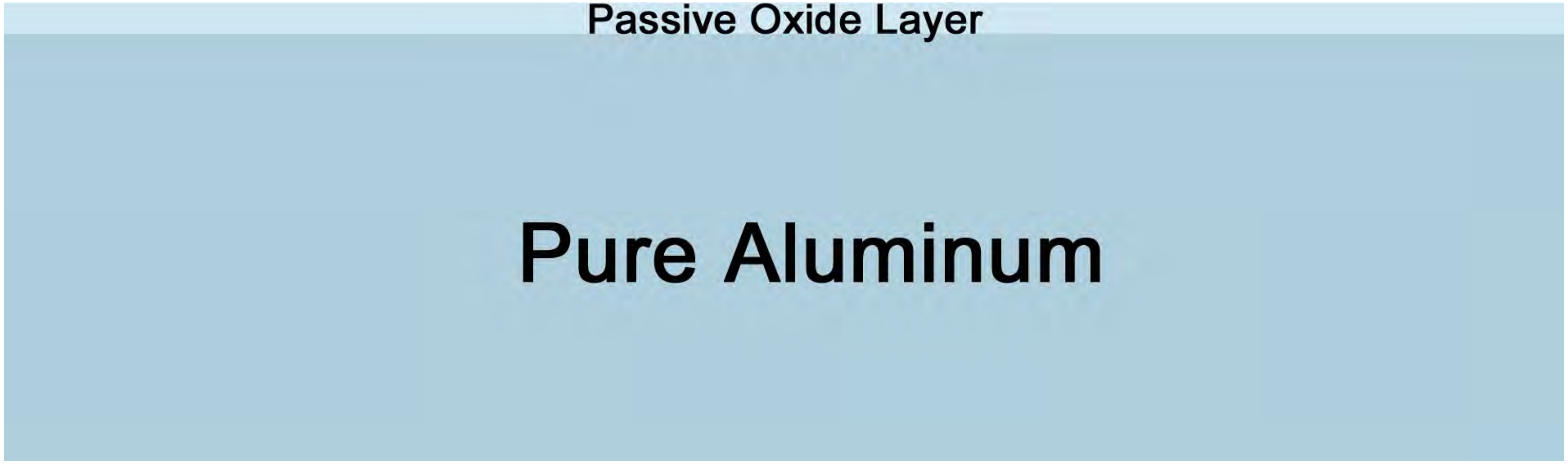
# Towards the modeling of microgalvanic coupling in aluminum alloys : the choice of boundary conditions

**Nicolas Murer*[1], Nancy Missert[2], Roland Oltra[3], Rudy Buchheit[1]**
[1]Fontana Corrosion Center, Ohio State University, 2041 College Road, Columbus, OH 43210
[2]Sandia National Laboratories, 1515 Eubank SE, Albuquerque, NM 87123
[3]Institut Carnot de Bourgogne, UMR 5613 CNRS, 21078 Dijon Cedex

*Corresponding author: murer.3@osu.edu

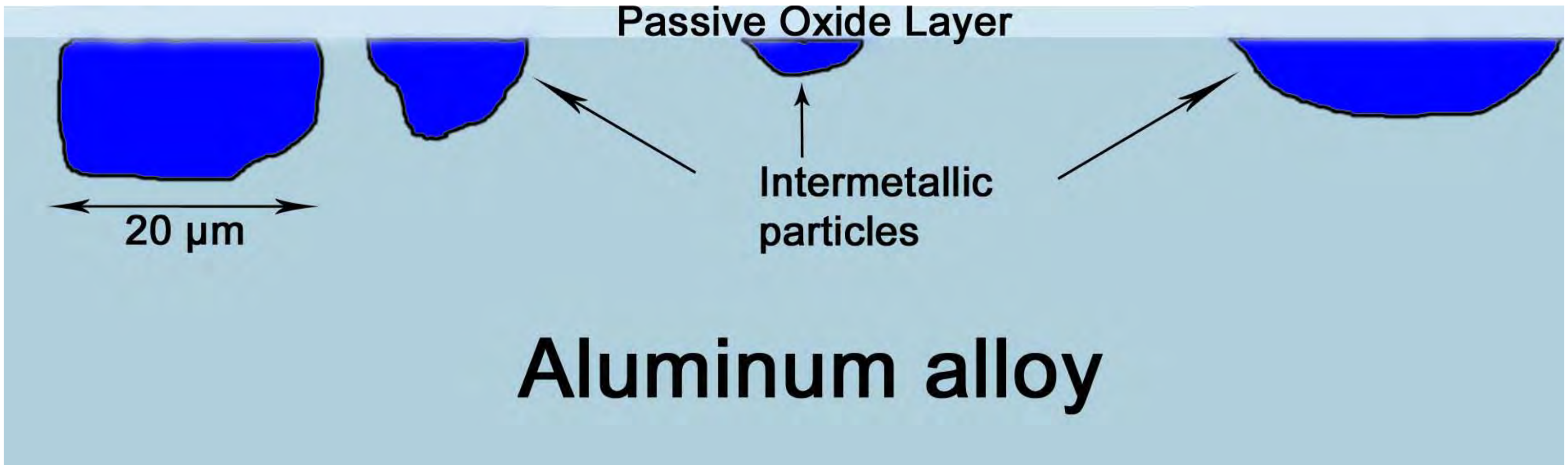
# Phenomenology of localized corrosion

Environment



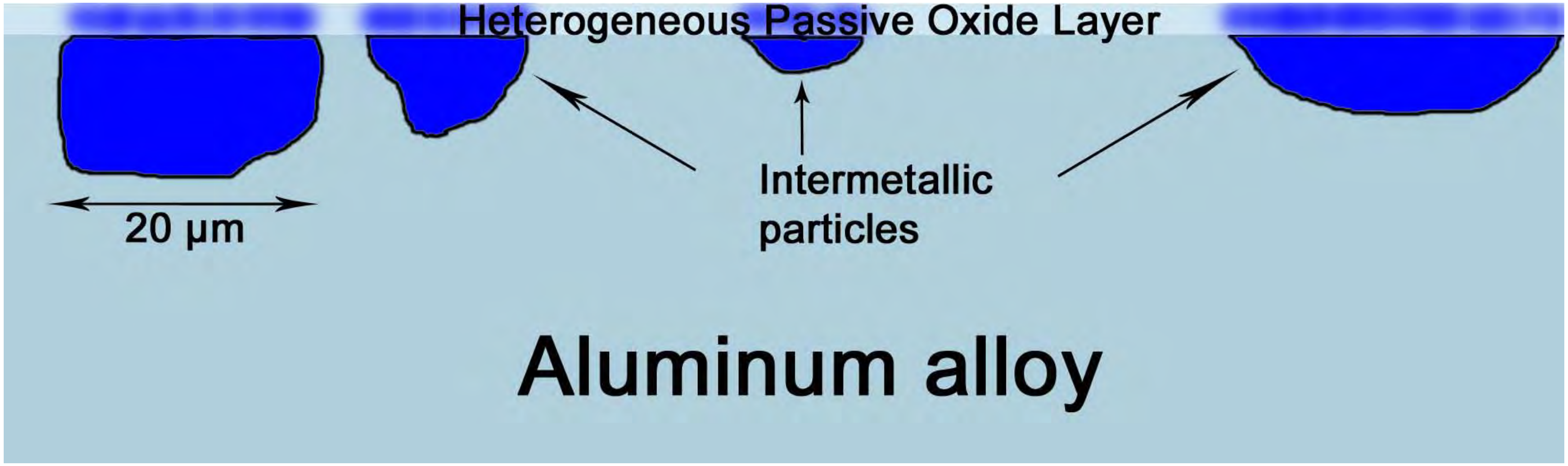
**Pure aluminum is passive in neutral, low conductive environments.**

# Phenomenology of localized corrosion



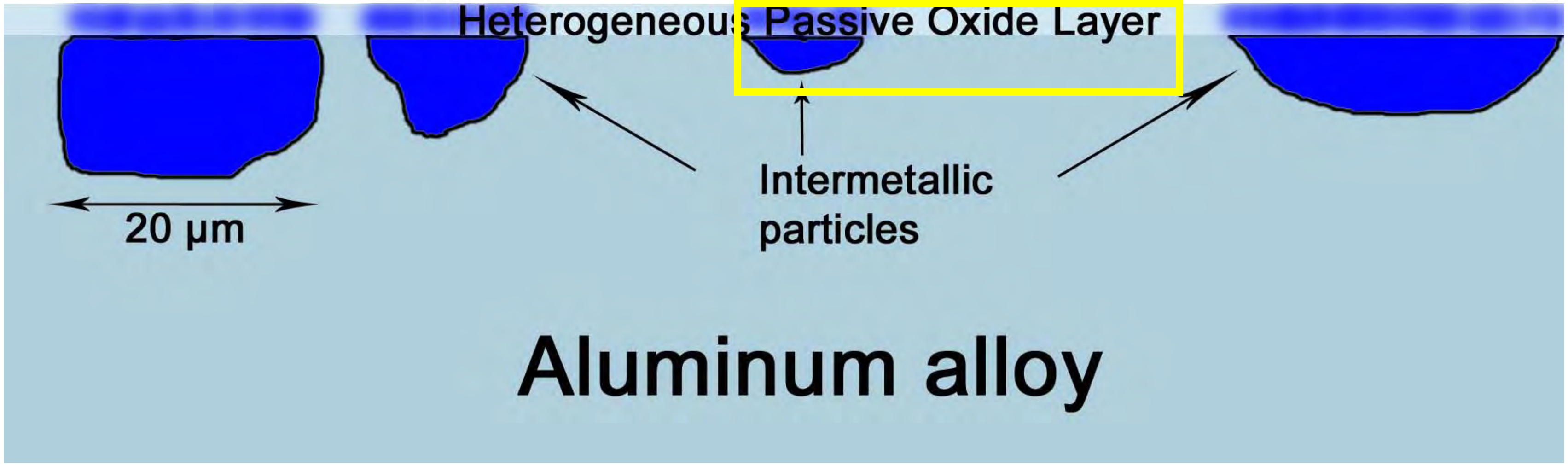
**During the fabrication process of structural aluminum alloys, microstructural heterogeneities are formed in the material.**

# Phenomenology of localized corrosion



**The presence of the particles modifies the composition of the oxide layer and reduces its passive character.**

# Phenomenology of localized corrosion

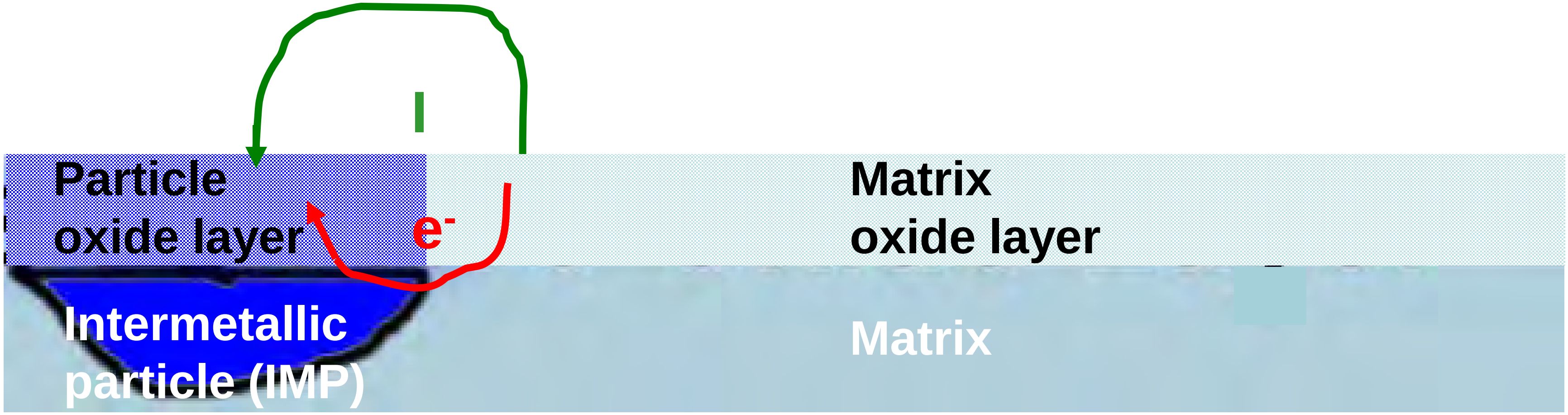


**Corrosion is likely to take place at the interface between the intermetallic particle and the matrix.**

**(More precisely at the interface between the aluminum oxide and the intermetallic oxide)**

# Phenomenology of localized corrosion

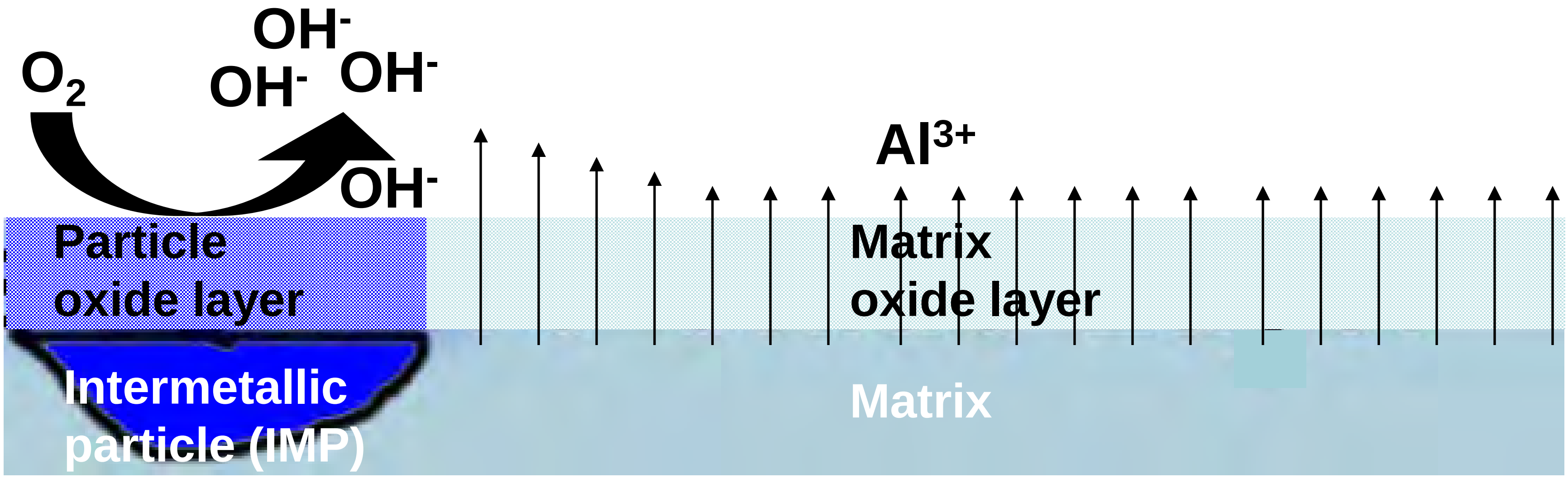
## Galvanic coupling



**In <u>low conductivity environments</u>, galvanic coupling takes place between the two phases. In most cases, IMP is the cathode and the matrix is the anode.**

# Phenomenology of localized corrosion

## Galvanic coupling : Redox reactions

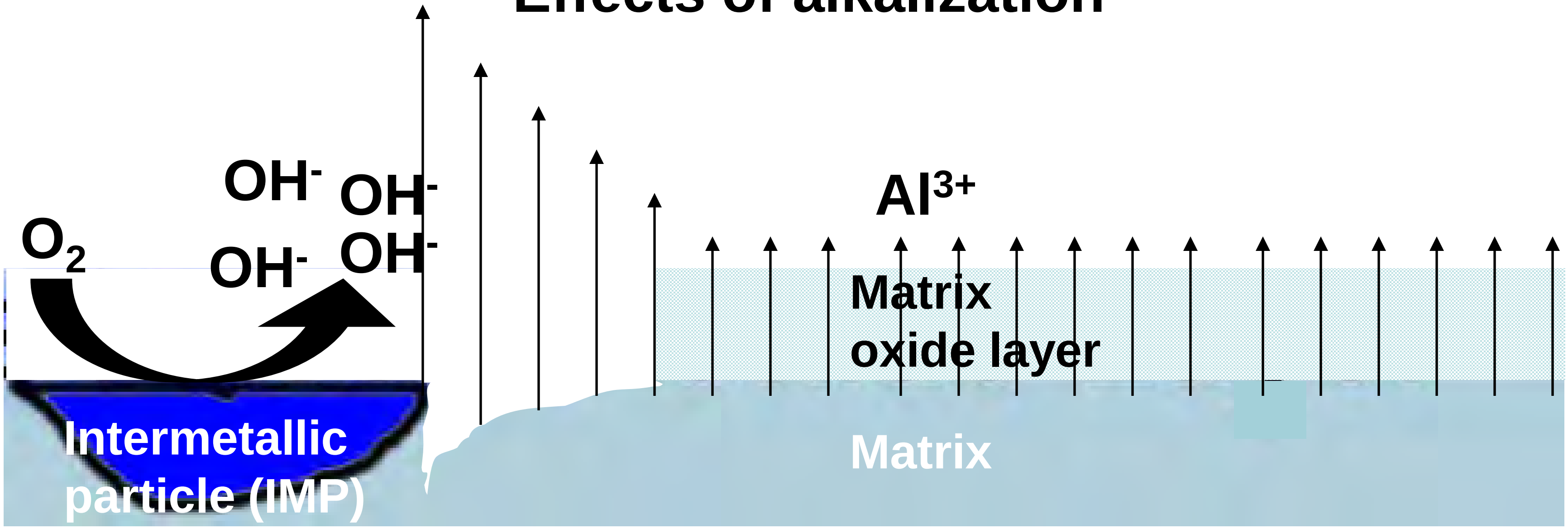


At the cathode : $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

At the anode : $Al \rightarrow Al^{3+} + 3e^-$

# Phenomenology of localized corrosion

## Effects of alkalization



- Dissolve oxide layers
- Increase the dissolution rate of the substrate

# Why modeling ?

The current and pH distributions in this type of configuration are very difficult to reach. The former phenomena have only been *qualitatively* experimentally highlighted[1-4].

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- the passive nature of aluminum and aluminum alloys

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The current and pH distributions in this type of configuration are very difficult to reach. The former phenomena have only been *qualitatively* experimentally highlighted[1-4].

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A predictive model is required if we want to quantitatively describe localized corrosion.

# OBJECTIVES

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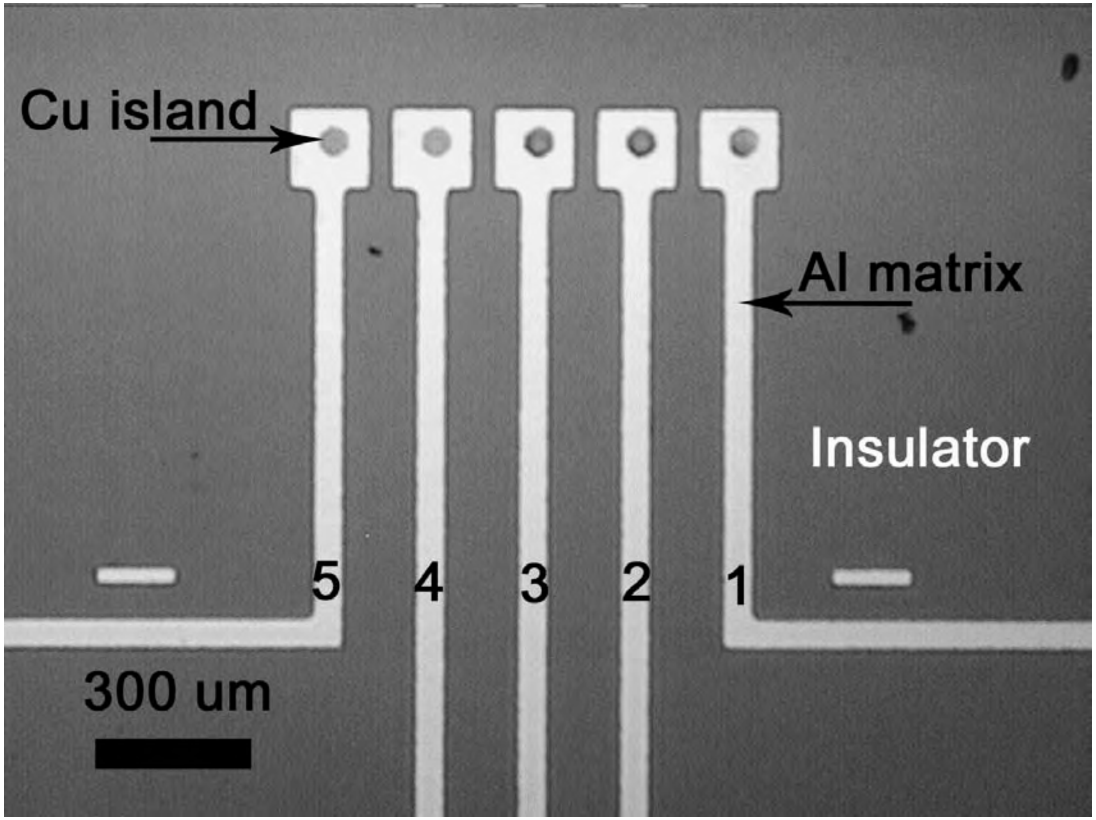
**We must use a model system that mimic real geometries and for which coupling currents can be monitored.**

# Experimental : the model system

Cu islands diameter is 50 µm

Electrolyte is NaCl
10 $mmol.L^{-1}$



All the Al/Cu channels are coupled.

Each net current originating from an Al/Cu channel can be monitored and compared to the simulated current profiles.

# Governing equations

Nernst – Planck equation in stationary regime assuming electroneutrality.

$$\nabla . N_i = \nabla . (-z_i u_i F c_i \nabla \varphi - D_i \nabla c_i) = R_i$$

$N_i$ is the total flux density of species i ($mol.m^{-2}.s^{-1}$)
$\varphi$ is the potential in the domain i.e. in the solution (V)
$u_i$ is the mobility of the species i ($m.s^{-1}$)
$c_i$ is the concentration of the species i ($mol.m^{-3}$)
$z_i$ is the charge number of the species i
$R_i$ is the production term, i.e. the flux of species due to reactions that are occurring in the bulk solution (i.e. subdomain) ($mol.m^{-2}.s^{-1}$)

Species : $Na^+$, $Cl^-$,$OH^-$,$H^+$, $Al^{3+}$,$O_2$

# Governing equations

Electroneutrality

$$\sum_{i}^{n} z_i c_i = 0$$

Electroneutrality assumption (i.e. infinite dilute solutions assumption) allows potential distribution calculation and complete solving of Nernst Planck equation.

Currents are due to the motion of the charged species

$$i = F\sum_{i} z_i N_i$$

# Boundary Conditions

Two active boundaries : the anode and the cathode.

Two different types of boundary conditions are possible to describe galvanic coupling.

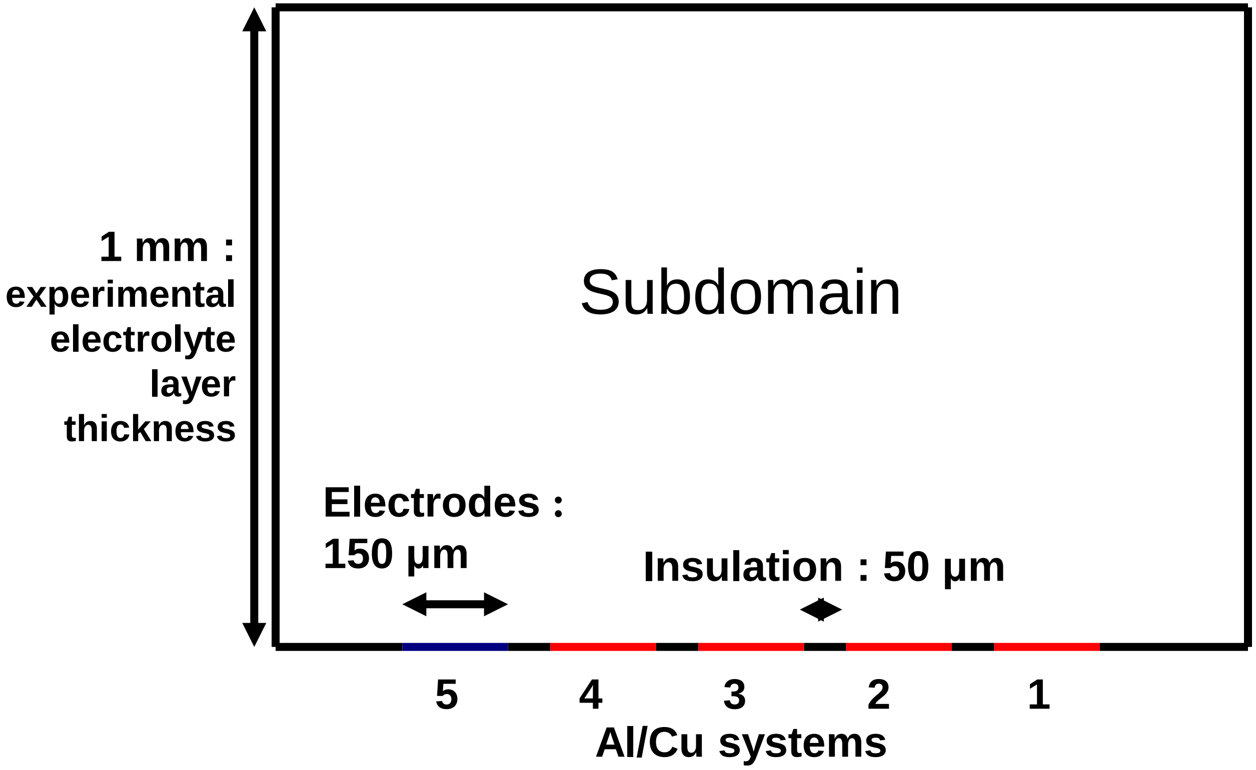
1. non-linear semi-empirical Butler-Volmer based current-potential relations[5]
2. $O_2$ diffusion limited cathodic reduction reaction[1-4]

# The Choice of the Boundary Conditions

To know which kind of conditions we have to use for the predictive model, we must compare the <u>simulated</u> current distributions obtained for either boundary condition, with the <u>experimental</u> current distribution.

# Model System used in COMSOL

Channel 5 : anodic net current
Channels 1, 2, 3, 4 : cathodic net currents → Simplification of the geometry



# Boundary Conditions

1. *Butler Volmer based potential-current relations.*

Cathodic channels (Cu) : presence of a cathodic current plateau

$$i_C = \frac{i_{c_C} \exp(E_C - (V_m - V)) / \beta_C)}{1 + \frac{(i_{c_C} \exp(E_C - (V_m - V)) / \beta_C))}{i_{diff}}}$$

Anodic channels (Al) : charge transfer regime

$$i_A = i_{c_A} \exp(E_A - (V_m - V)) / \alpha_A)$$

All parameters are determined with experimental polarization curves of Al and Cu in corresponding media.

# Boundary Conditions

2. *Galvanic coupling controlled by diffusion-limited cathodic reaction.*

**At each cathode j** : $C_{O2} = 0$ $i_{cj} = -4*F*J_{diff}O_2$

(Four moles of electrons are required to reduce one mole of $O_2$)

**At the anode :**

Sum of the currents densities integrated on each cathode divided by the length of the anode.

$$i_a = \left(\sum_j \int_0^c i_{cj}\,dx\right)/a$$

With a the anode length and c the cathode length

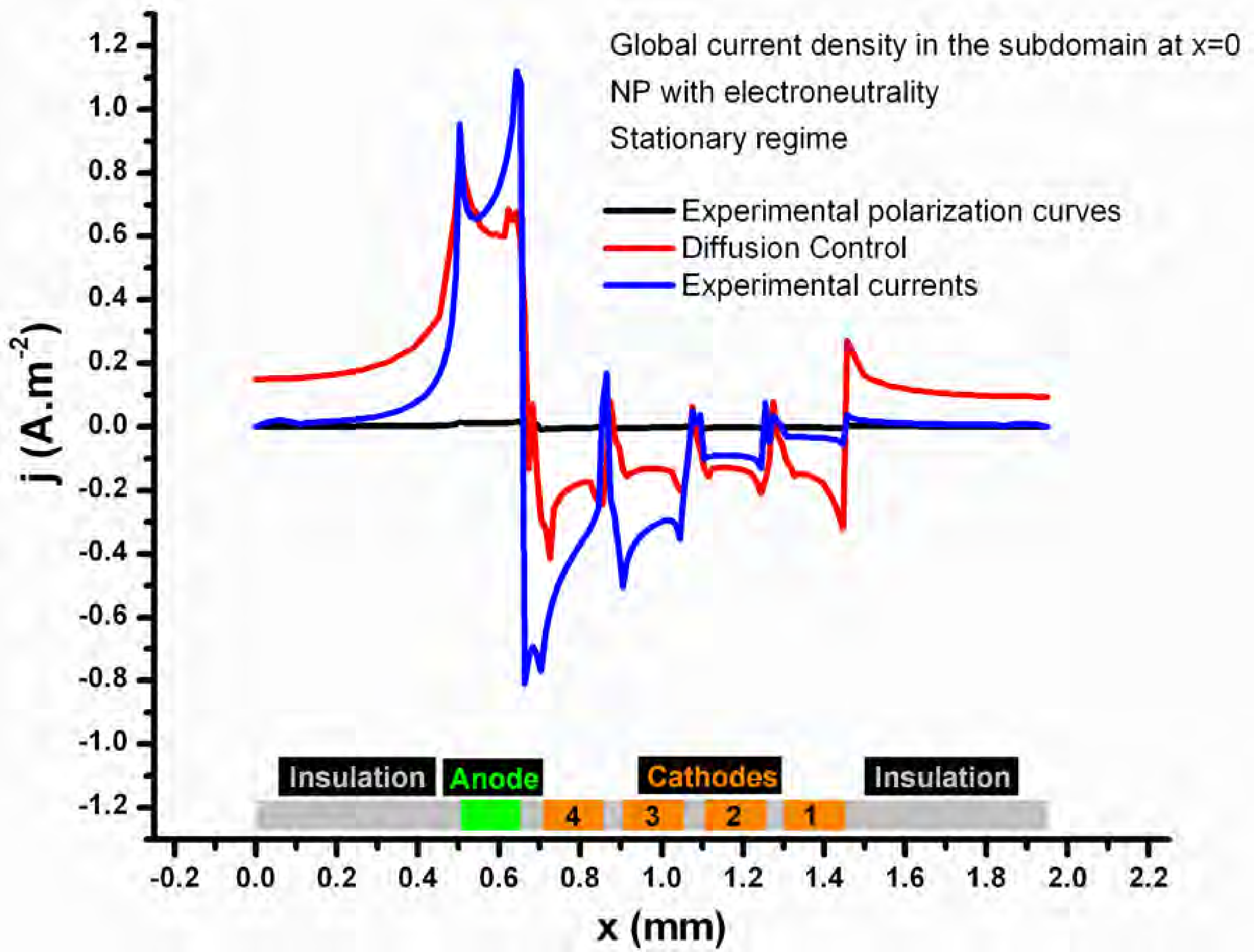
# Boundary Conditions

3. *Experimental currents*

**Cathodes** : for each channel, the current monitored with time was averaged and divided by the surface of the channel.
Each current density was then applied as a boundary condition.

**Anode** : the sum of the cathodic current densities was the current density applied at the anodic boundary.

# Results


Global current density in the subdomain at x=0
NP with electroneutrality
Stationary regime
Experimental polarization curves
Diffusion Control
Experimental currents
j (A.m$^{-2}$)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
Insulation
Anode
Cathodes
Insulation
4
3
2
1
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
x (mm)

# Results

**Boundary conditions that are the most accurate to describe galvanic coupling are based <u>on the assumption of a cathodic control by $O_2$ diffusion.</u>**

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This assumption will be used to describe galvanic coupling at the interface between a cathodic particle and an anodic matrix.

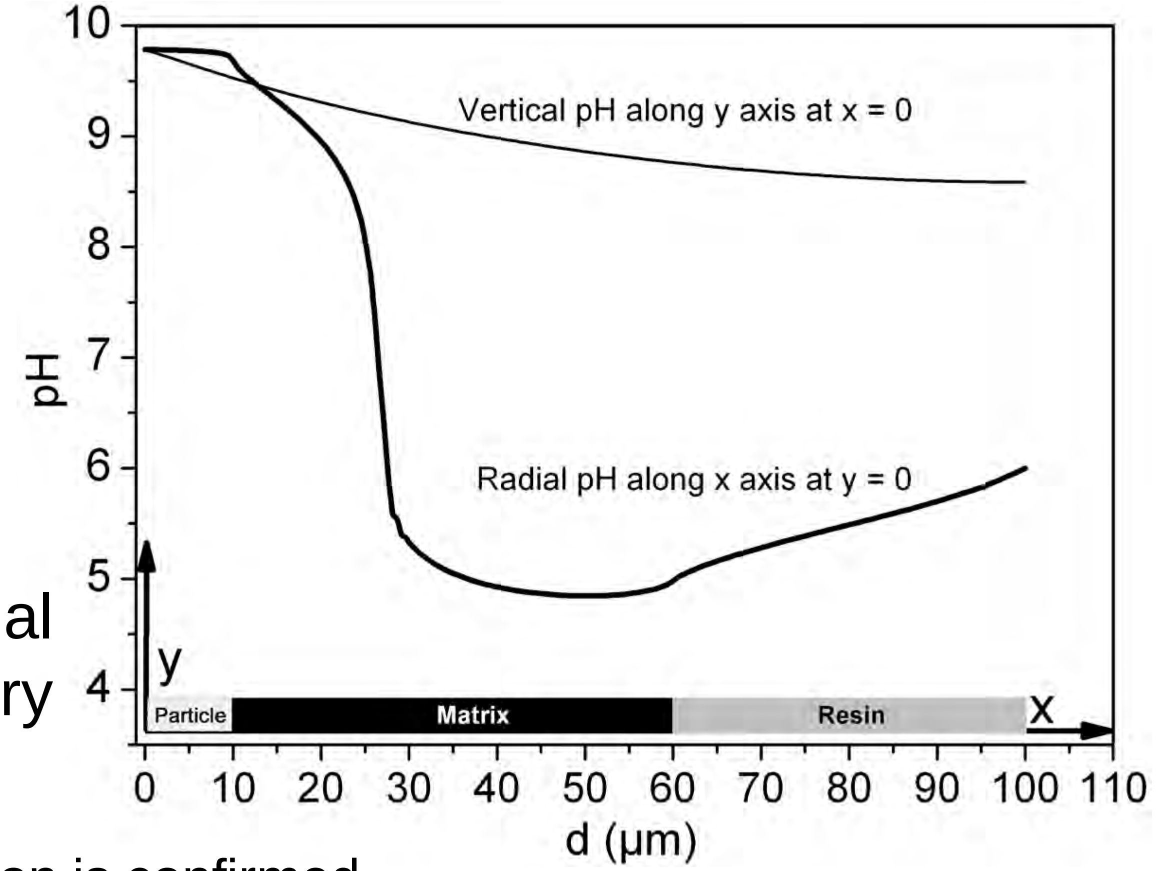
# Results

**Boundary conditions that are the most accurate to describe galvanic coupling are based on the assumption of a cathodic control by $O_2$ diffusion.**

This assumption will be used to describe galvanic coupling at the interface between a cathodic particle and an anodic matrix.

The pH distribution at the surface of this system can be predicted.

# Application : pH distribution[6]

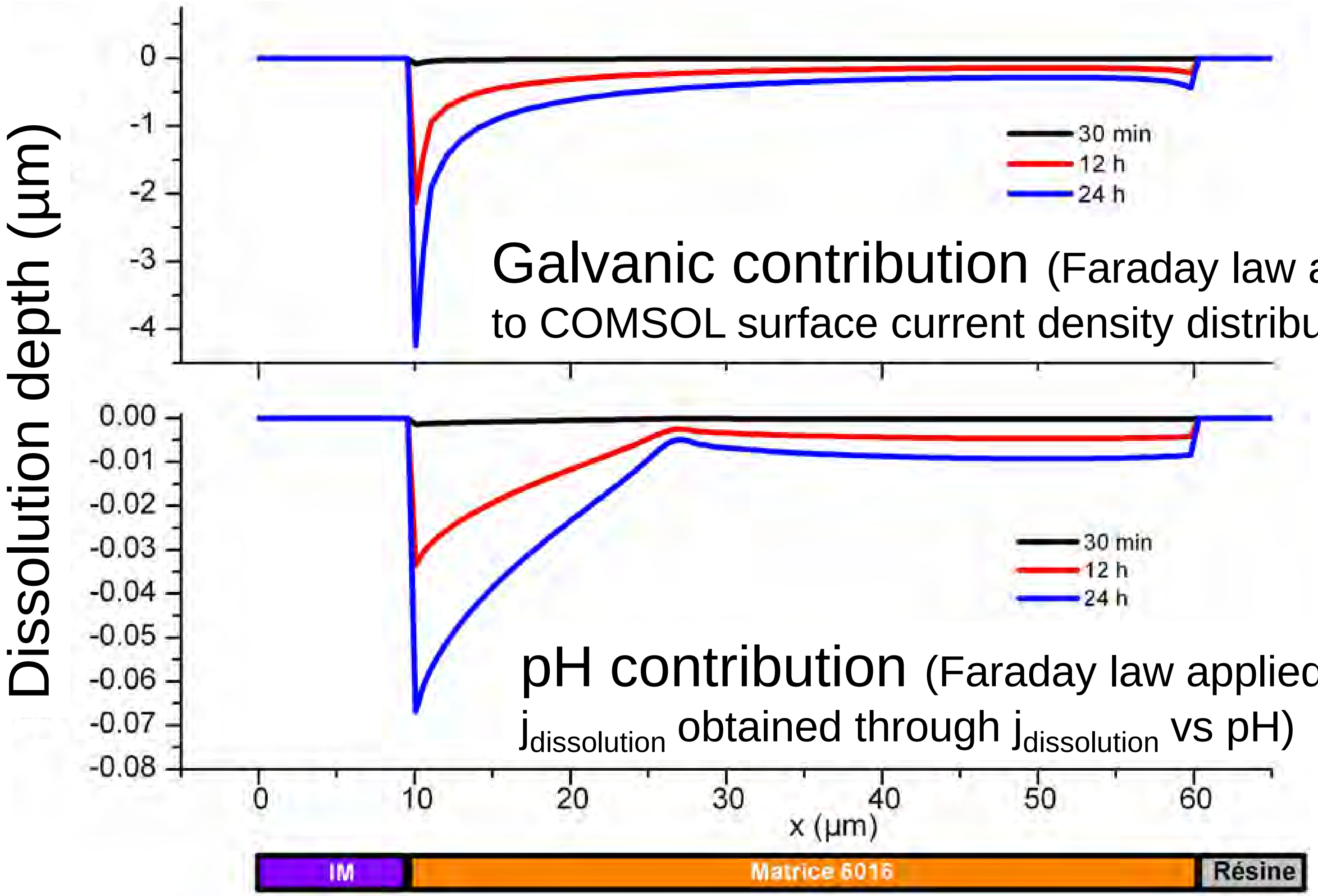


Axial symmetry

Alkalization is confirmed.

Knowing the dissolution current associated with pH ($j_{dissolution}$ = f(pH)), we can deduce the pH contribution to the damage.

# Application : effect of pH[6]



Galvanic contribution (Faraday law applied to COMSOL surface current density distribution)

pH contribution (Faraday law applied to $j_{dissolution}$ obtained through $j_{dissolution}$ vs pH)

N.Murer, Comsol Conference
Boston, October 10 2008

# Conclusions

- Nernst-Planck application mode with electroneutrality has been proven able to describe tertiary current distributions taking place during galvanic coupling.

- The designed model system allowed to determine that the most suitable boundary conditions must be based on the assumption of a mass transport limited cathodic control of the galvanic coupling.

- The actual alkalization occurring over the particle/anodic matrix interface has been highlighted.

- Its role in damage accumulation was shown to be less important than expected.

# Perspectives

- **Introducing time** : galvanic coupling in this configuration is NOT a stationary phenomenon.

  The role of galvanic coupling can be reduced with time as the electrolyte in the vicinity of the surface becomes more conductive.

- **Considering the oxide layers** : the cathodic reaction seems to be correctly modeled, but the effect of the pH on the anodic dissolution depends on the time-dependent stability of the matrix oxide layer, which is a semi-conductor.

# References

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3. *Park, Paik, Huang, Alkire, J. Electrochem. Soc.,* ***146*** *(2) 517-523 (1999)*

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5. *P. Bucaille, R. Oltra and T. Warner, Theoretical and experimental studies of galvanic corrosion between aluminium and Al-4% Cu alloys, Materials Science Forum,* ***242****, 207-212 (1997)*

6. *Murer, Oltra, Neel, Vuillemin, J. Electrochem. Soc., submitted*

Thank you for your attention