Use of COMSOL Multi-Physics® in Modeling Galvanic Corrosion

Kiran B. Deshpande

Senior Researcher, Material Characterization and Modeling Group
India Science Lab, General Motors Global Research and Development
GM Technical Centre India Pvt Ltd, Creator Building,
International Tech Park Ltd.
Whitefield Road, Bangalore - 560 066, INDIA

Email: kiran.deshpande@gm.com

COMSOL CONFERENCE 2010, BANGALORE
October 29 - 30, 2010

Motivation

Why Magnesium in Automobiles?

- Light weight increases fuel economy
- High strength to weight ratio makes it a good engineering material
- Good castability enables high production rate

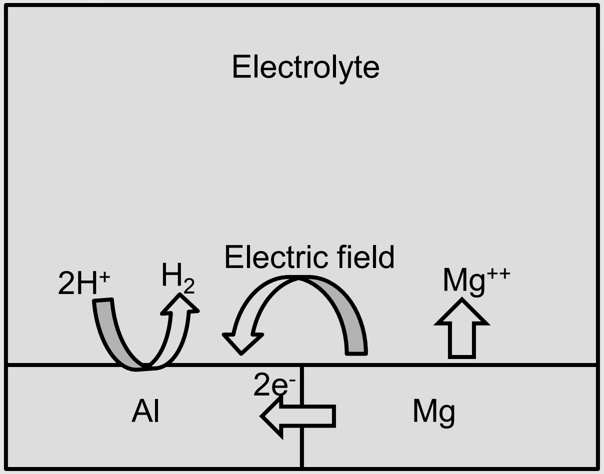
Challenges

- Poor corrosion resistance
  - Mg is not very suitable for automotive applications which are exposed to corrosion media
- High galvanic corrosion
  - Mg is very anodic to other metals such as Fe, Al – poor durability in dissimilar material joints and applications

Research Focus

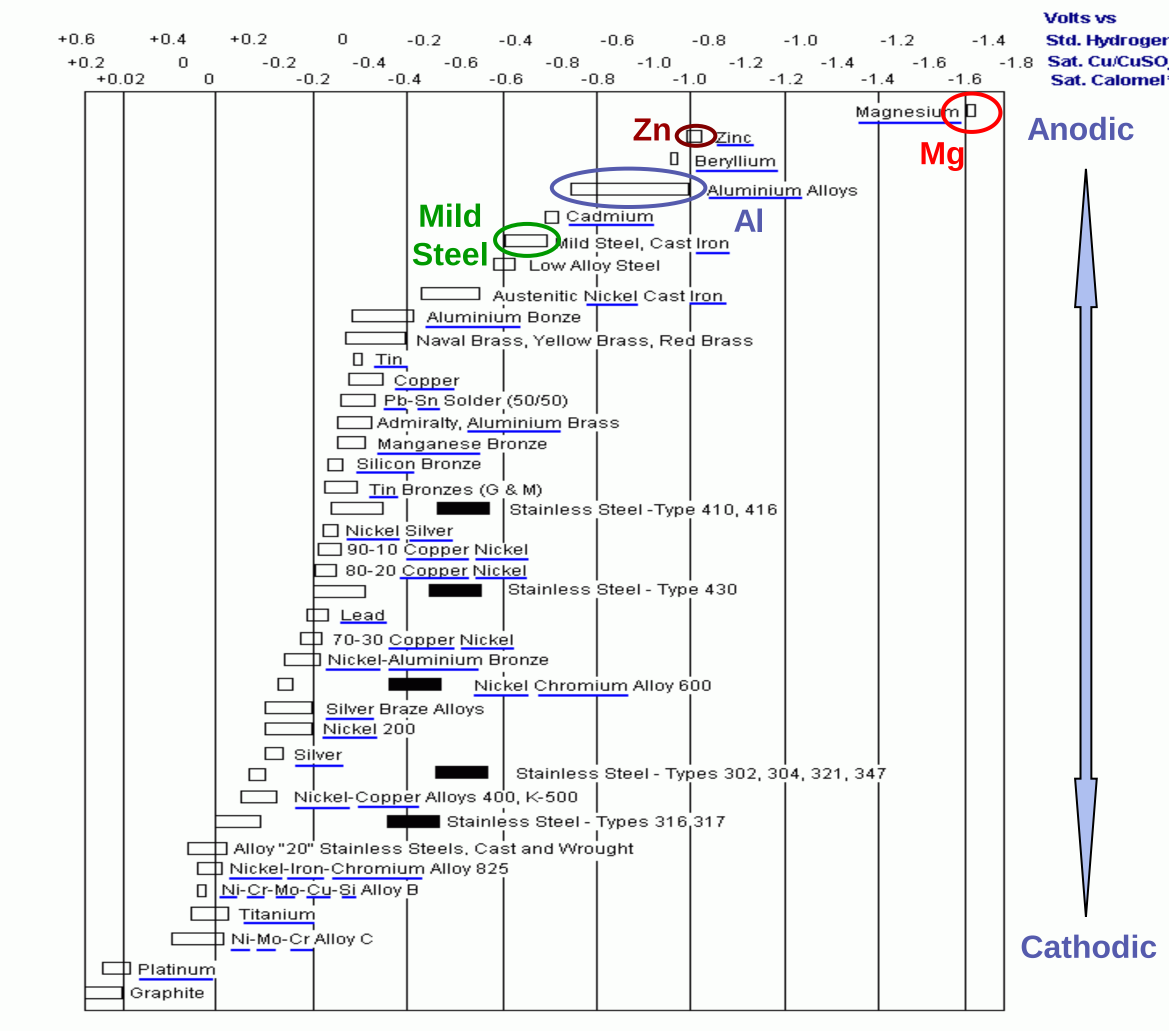
- Understanding macro-galvanic and micro-galvanic corrosion

What is galvanic corrosion?



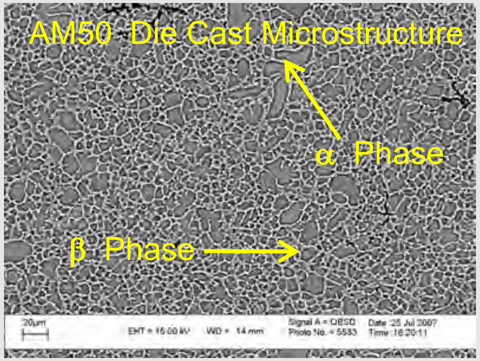
3 conditions for galvanic corrosion

- ➢Potential difference between dissimilar materials
- ➢Electrical contact between dissimilar material for electron transport
- ➢Exposure to conductive medium for ionic transport



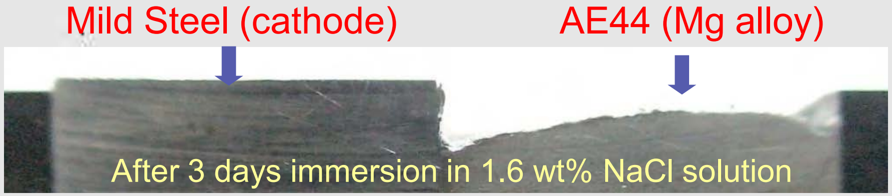
Modeling of Corrosion Phenomena

Micro-galvanic corrosion



Objective: To optimize the processing route to obtain the desirable microstructure for the better corrosion resistance

Macro-galvanic corrosion



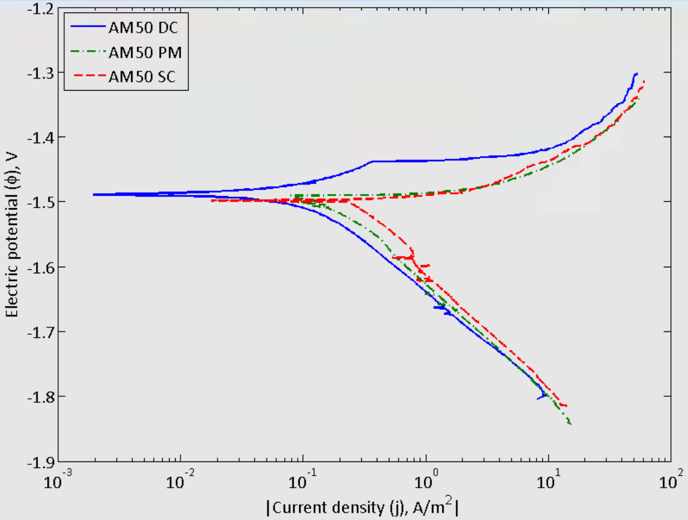
Objective: To develop a numerical tool to predict galvanic corrosion rate, which can provide design specifications

Microstructure – corrosion correlation

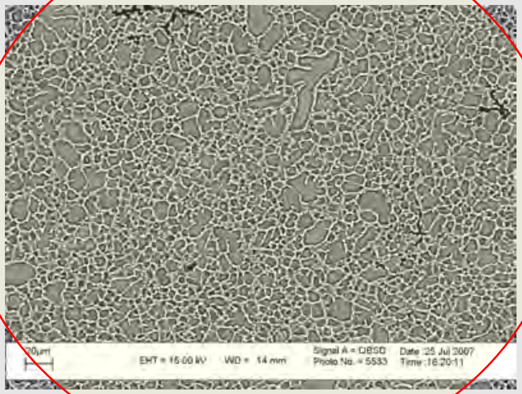
Alloy	Casting Process	E_{corr} (V)	β phase content %	i_{corr} (A/m^2)
AM50	Die Cast	-1.48	18.4	0.081
AM50	Permanent Mold	-1.5	1.08	0.182
AM50	Sand Cast	-1.5	0.61	0.269

E_{corr} - Corrosion Potential

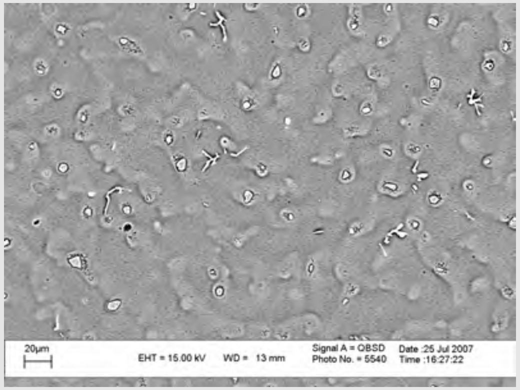
i_{corr} – Corrosion current density



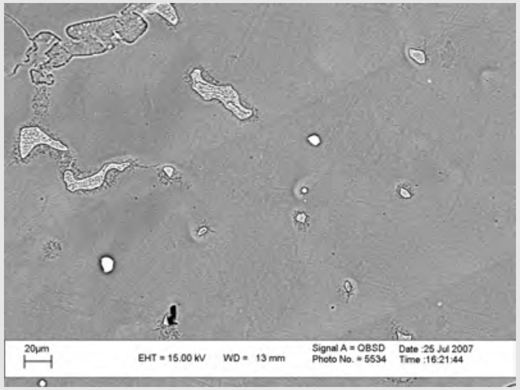
AM50 DC



AM50 PM



AM50 SC



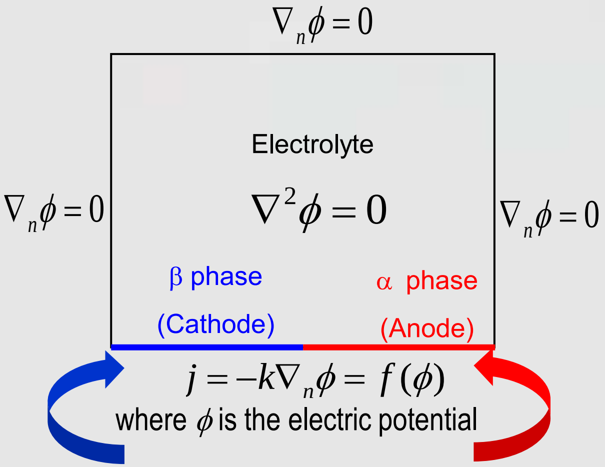
Microstructure effect on corrosion

- ☐ β phase fraction
- ☐ β phase Distribution
- ☐ Al content in the α phase

Reference: Sundarraj et al., Magnesium Technology 2008, TMS 2008.

Modeling approach

Model Schematic



$\nabla_n \phi = 0$

Electrolyte

$\nabla^2 \phi = 0$

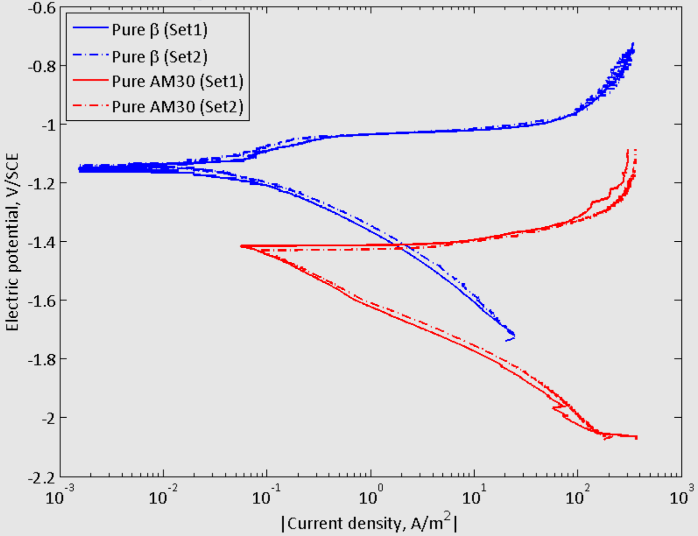
$\nabla_n \phi = 0$ $\nabla_n \phi = 0$

β phase (Cathode)

α phase (Anode)

$j = -k\nabla_n \phi = f(\phi)$

where ϕ is the electric potential



Assumptions

- ☐ Well mixed, incompressible and electro-neutral electrolyte solution
- ☐ Uniform Al content throughout alpha phase
- ☐ No interfacial resistance due to corrosion product is considered here
- ☐ The dissolution reaction is considered at the anode surface

Corrosion rate calculation

$$\boldsymbol{CR} = \boldsymbol{n}\cdot\mathbf{v} = K\frac{EW}{\rho}f_a(\phi),$$

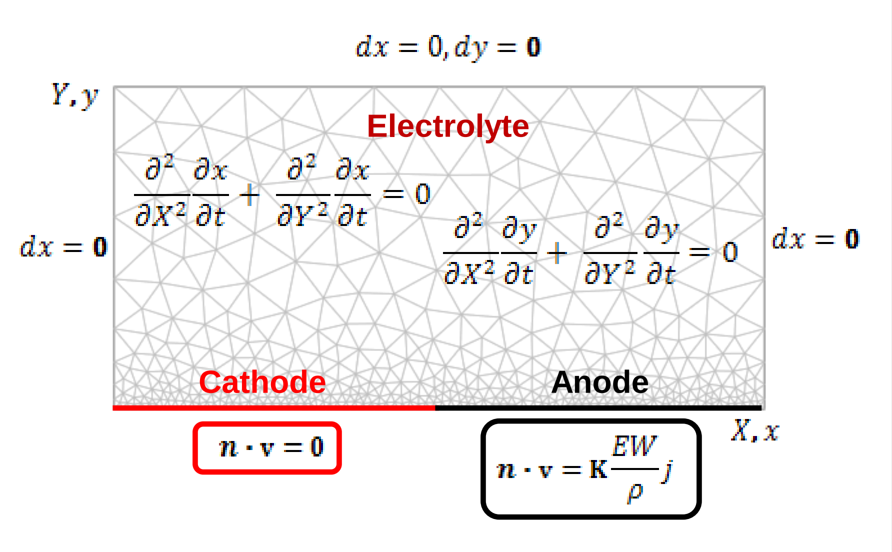
CR	Corrosion rate in m.sec^{-1}
$K = \frac{1}{F} = 1.03625 \times 10^{-5}$	mole.Amp^{-1}.sec^{-1}
EW	Equivalent weight in kg.mole^{-1}
ρ	Density in kg.m^{-3}
$f_a(\phi)$	anodic current density in Amp.m^{-2}

- ☐The model is capable of explicitly tracking the corroding phase.
- ☐The model predictions are based on non-linear polarization data.

Modeling Approach: moving boundary formulation

Arbitrary Lagrangian Eulerian (ALE) Method – COMSOL Multi-Physics®

Initial mesh


$dx = 0, dy = \mathbf{0}$

Y, y

Electrolyte

$$\frac{\partial^2}{\partial X^2}\frac{\partial x}{\partial t} + \frac{\partial^2}{\partial Y^2}\frac{\partial x}{\partial t} = 0$$

$$\frac{\partial^2}{\partial X^2}\frac{\partial y}{\partial t} + \frac{\partial^2}{\partial Y^2}\frac{\partial y}{\partial t} = 0$$

$dx = \mathbf{0}$

$dx = \mathbf{0}$

Cathode

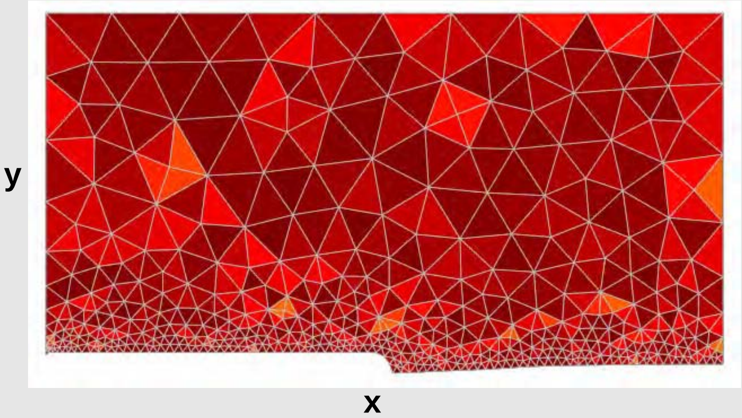
Anode

X, x

$\boldsymbol{n} \cdot \mathbf{v} = \mathbf{0}$

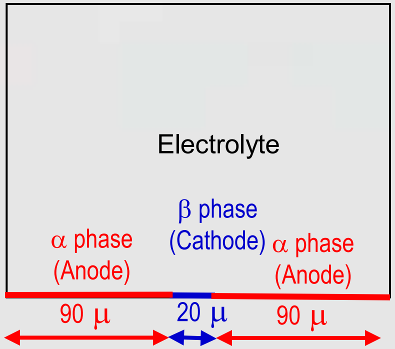
$\boldsymbol{n} \cdot \mathbf{v} = \mathrm{K}\frac{EW}{\rho} j$

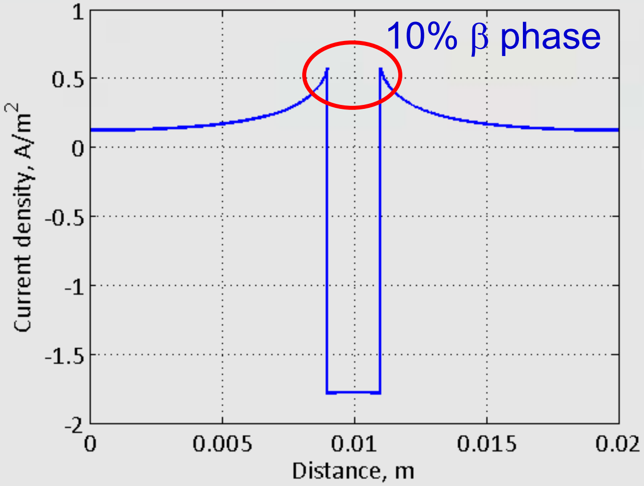
Deformed mesh

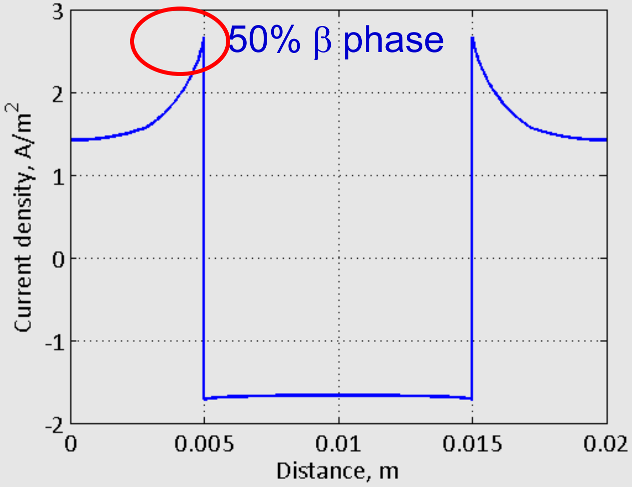


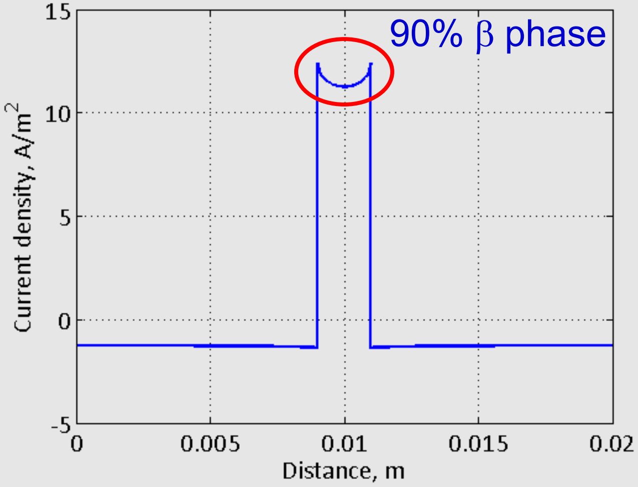
Effect of β phase fraction (area ratio)

Model Schematic







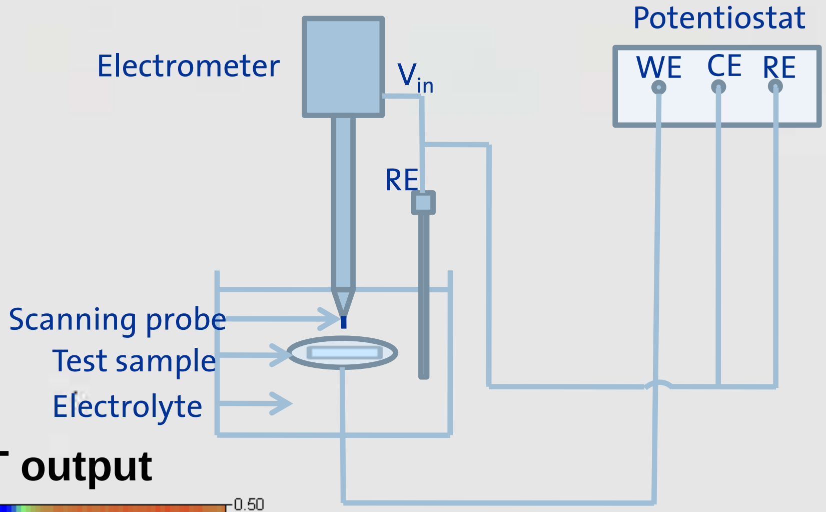


The maximum of anodic current density (corrosion rate)⇧ as β phase fraction⇧

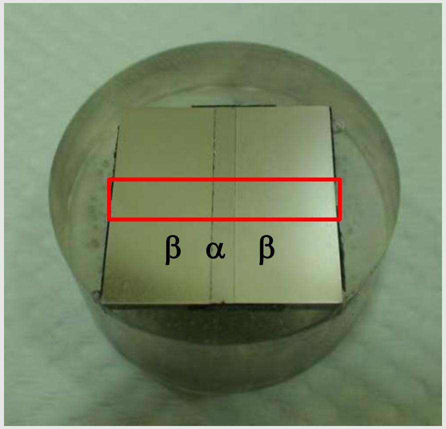
Scanning Vibrating Electrode Technique

Equipment

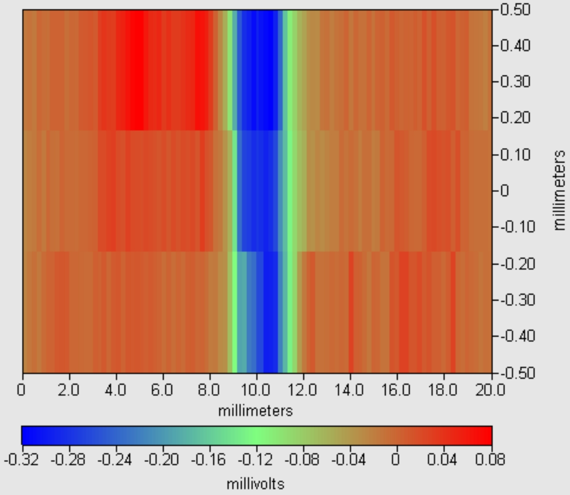
Schematic



Sample specimen



SVET output



Current density calculation

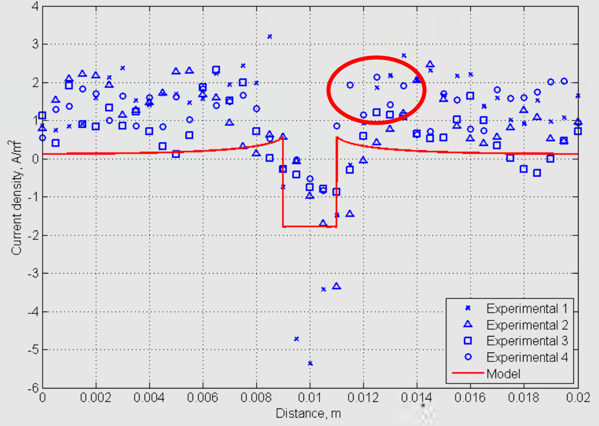
$$j = -\sigma \frac{\Delta E}{A}$$

j	Current density, Amp/m^2
σ	Conductivity, S/m
ΔE	Potential difference at the two extremes of amplitude of probe vibration, V
A	Amplitude of probe vibration, m

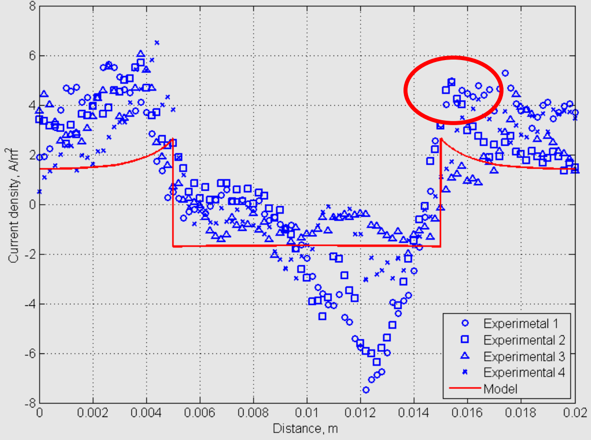
SVET experiments are performed on a galvanic couple where individual components are in direct physical and electrical contact, which eliminates IR drop.

Model - SVET Comparison

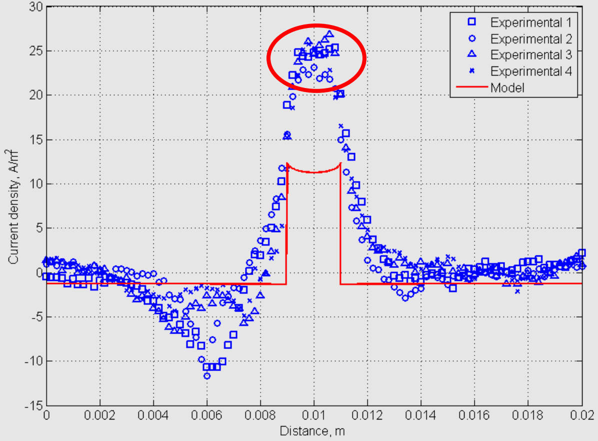
10% β phase



50% β phase



90% β phase



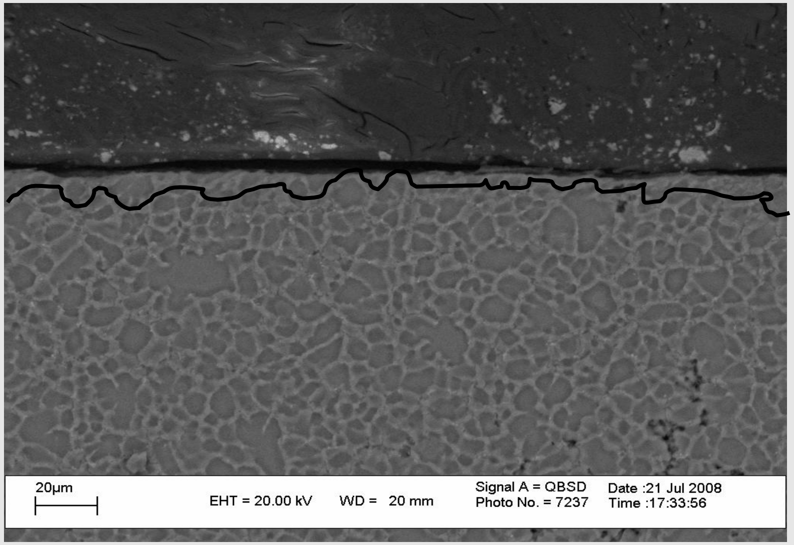
Model and SVET experiments : Corrosion rate ⇧ as β phase fraction ⇧

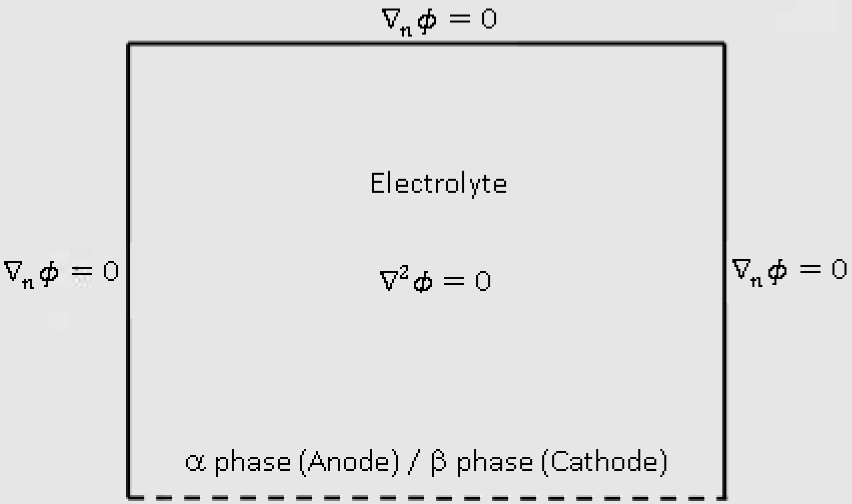
The corrosion rate AM50 dc was the lowest despite the highest β phase fraction

This behavior motivates us to investigate the effect of β phase distribution

Level set formulation

Microstructure of AM50 die cast along the depth





$$\nabla_n \phi = -\frac{f_a(\phi)}{\sigma} * (\phi_L > 0) - \frac{f_c(\phi)}{\sigma} * (\phi_L \leq 0)$$

❑A single boundary is used to specify the anode surface and the cathode surface using the level set function

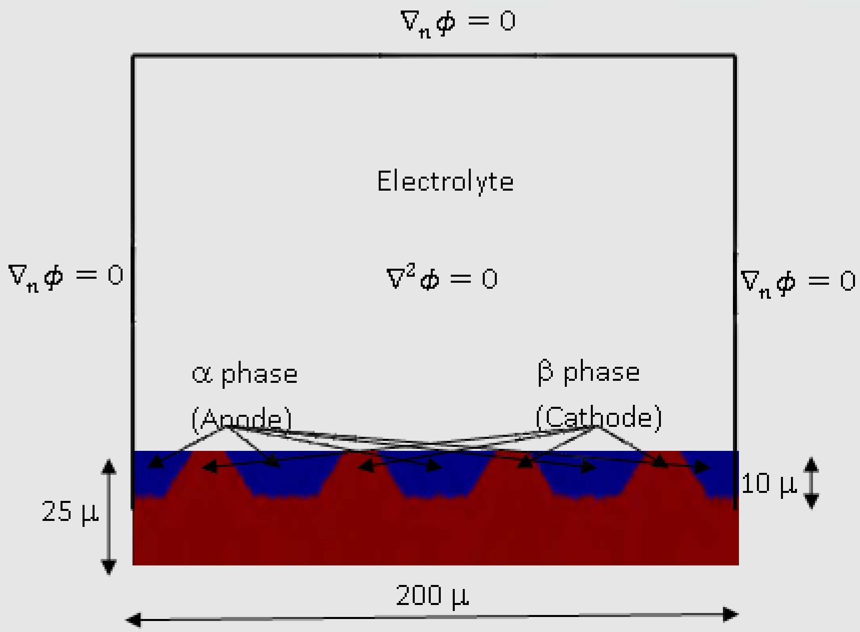
❑The above formulation can capture the varying ratios of the α phase and the β phase along the depth of the alloy

Acknowledgement: Shashank Tiwari for microstructure

Reference: K. B. Deshpande, Electrochimica Acta (2010), doi:10.1016/j.electacta.2010.09.044

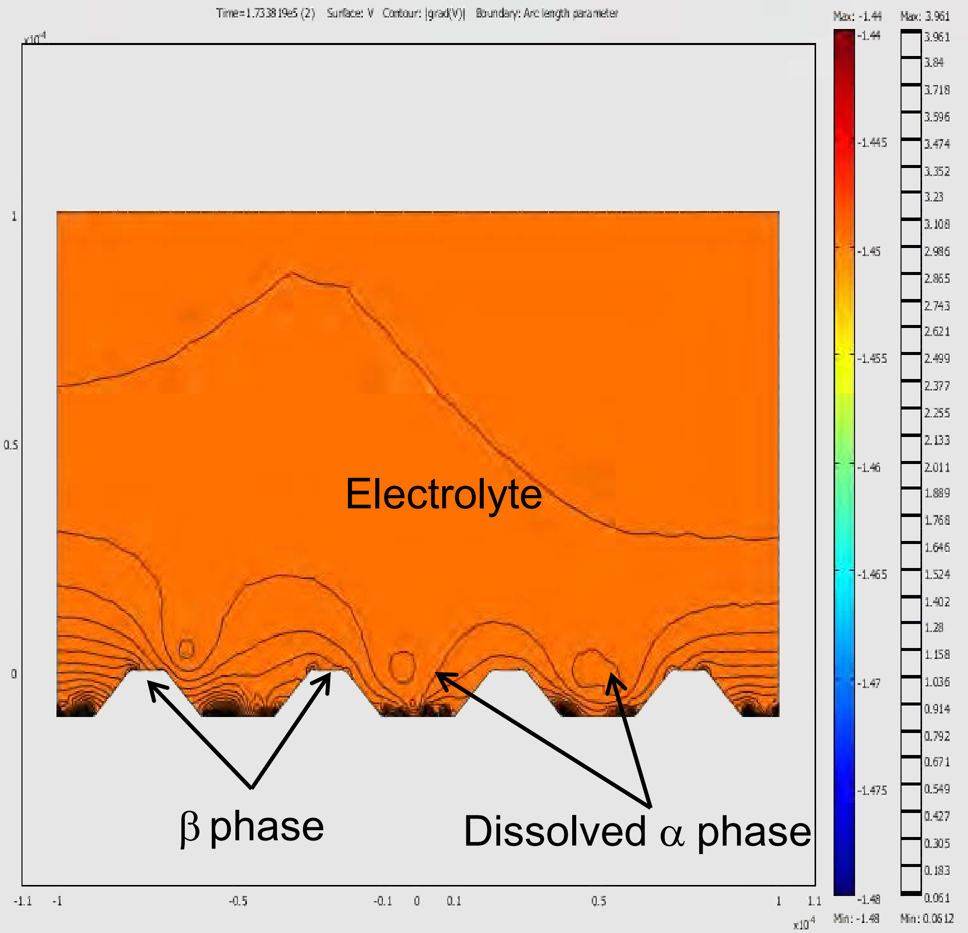
Continuous β phase network

Schematic of microstructure



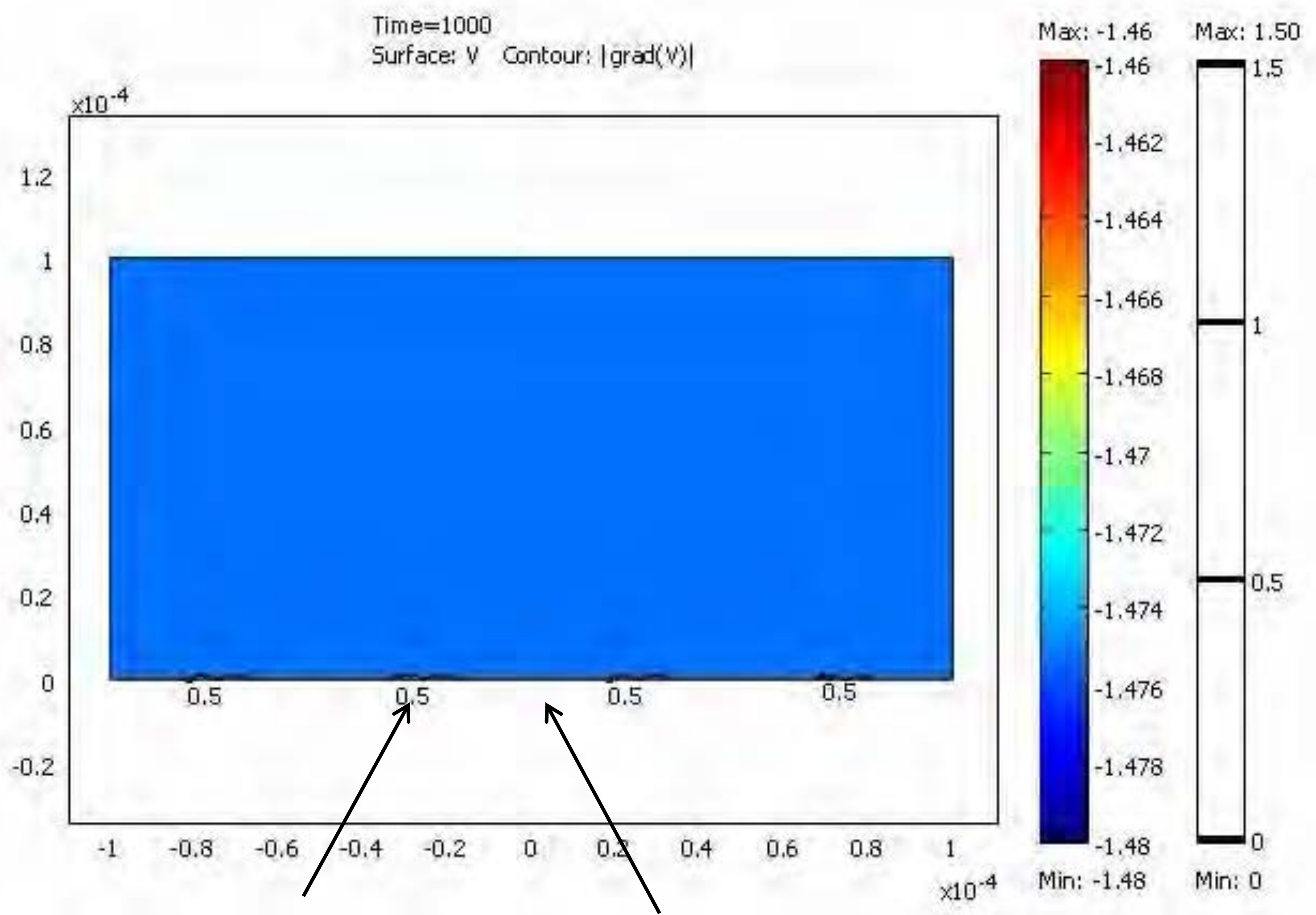
$$\nabla_n \phi = -\frac{f_a(\phi)}{\sigma} * (\phi_L > 0) - \frac{f_c(\phi)}{\sigma} * (\phi_L \leq 0)$$

Model prediction



α phase preferentially dissolves in electrolyte solution until continuous network of β phase is exposed to electrolyte solution after which corrosion is halted.

α phase dissolution

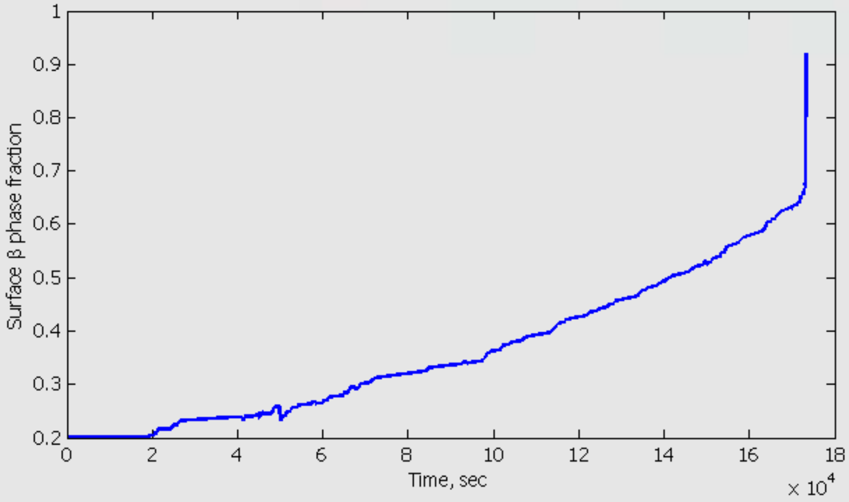


β phase

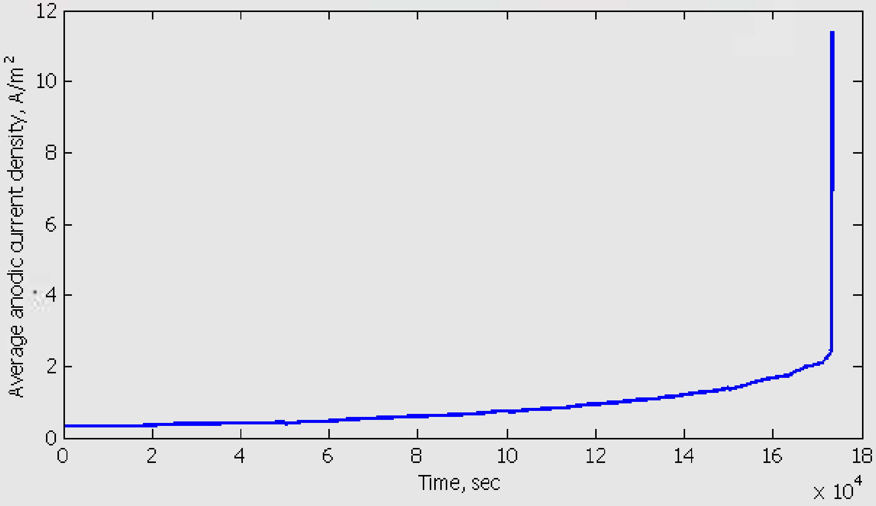
Dissolved α phase

Continuous β phase network

Surface β phase fraction evolution



Average anodic current density evolution



$$\text{Surface } \beta \text{ phase fraction} = \frac{\int_{\phi_L \le 0} d\Omega}{\int_{\phi_L \le 0} d\Omega + \int_{\phi_L > 0} d\Omega}$$

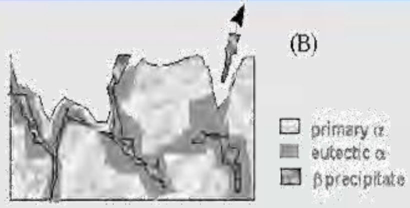
$$\text{Average anodic current density} = \frac{\int_{\phi_L > 0} f_a(\phi)\, d\Omega}{\int_{\phi_L > 0} d\Omega}$$

- Average anodic current density ⇧ as surface β phase fraction ⇧
- The corrosion activity is however halted after the α phase present on the surface is dissolved into the electrolyte solution.

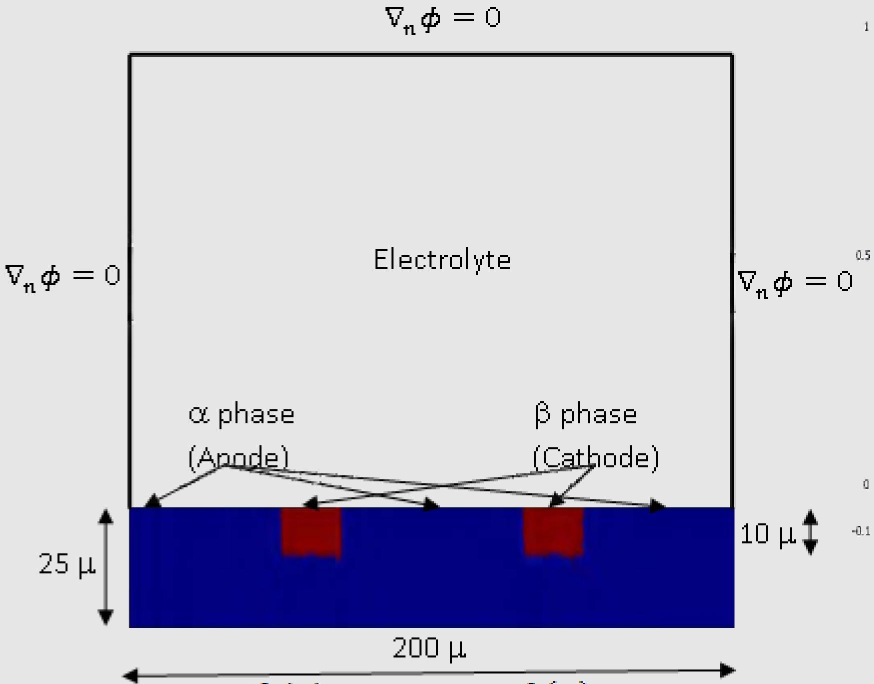
The total charge passed per square meter area = 1.3844×10^5 C/m²

The total mass of material removed per square meter area = 17.22 g/m²

Discrete β phase

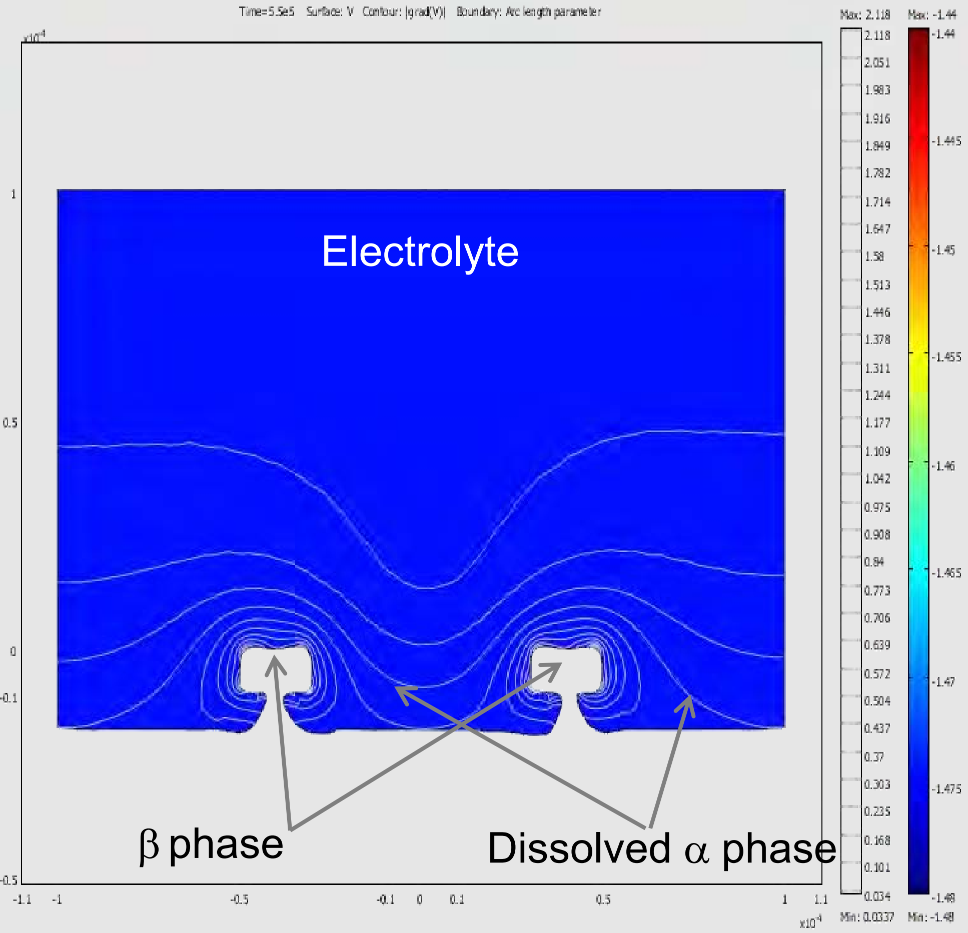


Schematic of microstructure



$$\nabla_n \phi = -\frac{f_a(\phi)}{\sigma} * (\phi_L > 0) - \frac{f_c(\phi)}{\sigma} * (\phi_L \leq 0)$$

Model prediction

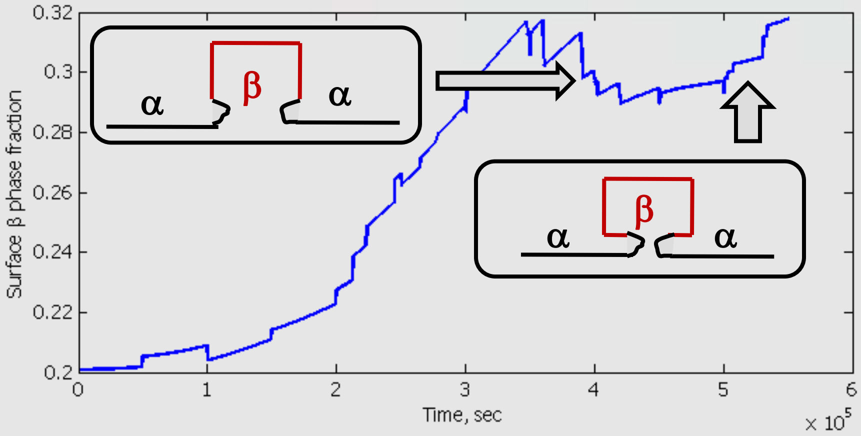


α phase continuously dissolves in the electrolyte solution as discontinuous β phase network assists corrosion. As discrete β phase is not well supported, β phase eventually spatters off.

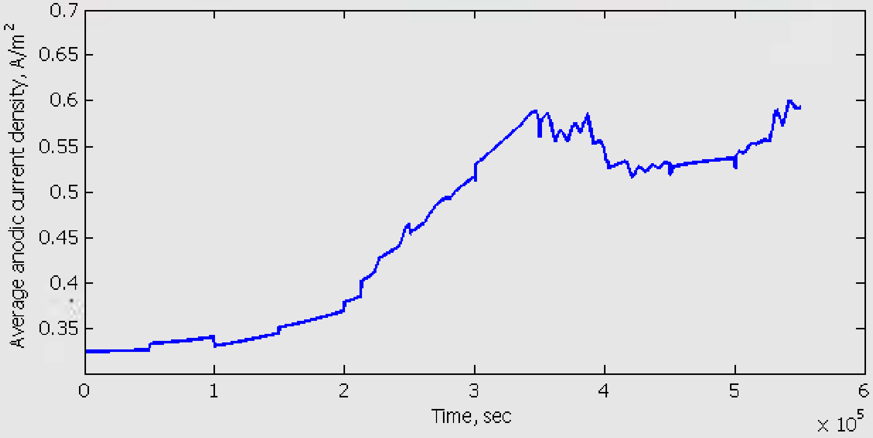
References: Ambat, et al., Corrosion Science, 42, 1433-1455 (2000); Song et al., Corrosion Science, 41, 249-273 (1999).

Discrete β phase

Surface β phase fraction evolution



Average anodic current density evolution



❑ Neck formation and neck thinning leading to β phase spattering is captured using the model.

❑ The corrosion activity lasts for a lot longer for discrete β phase than in continuous β phase network.

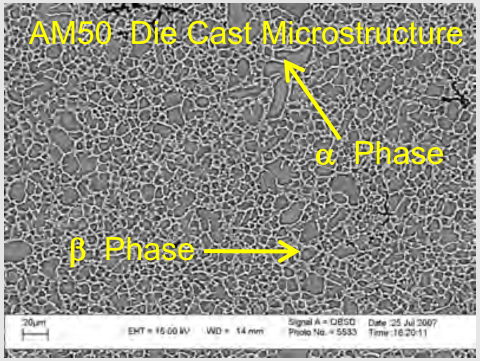
❑ The model captures the scenario leading to β phase spattering, but not the actual spattering as the model cannot capture topological changes.

The total charge passed per square meter area = 2.5060×10^5 C/m^2

The total mass of material removed per square meter area = 31.17 g/m^2

Modeling of Corrosion Phenomena

Micro-galvanic corrosion



Objective: To optimize the processing route to obtain the desirable microstructure for the better corrosion resistance

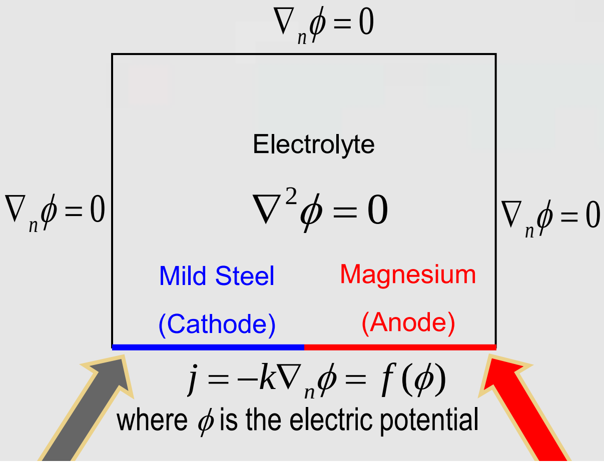
Macro-galvanic corrosion

After 3 days immersion in 1.6 wt% NaCl solution

Objective: To develop a numerical tool to predict galvanic corrosion rate, which can provide design specifications

Modeling approach

Model Schematic



$\nabla_n \phi = 0$

$\nabla_n \phi = 0$

Electrolyte

$\nabla^2 \phi = 0$

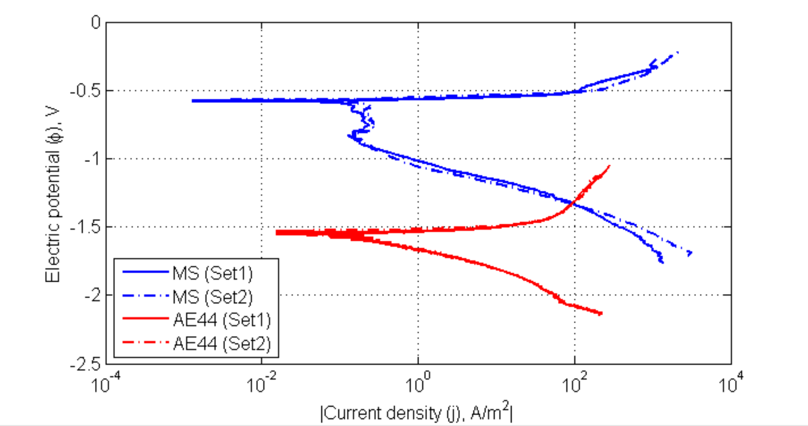
$\nabla_n \phi = 0$

Mild Steel (Cathode)

Magnesium (Anode)

$j = -k \nabla_n \phi = f(\phi)$

where ϕ is the electric potential



Assumptions

- ❑Well mixed, incompressible and electro-neutral electrolyte solution
- ❑No interfacial resistance due to corrosion product is considered here
- ❑Anode surface is assumed to be corroding and cathode surface is assumed to be non-corroding

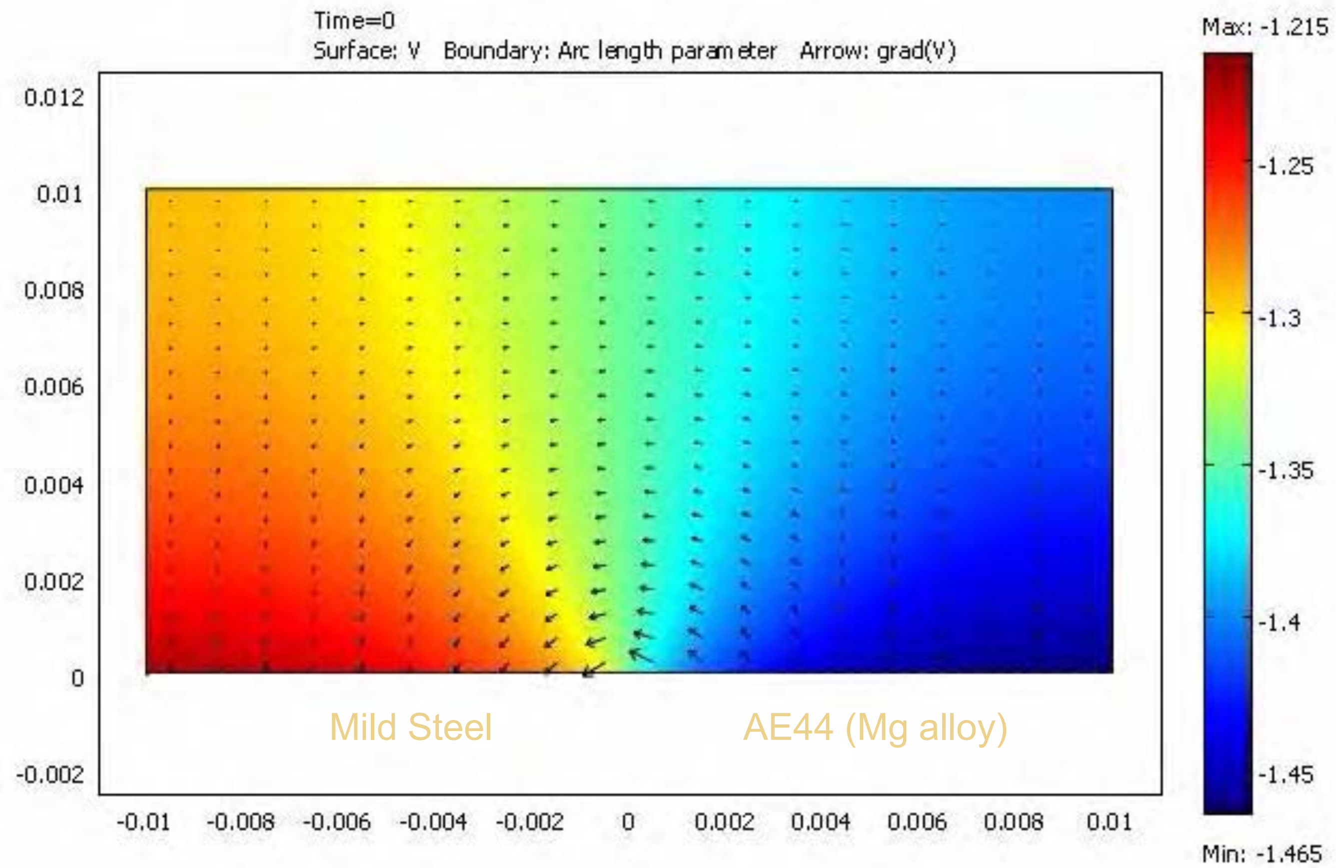
- ❑The model is capable of explicitly tracking the corroding phase.
- ❑The model predictions are based on non-linear polarization data.

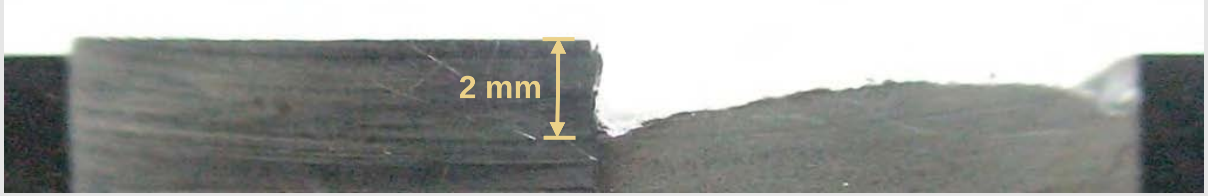
Corrosion rate calculation

$$CR = n \cdot \mathbf{v} = K \frac{EW}{\rho} f_a(\phi),$$

CR	Corrosion rate in m.sec^{-1}
$K = \frac{1}{F} = 1.03625 \times 10^{-5}$	mole.Amp^{-1}.sec^{-1}
EW	Equivalent weight in kg.mole^{-1}
ρ	Density in kg.m^{-3}
$f_a(\phi)$	anodic current density in Amp.m^{-2}

Animation capturing moving Mg surface

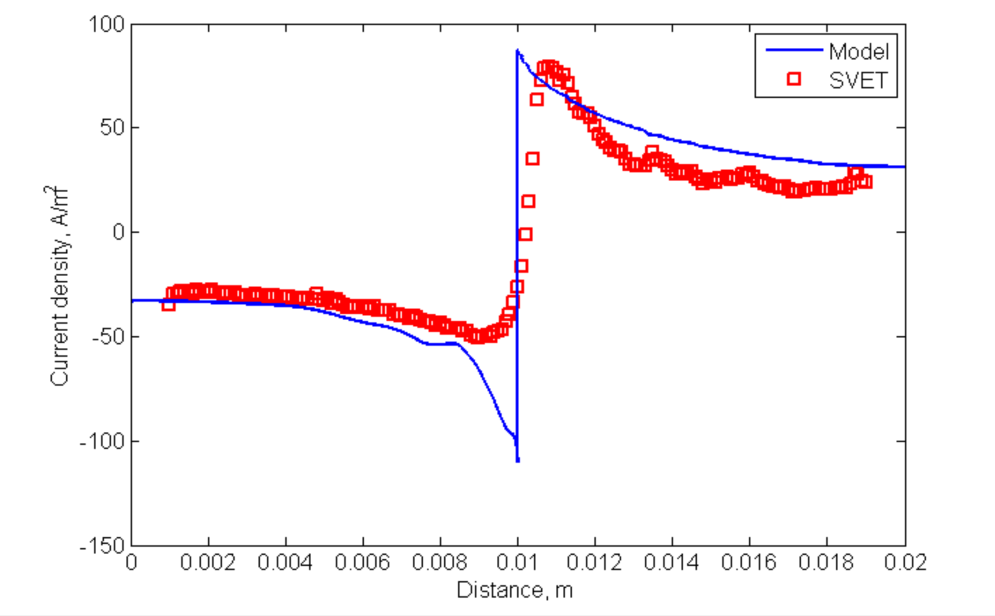




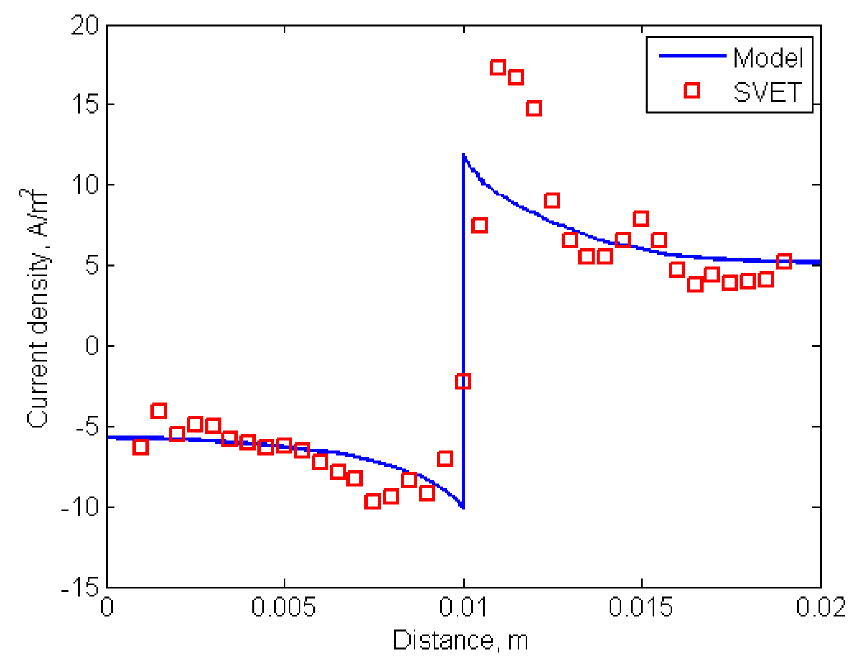
Photograph after cross-sectional cut of AE44 – MS couple after 3 days of immersion

SVET and model prediction

AE44 – Mild steel couple



AE44 – AA6063 couple

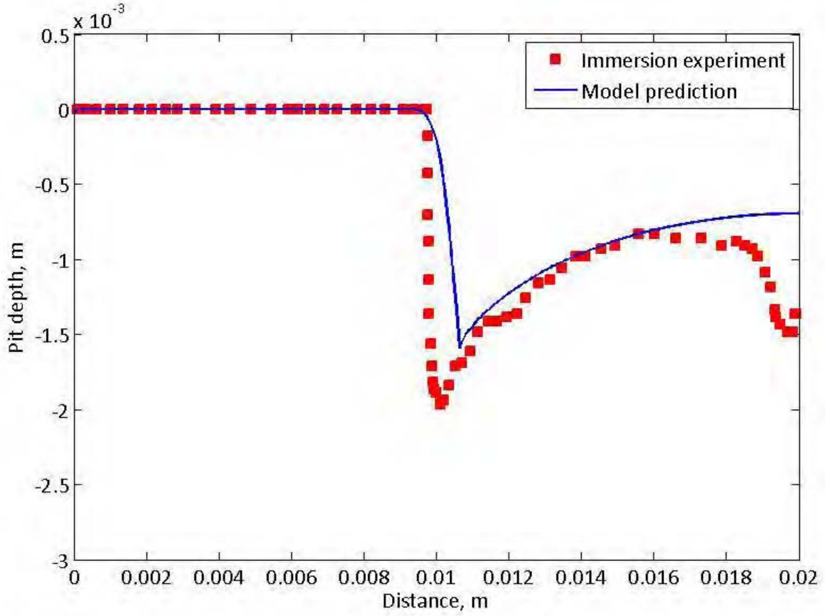


- The corrosion rate predicted using the numerical model is within +9% of that estimated using SVET analysis for AE44 – mild steel couple.
- The corrosion rate predicted using the numerical model is within -29% of that estimated using SVET analysis for AE44 – AA6063 couple.

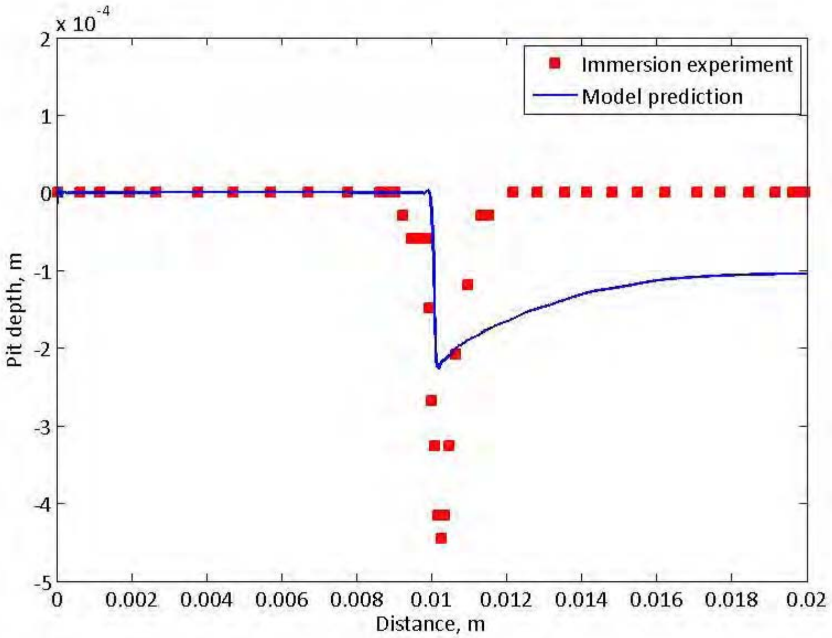
References: K. B. Deshpande, Corrosion Science, 52 (2010) 2819 – 2826
K. B. Deshpande, Corrosion Science, 52 (2010) 3514 - 3522

Immersion and model prediction

AE44 – Mild steel couple



AE44 – AA6063 couple



❑The corrosion rate predicted using the numerical model is within -20% of that estimated from immersion technique for AE44 – mild steel couple.

❑The corrosion rate predicted using the numerical model is within -47% of that estimated from immersion technique for AE44 – AA6063 couple.

Acknowledgement: Sampath Vanimisetti (Image digitization)

Summary

Galvanic Couples	Corrosion rate (mm/y)			
	SVET experiments	Immersion experiments	Mixed Potential Theory	ALE method
AE44 - MS	197	243	231	210
AE44 – AA6063	42	52	26	29

The corrosion rate predicted using the numerical model is in good agreement with that estimated from the two experimental techniques.

The galvanic corrosion behavior is demonstrated at both macro and micro scale using the numerical model developed using COMSOL Multi-Physics®.

Thank You!!