

Localized Corrosion Using the Phase Field Method

Introduction

This example models the galvanic corrosion between the two constituent phases of a metallic alloy. Since the two phases have different equilibrium potentials corrosion occurs when the alloy is exposed to an electrolyte solution. The Present model is similar to the Localized Corrosion Using the Level Set Method example, except that the Phase Field method is used here instead of the Level Set method to capture dissolution of a constituent phase.

This model example is based on a paper by Deshpande (Ref. 1).

Model Definition

The model geometry considered in this example is shown in Figure 1, along with a representative cross-sectional microstructure, which consists of the alpha and beta phases exposed to the electrolyte solution.



Figure 1: Model geometry along with cross-sectional microstructure comprising of the alpha and beta phases and exposed to the electrolyte solution.

The cross-sectional microstructure shown in Figure 1 is represented in terms of an interpolation function called "micro" which has a value of 0 and 1 for the alpha and beta

phases, respectively. The metal alloy geometry has a width of $200 \,\mu\text{m}$ and a depth of $40 \,\mu\text{m}$. The maximum depth of the beta phase is $10 \,\mu\text{m}$.

ELECTROLYTE CHARGE TRANSPORT

Use the Secondary Current Distribution interface to solve for the electrolyte potential, $\phi_l(V)$, over the electrolyte domain according to Ohm's law:

$$\mathbf{i}_l = -\sigma_l \nabla \phi_l$$
$$\nabla \cdot \mathbf{i}_l = 0$$

where \mathbf{i}_l (SI unit: A/m²) is the electrolyte current density vector.

The electrolyte conductivity, σ_l (SI unit: S/m), is defined for the electrolyte and electrode domains separately using the electrolyte volume fraction defined in terms of phase field variable, ϕ , according to

$$\sigma_l = \sigma_{ed} \times V_{f1} + \sigma_{el} \times V_{f2}$$

where σ_{el} is the electrolyte conductivity in the electrolyte domain and is considered to be equal to 2.5 S/m and σ_{ed} is the electrolyte conductivity in the electrode domain and is considered to be equal to 0.1 S/m. Furthermore, V_{f1} and V_{f2} are the electrolyte volume fractions in electrode and electrolyte domains, respectively. While the electrolyte conductivity in electrolyte domain describes the actual chemistry of the problem, the electrolyte conductivity in the electrode domain is defined only to aid numerical convergence.

Use the default Insulation condition for all exterior boundaries:

$$\mathbf{n} \cdot \mathbf{i}_{I} = 0$$

where **n** is the normal vector, pointing out of the domain.

Use an Electrolyte Current Source domain node to define the electrode kinetics at the corroding boundary:

$$Q_l = i_{loc}\delta$$

where i_{loc} (SI unit: A/m²) is the local electrode reaction current density and δ (SI unit: 1/m) is the phase field delta function.

Use a user-defined electrode kinetics expression to model the electrode reaction at the alpha and beta phases on the electrode surface.

Set the local current density for the alpha phase at the electrode surface to

$$i_{\text{alpha}} = f(\phi_{s, \text{ext}} - \phi_l) \times (1 - \text{micro}(x, y))$$

The 1-micro(x,y) factor ensures that the local current density is applied only at the alpha phase on the electrode surface.

Similarly, use the following expression for the local current density at the beta phase:

$$i_{\text{beta}} = f(\phi_{s, \text{ext}} - \phi_l) \times \text{micro}(x, y)$$

The interpolation function micro(x, y) ensures that the local current density is applied only at the beta phase on the electrode surface.

A relationship between the local current density and the electrolyte potential, $f(\phi_{s, \text{ext}} - \phi_l)$, is incorporated in the model using a piecewise cubic interpolation function for the experimental polarization data. The same polarization data as used in the Localized Corrosion example is used here for the alpha and beta phases.

Set the local current density for the alpha and beta phases at the electrode surface according to

$$i_{\rm loc} = i_{\rm alpha} + i_{\rm beta}$$

CORROSION INTERFACE TRACKING

Use the Phase Field interface to keep track of dissolution of the alpha phase. In the Phase Field interface the two-phase flow dynamics is governed by a Cahn-Hilliard equation. The equation tracks a diffuse interface separating the immiscible phases. The diffuse interface is defined as the region where the dimensionless phase field variable ϕ goes from -1 in the electrode domain to 1 in the electrolyte domain. When solved in COMSOL Multiphysics, the Cahn-Hilliard equation is split up into two equations

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \nabla \cdot \frac{\gamma \lambda}{\varepsilon^2} \nabla \psi$$
$$\psi = -\nabla \cdot \varepsilon^2 \nabla \phi + (\phi^2 - 1)\phi$$

where **u** is the interface velocity (m/s), γ is the mobility $(m^3 \cdot s/kg)$, λ is the mixing energy density (N) and ϵ (m) is the interface thickness parameter. The ψ variable is referred to as the phase field help variable. The following equation relates the mixing energy density and the interface thickness to the surface tension coefficient:

$$\sigma = \frac{2\sqrt{2}\lambda}{3\epsilon}$$

In the present model, the interface thickness parameter is set to $\varepsilon = h_{\text{max}}/32$, where h_{max} is the maximum mesh element size in the domain. The mobility parameter γ determines the time scale of the Cahn-Hilliard diffusion and must be chosen judiciously. It must be large enough to retain a constant interfacial thickness but small enough so that the convective terms are not overly damped. A suitable value for γ is the maximum velocity magnitude occurring in the model.

In this model formulation, it is assumed that the anodic dissolution reaction takes place at the alpha phase surface, and that the cathodic hydrogen evolution reaction (which is not associated with any loss of material) takes place at the beta phase surface. Hence, the alpha phase surface will move (dissolve) whereas the beta phase surface remains intact. This is achieved in the model by setting the alpha phase dissolution velocity in normal direction according to

$$\mathbf{u} = \mathbf{n} \cdot \left(\frac{i_{\text{loc}}}{2F} \frac{M_{\text{Mg}}}{\rho_{\text{Mg}}} \times (1 - \text{micro}(x, y))\right)$$

where M_{Mg} is the mean molar mass (23.98 g/mol) and ρ_{Mg} is the density (1770 kg/m³) of the magnesium alloy.

The interface normal **n** is calculated as:

$$\mathbf{n} = \frac{\nabla \phi}{|\nabla \phi|}$$

In the Phase Field interface, the volume fractions of the individual fluids are

$$V_{\rm f1} = 1 - V_{\rm f2}, \qquad V_{\rm f2} = \frac{1 + \phi}{2}$$

In the present model, the electrode domain is defined as Fluid 1 and the electrolyte domain as Fluid 2.

The phase field delta function is approximated by:

$$\delta = \frac{3}{4}(1 - \phi^2) |\nabla \phi|$$

Use the Inlet boundary node for the exterior boundaries of the electrolyte domain and set the phase field variable to 1 at those boundaries.

Use the Outlet boundary node for the exterior boundaries of the electrode domain.

To set the initial interface position, use the Initial Interface boundary node for the interior boundary between the electrolyte and electrode domains.

Results and Discussion

Figure 2 shows a surface plot of the electrolyte potential at time t = 300 h. It can be seen that the alpha phase, being electrochemically more active, is dissolving from the electrode surface whereas the beta phase, being relatively nobler, remains intact. With the preferential dissolution of the alpha phase, the underlying beta phase gets exposed to the electrolyte solution, resulting in an increase in the surface beta phase fraction at the electrode surface. It can be seen in Figure 2 that the alpha phase in the electrode domain, as shown in Figure 1, is dissolved in the electrolyte solution. The dissolved alpha phase and intact beta phase are highlighted in Figure 2 at time t = 300 h.



Figure 2: A surface plot of the electrolyte potential at time t = 300 h where the dissolved alpha phase and intact beta phase are highlighted.

Figure 3 shows a surface plot of the volume fraction of fluid 2 at time t = 300 h. The volume fraction of value 1 represents the electrolyte domain and 0 represents the electrode domain. The dissolved alpha phase, undissolved alpha phase and intact beta phase regions

of the electrode domain are highlighted in Figure 3 at time t = 300 h. Since the Phase Field method can handle topological changes, the computations are continued even after the beta phase falls off the electrode surface.



Figure 3: A surface plot of the volume fraction of fluid 2 at time t = 300 h where the value of 1 is the electrolyte domain and 0 is the intact beta phase and the undissolved alpha phase in the electrode domain.

Reference

1. K.B. Deshpande, "Numerical modeling of micro-galvanic corrosion," *Electrochimica Acta*, vol. 56, pp 1737–1745, 2011.

Application Library path: Corrosion_Module/General_Corrosion/ localized_corrosion_pf

Modeling Instructions

From the File menu, choose New.

NEW

In the New window, click 🔗 Model Wizard.

MODEL WIZARD

- I In the Model Wizard window, click **2D**.
- 2 In the Select Physics tree, select Electrochemistry>

Primary and Secondary Current Distribution>Secondary Current Distribution (cd).

- 3 Click Add.
- 4 In the Select Physics tree, select Mathematics>Moving Interface>Phase Field (pf).
- 5 Click Add.
- 6 Click 🔿 Study.
- 7 In the Select Study tree, select Preset Studies for Selected Physics Interfaces>Phase Field> Time Dependent with Phase Initialization.
- 8 Click **M** Done.

GEOMETRY I

Now, create the model geometry by adding two rectangles.

Rectangle 1 (r1)

- I In the Geometry toolbar, click Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- 3 In the Width text field, type 200e-6.
- 4 In the **Height** text field, type 100e-6.
- 5 Locate the **Position** section. In the **x** text field, type -100e-6.

Rectangle 2 (r2)

- I In the Geometry toolbar, click Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- 3 In the Width text field, type 200e-6.
- 4 In the **Height** text field, type 40e-6.
- 5 Locate the Position section. In the x text field, type -100e-6.
- 6 In the y text field, type -40e-6.
- 7 Click 🟢 Build All Objects.
- **8** Click the \longleftrightarrow **Zoom Extents** button in the **Graphics** toolbar.

GLOBAL DEFINITIONS

Now, create a predefined cross-sectional microstructure, which gets exposed to the electrolyte solution at the bottom boundary of the electrolyte domain, using an interpolation function. Please note that the interpolation function creates a similar microstructure as reported in Ref. 1.

Interpolation 1 (int1)

- I In the Home toolbar, click f(X) Functions and choose Global>Interpolation.
- 2 In the Settings window for Interpolation, locate the Definition section.
- 3 From the Data source list, choose File.
- 4 Click **Prowse**.
- 5 Browse to the model's Application Libraries folder and double-click the file localized_corrosion_ls_microstructure.txt.
- 6 Click **[]** Import.
- 7 Find the Functions subsection. In the table, enter the following settings:

Function name	Position in file
micro	1

8 Locate the Units section. In the Argument table, enter the following settings:

Argument	Unit
Column I	m

9 In the Function table, enter the following settings:

Function	Unit
micro	1

IO Click 🚮 Create Plot.

RESULTS

- 2D Plot Group 1
- I In the Settings window for 2D Plot Group, locate the Plot Settings section.
- 2 From the View list, choose View I.
- 3 In the Model Builder window, expand the 2D Plot Group I node.

Height Expression 1

I In the Model Builder window, expand the Results>2D Plot Group I>Function I node.

2 Right-click Height Expression I and choose Disable.

2D Plot Group : Cross-sectional microstructure

- I In the Model Builder window, under Results click 2D Plot Group I.
- 2 In the Settings window for 2D Plot Group, type 2D Plot Group : Cross-sectional microstructure in the Label text field.
- **3** Click the 4 **Zoom Extents** button in the **Graphics** toolbar.

The cross-sectional microstructure should look like this:



GLOBAL DEFINITIONS

Load the model parameters.

Parameters 1

- I In the Model Builder window, under Global Definitions click Parameters I.
- 2 In the Settings window for Parameters, locate the Parameters section.
- **3** Click **b** Load from File.
- **4** Browse to the model's Application Libraries folder and double-click the file localized_corrosion_parameters.txt.

DEFINITIONS

Now, create interpolation functions for the alpha phase and beta phase to prescribe a piecewise cubic relationship between the local current density and the electrolyte potential obtained from the experimental polarization data (Ref. 1).

Interpolation 2 (int2)

- I In the Home toolbar, click f(x) Functions and choose Local>Interpolation.
- 2 In the Settings window for Interpolation, locate the Definition section.
- **3** In the **Function name** text field, type i_alpha.
- 4 Click **b** Load from File.
- 5 Browse to the model's Application Libraries folder and double-click the file localized_corrosion_i_alpha.txt.
- 6 Locate the Interpolation and Extrapolation section. From the Interpolation list, choose Piecewise cubic.
- 7 From the Extrapolation list, choose Linear.
- 8 Locate the Units section. In the Argument table, enter the following settings:

Argument	Unit
t	V

9 In the **Function** table, enter the following settings:

Function	Unit
i_alpha	A/m^2

IO Click 💿 Plot.

The interpolation plot for the alpha phase should look like this:



Interpolation 3 (int3)

- I In the Home toolbar, click f(X) Functions and choose Local>Interpolation.
- 2 In the Settings window for Interpolation, locate the Definition section.
- 3 In the Function name text field, type i_beta.
- 4 Click 📂 Load from File.
- 5 Browse to the model's Application Libraries folder and double-click the file localized_corrosion_i_beta.txt.
- 6 Locate the Interpolation and Extrapolation section. From the Interpolation list, choose Piecewise cubic.
- 7 From the Extrapolation list, choose Linear.
- 8 Locate the Units section. In the Argument table, enter the following settings:

Argument	Unit
t	V

9 In the **Function** table, enter the following settings:

Function	Unit
i_beta	A/m^2

10 Click 💿 Plot.

The interpolation plot for the beta phase should look like this:



Variables I

Now, load the model variables.

- I In the Home toolbar, click a= Variables and choose Local Variables.
- 2 In the Settings window for Variables, locate the Variables section.
- **3** Click **b** Load from File.
- **4** Browse to the model's Application Libraries folder and double-click the file localized_corrosion_pf_variables.txt.

SECONDARY CURRENT DISTRIBUTION (CD)

Now set up the physics for the current distribution. First, set the electrolyte conductivity and then prescribe the electrode kinetics for both the alpha phase and beta phase making use of the interpolated function, micro(x,y). Also, note that the electrode kinetics is

prescribed as an electrolyte current source term using the phase field delta function, pf.delta.

Electrolyte I

- I In the Model Builder window, under Component I (compl)> Secondary Current Distribution (cd) click Electrolyte I.
- 2 In the Settings window for Electrolyte, locate the Electrolyte section.
- **3** From the σ_l list, choose **User defined**. In the associated text field, type sigmae.
- **4** Click the **5** Show More Options button in the Model Builder toolbar.
- 5 In the Show More Options dialog box, in the tree, select the check box for the node Physics>Advanced Physics Options.
- 6 Click OK.

Electrolyte Current Source 1

- I In the Physics toolbar, click 🔵 Domains and choose Electrolyte Current Source.
- 2 Click in the Graphics window and then press Ctrl+A to select both domains.
- **3** In the Settings window for Electrolyte Current Source, locate the Electrolyte Current Source section.
- **4** In the Q_1 text field, type i_loc*pf.delta.

PHASE FIELD (PF)

Now, set up the phase field physics to track the position of dissolving alpha phase interface. Set up the Phase Field model by specifying the parameter controlling interface thickness, mobility tuning parameter, and velocity field.

Phase Field Model I

- I In the Model Builder window, under Component I (comp1)>Phase Field (pf) click Phase Field Model I.
- 2 In the Settings window for Phase Field Model, locate the Phase Field Parameters section.
- **3** In the ε_{pf} text field, type pf.hmax/16.
- 4 From the Mobility tuning parameter list, choose Calculate from velocity.
- 5 In the U text field, type max(Vn,eps).
- 6 Locate the Convection section. Specify the u vector as

Vn*pf.intnormx x

Vn*pf.intnormy y

Initial Values 1

Set the initial value of phase field function to -1 for the electrolyte domain and 1 for the electrode domain.

Initial Values, Fluid 2

I In the Model Builder window, click Initial Values, Fluid 2.

2 Select Domain 1 only.

Inlet 1

Set the inlet for phase field function.

I In the Physics toolbar, click — Boundaries and choose Inlet.

2 Select Boundary 5 only.

Outlet I

Set the outlet for phase field function.

I In the Physics toolbar, click — Boundaries and choose Outlet.

2 Select Boundary 2 only.

MESH I

Now, mesh a computational domain with a finer resolution at the electrode surface.

Size

- I In the Model Builder window, under Component I (comp1) right-click Mesh I and choose Edit Physics-Induced Sequence.
- 2 In the Settings window for Size, locate the Element Size section.
- 3 From the Predefined list, choose Normal.

Size 1

- I In the Model Builder window, right-click Free Triangular I and choose Size.
- 2 In the Settings window for Size, locate the Geometric Entity Selection section.
- 3 From the Geometric entity level list, choose Domain.
- **4** Select Domain 2 only.
- 5 Locate the Element Size section. From the Calibrate for list, choose Fluid dynamics.

Size 2

- I Right-click Free Triangular I and choose Size.
- 2 In the Settings window for Size, locate the Geometric Entity Selection section.
- 3 From the Geometric entity level list, choose Domain.

- **4** Select Domain 1 only.
- 5 Locate the Element Size section. From the Calibrate for list, choose Fluid dynamics.
- **6** From the **Predefined** list, choose **Extremely fine**.
- 7 In the Model Builder window, right-click Mesh I and choose Build All.

The mesh should look like this:



STUDY I

Finally, clear solve for check box for Secondary Current Distribution interface in Phase Initialization study node and set the time steps for time dependent solver.

Step 1: Phase Initialization

- I In the Model Builder window, under Study I click Step I: Phase Initialization.
- **2** In the **Settings** window for **Phase Initialization**, locate the **Physics and Variables Selection** section.
- 3 In the table, clear the Solve for check box for Secondary Current Distribution (cd).

Step 2: Time Dependent

- I In the Model Builder window, click Step 2: Time Dependent.
- 2 In the Settings window for Time Dependent, locate the Study Settings section.

- 3 From the Time unit list, choose h.
- 4 In the **Output times** text field, type range(0,1,300).

Solution 1 (soll)

I In the Study toolbar, click **Show Default Solver**.

Store the actual steps taken by the solver to avoid interpolation issues in the stored solution.

- 2 In the Model Builder window, expand the Solution I (soll) node, then click Time-Dependent Solver I.
- 3 In the Settings window for Time-Dependent Solver, locate the General section.
- 4 From the Times to store list, choose Steps taken by solver closest to output times.

The model is now ready to be solved.

5 In the **Study** toolbar, click **= Compute**.

RESULTS

Surface plots of the electrolyte potential and volume fraction of fluid 1 representing dissolution of alpha phase are plotted by default. Update these default plots by following the below steps to reproduce the plots from the Results and Discussion section.

Surface 1

In the Model Builder window, expand the Electrolyte Potential (cd) node, then click Surface I.

Filter I

- I In the Electrolyte Potential (cd) toolbar, click 🔫 Filter.
- 2 In the Settings window for Filter, locate the Element Selection section.
- **3** In the **Logical expression for inclusion** text field, type phipf<=0.

Streamline 1

- I In the Model Builder window, under Results>Electrolyte Potential (cd) click Streamline I.
- 2 In the Settings window for Streamline, locate the Coloring and Style section.
- 3 Find the Point style subsection. From the Arrow length list, choose Normalized.
- 4 Select the Scale factor check box. In the associated text field, type 2e-6.

Filter I

- I Right-click Streamline I and choose Filter.
- 2 In the Settings window for Filter, locate the Element Selection section.

3 In the **Logical expression for inclusion** text field, type phipf<=0.

Electrolyte Potential (cd)

- I In the Model Builder window, under Results click Electrolyte Potential (cd).
- 2 In the Electrolyte Potential (cd) toolbar, click 🗿 Plot.

The plot should look like Figure 2.

Contour I

- I In the Model Builder window, expand the Volume Fraction of Fluid I (pf) node, then click Contour I.
- 2 In the Settings window for Contour, locate the Coloring and Style section.
- **3** From the **Color** list, choose **Black**.
- 4 In the Volume Fraction of Fluid I (pf) toolbar, click 🗿 Plot.

The plot should look like Figure 3.

Animation I

Plot the animation of volume fraction of fluid 1 to better visualize the evolution of the alpha phase dissolution.

- I In the **Results** toolbar, click **Animation** and choose **File**.
- 2 In the Settings window for Animation, locate the Scene section.
- 3 From the Subject list, choose Volume Fraction of Fluid I (pf).
- 4 Locate the Target section. From the Target list, choose Player.
- 5 Locate the Animation Editing section. From the Time selection list, choose Interpolated.
- 6 In the Times (h) text field, type range(0,1,300).
- 7 Locate the Frames section. From the Frame selection list, choose All.
- 8 Click the **Play** button in the **Graphics** toolbar.