



A quantitative phase-field model for crevice corrosion

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ABSTRACT

A quantitative phase-field model is developed for the investigation of crevice corrosion of iron in salt water. Six types of ionic species and some associated chemical reactions have been considered. In addition to the transient distributions of ion concentrations and electric potential in the electrolyte, some physical and chemical properties related to corrosion, such as overpotential, pH value and corrosion rate, under different metal potentials are studied. Benchmarking of the phase-field model against a sharp interface model is conducted. The corrosion rates predicted by the models are in the same order of magnitudes with experimental results.

1. Introduction

Crevice and pitting corrosion are localized corrosion in which there is intensive corrosion attack at localized sites on the metal surface inside crevices or pits. Those metals that resist corrosion by forming passive films, such as stainless steel, are vulnerable to crevice and pitting corrosion because of the breakdown of protective oxide film. In crevice corrosion for example, the anodic reactions mainly occur within the crevice and cathodic reactions mainly occur outside the crevice, and the cathodic region surface area is far larger than that of anodic region, which usually leads to pitting of the metal without large loss of metal mass by faster corrosion reaction inside the crevice. The propagation of pitting results in the degradation of the mechanical properties of the metallic material. Due to the extremely secluded geometry of crevice and pitting which is often hidden from view, crevice and pitting corrosion are very difficult to be detected.

There has been extensive investigation on crevice corrosion in the past decades. Two theories, i.e., critical crevice solution theory and IR drop theory have been proposed to describe crevice corrosion [1,2]. In the critical crevice solution theory, it is assumed that the reaction of oxidants, such as oxygen, depletes the oxidant in the crevice. Due to the restrictive geometry of the crevice, the replenishing of oxidant from outside of the crevice is too slow to maintain the cathodic reaction in the crevice. The anions, such as Cl^- , are transported into the crevice in order to neutralize the metal cation due to the dissolution of metal ions into the electrolyte. The hydrolysis of metal ions with water molecules generates H^+ ions that result in acidity in the crevice. When the concentrations of Cl^- and H^+ reach critical values, the passive film that protects the metal from the environment breaks down, and the

accelerated corrosion in crevice starts. In the IR drop theory, it is assumed that there is an IR voltage drop in the solution produced by the separation of anodic and cathodic reactions. The IR voltage drop is proportional to the ionic current (I) flowing through a solution with a resistance (R) determined by the length of the current path, the cross-section area of crevice and the conductivity of solution in the crevice. If the voltage IR drop is large enough, the electrode potential in the crevice will shift from the passive region into the active region in the polarization curve, corresponding to the occurrence of crevice corrosion. A number of mathematical and numerical models based on the critical crevice solution theory [3–9], IR drop theory [10] and both theories [11,12], have been developed for crevice corrosion.

Crevice corrosion of an active metal is a very complex phenomenon and involves multiscale physical and chemical processes. The metal ions get into electrolyte in the dissolution process of metal under the gradient of electrochemical potential via an electrical double layer (DL) which separates the metal phase from the electrolyte phase. There is net electric charge which forms a dipole in the DL (a layer with a thickness in the order of nanometers), in which the electrochemical reactions mainly occur. The metal ion and other ions may chemically react with each other and are transported in the crevice solution over a typical length scale of millimeters. The solution part extent is much larger than the thickness of DL. The electrical potential gradients and composition gradients of metal ions are very large in DL and relatively small in the crevice solution. Due to the presence of net electrical charge, thin DL, and huge drop of electrical potential and concentration of metal ion across the DL, the numerical simulation of physical and chemical processes within the vicinity of DL is difficult. Thus, the electrochemical reactions inside the DL have not been taken into account in the reported

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Nomenclature	
A_c	a constant related to the interface
c_i	composition of species i
c_{ib}	composition of species i close to the metal surface in the electrolyte
c_{1s}	composition of Fe^{2+} at standard state in the electrolyte
C_i	concentration of species i (mol/m ³)
C_{ib}	concentration of species i close to the metal surface in the electrolyte (mol/m ³)
C_{1s}	concentration of Fe^{2+} at standard state in the electrolyte (mol/m ³)
D_i	diffusion coefficient of species i in the electrolyte (m ² /s)
D_m	self-diffusion coefficient of iron atom (m ² /s)
D_{1r}	diffusion coefficient of Fe^{2+} at a reference state when $\phi_M = -0.4$ V (m ² /s)
D_{ml}	diffusion coefficient of Fe^{2+} within the interface (m ² /s)
E	free energy functional (J)
E_b	bulk free energy (J)
E_i	interfacial energy (J)
f_b	bulk free energy density (J/m ³)
f_i	gradient free energy (J/m ³)
F	Faraday's constant (96,485C/mol)
j_1	flux of Fe^{2+} from metal into electrolyte (A/m ²)
j_{10}	exchange current density of Fe^{2+} (A/m ²)
j_5	reduction rate of hydrogen ion at the anodic electrode (A/m ²)
j_{50}	pre-exponential factor of j_5 (A m ³ /mol/m ²)
j_6	reduction rate of water ion on the anodic electrode (A/m ²)
j_{60}	pre-exponential factor of j_6 (A/m ²)
j_{ml}	flux of Fe^{2+} under any electrode potential any given ϕ_M with $\phi_l + \eta_c$ setting to be 0 (A/m ²)
j_{1r}	flux of Fe^{2+} at a reference state when $\phi_M = -0.4$ V (A/m ²)
k_{1F}	forward reaction rate constant of the hydrolysis of Fe^{2+} (s ⁻¹)
k_{1B}	backward reaction rate constant of the hydrolysis of Fe^{2+} (m ³ /mol/s)
k_{2F}	forward reaction rate constant of self-ionization of water (mol/m ³ /s)
k_{2B}	backward reaction rate constant of self-ionization of water (m ³ /mol/s)
K_1	equilibrium constant of hydrolysis reaction of Fe^{2+} (mol/m ³)
K_2	self-ionization constant of water (mol ² /m ⁶)
$M(c_1)$	mobility of Fe^{2+} (mol m ² /J/s)
n_x	number of grids used in SIM
n_{xt}	number of grids in electrolyte used in PFM
r	coordinate in whole system domain (m)
R	gas constant (8.314 J/mol/K)
T	absolute temperature (K)
V_m	molar volume of pure water (m ³ /mol)
V_{Fe}	molar volume of iron (m ³ /mol)
x	a dimensionless variable from 0 to 1
z_i	charge of species i
<i>Greek</i>	
α	gradient energy coefficient (J m ² /mol)
α_1	charge transfer coefficient of Fe^{2+}
α_5	charge transfer coefficient of H^+
α_6	charge transfer coefficient of reduction of water
ΔG	the energy barrier between the electrolyte phase and metal phase
Δl	grid size (m)
Δt	time step (s)
η_a	total overpotential (V)
η_c	concentration polarization overpotential close to metal-electrolyte interface (V)
σ_s	surface tension (J/m ²)
ϕ	electrostatic potential in electrolyte (V)
ϕ_M	electric potential in the metal (V)
ϕ_l	electric potential in the electrolyte close to metal-electrolyte interface (V)
$\phi_{eq,M}$	standard electrode potential of iron (V)

mathematical and numerical models for crevice corrosion. And, for simplicity, the electrolyte was usually treated as electrically neutral in those studies.

During crevice corrosion, the interface between metal and solution moves due to the dissolution of metal, and new phases, such as hydrogen gas and/or corrosion products might form if the crevice solution is supersaturated [1]. Both the interface migration and new phase formation modify the crevice geometry and physical environment, which, in turn, influence the local chemical potential and the crevice corrosion kinetics. Thus, the interface should be treated as a moving boundary for a quantitative model of crevice corrosion. A moving boundary is difficult to deal with, especially for crevices with complex topological geometries. The traditional way to deal with the moving boundary problem was to use sharp interface model (SIM) in which the position of interface was tracked explicitly in the simulations. To model crevice corrosion or pitting corrosion, some complex algorithms of moving mesh were developed to track the moving interface using some numerical techniques, such as finite element method [8,13–18], finite volume method [19], boundary element method [20–22] and arbitrary Lagrangian–Eulerian model [23]. It is difficult to successfully cope with both the multiphysics calculation and the smooth moving interface of arbitrary crevice shapes while maintaining conservation of mass and

electroneutrality. Special methods are needed to guarantee the conservation of mass and electroneutrality when the interface moves [19].

In the past two decades, phase-field methods (PFM) based on a diffusive interface concept without the need of tracking the interface position explicitly [24,25], have advanced very rapidly. Significant phase-field modeling work has been done on electrochemical systems. PFM offers an alternative method to model crevice or pitting corrosion. Guyer et al. developed a one-dimensional PFM of an electrochemical system that can handle both the electro-dissolution and electro-deposition, including the net charges present in the interface by incorporating the Poisson equation into the model [26,27]. Basing on Guyer's model, Gathright et al. built phase-field model to simulate solid-electrolyte gas sensor [28] and electrochemical impedance spectroscopy experiments [29]. However, due to the restriction of electric double layer size, the model can only handle systems with a size about tens of nanometers. Later on, PFM was implemented on the studies of thermal oxidation [30–33], electrochemical processes [34], especially the reverse process of corrosion, such as metal refining [35], electro-deoxidation [36] and electro-deposition [37–40].

One recent attempt has been made to use PFM to study corrosion [41,42]. Mai et al. studied activation-controlled and diffusion controlled pitting corrosion processes, electropolishing processes and stress

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