

Experimental and Numerical Study of the Selective Dissolution Mechanism of a Super Duplex Stainless Steel

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Abstract

Duplex stainless steels are commonly used in oil and gas production due to their high mechanical properties and good resistance to stress corrosion cracking. In particular, URTM 2507 (EN 1.4410) exhibits good resistance to stress corrosion cracking in an acidic environment containing chlorides at low partial pressures of hydrogen sulfide (H₂S). At high H₂S partial pressures, samples do not exhibit cracking, but the selective dissolution of a phase is visible on the sample surface. Even if no cracking occurs, surface dissolution is sufficient to conclude that the stress corrosion cracking resistance is not suitable for this environment. Therefore, a deeper understanding of the dissolution mechanism is necessary to further expand the application range of the grade. The study of the dissolution mechanism was explored using a numerical approach with COMSOL Multiphysics[®] software. The model has been adapted from “Localized corrosion using phase field model” example from Application Libraries. The actual microstructure of the grade was implemented in the model after some image processing. Then, the electrochemical behavior of each phase (austenite and ferrite) in H₂S environment was determined using laboratory-synthesized castings and implemented in the model. Using a phase-field methodology, the dissolution kinetics and morphology were studied as a function of several microstructural parameters (sampling direction, grain size). The model made it possible to quantify the effect of dissolution on the initiation of stress corrosion cracking in the grade.

Keywords: Add keywords here.

Introduction

The URTM 2507 (EN 1.4410) super-duplex grade exhibits good resistance to stress corrosion cracking in H₂S-containing environments. However, its operating range is limited to an H₂S partial pressure of 0.2 bar, regardless of chloride concentration or pH. Indeed, above this partial pressure, although no specimen failure due to stress corrosion cracking was observed, the grade is susceptible to surface corrosion identified as the selective dissolution of the ferrite phase [1]. This phenomenon has previously been investigated using electrochemical characterization [2]. These studies demonstrated that such dissolution occurs in the presence of chlorides and H₂S and that the depth of dissolution remains below 200 µm under all experimental conditions. The austenite phase appears to act as a physical barrier, and metallic sulfides are formed during dissolution which could have an effect on dissolution kinetics. The electrochemical behavior of the grade in this environment, as well as that of each of the two phases of the microstructure, was characterized using model materials. Experimental characterization of the phenomenon has enabled the formulation of hypotheses regarding the selective dissolution mechanism. However, it did not rule out the possibility that selective dissolution could act as an initiation site for stress corrosion cracking. Therefore, the present

study investigates this same dissolution phenomenon using a COMSOL Multiphysics[®] model. The initial objective of the model is to reproduce the observed selective dissolution morphology by utilizing the actual microstructure and polarization curves obtained for the ferrite and austenite phases.

Theory

General physics of the model

The selective dissolution of ferrite will be studied using a phase-field model. A phase-field function, ϕ , is defined to distinguish between the liquid and solid phases within the model. Within the solid, reactivity is predefined at every point in the material by considering the microstructure and utilizing polarization curves obtained for each phase. Consequently, when a point in the material lies at the liquid/solid interface, the local current is determined using the polarization curve, thereby allowing the local dissolution rate to be defined.

Model geometry

In this model, we consider an interface between duplex stainless steel and the electrolyte that is 200 μm in length (Figure 1). The represented electrolyte thickness is 150 μm , and the stainless steel thickness considered is 150 μm .

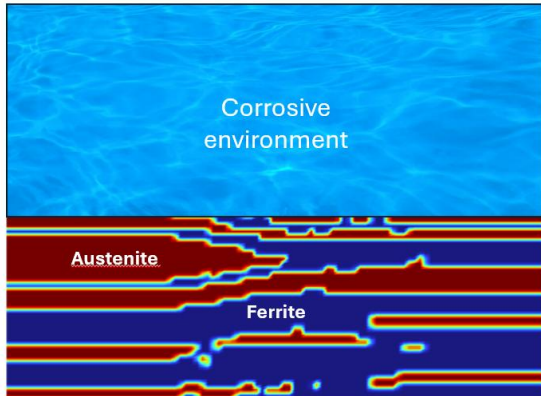


Figure 1. Geometry of the model.

A function, $micro(x,y)$, is defined within the stainless steel domain. This function equals 0 when the coordinates (x,y) correspond to a point in the ferrite phase and equals 1 when they correspond to a point in the austenite phase. To determine the $micro(x,y)$ function, an actual micrograph of a duplex structure was used. Using ImageJ software, the image was converted into a binary image to identify the pixels associated with each of the two phases (Figure 2). Thus, a pixel located in the ferrite is assigned to a value of 0, while a pixel located in the austenite is assigned to a value of 1. A table containing the coordinates of each pixel and its corresponding value (0 or 1) is then constructed for input into COMSOL Multiphysics®. Only a portion of the micrograph is utilized in the model, as a 200 x 150 μm section is used to represent the steel.



Figure 2. Microstructure of duplex stainless steel implemented in the model to define $micro(x,y)$.

Governing Equations and Numerical Model Electrochemical Kinetics

The Secondary Current Distribution interface is used to calculate the electrolyte potential, ϕ_l (V), over the electrolyte domain, in accordance with Ohm's law:

$$\begin{aligned} i_l &= -\sigma_l \nabla \phi_l \\ \nabla \cdot i_l &= 0 \end{aligned}$$

where i_l (A/m²) is the electrolyte current density vector.

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

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

where σ_{el} is the electrolyte conductivity in the electrolyte domain (1.8 S/m) and σ_{me} is the electrolyte conductivity in the metallic domain (0.1 S/m). Furthermore, V_{f1} and V_{f2} are the electrolyte volume fractions in the electrode and electrolyte domains, respectively. Electrolyte conductivity in metal is implemented to help numerical convergence.

An insulation condition is defined by default for all external boundaries:

$$n \cdot i_l = 0$$

where n is the outward-pointing normal vector of the domain.

Dissolution kinetics boundary condition is described through and electrolyte current source:

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

where i_{loc} (A/m²) is the local electrode reaction current density and δ (m⁻¹) is the phase-field delta function (Dirac function defining the interface). An expression for dissolution kinetics is separately defined to model the reaction involving ferrite and austenite at metal surface. The local current density for ferrite at the electrode surface is:

$$i_{ferrite} = f_{ferr}(\phi_{s,ext} - \phi_l) * (1 - micro(x,y))$$

Similarly, the following expression is defined for the local current density at the austenite:

$$i_{austenite} = f_{aust}(\phi_{s,ext} - \phi_l) * micro(x,y)$$

A relationship between the local current density and the electrolyte potential, $f(\varphi_{s,ext} - \varphi_l)$, is incorporated into the model using a polynomial interpolation function based on experimental polarization data obtained for each phase. The local current density at the metal surface is then defined as:

$$i_{loc} = i_{ferrite} + i_{austenite}$$

Electrochemical behaviors of austenite and ferrite phases

The duplex stainless steel microstructure is composed of two phases (austenite and ferrite) with two different chemical compositions. To characterize the electrochemical behavior of both phases, synthetic heats matching the chemical composition of the two phases were used. Specifically, the composition of both phases was analyzed via EDS, and the resulting chemical data were used to produce laboratory-scale heats. The chemical analyses of these materials tested in this study are summarized in Table 1.

Table 1: Chemical composition of the tested grades (wt%)

Grade	C	Cr	Ni	Mo	Mn	N
UR TM 2507	0.019	24.8	6.4	3.7	0.9	0.27
Austenite	0.016	23.5	9.2	2.8	2.0	0.49
Ferrite	0.011	26.7	4.9	4.4	1.0	0.03

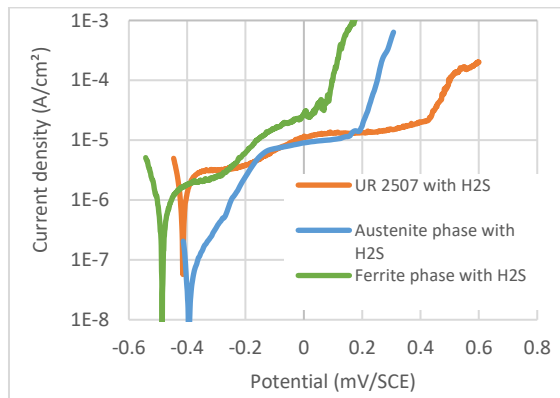


Figure 3. Polarization curves of tested grades in 150 g/L NaCl, pH=3.3, 0.3 bar H₂S/N₂, 90°C

Figure 3 shows the polarization curves obtained for the three samples in a medium containing 150 g/L NaCl and H₂S at pH 3.3 and 90°C, which is representative of environment where dissolution is

observed. Several key points emerge from these polarization curves. First, the URTM 2507 grade exhibits a relatively low corrosion current (in the $\mu\text{A}/\text{cm}^2$ range) and anodic behavior characterized by two plateaus. The first plateau corresponds to the passive region, while the second corresponds to the selective dissolution of the ferrite phase. The austenite phase displays behavior more typical of stainless steel, with a very low corrosion current (in the 100 nA/cm² range). Its anodic behavior shows a passive plateau followed by a rise in current, likely linked to the dissolution of residual ferrite present in the microstructure. Finally, ferrite exhibits a corrosion current and anodic behavior similar to those of the URTM 2507 grade, although the plateaus occur over narrower potential ranges. It is important to note that the laboratory samples exhibit more degraded behavior than the industrial material (URTM 2507) due to their inferior metallurgical quality (regarding phases, inclusions, and sulfur content).

Thus, in the COMSOL Multiphysics® model, the polarization curve for each phase is used to describe $f_{ferr}(\varphi_{s,ext} - \varphi_l)$ and $f_{aust}(\varphi_{s,ext} - \varphi_l)$.

Evolution of the corrosion interface

A Phase Field in Fluids interface is used to track the dissolution of ferrite. In this interface, the dynamics of the two-phase flow are governed by a Cahn-Hilliard equation. This equation expresses two immiscible phases with diffuse interface between these two phases. At this interface, dimensionless phase field variable φ varies from -1 in the metallic domain to 1 in the electrolyte domain. In COMSOL Multiphysics®, the Cahn-Hilliard equation is split into two equations.

$$\begin{cases} \frac{\partial \varphi}{\partial t} + u \nabla \varphi = \nabla \cdot \frac{\gamma \lambda}{\varepsilon^2} \nabla \psi \\ \psi = -\nabla \varepsilon^2 \nabla \varphi + (\varphi^2 - 1) \varphi \end{cases}$$

Where u is the interface velocity (m/s), γ is the mobility ($\text{m}^3 \cdot \text{s}/\text{kg}$), λ is the mixing energy density (N), and ε (m) is the interface thickness. The variable ψ is called the phase-field auxiliary variable.

Mixing energy density, interface thickness and the surface tension coefficient can be related by:

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

In this model, the interface thickness parameter is set to $\varepsilon = h_{max}/32$, where h_{max} is the maximum mesh element size in the domain (7 μm in our case). The mobility parameter γ determines the time scale of Cahn-Hilliard diffusion and is set as the maximum velocity magnitude occurring in the model. In this model, anodic dissolution reaction occurs at the

ferrite surface, while the cathodic reaction (which involves no metallic dissolution) occurs at austenite surface. Consequently, only ferrite surface moves (dissolves). It is implemented in the model by setting the ferrite dissolution velocity in the normal direction according to:

$$u = n \left(\frac{i_{loc} M_{Fe}}{2F \rho_{Fe}} * (1 - micro(x, y)) \right)$$

where M_{Fe} is the average molar mass (55.8 g/mol) and ρ_{Fe} is the density (8000 kg/m³) of the stainless steel. The interface normal n is calculated as follows:

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

In the phase-field interface, the volume fractions of the individual phase are

$$V_{f1} = 1 - V_{f2} \text{ and } V_{f2} = \frac{1+\phi}{2}$$

As a reminder, the metallic domain is defined as Fluid 1 and the electrolyte domain as Fluid 2.

The phase-field delta function is approximated by:

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

Thus, the phase-field variable is set to 1 at the upper boundary of the electrolyte as an inlet boundary condition. The "Outlet boundary" condition applies to the outer boundaries of the metallic domain.

Results and Discussion

Rolling direction

Figure 4 illustrates the progression of the liquid front into the metal after five years. Comparing the two figures is instructive: it is evident that corrosion initiated in the ferrite phase and propagated primarily through it. Furthermore, the dissolution morphology is similar to that observed in actual samples (Figure 5). Thus, by using the polarization curves for each phase and the material's initial microstructure, it was possible to reproduce the dissolution morphology of the duplex grade.

However, experimentally, the maximum dissolution depth is reached after only a few days, whereas the numerical model takes several years to reach this maximum. This suggests that while the model accurately captures the reactions involved in this dissolution process, the calculated kinetics are too low. One hypothesis is that the polarization curves for the individual phases do not adequately account for the galvanic coupling between them. So, the current densities determined with polarization curves are underestimated. It could be interesting to evaluate the reactivity of both phases using local electrochemistry techniques such as Scanning Electrochemical Microscopy (SECM). It would

highlight the reactivity of each phase considering the possible galvanic coupling.

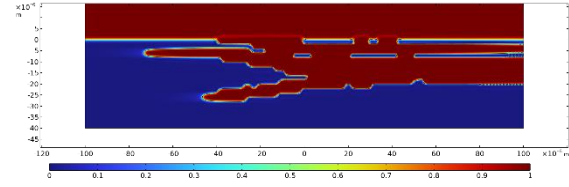


Figure 4. Dissolution front obtained in numerical model for microstructure in rolling direction. Phase-field volume fraction equals 0 in metallic domain.

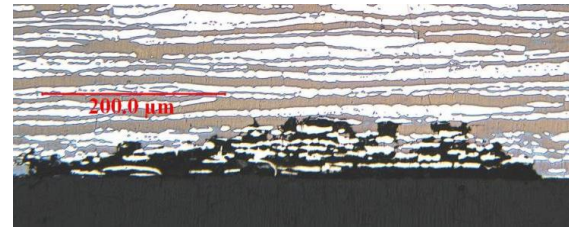


Figure 5. Dissolution front obtained experimentally with duplex stainless steel in H₂S environment sampled in rolling direction

Normal direction

Experimental observations showed that the dissolution depth was significantly greater when the sample was taken in the normal direction. To verify that the model accurately reproduces this phenomenon, a calculation was performed using the duplex microstructure in the normal direction, without altering the other parameters.

Figure 6 shows the progression of the liquid front into the metal after 3 years. The dissolution indeed propagated deeper than with the microstructure oriented in the rolling direction. Furthermore, the dissolution morphology resembles that observed in actual samples (Figure 7). However, the numerical model predicts a dissolution depth of approximately 120 μm after 3 years of exposure, whereas experimentally, this depth is reached after only a few days. These results confirm that while the model appears to capture the physical phenomena involved, it does not reproduce the correct kinetics. Moreover, it is interesting to note that the dissolution process does not appear to slow down over time to reach a maximum depth, as was observed experimentally. In the model, dissolution continues as long as any ferrite remains in contact with the electrolyte. This suggests that the model lacks a physical mechanism to account for this slowing of corrosion. The formation of corrosion products in place of the ferrite following dissolution could play a significant role in the dissolution kinetics; the more ferrite dissolves, the thicker the layer of corrosion products the electrolyte must penetrate. Consequently, the diffusion of the electrolyte through the corrosion product layer

should be considered, as this would likely lead to a maximum corrosion depth.

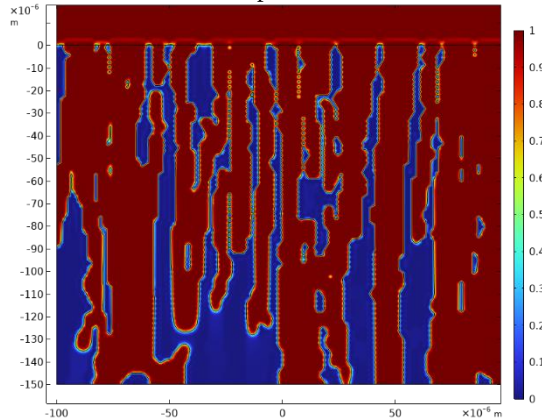


Figure 6. Dissolution front obtained in numerical model for microstructure in normal direction. Phase-field parameter equals 0 in metallic domain

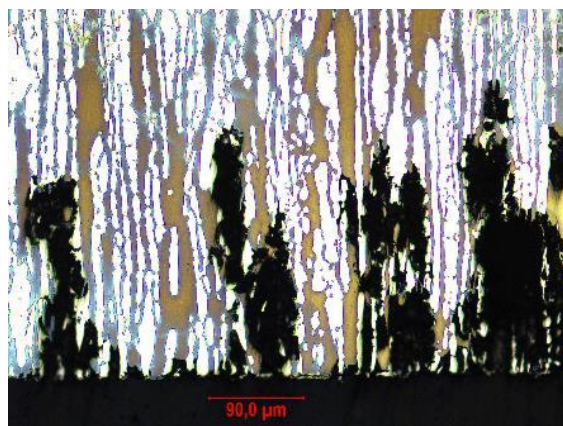


Figure 7. Dissolution front obtained experimentally with duplex stainless steel in H_2S environment sampled in normal direction

Conclusions

The URTM 2507 super duplex grade is susceptible to a form of corrosion characterized by the selective dissolution of the ferrite phase. This corrosion mechanism was modeled in COMSOL Multiphysics[®] using a phase-field approach capable of representing such dissolution. Furthermore, polarization curves obtained from model materials made it possible to correlate the behavior of each phase present in the microstructure. The dissolution morphology produced by the model is closely like that observed experimentally. This supports the view that selective dissolution is primarily driven by the difference in reactivity between the ferrite and austenite phases. However, the dissolution propagation rate in the model is significantly slower than that observed experimentally. One hypothesis is that the galvanic coupling between the two phases—a factor not accounted for when using

model materials—significantly influences dissolution kinetics. Employing a localized electrochemical technique, such as SECM, could enable the determination of polarization curves for both phases within the super duplex microstructure. Experimentally, dissolution appears to stop at a specific depth, which depends on the sampling orientation. While the model predicted a stabilization of dissolution depth in the rolling direction, this was not the case for the normal direction. This suggests that a specific phenomenon is likely missing from the corrosion description. Electrolyte diffusion through the layer of corrosion products formed following dissolution appears to be a promising avenue for investigation. However, implementing this phenomenon in the COMSOL Multiphysics[®] model requires characterizing the physical properties of the corrosion product layer; specifically, measuring the layer's permeability and adhesion would provide crucial data for validating this hypothesis.

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