Numerical Simulation of Micro-Galvanic Corrosion in Al Alloys: Steric Hindrance Effect of Corrosion Product

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An improved finite element model was established to demonstrate the steric hindrance effect of the precipitated corrosion product (Al(OH)₃) on micro-galvanic corrosion triggered by intermetallic particles (IMPs) in an Al-matrix. In this model, the precipitation/dissolution of the corrosion product could occur in the whole liquid field as the result of a reversible reaction. Simulation results show that the precipitated insulating Al(OH)₃ on the electrode surface can inhibit further corrosion by reducing the conductivity of the solution and the active electrode surface area. Meanwhile, the steric hindrance effect of the precipitated Al(OH)₃ also slows down the diffusion and migration of species in the solution. Moreover, considering the porous nature of precipitated Al(OH)₃, a porosity parameter ε and a critical minimum value εc under a specific corrosion situation. Compared to the previous work in which a surface coverage parameter was used to describe the blocking effect of Al(OH)₃ on surface activity, the present model is more realistic in mimicking the micro-galvanic corrosion, and also useful for the simulation of the transition from metastable pit formation to pit propagation.

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Al alloys are widely used in many fields as structural materials because of their high strength/weight ratio. Although many Al alloys show high corrosion resistance due to spontaneous formation of a protective oxide layer on the surface, some of them are vulnerable to local corrosion when exposed to aqueous solutions containing halide ions, e.g., Cl⁻. Particularly, the surface heterogeneity may provide initiation sites for localized corrosion. A precise and comprehensive understanding of the localized corrosion behavior of Al alloys is of great importance.

In our series of studies, a finite element model has been established to investigate micro-galvanic corrosion induced by cathodic intermetallic particles (IMPs), i.e., trench formation, by taking into account electrochemical kinetics of the single phases involved, homogeneous reactions occurring in the electrolyte, a moving dissolution interface, and blocking effect of the precipitated corrosion product. However, in the model reported previously, the precipitation was assumed to occur only on the electrode surface, and the blocking effect of the precipitated corrosion product was simply described by a surface coverage parameter (θ). In that case, the precipitation within the liquid phase and multi-dimensional growth of the precipitated corrosion product were not considered, and the steric hindrance on the mass transport was neglected. Such a simplification limits the applicability of the model for simulating practical systems, since the steric hindrance effect of the precipitated corrosion product has been widely recognized to be critical for the development of pitting-like localized corrosion.

For instance, Frankel et al. suggested that metastable pitting on stainless steel is stabilized by the ohmic drop associated with the porous pit cover, since the average metastable pit current density was found to increase with increasing applied potential. When the cap on the pit was broken and the pit solution was diluted by the bulk solution, repassivation was expected to occur. Pisorsius and Burstein proposed that a perforated pit cover is required for pitting stabilization in stainless steel by providing a barrier to mass transport, which is necessary to isolate the anolyte environment within the occluded volume. They concluded that the metastable pit growth is always under mass transport control. Besides decreasing the conductivity of the electrolyte and suppressing the diffusion of species in the electrolyte, the precipitated corrosion product has been found to also largely impact the activity of the metal surface. Payer et al. suggested that a corrosion product film capable of high ionic transport is required for the corrosion to continue. With sufficient electronic conductivity, the corrosion product can serve as cathode for subsequent metal corrosion and influence ion migration in the electrolyte. Similar observations have also been found for pitting corrosion of other alloys, e.g., Zn alloys, Cu alloys, and Mg alloys. During in-situ atomic force microscopy (AFM) measurement of an Al7075 alloy, we observed precipitation of corrosion products on the surface of the sample after 42 hours immersion. Thus, most likely the aforementioned steric hindrance effect of a precipitated corrosion product also plays an important role in the localized corrosion of Al alloys with active dissolution occurring inside an occluded volume.

The precipitated corrosion product cover makes it extremely difficult to perform in-situ investigations of localized corrosion kinetics experimentally. Recent decades have seen development of modeling and simulation in this field. However, to our knowledge, there is no modeling work taking into account the steric hindrance effect of the precipitated corrosion product and its multi-dimensional growth.

In the present work, in order to investigate the steric hindrance effect of precipitated corrosion products, our previously proposed model has been further improved by taking into account the precipitation-dissolution equilibrium of Al(OH)₃ both on the metal surface and in the liquid phase, as well as its impact on the mass transport in the electrolyte, the conductivity of the electrolyte and the surface activity of the electrode. A porosity parameter with a critical minimum value has been introduced to describe the degree of compactness of the corrosion product, and to evaluate the influence of the corrosion product on the development of localized corrosion.

Physical and Mathematical Model Description

The local corrosion cell consists of one cathodic IMP with radius of 2 μm and a circular anodic ring of 1 μm width in an Al matrix without passive film, as schematically illustrated in Fig. 1. The passive film on the surface area surrounding the anodic and cathodic areas was assumed to be inert. The electrolyte (corrosive solution) was 0.1 M NaCl solution with initial pH = 7. In addition to the local electrochemical reactions occurring on the electrode surface, the considered physical-chemical processes include diffusion, migration and homogeneous reactions taking place in the electrolyte. A more detailed description

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can be found in our previous report. Herein, only the improvements of the model related to the hindrance effect of the corrosion product are described in the following sections.

**Precipitation of porous corrosion product.**—Besides the surface coverage of the corrosion product, the volume and critical porosity of the precipitated corrosion product (Al(OH)₃) were introduced in the present model. Moreover, it was assumed that the precipitation occurs not only on the solid surface but also in the electrolyte. Consequently the precipitation of corrosion product affects the surface activity of the electrodes and the homogeneous reactions in the solution simultaneously.

As a result of the local anodic and cathodic reactions, Al³⁺ and OH⁻ ions are generated at the solid/liquid interface, spreading into the electrolyte through diffusion and migration. Hydrolysis of Al³⁺ leads to formation of soluble Al(OH)₃ through homogeneous reactions in the electrolyte. The generated soluble Al(OH)₃ species not only concentrate in the vicinity of the electrode surface, but also distribute widely into the bulk solution. Once its local concentration reaches oversaturation, the precipitation of Al(OH)₃ occurs both on the surface and in the bulk solution. During our in-situ AFM experiments over several hours immersion, verifying that precipitation of Al(OH)₃ occurred both on the sample surface and in the bulk solution. In addition, the re-dissolution of precipitated Al(OH)₃ was also considered in the present model, and the precipitation/dissolution process was assumed to be fast enough to stay in equilibrium (as shown by Equation 1), with the reaction moving forward or backward depending on the concentration of Al(OH)₃ (C_{Al(OH)₃}) and the equilibrium constant (K_{eq}):

\[ \text{Al(OH)₃} (aq) \leftrightarrow \text{Al(OH)₃} (s) \quad \text{[1]} \]

\[ K_{eq} = \frac{1}{C_{Al(OH)₃}} \quad \text{[2]} \]

where \( a \) is the standard chemical activity of soluble Al(OH)₃, with a value of 1 mol/L, because the electrolyte was assumed to be a dilute solution in the present model.

A parameter \( \varepsilon \) representing the porosity of precipitated Al(OH)₃ was introduced by considering the mole number per unit volume (molar concentration) of the precipitated corrosion product. For dense precipitated Al(OH)₃, with porosity of zero, \( C_{\text{compact}} \) (mol/m³) was defined by Equation 3, in which \( \rho_{\text{Al(OH)₃}} \) and \( M_{\text{Al(OH)₃}} \) are the density and molar mass of the compact solid Al(OH)₃, respectively.

\[ C_{\text{compact}} = \frac{\rho_{\text{Al(OH)₃}}}{M_{\text{Al(OH)₃}}} \quad \text{[3]} \]

With accumulation of the corrosion product, the porosity (0 ≤ \( \varepsilon \) ≤ 1) of precipitated Al(OH)₃ was changing according to Equation 4.

\[ \varepsilon = 1 - \frac{C_{\text{cp}}}{C_{\text{compact}}} \quad \text{[4]} \]

where \( C_{\text{cp}} \) is the cumulative molar concentration of the precipitated Al(OH)₃ in each calculated electrolyte mesh. \( \varepsilon_{c} \) was set to be the minimum porosity of the precipitated Al(OH)₃ corresponding to the most dense state under a certain condition. This implies that the precipitation of Al(OH)₃ can only occur when \( \varepsilon \) is larger than \( \varepsilon_{c} \). At any site where \( \varepsilon = \varepsilon_{c} \), no further precipitation can occur.

When covered by a precipitated porous corrosion product, the extent of blocking of the electrode surface by the corrosion product can be described quantitatively by the coverage (\( \theta \)) of the precipitated corrosion product on the electrode surface. Since the variables within one mesh cell are assumed to be uniform in the finite element model, the coverage (\( \theta \)) can be calculated according to Equation 5, in which \( \varepsilon \) refers to the porosity of the corrosion product within the monolayer meshes along the electrode surface.

\[ \theta = 1 - \varepsilon \quad \text{[5]} \]

The description of the porous corrosion product and use of a porosity parameter are believed to better mimic the realistic conditions in practice, as compared to the model in the previous work.⁶⁷

**Mass transport and homogeneous reactions.**—The ongoing local electrochemical reactions leads to generation of Al³⁺ ions at the anode area and OH⁻ ions at the cathode area, while \( O_{2} \) is consumed at the cathode area.⁶ In the present model, the steric hindrance effect of the precipitated Al(OH)₃ has an influence on the local concentration of the

![Figure 1. Schematic diagram of the micro-galvanic corrosion model for one cathodic IMP particle surrounded by an active anodic matrix ring. Accumulation of Al(OH)₃ precipitate leads to a decreasing porosity with time, which gradually reaches a critical value.](C1036)
relevant species, the homogeneous reactions, and the mass transport (diffusion and migration) in the electrolyte.

In reality, due to the tortuous pore channels in the porous Al(OH)₃ formed, the real diffusion and migration distance of the species is much larger than the thickness of the corrosion product layer. Thus, in the simulation herein, the diffusion coefficients of different species [6,20,21] should be modified by considering the porosity in this mesh at each time moment. [23] In order to simplify the calculation, the correlation between the diffusion coefficient and the porosity was assumed to be linear, [23] therefore, the effective diffusion coefficient, $D_{\text{eff}}$, was defined by Equation 6:

$$D_{\text{eff}} = D_i \times \varepsilon$$  \[6\]

where $D_i$ is diffusion coefficient of species $i$ in the aqueous solution.

The effective migration mobility, $m_{\text{eff}}$, was given by the Nernst–Einstein relationship (Equation 7), where $R$ is the gas constant and $T$ the thermodynamic temperature.

$$m_{\text{eff}} = D_{\text{eff}} / RT$$  \[7\]

The conductivity $\sigma_i$ (S/m) of the electrolyte, having a great influence on the corrosion kinetics, was determined by Equation 8, where $F$ is Faraday’s constant.

$$\sigma_i = -F \sum_i (-Z_i^2 m_{\text{eff},i} F c_i)$$  \[8\]

Taking the formation of a porous corrosion product into account, the Nernst-Planck equations for conservation of all species including diffusion, convection and migration terms also need to be modified. Due to the reduction of the effective volume caused by densification of the corrosion product, the rate of the concentration change $\frac{d(C_i)}{dt}$ can also be influenced, in addition to the abovementioned factors. Accordingly, the modified Nernst-Planck equation is shown by Equation 9:

$$\frac{d(C_i)}{dt} = \nabla \cdot (-D_{\text{eff}} \nabla C_i - Z_i m_{\text{eff},i} F C_i \nabla \Phi_i) + u \cdot \nabla C_i = R_{\text{eff}}$$  \[9\]

where $t$ is time, and $u$ is the flow velocity of the electrolyte. The calculation in this work was done within the diffusion layer, thus $u \cdot \nabla C_i$ equaled to zero all the time. $\Phi_i$ is the potential in the electrolyte, and the potential gradient $\nabla \Phi_i$ is the driving force for the migration of the ionic species. The effective production rate of species $i$, $R_{\text{eff}}$, was introduced to amend the effect of electrolyte volume change caused by the change in the volume of the solid corrosion product. $R_{\text{eff}}$ was given by:

$$R_{\text{eff}} = \varepsilon \times \left( k_{\text{forward}} \sum_i C_i (r, \theta, z, t) - k_{\text{backward}} \sum_i C_i (r, \theta, z, t) \right)$$  \[10\]

Here, $k_{\text{forward}}, k_{\text{backward}}$ are forward and backward reaction rate constants of the homogeneous reaction, and $C_i$ the corresponding concentration. $r$, $\theta$, and $z$ are radial, angle and axial coordinates, respectively, for the cylindrical coordinates. All the homogeneous reactions considered in this model and corresponding kinetic parameters are listed in Table I [6,20,21,24]. Water dissociation reaction was considered in equilibrium state all the time.

The material conservation (Equation 9) gives one equation per species, and the electroneutrality condition (Equation 11) gives another equation.

$$\sum_i Z_i C_i = 0$$  \[11\]

By solving the above equations the concentration field and the potential distribution can be obtained.

Transport of charged species including both diffusion and migration yields the current density in the electrolyte (Equation 12), in which $i$ denotes the ionic current density vector. Since there was no source and sink in the current for the electrolyte, Gauss’s law (Equation 13) was used to determine the current vector.

$$i = F \sum_i Z_i (-D_{\text{eff}} \nabla c_i - Z_i m_{\text{eff},i} F c_i \nabla \Phi_i)$$  \[12\]

$$\nabla i = 0$$  \[13\]

where $F$ is the Faraday constant, $c_i, Z_i$ the concentration and charge number of species $i$, respectively. Table II gives all the constants and the parameters used in the present model.

### Numerical Method

COMSOL Multiphysics was utilized to obtain a numerical solution for this time-dependent model with a coupled built-in interface, and the arbitrary Langrangian Eulerian method was used to accomplish the moving boundary trace, as reported previously [7,25].

Following simplifications were made in the simulation: 1) the cathode particle is hemispherical, so that the three-dimensional model can be converted into a two-dimensional one by using rotational symmetry to reduce the calculation; 2) the distribution of corrosion product is not affected by gravity; 3) the adsorption and interaction between Cl⁻ ions and the passive layer or the generated precipitates are ignored due to lack of kinetic information.

It should be added that oxygen reduction was assumed to be the only cathodic reaction in this model, i.e., hydrogen evolution did not consume electrons from Al dissolution. The reason for such an assumption is that the simulated micro-galvanic corrosion is different from many other pitting systems studied, primarily because much smaller driving force for metal dissolution is presumably not sufficient to supply an auto-catalytic dissolution within the occluded volume. Thus, the pH of the anolyte solution is not acidic enough to result from many other pitting systems studied, primarily because much smaller driving force for metal dissolution is presumably not sufficient to supply an auto-catalytic dissolution within the occluded volume.

### Table I. Homogeneous reactions and corresponding kinetic parameters.

| No. | Homogeneous reactions | $k_{\text{forward}}$ | $k_{\text{backward}}$ | Ref. |
|-----|----------------------|----------------------|-----------------------|-----|
| 1   | $\text{Al}^{3+} + H_2O \rightarrow \text{Al(OH)}^{2+} + H^+$ | $1.09 \times 10^5$ s⁻¹ | $4.4 \times 10^4$ M⁻¹s⁻¹ | 23,32 |
| 2   | $\text{Al(OH)}^{2+} + H_2O \rightarrow \text{Al(OH)}_2^+ + H^+$ | $1.90 \times 10^5$ s⁻¹ | $4.4 \times 10^4$ M⁻¹s⁻¹ | 23,32 |
| 3   | $\text{Al(OH)}_2^+ + H_2O \rightarrow \text{Al(OH)}_3^+ + H^+$ | $5.58 \times 10^5$ s⁻¹ | $2.8 \times 10^4$ M⁻¹s⁻¹ | 29 |
| 4   | $2\text{Al}^{3+} + \text{Cl}^- \rightarrow \text{Al}_2\text{Cl}_4$ | $10^{-2}$ M⁻¹s⁻¹ | $10^5$ M⁻²s⁻¹ | 23,32 |
| 5   | $\text{Al}^{3+} + \text{Cl}^- \rightarrow \text{AlCl}_3$ | $226 \text{M}^{-3}\text{s}^{-1}$ | $(7.5 - k_f \cdot (C_{\text{Al}}^{3+} - C_{\text{Al(OH)2+}})) \text{s}^{-1}$ | 23,32 |
| 6   | $\text{Al(OH)}^{2+} + \text{Cl}^- \rightarrow \text{Al(OH)Cl}_2$ | $1.9 \times 10^3$ M⁻¹s⁻¹ | $(5.7 \times 10^3 - k_f \cdot C_{\text{Al(OH)2+}}) \text{s}^{-1}$ | 23,32 |
| 7   | $2\text{AlCl}^{4+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_2\text{Cl} + 2\text{H}^+$ | $4 \times 10^{-6}$ s⁻¹ | — | 23,32 |
| 8   | $\text{Al(OH)}\text{Cl}_2^+ + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_2\text{Cl} + \text{H}^+$ | $4 \times 10^{-6}$ s⁻¹ | — | 23,32 |
| 9   | $2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{O}_2^{-}$ | $2.6 \times 10^{-5}$ s⁻¹ | $1.3 \times 10^{13}$ M⁻¹s⁻¹ | 23,32 |

$C_{\text{Al}^{3+}}, C_{\text{Al(OH)2+}}$ are concentration of $\text{Al}^{3+}$, and $\text{Al(OH)}^2+$, respectively.
Results and Discussion

To illustrate the steric hindrance effect of precipitated Al(OH)₃ on the kinetics of the localized corrosion, the results from the simulation are presented below, showing that the corrosion product accumulates and finally forms a dense precipitate layer with critical porosity εₖ equal to 0.01.

**Corrosion product distribution and precipitation/dissolution rate.** Figure 2 shows the profile of the electrode surface after 2, 4, 6 and 70 hours, respectively, with the color scale representing the porosity of precipitated Al(OH)₃. A porosity value equal to 1 indicates the aqueous solution without precipitate. It can be seen from Fig. 2a that the Al(OH)₃ precipitates in the vicinity of the metal dissolution front and even in the areas of the nearby cathode and above the occluded dissolving volume. Al(OH)₃ is found to preferentially form in the middle of the anode area initially (Fig. 2a), thus the corrosion rate at the central area becomes lower than at the other areas resulting in a shallower position therein (seen in Figs. 2b and 2c). However, as the bottom surface of the anode is fully covered with precipitated Al(OH)₃, the corrosion rate on the anode becomes uniform again (Fig. 2d). Besides, the color scale in Fig. 2 indicates that the lowest porosity after corrosion for 2 hours is 0.277, this value drops to 0.048 at 4 hours, and reaches the critical value of 0.01 at 6 hours. Afterwards, the area with porosity equal to the critical value extends with time in the corroding volume. Meanwhile, there is also some more porous precipitate with a gradient of porosity present within and away from the corroding volume. Moreover, it is interesting that the lowest calculated precipitation rate is a negative value in Fig. 3d, although very small, which indicates a possible dissolution of the corrosion product in the system.

**Conductivity and current density distribution in electrolyte.**— Due to the difficulty of diffusion and migration through the compact corrosion product layer, the transport of Al³⁺ ions and their hydrates away from the anode surface is effectively retarded. This has an impact on the electrolyte conductivity and current distribution in the electrolyte, as can be seen in Fig. 4. After 70 hours, when a dense Al(OH)₃ layer is formed, Fig. 4a, the calculated local conductivity of the electrolyte in the corroding volume including the mouth area drops to ~0.0126 S/m, which is two orders of magnitude smaller than the conductivity of the bulk electrolyte without corrosion product precipitation (ε = 1). In contrast, Fig. 4d shows calculated electrolyte conductivity distribution after 42 hours, considering only the coverage of the Al(OH)₃ on the electrode surface but not the steric hindrance effect. In this case, the conductivity of the electrolyte is uniform in the electrolyte phase, with a value of 1.26 S/m that is determined by the concentration of all ionic species. This comparison demonstrates that the steric hindrance effect of the precipitated Al(OH)₃ leads to a non-uniform distribution and greatly decreased local conductivity of the electrolyte in the corroding volume and its vicinity.

As a result of the modified electrolyte conductivity distribution, the current density distribution in the electrolyte is also modified in the same way. As shown in Fig. 4b, by considering the steric hindrance effect of the precipitated Al(OH)₃, the current density is lower in the metal dissolution front in the presence of a dense corrosion product, whereas it is much higher near the cathode surface where no dense corrosion product is formed. On the contrary, as shown in Fig. 4b’, when the steric hindrance effect of corrosion product is not considered, the current density is much more uniformly distributed. Moreover, the absolute value of the current density in Fig. 4b’ is much higher than in Fig. 4b, suggesting that the steric hindrance effect of the precipitated corrosion product not only affects the distribution of the current density, but also decreases the current density in the electrolyte and, consequently, hinders the whole kinetic corrosion process. This is clearly demonstrated by a smaller corroded volume after 70 hours (Figs. 4a and 4b) as compared to that after 42 hours.

### Table II. Parameters used in the present model.

| Parameters         | Values                          | Meanings                                    | Ref. |
|--------------------|---------------------------------|---------------------------------------------|------|
| DO₂                | 1.980 × 10⁻⁵ cm² s⁻¹           | O₂ diffusion coefficient                     | 20,21|
| DH⁺                | 9.311 × 10⁻⁵ cm² s⁻¹           | H⁺ diffusion coefficient                     | 20,21|
| DA¹⁺               | 5.273 × 10⁻⁵ cm² s⁻¹           | Al¹⁺ diffusion coefficient                  | 20,21|
| DA(OH)₂⁺           | 0.541 × 10⁻⁵ cm² s⁻¹           | Al(OH)₂⁺ diffusion coefficient              | 20,21|
| DA(OH)₃           | 0.541 × 10⁻⁵ cm² s⁻¹           | Al(OH)₃ diffusion coefficient               | 20,21|
| DA(OH)₂Cl⁻        | 0.541 × 10⁻⁵ cm² s⁻¹           | Al(OH)₂Cl⁻ diffusion coefficient            | 20,21|
| DA(OH)₃Cl⁻        | 0.541 × 10⁻⁵ cm² s⁻¹           | Al(OH)₃Cl⁻ diffusion coefficient            | 20,21|
| Na⁺                | 1.334 × 10⁻⁵ cm² s⁻¹           | Na⁺ diffusion coefficient                   | 20,21|
| Cl⁻                | 2.032 × 10⁻⁵ cm² s⁻¹           | Cl⁻ diffusion coefficient                   | 20,21|
| a                  | 1 mol/L                        | molar gas constant                          | —    |
| R                  | 8.314 J/(mol K)                | Faraday constant                            | —    |
| F                  | 96485 C/mol                    | Critical porosity                           | this work |
| εₖ                 | 0.01                            | dense precipitated Al(OH)₃ with porosity of zero | — |
| ρ₃AOH3             | 2.4 g/cm³                       | Molar mass of corrosion product              | —    |
| M₃AOH3             | 78 g/mol                       | temperature                                 | —    |
| T                  | 293.15 K                       | equilibrium constant                        | 33,34|
| Kₐ0               | 5.39 × 10⁻⁵                    | —                                           | —    |

It should be stressed that the investigated system in our study concerns micro-galvanic corrosion induced by one cathodic IMP. The driving force is much smaller than in typical pitting experiments under anodic polarization, leading to a much slower dissolution process. According to the simulation results performed in this work, the formation of an Al-chloride salt film due to oversaturation is unlikely, although such a scenario has been widely discussed for active pitting processes.26,27,30

Figure 3 displays the spatial variation of the precipitation rate (color scale, in mol/(m² s)) of Al(OH)₃ after 2, 4, 6, and 70 hours, respectively. In general, the precipitation rate decreases with increasing time, see the color scale in Fig. 3a–3c. With accumulation of the corrosion product, when ε reaches εₖ, the precipitation process terminates, which is seen in Figs. 3c and 3d, where the precipitation rate inside the corroding volume is almost equal to zero. Meanwhile, a relatively high precipitation rate is located along the mouth of the corroding volume. Moreover, it is interesting that the lowest calculated precipitation rate is a negative value in Fig. 3d, although very small, which indicates a possible dissolution of the corrosion product in the system.
when the steric hindrance effect is not considered in the calculation (Figs. 4a’ and 4b’).

**Oxygen flux and pH distribution in electrolyte.**—Oxygen transport to the surface of the local cathode is crucial for the localized corrosion development. Figure 5a displays the diffusional flux of oxygen after 70 hours including the steric hindrance effect of the dense Al(OH)$_3$ with $\varepsilon_c = 0.01$. For comparison, Fig. 5a’ displays the simulation result, considering only the effect of surface coverage of the Al(OH)$_3$, but not the steric hindrance effect.

The oxygen flux varies in the electrolyte because it is determined by the oxygen concentration gradient and its diffusion coefficient. The cathodic oxygen reduction reaction consumes oxygen, resulting in a large concentration gradient in the vicinity of the local cathode, and therefore the oxygen flux near the local cathode is much larger than that near the local anode. Interestingly, due to the decreased surface activity and the reduced diffusion rate caused by the generated dense Al(OH)$_3$, the oxygen flux near the cathode surface, at the mouth of and inside the corroding volume in Fig. 5a is significantly lower than that in Fig. 5a’.

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**Figure 2.** Distribution of the Porosity (color scale) of the corrosion product after 2 (a), 4 (b), 6 (c), 70 hours (d), respectively.

**Figure 3.** Distribution of the precipitation rate (color scale) of the corrosion product after 2 (a), 4 (b), 6 (c), 70 hours (d), respectively.
pH is another important factor affecting the kinetics of localized corrosion of Al alloys. It has been reported that when pH is lower than 4 the precipitation of Al(OH)₃ is not possible. Based on the simulation results in this work, the pH distributions calculated with and without considering the steric hindrance effect of precipitated Al(OH)₃ are displayed in Figs. 5b and 5b', respectively. The highest pH locates near the surface of the local cathode owing to the cathodic reduction of oxygen releasing OH⁻, while the local pH in the vicinity of the local anode is lower due to the hydrolysis of the Al³⁺ releasing H⁺. Remarkably, since the steric hindrance effect of the precipitated corrosion product can hinder the whole kinetic corrosion process, the amount of Al³⁺ generated from metal dissolution and thus the amount of released H⁺ should be smaller in Fig. 5b than in Fig. 5b'. However, the lowest pH value (5.57, with the steric hindrance effect) shown in Fig. 5b is unexpectedly lower than the lowest pH value (6.38, without the steric hindrance effect) shown in Fig. 5b'. This is probably due to
the fact that the dense Al(OH)$_3$ can effectively hinder the transport of H$^+$, Al$^{3+}$ and OH$^-$, simultaneously. The reduced rate of inward transport of OH$^-$ and outward transport of Al$^{3+}$ and H$^+$ through the dense precipitated Al(OH)$_3$ causes the more severe acidification inside the corroding volume.

Time dependence of electrode surface condition.—Figure 6 displays the evolution of the coverage of precipitated Al(OH)$_3$, the distribution of current density, the pH value and the concentration of dissolved oxygen, respectively, along the electrode surface within 42 hours. The vertical axis of the plots in Figs. 6a–6d is the distance from the zero point (the center of the IMP) to the point on the active surface along the 2-dimensional solid surface. The total length of active area extends as the corrosion proceeds. Figures 6a–6d present the surface distribution of these parameters by showing the data from Figs. 6a–6d at time intervals of 0, 2.5, 5, 10, 20, and 40 hours, respectively.

Both Fig. 6a and Fig. 6a’ show that Al(OH)$_3$ preferably precipitates in the middle part of the anode area, then extends and accumulates rapidly on the entire anode surface, resulting in gradually increase of the coverage of precipitated corrosion product on the electrode surface (θ), up to 0.99 after 6 hours. For a better illustration, the boundary between the anode and the cathode is traced as the black curve in
The precipitated Al(OH)₃ acts as a protective barrier, reducing the electrode activity. Consequently, the corrosion current density initially decreases faster in the central part of the anode surface, forming a saddle shaped current distribution curve. As the surface activity drops rapidly with time, the corrosion current becomes negligible (0.045 A/m²) on the entire surface after 8 hours, indicating an effective protection by the dense corrosion product. Consequently, the corrosion current density initially decreases faster in the central part of the anode surface, forming a saddle shaped current distribution curve. As the surface activity drops rapidly with time, the corrosion current becomes negligible (0.045 A/m²) on the entire surface after 8 hours, indicating an effective protection by the dense corrosion product. Thus, the mass transport of OH⁻ in homogeneous reactions can gradually balance and even become faster than the generation of OH⁻, leading to a pH decrease and reaching a stable value.

Moreover, as shown in Fig. 6c and Fig. 6c', the pH near the dissolving anode surface decreases during the first 3 hours, followed by a slight pH increase from 3 to 6 hours, and finally drops again as corrosion continues, leading to a local pH equal to 5.85 after 40 hours. The first pH decrease is simply due to the hydrolysis of Al³⁺. The following pH increase is the result of a decreased metal dissolution rate at the precipitate covered anode. Afterwards, the accumulated precipitated Al(OH)₃ in the electrolyte starts to retard the outward transport of H⁺, Al³⁺ and inward transport of OH⁻, leading to the pH drop near the anode surface.

Unlike the local pH, which is related to both anodic and cathodic reactions, the change in concentration of dissolved oxygen is only due to its consumption in the cathodic reaction. As seen in Figs 6d and 6d', the oxygen concentration is always lower near the cathode surface, and increases with the distance from the center of the cathode. Even though Fig. 6d displays an obvious color contrast for oxygen concentration distribution near the cathodic surface, the absolute value of the concentration difference shown by Fig. 6d' is quite small, evidenced by the lowest concentration of 0.2573 mol/m³ compared to 0.2580 mol/m³ in the bulk solution. Compared with typical pitting corrosion, we interpret that the galvanic process investigated in the present work is not controlled by the cathodic oxygen reduction, but controlled by the anodic activity. That is, the activity of the local anode is the limiting step for the whole kinetic process. In time domain, the oxygen concentration is lowest around 2 hours, followed by a gradually increase prior to stabilization, which reflects the balance between surface consumption and diffusional transport from the bulk solution.

**Integrated anodic & cathodic currents and corroded volume.**

Fig. 6a. It is clear that the corrosion product precipitates not only inside the corroding volume but also on the edge of the cathode top surface. The precipitated Al(OH)₃ acts as a protective barrier, reducing the electrode activity. Consequently, the corrosion current density initially decreases faster in the central part of the anode surface, forming a saddle shaped current distribution curve. As the surface activity drops rapidly with time, the corrosion current becomes negligible (0.045 A/m²) on the entire surface after 8 hours, indicating an effective protection by the dense corrosion product. Thus, the mass transport of OH⁻ in homogeneous reactions can gradually balance and even become faster than the generation of OH⁻, leading to a pH decrease and reaching a stable value.

Figure 7. Time evolution of the integrated anodic/cathodic current (a) and corroded volume (b) for the three models: 1) no precipitation of corrosion product, 2) considering only the surface coverage effect of precipitated corrosion product, and 3) considering the steric hindrance effect of precipitated corrosion product in the whole electrolyte.

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Moreover, as shown in Fig. 6c and Fig. 6c', the pH near the dissolving anode surface decreases during the first 3 hours, followed by a slight pH increase from 3 to 6 hours, and finally drops again as corrosion continues, leading to a local pH equal to 5.85 after 40 hours. The first pH decrease is simply due to the hydrolysis of Al³⁺. The following pH increase is the result of a decreased metal dissolution rate at the precipitate covered anode. Afterwards, the accumulated precipitated Al(OH)₃ in the electrolyte starts to retard the outward transport of H⁺, Al³⁺ and inward transport of OH⁻, leading to the pH drop near the anode surface.

Unlike the local pH, which is related to both anodic and cathodic reactions, the change in concentration of dissolved oxygen is only due to its consumption in the cathodic reaction. As seen in Figs 6d and 6d', the oxygen concentration is always lower near the cathode surface, and increases with the distance from the center of the cathode. Even though Fig. 6d displays an obvious color contrast for oxygen concentration distribution near the cathodic surface, the absolute value of the concentration difference shown by Fig. 6d' is quite small, evidenced by the lowest concentration of 0.2573 mol/m³ compared to 0.2580 mol/m³ in the bulk solution. Compared with typical pitting corrosion, we interpret that the galvanic process investigated in the present work is not controlled by the cathodic oxygen reduction, but controlled by the anodic activity. That is, the activity of the local anode is the limiting step for the whole kinetic process. In time domain, the oxygen concentration is lowest around 2 hours, followed by a gradually increase prior to stabilization, which reflects the balance between surface consumption and diffusional transport from the bulk solution.

**Integrated anodic & cathodic currents and corroded volume.**

To illustrate the blocking effect of the precipitated Al(OH)₃ quantitatively, Figs. 7a and 7b display the time evolution of the integrated current (cathodic current and anodic current are always equal) and the corresponding time evolution of the corroded volume, respectively. Besides the results shown in Fig. 7 and based on the present model, Fig. 7 also shows results from the previous two models. The first model was developed without considering the formation of precipitated corrosion product. In the second model precipitated corrosion products were considered on the electrode surface having no physical extension and resulting in blocking effects and concomitant reduction of the activity of the electrode surface.

Figure 7a shows that using a simple model without the precipitation of Al(OH)₃, the integrated current increases continuously during the micro-galvanic corrosion process, which is due to the increase of active area of the electrodes. Using the model considering the surface coverage of precipitated Al(OH)₃, the electrode area extends with time while gradual precipitation of Al(OH)₃ on the electrode surface reduces the surface activity. As a result, the integrated current increases initially, reaching a maximum level around 36 hours, and then decreases with time. Using the improved model taking into account the steric hindrance effect of precipitated porous Al(OH)₃, the integrated current decreases rapidly as a result of precipitation of Al(OH)₃ and then reaches a minimum level after 6 hours, indicating that precipitated Al(OH)₃ results in effective protection against localized corrosion under the simulated conditions.

Figure 7b shows the evolution of the corroded volume for the three different models, calculated from the time integration of the corresponding total anodic current in Fig. 7a. In the simple model without any blocking effect of the corrosion product, the corroded volume increases continuously, eventually leading to removal of the IMP (local cathode). In the model considering the blocking effect of a precipitated Al(OH)₃ layer, but without any steric hindrance effect, the corroded volume also increases faster with time, but gradually becomes smaller than without a corrosion product layer, as seen in the insert in Fig. 7b. In the present model and considering the steric hindrance effect of the precipitated Al(OH)₃, the corroded volume increases much slower with time, suggesting a quite slow local corrosion process in this case.
These results demonstrate that the steric effects of precipitated porous \( \text{Al(OH)}_3 \) in the solution and on the surface plays an important role in the development of localized corrosion.

**Implications of the simulation results.**—According to the simulation results above, gradual precipitation and accumulation of the porous corrosion product (\( \text{Al(OH)}_3 \)) in the electrolyte can reduce the activity of the dissolving anode and nearby cathode. Moreover, the precipitated \( \text{Al(OH)}_3 \) acts as an effective barrier for the diffusion of the reactants and reaction products, resulting in more serious acidification within the occluded corroding volume (Fig. 5b). Besides, accumulation of precipitated insulating \( \text{Al(OH)}_3 \) in the electrolyte also reduces the conductivity of the electrolyte as much as two orders of magnitude. The total corrosion current flowing between the local anode and the local cathode decreases dramatically due to the combined blocking effect on the active surface area and steric hindrance for transition from meta-stable pitting to stable pitting corrosion.\(^{32}\)

If the \( \text{pH} \) at the bottom of the corroding volume reaches 4 or lower, the local acidic environment will prevent the formation of insoluble \( \text{Al(OH)}_3 \) and cause re-dissolution of the precipitated corrosion product.\(^{31}\) It follows that the local metal dissolution at the bottom of the corroding volume will continue to occur, and leave some amount of the corrosion product precipitates around the mouth of the corroding volume due to a larger \( \text{pH} \) in that area. This situation is similar to the formation of a cap on top of an active pit. The cap-like precipitate at the mouth will slow down the mass transport inward or outward the corroding volume, consequently, the meta-stable corrosion may transform into a stable state of localized corrosion. This transition process is typical for transition from meta-stable pitting to stable pitting corrosion.\(^{32}\)

Further modeling work is needed for the demonstration of this process.

**Conclusions**

An FEM model has been developed to simulate the effect of corrosion product precipitation on micro-galvanic corrosion of Al matrix caused by a cathodic IMP. In the present model, several important processes are considered and their influence of the localized corrosion process are explored: 1) the corrosion product (\( \text{Al(OH)}_3 \)) precipitates not only on the solid surface but also in the solution when its concentration becomes saturated; 2) the backward process, i.e., re-dissolution of precipitated corrosion product is also possible as long as the precipitation equilibrium allows its occurrence; 3) the steric hindrance effect is taken into account, as well as its influences on the concentration of the involved species, on the homogeneous reactions, the electrolyte conductivity, and the mass transport. These key improvements of the previously reported model enable the present model to better mimic real micro-galvanic corrosion situations. The present model is also relevant for other general localized corrosion processes involving generation of solid corrosion products.

The simulation results demonstrate that the steric effect of the precipitated \( \text{Al(OH)}_3 \) leads to a larger hindrance of the corrosion process due to its influences on both surface activity and mass transport in the solution containing precipitated \( \text{Al(OH)}_3 \). This causes significantly reduced current density, oxygen flux around the cathode, and acidification in the occluded corroding volume.

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