A finite element model for simulating the propagation of micro-galvanic corrosion of Al alloys induced by intermetallic particle was established to reveal the dynamic changes including a moving dissolution boundary, deposition of reaction products and their blocking effect. This model has previously been used to study the influence of geometrical factors such as the particle size and width of the anodic ring. In this work, we explore effects of chemical factors including pH and bulk concentration of O2 by using chemical-dependent electrochemical kinetics as input parameters. The simulations reveal that the micro-galvanic corrosion rate is slowest at pH = 6. For pH > 6, the rise of pH increases the dissolution rate of Al and also the deposition rate of Al(OH)3, leading to a faster but more short localized Al dissolution. For pH < 6, the decline of pH accelerates Al dissolution and inhibits Al(OH)3 deposition, leading to a faster and more long lasting Al dissolution. At pH ≤ 4, deposition of Al(OH)3 becomes negligible, and localized corrosion will propagate continuously. Within the O2 concentration range relevant for atmospheric conditions, a lower O2 concentration in the solution leads to a slower rate of micro-galvanic corrosion.

For multi-element alloys with heterogeneous microstructures, micro-galvanic couplings exist between different constituent components due to their difference in relative nobility, implying a risk for localized corrosion when exposed to a corrosive environment. In the case of aluminum (Al) alloys, depending on the composition and thermo-mechanical processing, different types of intermetallic particles (IMPs), with micron- or nanometer sizes, are formed in the microstructure. Most of the IMPs exhibit cathodic character while some type of IMPs exhibit anodic character, relative to the alloy matrix. Localized corrosion of Al alloys is commonly observed to be associated with relatively large cathodic type IMPs which contain more ‘noble’ elements (i.e. Cu, Fe, Mn, etc.), leading to enhanced dissolution of surrounding matrix, named ‘trench formation’. There are extensive literature reports on investigations of localized corrosion of Al alloys, providing substantial knowledge about the effect of the microstructure. In contrast, despite of some experimental observations, little is known at a fundamental level about the influence of pH on the corrosion of Al alloys. Several decades ago, Chatalov and Pourbaix et al. found that the corrosion rate depends logarithmically on the pH, with a minimum corrosion rate at pH close to 6. By using stereological methods, Birbilis et al. observed that the mode of corrosion of AA7075-T651 alloy also depends on the pH of the solution: stochastic at acid pH, general at alkaline pH, and strongly influenced by the microstructure and electrochemistry of the intermetallics at a near neutral pH. They pointed out that the environment is of similar critical influence as the microstructure for the corrosion of Al alloys, and the ultimate damage depends on a combination of the two factors. The same trend has also been found by Cavanaugh. The interplay between the complicate microstructure and the chemical environment gives rise to a huge obstacle for achieving fundamental understanding of localized corrosion of Al alloys. Furthermore, once the corrosion commences, the situation becomes further complicated by matrix etching, IMPs dealloying, homogeneous reactions, and corrosion product deposition on the surface, leading to significant changes in the local electrochemical activity and local environment. In general, the cathodic IMPs in Al alloys are commonly regarded as the preferred sites for oxygen reduction. From this follows that the OH− ions generated from the cathodic reaction should cause a local pH increase near the surface of these IMPs in a nominally neutral bulk solution. As an example, the electrochemical activity of the IMPs and the bulk alloys can be enhanced under alkaline environment, which promotes preferential dissolution of the alloy matrix surrounding the IMPs. This mechanism is known as the cathodic model for the formation and trench propagation in Al alloys, originally proposed by Nisancioglu et al. Park et al. measured the pH around an AlFe particle in Al6060 and found an alkaline solution around the inclusions, providing direct evidence supporting the cathodic model. However, by computational means, Alodan and Smyrl simulated the pH close to a single IMP for different bulk pH solutions, and their results showed that no local alkalization occurs for acidic bulk environment. Thus, although trench formation has been discussed extensively, the interplay between the microstructure and the local environment is still not clear.

Because of the multitude of coupled factors that influence localized corrosion, such as the microstructure, chemical environment, electrochemical conditions which are varying in space and time, it is extremely challenging for experimentalists to clearly differentiate the role of each individual factor and gain a thorough understanding of the mechanism of such localized corrosion. Recent decades have seen the development of modelling and numerical simulation in the context of rationalising and quantifying the phenomenology of localized corrosion. Such models have been established based on theoretical analysis of the general and local chemistry and electrochemistry involved in a given localized corrosion scenario. But, for the existing models, the effect of chemical environments has rarely been discussed. Further efforts are needed to take into account the effect of heterogeneous chemical environments on the local electrochemical kinetics. Previously we have established a localized corrosion model that simultaneously takes into account coupled reactions and mass transport, allowing for a moving dissolution boundary and also considering the deposition of the corrosion product. In this work, we explore the effects of chemical factors including the pH and O2 concentration of the bulk solution on the localized corrosion of Al alloys. For the first time, chemical-dependent electrochemical kinetics is used as input parameters in the model to address the coupling effect of the alloy microstructure and its service environment quantitatively. This study, together with a previous work investigating the effect of geometric factors, aims at forming a comprehensive model for the evolution of an anodic ring around an IMP, regarded as a precursor for the initiation of localized corrosion.
ing the equation of charge conservation (equation 4). Coverage ($\theta$) of deposited Al(OH)$_3$ is used to quantitatively describe its blocking effect. The dynamic change of the coverage is directly related to the deposition rate (equation 5).

$$ \frac{\partial C_i}{\partial t} = -\nabla \cdot (D_i \nabla C_i + C_i m_i \mathbf{F} C_i \nabla \phi_i) + R_i $$  \hspace{1cm} [1]

$$ \sum Z_i C_i = 0 $$  \hspace{1cm} [2]

$$ i_j = F \sum_{j=1}^n Z_i (-D_i \nabla C_i - Z_i m_i F C_i \nabla \phi_i) $$  \hspace{1cm} [3]

$$ \nabla \cdot i_i = 0 $$  \hspace{1cm} [4]

$$ \frac{d\theta}{dt} = \frac{1}{\delta} \times \frac{t_{dep} \times M_{Al(OH)_3} \times V_{mesh}}{PA_{Al(OH)_3}} $$  \hspace{1cm} [5]

In above equations, $t$ is the time, $F$ is the Faraday constant. $C_i$, $D_i$, $Z_i$, $m_i$ are the concentration, diffusion coefficient, charge number and mobility of species $i$. $R_i$ is the concentration variation caused by the homogeneous reactions in the electrolyte. $i_j$ is the ionic current density vector. Moreover, $M_{Al(OH)_3}$ and $PA_{Al(OH)_3}$ are the molar mass and density of Al(OH)$_3$. $\delta$ is the thickness of the deposit layer that blocks the active surface completely. $V_{mesh}$ is the volume and $S_{mesh}$ the projected area of the calculated mesh unit along the active surface. More details can be found in Ref. 33.

COMSOL Multiphysics was used to obtain the numerical solution. By using the Arbitrary Lagrangian-Eulerian Formulation (ALE) method, the moving boundary of the domain with free deformation was traced. The same initial and boundary conditions defined previously$^{33}$ were also used here.

**Chemical-Dependent Electrochemical Kinetics**

During the galvanic corrosion, the local chemical environment varies due to the coupled local anodic dissolution and cathodic oxygen reduction, as well as the homogeneous reactions and the mass transport of species in the solution. In turn, this uneven and time-dependent local chemical environment affects the kinetics of the electrochemical reactions locally. Therefore chemical-dependent electrochemical kinetics is needed as input data for the simulation. For simplicity, an interpolation surface (three variables) or volume (four variables) were extracted from available electrochemical polarization curve measured on a single phase (Al,Fe) and an Al7075 matrix under different conditions$^{10}$ in order to approximate the chemical-dependent electrochemical kinetics. It should be mentioned that the polarization curves used were obtained in oxygen-saturated solution. The coupling between such curves might lead to some unavoidable underestimates in predictions of damage accumulation or pH change, since each phase supports both anodic and cathodic currents in the potential range of interest.

**$pH$-dependent electrochemical kinetics.—**The susceptibility and extent of corrosion damage of Al-alloys are highly pH dependent$^{20,27,30,35,36}$ In the simulation herein, polarization curves measured on respective single phases (Al,Fe and matrix) in 0.1 M NaCl solution with $pH = 2.5, 6, 10$ reported in literature$^{19}$ were used to perform the linear interpolation. Fig. 2a–2b shows the three-dimensional interpolated $pH$-dependent electrochemical kinetic surface for the cathodic particle (Al,Fe) and the Al7075 matrix, respectively, in which the x-axis represents $pH$, y-axis the electrode potential and z-axis (color scale) the cathodic or anodic current density. Fig. 2c–2d are corresponding contour plots for (a) and (b), respectively. In this work, the cathodic current density was defined to be negative. Basically, from the figure, we can interpret that for both cathode and anode, the reaction rate (current density) at given electrode potential was the lowest at $pH = 6$, i.e., both acidic and alkaline environments can enhance the corrosion process. It should be mentioned that this interpolated pH-dependent electrochemical kinetics is rather coarse,
Figure 2. (a)-(b) Three dimensional interpolated electrochemical kinetic surfaces for the cathodic particle (Al\textsubscript{3}Fe) and anodic electrode (Al7075 matrix), respectively. The x-axis represents pH, y-axis the electrode potential, and z-axis (color scale) the cathodic or anodic current density. (c)-(d) Corresponding contour plots for (a)-(b), respectively.

because of only limited amount of available polarization curves measured on the relevant single phases. Hence, quantitative conclusions should be done with caution. But as a first attempt, this work intends to provide some valuable insights about the role of pH on micro-galvanic corrosion of Al alloys.

**pH-O\textsubscript{2} concentration-dependent electrochemical kinetics.**—Besides pH, the concentration of dissolved O\textsubscript{2} in the environment sometimes also can be critical for corrosion of Al alloys.\textsuperscript{24,37} Hence, it is also taken into account in this simulation. Here, based on the interpolated surface with three variables (pH, potential, current density) for pH-dependent electrochemical kinetics, an interpolated volume with four variables (pH, O\textsubscript{2} concentration, potential, current density) was established to describe the pH-O\textsubscript{2} concentration-dependent electrochemical kinetics. To do so, the electrochemical polarization curves measured with different O\textsubscript{2} concentrations (e.g., 0.1, 0.2, 0.5 times c\textsubscript{sat}, where c\textsubscript{sat} = 0.258 mol/m\textsuperscript{3} for aqueous solutions in equilibrium with air) for all selected pH values (here, pH = 2.5, 6, 10) are needed. Since it is difficult to set different O\textsubscript{2} concentrations in practice, especially for in-situ electrochemical measurements of micro-scale systems, the electrochemical polarization curves with different O\textsubscript{2} concentrations are not available. To solve the problem, the Nernst equation and the definition of exchange current density were used to derive the polarization curves with different O\textsubscript{2} concentrations from the curves measured with c\textsubscript{sat}, which are available for different pH values. The interpolation to get the pH-O\textsubscript{2} concentration-dependent electrochemical kinetics is similar to the operation to get the pH-dependent electrochemical kinetics, the only difference being the change from three-dimensional to four-dimensional relationship. The results turn out to be a four-dimensional volume, in contrast to the three-dimensional surface for the pH-dependent kinetics, and the typical two-dimensional polarization curves for the non-chemical-dependent kinetics.

Fig. 3a displays a sectional view to present a four-dimensional plot, in which, x-axis stands for pH, y-axis for O\textsubscript{2} concentration, z-axis for electrode potential, and the color scale for cathodic current density of the cathodic particle. Fig.3b displays a x-z view showing the pH effect on the cathodic current density at O\textsubscript{2} concentration of 0.15 mol/m\textsuperscript{3}, i.e., both acidic and alkaline environments increase the electroactivity of the cathodic particle for the O\textsubscript{2} reduction reaction. Fig. 3c and 3d display y-z views showing the effect of O\textsubscript{2} concentration at pH = 4 and 6, respectively. At a given pH value, a higher O\textsubscript{2} concentration gives a higher cathodic current density. It should be noted that the pH-O\textsubscript{2} concentration-dependent electrochemical kinetics reflects a reasonable trend for the influence of pH and O\textsubscript{2}. However, it does not have a high accuracy because of the limited amount of measured polarization curves available for interpolation.

To check eventual effects of H\textsubscript{2} evolution on the electrochemical kinetics, the derived polarization curve for c\textsubscript{O\textsubscript{2}} = 0.1c\textsubscript{sat} at pH = 2.5, the most favorable condition for H\textsubscript{2} evolution, was compared to the polarization curve measured in the same electrolyte with N\textsubscript{2} bubbling to remove O\textsubscript{2}. The results show that both E\textsubscript{corr} and i\textsubscript{corr} are much higher for the sample without N\textsubscript{2} bubbling (in which the cathodic branch
includes O2 reduction and H2 evolution) than with N2 bubbling (the cathodic branch includes only H2 evolution). This indicates that O2 reduction is the dominant cathodic reaction, whereas the effect of H2 evolution is negligible within the investigated O2 and pH range. This justifies the assumption that O2 reduction is the dominant cathodic reduction reaction.

**Temporal evolution of the micro-galvanic coupling process.**—Following the mixed potential theory and Evan’s diagram, in most of the reported modelling work on galvanic corrosion, the mixed potential was determined by coupling anodic and cathodic polarization curves or two Butler-Volmer equations (i.e., with no external polarization applied to the sample), and the driving force (over-potential) was determined by the mixed potential without considering the effect of local chemical factors. In our model, by using the above mentioned chemical-dependent electrochemical kinetics as input data, the effect of local pH and O2 concentrations can be taken into account. Since pH affects both local anodic and cathodic kinetics, two interpolated surfaces (pH-dependent kinetics for both anodic and cathodic reactions) were used to perform the coupling of anodic and cathodic polarization curves. On the other hand, by assuming that O2 does not affect anodic dissolution of Al, when investigating the effect of O2 concentration, we used the pH-dependent interpolated surface to describe the anodic kinetics and the pH-O2 concentration-dependent interpolated volume to describe the cathodic kinetics. In this way, the galvanically driven kinetics was based on the coupling between one surface (pH dependence) and one volume (pH-O2 dependence) in the simulation. By equaling the local anodic current to the cathodic current at all times, the mixed electrolyte potential is determined kinetically.

**Results and Discussion**

**Influence of bulk pH.**—The chemical environment considered in this work represents relatively mild corrosion environments, and the O2 reduction is regarded as the dominant cathodic reaction in the corroding system.

**Influence of bulk pH on anodic and cathodic current densities.**—As shown in Fig. 4, the cathodic and the anodic current density distributions are plotted as a function of distance from zero point along the active surface for different bulk pH values. At the beginning (Fig. 4a), the cathodic reaction (O2 reduction) occurs only on the...
increase of cathodic area with time, which is reflected by a shifting values (pH). The current density drop is more pronounced for higher bulk pH. One interesting observation is that micro-galvanic corrosion seems to be more sensitive to alkaline environments, which is reflected by a much higher cathodic current density in alkaline environments than in acidic environments.

The results show a strong influence of bulk pH on the deposition of Al(OH)$_3$ and the blocking effect, i.e., the surface coverage decreases with decreasing bulk pH. After 11 h, the average coverage values are ca. 0.9, 0.7, 0.6, 0.3, 0.3 and 0 for bulk pH of 9, 8, 7, 6, 5 and 4, respectively. Obviously a higher OH$^-$ ion concentration under higher bulk pH conditions favors the deposition of Al(OH)$_3$. In contrast, the coverage = 0 for bulk pH = 4, not only at 11 h, but also during the whole simulation process (ca. 42 h). This result is in accordance with the reported thermodynamic stability of Al(OH)$_3$ in aqueous solution. It is possible that when the bulk pH = 4, the environment is enough acidic to inhibit hydrolysis of Al$^{3+}$ ions and formation of Al(OH)$_3$, keeping soluble Al(OH)$_3$ in the solution at unsaturated level and thus preventing deposition of Al(OH)$_3$.

**Influence of bulk pH on the deposition of Al(OH)$_3$.**—In addition to the above mentioned expansion of the anodic surface, the blocking effect of the deposited Al(OH)$_3$ can also lead to decreasing anodic current density with time. To demonstrate the blocking effect of the deposited Al(OH)$_3$, the calculated coverage ($\theta$) after 11 h is plotted in Fig. 5a for different bulk pH values. For bulk pH = 9, the coverage is higher than 0.9 for most part of the anodic area, which means that the active dissolving surface has almost been completely blocked by the deposited corrosion product. This is also the reason for choosing the results after 11 h for comparison.

The current density gives an indication of the dynamic change of the corroding process, two-dimensional profiles revealing the position of the dissolving surface after 11 h are shown in Fig. 5b–5d for bulk pH = 9, 6, 4, respectively, with color scale indicating the local pH distribution. To visualize the development of the micro-galvanic corrosion process, two-dimensional profiles revealing the position of the dissolving surface after 11 h are shown in Fig. 5b–5d for bulk pH = 9, 6, 4, respectively, with color scale indicating the local pH distribution.

The results show a strong influence of bulk pH on the deposition of Al(OH)$_3$ and the blocking effect, i.e., the surface coverage decreases with decreasing bulk pH. After 11 h, the average coverage values are ca. 0.9, 0.7, 0.6, 0.3, 0.3 and 0 for bulk pH of 9, 8, 7, 6, 5 and 4, respectively. Obviously a higher OH$^-$ ion concentration under higher bulk pH conditions favors the deposition of Al(OH)$_3$. In contrast, the coverage = 0 for bulk pH = 4, not only at 11 h, but also during the whole simulation process (ca. 42 h). This result is in accordance with the reported thermodynamic stability of Al(OH)$_3$ in aqueous solution. It is possible that when the bulk pH = 4, the environment is enough acidic to inhibit hydrolysis of Al$^{3+}$ ions and formation of Al(OH)$_3$, keeping soluble Al(OH)$_3$ in the solution at unsaturated level and thus preventing deposition of Al(OH)$_3$.

**Influence of bulk pH on the propagation of active surface.**—To visualize the development of the micro-galvanic corrosion process, two-dimensional profiles revealing the position of the dissolving surface after 11 h are shown in Fig. 5b–5d for bulk pH = 9, 6, 4, respectively, with color scale indicating the local pH distribution. Together with the coverage plot in Fig. 5a, Fig. 5b presents the final position of the dissolving surface for bulk pH = 9 after 11 h, which is totally blocked by deposited Al(OH)$_3$. However, for lower bulk pH values, e.g., 6 and 4, the anodic surface is still quite active. For bulk pH = 4, as discussed above, the deposition of Al(OH)$_3$ is inhibited so that the Al matrix will continue to dissolve, and the cathode particle will be removed from the matrix after sufficient time.

Regarding the effect of bulk pH on the metal dissolution rate, Fig. 5 displays a consistent result with the current density plots shown in Fig. 4, illustrating that both acidic and alkaline environments can lead to a faster propagation of the dissolving front.

Once the micro-galvanic corrosion commences, owing to the electrochemical reactions taking place on the surface of the local anode and cathode, the pH is no longer uniform. The OH$^-$ ions generated from oxygen reduction leads to a local alkalization on the surface of cathodic particle, while the hydrolysis of Al$^{3+}$ ions in the dissolving volume most likely decreases the local pH near the dissolving front, as can be seen from the color scale in Fig. 5b–5d. Moreover, the pH difference shown in Fig. 5 is the largest for bulk pH = 6, smaller for bulk pH = 9, and almost negligible for bulk pH = 4. This result is consistent with the work by Alodan and Smyrl, in which they also calculated the pH close to a single cathodic intermetallic particle in solutions with different bulk pH, and found that no local alkalization occurs with a bulk pH of 4, whereas local alkalization occurs in neutral bulk solution.

For studying corrosion of Al alloys, although investigations have been done to simulate the heterogeneous environment by setting different bulk pH values, the effects of real time change in local chemical environment (e.g., pH) on the electrochemical kinetics have rarely been considered. In this work, by using the pH-dependent electrochemical kinetics, not only the effect of bulk pH, but also the effect of unevenly distributed local pH is taken into account. More details will be discussed in the following sections.

**Influence of bulk pH on integrated anodic and cathodic currents.**—The temporal evolution of integrated anodic or cathodic current gives an indication of the dynamic change of the corrosion process.
rate on the whole active surface. As shown in Fig. 6, the total anodic current equals the total cathodic current at all times owing to the galvanic coupling. In the early stage, the expansion of the dissolving surface and increase of the open surface of the cathodic particle leads to an increasing total current for all the examined pH values.

The integrated current is the lowest for bulk pH = 6, and it increases slowly with time. After ca. 32 h, the integrated current starts to decrease because of the blocking effect of Al(OH)$_3$, and the active surface is almost totally blocked after ca. 42 h resulting in the termination of corrosion. For the bulk pH values = 7, 8, 9, respectively, the integrated current is much higher than that at pH = 6, but it starts to decrease after a short period. For example, at bulk pH = 9 the current starts to decrease at 10 h and the active dissolving surface is blocked totally after 11 h. Together with the data of anodic and cathodic current densities (Fig. 4) and the calculated coverage of deposited Al(OH)$_3$ (Fig. 5a), these results suggest that for a bulk pH in the range from 6 to 9, a higher pH (alkaline environment) improves the electroactivity of the cathodic particle for oxygen reduction. This means that the particle can provide more galvanic current, leading to faster metal dissolution (releasing Al$^{3+}$ ions) and subsequently promoting formation and deposition of Al(OH)$_3$. To summarize under current modeling conditions in neutral and weak alkaline environments, the higher pH enhances the micro-galvanic dissolution of the Al matrix as well as the Al(OH)$_3$ deposition, leading to a fast but short micro-galvanic corrosion process.

For weak acidic environments (pH = 4, 5), the integrated currents are also higher than that for pH = 6. Different from alkaline environment, the acidic environment not only enhances the galvanic dissolution, but also inhibits the deposition of Al(OH)$_3$, leading to a relatively faster and more long lived micro-galvanic corrosion process. For pH = 4, the deposition of Al(OH)$_3$ is not possible (Fig. 5a), from which follows that the integrated current increases with time, and the micro-galvanic corrosion continues until the removal of the cathodic particle from the Al matrix.

**Influence of dissolved CO$_2$ in the solution.**—CO$_2$ is present in air and its dissolution in aqueous solutions causes a shift of pH toward a lower value. Effect of dissolved CO$_2$ on the corrosion process is of great interest in atmospheric corrosion. Since no stable compounds are formed between Al$^{3+}$ ions and CO$_3^{2-}$/$\text{HCO}_3^-$ ions in aqueous solutions, the effect of dissolved CO$_2$ is mainly related to the decreased bulk pH of the solution. According to thermodynamic calculation, the pH of aqueous solution in equilibrium with aerated dissolved CO$_2$ is 5.65. Based on the simulation results, temporal evolution of the integrated current is plotted in Fig. 7 for neutral conditions (bulk pH = 7) and a slightly acidic solution with dissolved CO$_2$ (bulk pH = 5.65). It can be seen that the active surface is blocked by deposited Al(OH)$_3$ after a short period under neutral condition. With dissolved
CO₂, on the other hand, micro-galvanic dissolution continues for a longer time period although the integrated current is lower.

Influence of local pH on the electrochemical kinetics (at bulk pH = 6).—As shown in Fig. 5, when micro-galvanic corrosion commences, the local pH distribution across the active surface becomes uneven and changes with time, due to ongoing local cathodic oxygen reduction and hydrolysis of Al³⁺ ions. In order to gain insights into how the local pH influences the electrochemical kinetics of the micro-galvanic corrosion, we compare the simulation results calculated with pH-dependent electrochemical kinetics (Fig. 2) and non-pH dependent electrochemical kinetics, taking the example of bulk pH = 6. For the calculation with non-pH-dependent electrochemical kinetics, the anodic polarization curve measured on Al 7075 matrix and cathodic polarization curve measured on Al₃Fe, all under bulk pH = 6, are used solely as input data to describe the electrochemical kinetics for the whole active electrode surface.

Influence of local pH on anodic and cathodic current densities.—For comparison, Fig. 8a displays the current density along the active cathodic and anodic surface at zero time and after 11 h, calculated with non-pH dependent and pH-dependent kinetics. At zero time, the current density calculated with pH-dependent (circle symbols) and non-pH-dependent (square symbols) kinetics are exactly the same, which is expected because at the beginning the local pH along the surface is uniform and equal to the bulk pH.

After 11 h, the local pH along the active surface becomes uneven, as indicated by the solid curve and values corresponding to the y-axis on the right hand side in Fig. 8a. The increased local pH on the cathodic surface is a result of oxygen reduction, while the decreased local pH on the anodic surface is due to the hydrolysis of the released Al³⁺ ions. The cathodic current density calculated with non-pH-dependent kinetics (triangle symbols) is quite uniform on the upper surface of the original cathodic particle, while it drops rapidly along the newly exposed particle surface (x ≥ 2 μm) due to the blocking effect of deposited Al(OH)₃. Interestingly, the cathodic current density calculated with pH-dependent kinetics is higher than that calculated with non-pH-dependent kinetics, and shows a tendency to increase toward the zero point. This trend is consistent with the extent of local alkalization, which is most severe in the center of the particle (zero point). This result provides quantitative and direct evidence supporting the explanation for the well-known “trench” corrosion induced by IMPs in Al alloys.

The effect of local pH on the anodic current density can be explained in terms of the Al(OH)₃ deposition and the blocking effect on the actively dissolving surface. Fig. 8a shows that the difference of
pH along the actively dissolving surface is quite small, and the anodic current density is similar for the calculations with non-pH dependent and pH-dependent kinetics. For the given micro-galvanic couple, the effect of local pH on the anodic current density is not pronounced.

**Influence of local pH on the integrated anodic and cathodic currents.**—Fig. 8b displays the temporal evolution of integrated anodic and cathodic currents (always equal) across the whole active surface. Calculated with non-pH-dependent kinetics, the integrated current increases during the first 40 h and then decreases with time due to the blocking effect of deposited Al(OH)$_3$, and the actively dissolving surface is totally blocked after ca. 50 h. With the pH-dependent kinetics, the integrated current increases to higher values within a shorter period (ca. 35 h) and then decreases with time, and the actively dissolving surface is totally blocked after ca. 42 h. Since the pH-dependent kinetics takes into account the enhancement of localized alkalization and acidification in micro-galvanic corrosion, it is reasonable that the anodic dissolution and cathodic reduction rates proceed faster than with non-pH-dependent kinetics.

Due to the small size of the micro-galvanic couple, it should be noted that the extent of the corrosion attack is quite limited and the difference of local pH across the whole active surface is relatively small according to the simulation results. This is different from traditional pitting corrosion that proceeds through self-catalytical propagation whereby the local pH may become extremely low within the corroding volume. However, owing to its general form, it is possible to extend or apply the present model to a variety of local corrosion systems, providing a potent method to evaluate the distinct roles of the solution chemistry (e.g., pH) and the galvanic effects on the initiation, propagation and repassivation of localized corrosion.

**Influence of bulk O$_2$ concentration.**—O$_2$ concentration in the solution is another important factor affecting the corrosion process, especially for localized corrosion (e.g., pitting and crevice corrosion) occurring in an occluded volume. To explore the effect of local pH and O$_2$ concentration simultaneously, the pH-O$_2$ concentration-dependent kinetics (Fig. 3) is used as input to describe the electrochemical kinetics in the simulation. Fig. 9a–9b show calculated anodic and cathodic current densities for different bulk O$_2$ concentrations with a bulk pH at zero time and after 42 h, respectively, plotted as a function of distance from zero point along the active surface. In the beginning, a higher O$_2$ concentration gives a higher cathodic current density along the original surface of cathodic particle ($x = 0–2 \ \mu$m) and also a higher anodic current density ($x = 2–3 \ \mu$m). Both anodic and cathodic current densities are uniformly distributed along the active surface.

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**Figure 9.** Current density along the active surface for different O$_2$ concentrations: (a) at 0 h, (b) at 42 h. (c) Local pH distribution along the active surface after 42 h for different bulk O$_2$ concentrations. The simulated electrolyte is 0.1 M NaCl with bulk pH = 6.
Figure 10. (a)-(d) Position of the anodic dissolution front after 42 h for O₂ concentration of 0.1csat, 0.2csat, 0.5csat, csat, respectively. The contour color profile indicates the local pH value. The simulated electrolyte is 0.1 M NaCl with bulk pH = 6.

The calculated anodic and cathodic current densities after 42 h are shown in Fig. 9b. Compared to the current density in the beginning, the anodic current density slightly drops with distance to zero point, a tendency which is more pronounced at higher O₂ concentration. The rightward shift of the borderline indicates the expansion of the electrochemically active surface, including both the Al matrix (anode) and the particle (cathode). To visualize the propagation of the micro-galvanic corrosion, two-dimensional plots in Fig. 10 show the position of the dissolving front after 42 h, with the color scale displaying the local pH distribution. Clearly, a higher O₂ concentration promotes the corrosion process by supplying more galvanic current.

During the micro-galvanic corrosion, localized alkalinization occurs on the surface of the cathodic particle due to the local oxygen reduction, and localized acidification occurs near the surface of the actively dissolving front through the hydrolysis caused by released Al³⁺ ions. The simulation can quantitatively predict these changes. Fig. 9c displays the local pH distribution along the active surface as function of the distance to zero point after 42 h. Clearly a higher O₂ concentration leads to more severe local alkalinization on the surface of the particle, and more severe local acidification along the surface of the dissolving front, thus the difference between the lowest and the highest pH values increases with increasing bulk O₂ concentration.

The pH-dependent electrochemical kinetics indicates that both alkaline and acidic environments can promote the micro-galvanic corrosion process. Comparing Fig. 9b and 9c, the local alkalinization on the particle surface indeed increases the local cathodic current density. Moreover, the results also reflect the gradually weakened effect of the local alkalinization with increasing distance away from the particle center. On the other hand, the actively dissolving front far from the particle turns out to be the most acidic area (see Fig. 10). However, the anodic current density on this point is relatively low (Fig. 9b), which can be explained by the blocking effect of deposited Al(OH)₃, as discussed below.

Influence of bulk O₂ concentration on deposition of Al(OH)₃.— As the corrosion proceeds, both the extension of the anodic area and the deposition of Al(OH)₃ lead to decreased anodic current density. Fig. 11a illustrates the Al(OH)₃ coverage and blocking effect after 42 h for different O₂ concentrations with bulk pH = 6. For saturated O₂ (cO₂ = csat), the coverage is higher than 0.9 on the anodic surface so the dissolving surface is almost totally blocked by the deposited Al(OH)₃. The surface coverage is lower for lower O₂ concentration, with average values of 0.7, 0.5, 0.3 for 0.5csat, 0.2csat, 0.1csat, respectively. Although the hydrolysis caused by Al³⁺ ions leads to local acidification inside the dissolving volume, the lowest pH value among all the investigated O₂ concentrations is higher than 5.8 (Fig. 9 and Fig. 10), which is not acidic enough to inhibit the deposition of Al(OH)₃.

Fig. 11b displays the temporal evolution of the integrated current for different O₂ concentrations. For cO₂ = 0.1csat and 0.2csat, the total current is relatively low and increases gradually for more than 100 h,
Nisancioglu et al. proposed that the oxygen reduction makes the model more realistic by considering the impact of heterogeneous electrochemical kinetics as input parameters in which the local alkalization seems not possible. Frankel et al. have been challenged by the trench formation in acidic environment, as trenches, which has been debated for a long time. Such a mechanism action was critical for initiation of circumferential pits, also referred to 42 h, respectively. It starts to decrease after 40 h and 30 h, and the active surface is totally blocked after 55 h and the beginning, and is followed by a more rapid blocking of the dissolving deposition. As a result, the localized corrosion proceeds fast in the beginning, and is followed by a more rapid blocking of the dissolving surface. How fast the dissolving front propagates is determined by the competition between these two processes.

Implications of the simulation results.—The major contribution of our serial work is to build a comprehensive model taking into account the involved multi kinetic physicochemical processes, opening possibilities to investigate the effects of geometric and chemical factors on the micro-galvanic corrosion of Al alloys. The effects of bulk pH, dissolved CO₂ concentration and deposition of corrosion product and its blocking effect on surface reactions. The implications of the simulation results indicate that the concentration of the chlor-alkali compound (Al(OH)₃Cl) is much lower than its solubility, i.e., the deposited product is mainly Al(OH)₃, even when bulk Cl⁻ ions concentration is increased to 0.6 M. In reality, Cl⁻ ions may affect the localized corrosion of Al alloys in other ways. Specific adsorption of Cl⁻ ions, for instance, may lead to local concentrations of Cl⁻ ions. Interaction between Cl⁻ ions and the passive layer may furthermore lower the pitting potential locally, and interaction between Cl⁻ ions and the deposited Al(OH)₃ reduce the blocking process. To fully consider the effect of Cl⁻ ions on the localized corrosion of Al alloys, the present model needs to be further elaborated.

Conclusions

A finite element model has been developed for simulation of micro-galvanic corrosion of Al alloys which takes into account coupled local electrochemical reactions, mass transport, homogeneous chemical reactions in the solution, as well as a moving dissolution boundary, deposition of corrosion product and its blocking effect on surface reactions. The effects of bulk pH, dissolved CO₂ concentration and dissolved O₂ concentration in the solution have been investigated, and the following conclusions have been drawn:

- pH-dependent electrochemical kinetics of the cathodic particle and dissolving Al matrix have been obtained by interpolating the electrochemical polarization curves measured at pH = 2.5, 6, 10, respectively. The interpolated kinetic surface shows that both acidic and alkaline conditions enhance Al dissolution and oxygen reduction rates, with pH = 6 exhibiting a minimum.
- Use of the pH-dependent electrochemical kinetics as input data enables evaluation of the effects of unevenly distributed localized pH across the active surface. For a given bulk pH, localized alkalization due to the cathodic oxygen reduction on the particle surface further promotes the cathodic reaction, supplying more galvanic current for faster Al dissolution.
- Within the bulk pH range from 4 to 9, under weak alkaline condition (pH > 6), a higher bulk pH results in a faster galvanic...
dissolution rate but a shorter time before the active surface is blocked totally. Under weak acidic condition (pH < 6), a lower pH leads to a faster galvanic dissolution rate and a longer time because the low pH inhibits the deposition of Al(OH)₃. When the bulk pH = 4, Al(OH)₃ deposition does not occur, which is consistent with experimental observations.

- Compared to a neutral solution (pH = 7), dissolved CO₂ in the solution (pH = 5.6) leads to a decreased rate but a longer time during which micro-galvanic corrosion operates.
- A four dimensional volume representing pH-O₂-dependent electrochemical kinetics has been built and successfully used as input data for the simulation. This broadens the application of the model for investigation of localized corrosion by taking into account the bulk O₂ concentration in the solution.
- A higher bulk O₂ concentration leads to more severe local alkalization on the cathodic particle and local acidification along the solution (pH beginning, followed by a quick blocking of the dissolving surface.
- By considering geometrical and chemical factors independent of each other, this physicochemical model may provide a deeper understanding of the mechanisms of micro-galvanic corrosion and other local corrosion phenomena.

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