Frankel and coworkers\(^1\) considered the anisotropy of the intergranular corrosion process and performed foil penetration tests using various electrochemical conditions. They proposed that the propagation rate of intergranular corrosion followed a power law of the following type:

\[
d = at^n
\]  

where \(d\) is either the nominal thickness of the full penetrated foil or the resulting IG path length, \(a\) and \(n\) are constants (\(n\) is between 0 and 1) and \(t\) the time for the full penetration. To discuss these results in terms of IG propagation rate the raw data can be inverted and expressed as the depth of the fastest growing site as a function of time. However the physical meaning of the exponent and its value as function the nature of the alloy have not been discussed to our knowledge. Nevertheless, interesting work described in Ref. \(^2\) illustrated application of such a law (relation 1) deduced from laboratory experiments to operational aircraft. In these practical cases there was a large variation in corrosion growth rates from one section of a wing to the next or from an aircraft to the next. But it was demonstrated that it was possible to provide a distribution for coefficients of relation (1), especially for coefficient \(a\), which could be deduced from documented corrosion data collected, for example, from repair data.

Relation (1) which means that the intergranular (IG) propagation rate on aluminum alloys (AA2024) is decreasing as function of the IG path length has been validated under potentiostatic conditions.\(^1\) Moreover this trend has been also frequently discussed in other studies under free corrosion conditions.\(^3,4\) Nevertheless, the origin of this feature has not been largely discussed quantitatively, especially as the inner surface of the “IG crevice” behind the active anodic head at the point of attack\(^5\) can also suffer dissolution at a reduced rate and at long exposures as illustrated in different works showing a blunting of the IG path,\(^6,7\) Consequently the mass transport and/or the ohmic drop can control the intergranular penetration as it has been discussed for crevice corrosion\(^8\) even if the geometry of the active anodic area is different.

Under potentiostatic control or under free corrosion conditions, for which rapid penetration attack, e.g. 60 \(\mu\)m after 2 hours of immersion in 0.1M \(\text{NaCl}\) solution has been reported for an AA2024,\(^9\) the same questions about the controlling factors arise.

The most advanced discussion on the electrochemical current variation during potentiostatic tests on a geometry close to that of IG paths was reported by Akiyama and Frankel\(^9\) for an artificial crevice cell consisting of a sandwich of Al foil/transparent sheets which presented a geometry similar to the confined geometry of a 1D-artificial pit electrode. Assuming the dissolution of the precipitated free zone (pfz) at the head of the “IG crevice” as the controlling process, from the total current which would decrease as function of the “length” of active IG paths, it would be possible to define a current by applying the Faraday’s law to predict the IG propagation rate. But as already discussed in a previous paper,\(^9\) the same approach based on the analysis of the time evolution of the net anodic current of the head of the cavity was difficult to apply to IGC.

As mentioned by Glenn and coworkers,\(^9\) the IG attack can be attributed simply to the acidic environment at the “head” of the IG attack compared to solution in the “IG crevice” behind the active front. To support this assumption, the authors assumed that the dissolution of the pfz and the precipitates would lower the pH due to hydrolysis of aluminum ions. The location of the cathodic areas, inside or outside the IG paths, can affect the chemical gradients inside the IG paths and affect the role of the ohmic drop. Electrochemical reduction reactions can occur in the “IG crevice” walls which are decorated by Cu particles coming from the selective dissolution of the precipitates.\(^9,10\) However, the location of the main cathodic contribution (inside or outside the “IG crevice”) counterbalancing the dissolution of the head remains an open question. The existence of a pH gradient inside the “IG crevice”, which is assumed by Glenn and coworkers\(^9\) was difficult to validate by pH probing. The presence of a pH gradient was easier to discuss through modelling as proposed recently.\(^12\)

In this paper we present an alternative detection method for the foil penetration technique\(^1\) to strengthen the robustness of the measurement of the penetration rates of IG “fissures”.\(^13\) The complementary methodology improvements, i.e. the control of the IGC initiation and the chemical analysis of the electrolyte trapped inside the grain boundary network, will be described and applied to assess quantitatively the IGC propagation on Al-Cu alloys.

The first improvement consisting of a well-controlled pre-corrosion procedure allowed the reduction in scattering of data on the IG propagation rate. The second one, based on the possibility to very easily collect the purged electrolyte from full penetrated foils, was used to probe the chemistry inside the “IG crevice”. The measured value of the pH of the purged electrolyte was validated by mass transport and reaction models which were numerically solved considering the grain boundary cavity, i.e. the “IG crevice”, as a pore-shape electrode. Moreover, the foil penetration results obtained for free corrosion conditions were used to evaluate the relevance of these models with several configurations for the location of cathodic areas.

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Experimental Part: Results and Discussion

In this experimental section, experimental procedure, results and their interpretation will be described.

Experimental.—Material and samples.—Foils of varying thicknesses (defined as the nominal thickness) 210, 320 and 520 μm were machined in thick plates of a 2024-T3 aluminum alloy in the longitudinal (L) direction. The average grain sizes within the plate were respectively 100, 300 and 700 μm in the short transverse (ST), long transverse (LT) and L direction. The face exposed to the corrosive solution - a 0.1M NaCl aerated solution - was the LT – ST face. The choice of studying the propagation in the L direction was made in order to approach the intrinsic propagation rate for a wide range of thicknesses because the average grain size can reach, as mentioned previously, 700 μm in this direction. Consequently the morphology of the IG defects corresponding to sharp “fissures” in 2D metallographic cross section as shown in Figure 1b, allowed to assume that the length of a full penetrating IG path through a thin foil (up to few hundred of μm-thick) was equal to the thickness of the foil.

Foil penetration set up.—To measure the IGC penetration rate, a direct optical interrogation of the rear side of the foils (see Figure 2) was performed recording the arrival of the full penetrating IG paths as described in a previous paper.13 Compared to this preliminary work13 carried on TL-L exposed surfaces for which penetrating IG paths presented an important tortuosity, in this work, the IGC propagation was studied in the L direction to approach the intrinsic propagation rate, as explained before. The optical detection consisted in detecting the purged electrolyte trapped in the “IG crevice” cavities emerging along full penetrating defects and forming droplets (Figure 2a). Typical minimum size of the detected droplets was approximately 50 micrometers.

What an electrolyte droplet represents?.—The detected droplets can be considered only as apparent indicators resulting from the emergence of the electrolyte trapped inside the dissolved grain boundaries. By following in detail a network of droplets it was illustrated that, as shown in Figure 2b1, initially a small “crack”, resulting from the full penetration of a grain boundary, appeared and was followed by electrolyte leakage through this “crack” forming a first droplet. After this, the “crack” grew, revealing a longer trace of a full penetrating grain boundary (see the arrow on the pictures in Figure 2b1). Then other droplets could appear or existing droplets could grow.

From a phenomenological point of view the optical detection of full penetrating IG paths contributes to image the propagation regime along a grain boundary as shown in the 3D schematic diagram in Figure 2b2. It can be determined that the dissolution along a grain boundary (3D) is not uniform because only segmented parts of a grain boundary intercepting with the image plane were revealed.

Undoubtedly, the time of the first emerging crack can be considered as a maximum value for the propagation regime. From the practical point of view the value of the full penetration time (FPT) was defined by the emergence of the first detectable droplet for a rear side surface of 5.3 × 7 mm. The average propagation rate (APR) was calculated by dividing the nominal thickness of the tested plate by the time that it takes for the fastest intergranular defect to fully penetrate the foil (FPT). Manual counting of the arrival of droplets along full penetrating defects on the recorded video sequence allowed to plot the variation of the cumulative number of droplet arrivals as function of time (Figure 3).

The time distribution of the emerging droplet is more difficult to analyze. It is clear from Figure 2 that the tempting assumption that one droplet is equal to one independent full penetrating defect cannot be made. Nevertheless, the cumulative number of droplets represents an indicator of the level of intergranular damage which could be used for ranking. Due to its complexity the time distribution of the emerging droplets will not be further analyzed in this work but a better understanding of this parameter is clearly of interest because it contains information about the initiation regime and the 3D volume propagation of IGC which are not well-documented in the literature.

Electrochemical conditions.—In this paper all the potentials were defined versus the saturated calomel electrode (SCE). Potentiodynamic polarization experiments were performed to electrochemically characterize the material. For the selected AA2024, the breakdown potential occurred at ~580 mV in 0.1M NaCl solution. Foil penetration experiments under potentiostatic conditions have been conducted imposing potential above and below the breakdown potential. The open circuit potential (OCP) was measured during five minutes before the potentiostatic tests. Before switching to the desired potential, a cathodic sweep occurred at 580 mV in 0.1M NaCl solution. Foil penetration experiments were also performed under free corrosion conditions, in full immersion and under small droplets measuring 3 mm in diameter. The diameter of the droplets was defined by a PTFE mask. The droplets were formed by a careful salt solution deposition using a microsyringe. In this case, the electrochemical cell was set up inside a small hermetic chamber containing a distilled water reservoir to limit the droplet evaporation.

pH measurement of the electrolyte trapped inside the “IG crevice”.—On the rear side of the foils the leaching of the electrolyte trapped inside the “IG crevice” allowed to proceed to a pH measurement using a pH-indicator paper. The modified foil penetration experiments13 provided an “easy” access to the rear side of the foil. The initial version of the foil penetration method was, in fact, based on this leaching which soaked the filter paper which was replaced in this work by a pH-indicator paper. The same approach was discussed in pioneering works of Boehni for pitting detection15 but it was concluded that the pH information was insufficient and did not allow further conclusions concerning the chloride concentration within the pit.

Figure 1. Metallographic cross section of an “as-received” specimen (nominal thickness = 210 μm). (a) before IGC test. (b) after corrosion in NaCl 0.1M solution showing sharp “fissures” corresponding to full penetrating IG paths in L direction.
Experimental results.—IG propagation kinetics on AA2024 under potentiostatic conditions.—Analysis of the scattering of data.—A first set of foil penetration experiments were performed on 210-μm thick foils at different potentials above the breakdown potential (-580 mV). The targeted potential was applied immediately after the cathodic sweep and the FPT was measured. The time zero was defined at the beginning of the potentiostatic step. As summarized in the first part of Table I, the full penetration time exhibits a large scattering for low potentials.

This scattering might be due to the IGC initiation which could be less controlled for lower potentials. Indeed, Zhang and Frankel have shown that the number of attacked boundaries per unit of cross-sectional area increased as function of the potential. To test this hypothesis, the foil penetration test sequence was modified as follows. After the initial potentiodynamic sequence, the samples were pre-corroded for five minutes at -480 mV, which is 100 mV higher than the breakdown potential previously defined. At the end of this pre-corrosion step, SEM observations showed sharp “fissures” which were homogeneously distributed all along the surface with a maximum depth of 60 μm (Figure 4). It induced a regular network of IG defects which were considered as controlled initiation sites. After this pre-corrosion step, the potential was switched to the desired potential and the time for IG defects to penetrate the rest of the foil was measured.

To check the validity of the 60 μm maximum depth obtained for IG defects after the pre-corrosion procedure, a 210-μm thick foil was thinned to 60 μm by mechanical polishing and a foil penetration experiment was carried out. It was confirmed that it took around 5 minutes for the fastest IG defect to fully penetrate the foil at -480 mV.

It must be noted that other authors also proposed to reduce the randomness of initiation by artificially initiating IGC using electrochemical polarization but inducing just a form of selective grain attacks.
Figure 3. Typical time distribution of the formation of droplets along full penetrating defects for a 210 \( \mu \text{m} \) thick foil (\( E = -480 \text{ mV} \)). Pictures of the rear side of the foil at different times (\( t = 0 \) and \( t = 60 \text{ min} \)) are also presented. The white circles represent the droplets emerging from the defects.

rather than a real IG “fissures”. The same approach was proposed by Zhang and Frankel\(^1\) who had also included a polarization step at high potential in order to control the IGC to obtain reproducible propagation laws, but the potential was much higher (-290 mV) and the polarization time much lower (one second).

In the following, the modified experimental procedure was then applied to determine the apparent average propagation rate (\( \text{APR}^* \)).

Variation of the average propagation rate as function of the apparent thickness.—The experimental procedure including the pre-corrosion step was applied for foils of nominal thicknesses of respectively 210, 350 and 520 \( \mu \text{m} \) for three anodic potentials and for \( -600 \text{ mV} \) which was lower than the breakdown potential. As illustrated in the second part of Table I, the scattering of FPTs was drastically reduced. This confirmed that the IGC initiation

| Imposed potential (SCE) / mV | Free corrosion conditions |
|-----------------------------|--------------------------|
|                             | immersion | droplet 3mm |

\( \text{APR}^* = (\text{nominal thickness} - 60 \mu\text{m}) / (\text{FPT} - 5 \text{ min}) \) calculated for the minimum FPT value whereas \( \text{APR} = \text{nominal thickness} / \text{FPT} \).
had to be controlled to determine accurately the IGC propagation rate.

Considering the modified experimental procedure, the FPT represents the time for the IG defect to grow from 60-μm depth to the depth corresponding to the nominal thickness (the total depth minus the pre-corrosion step). This difference was defined as the apparent thickness. The APR\(^\ast\) was then calculated by dividing the apparent thickness by the minimum value of the full penetration time deducing the pre-corrosion time. For example, for a 210-μm thick sample and a pre-corroded depth of 60 μm, the apparent thickness was 150 μm, so to obtain the APR\(^\ast\), the 150 μm was divided FPT minus 5 min of pre-corrosion step.

As shown in the second part of Table I, the APR\(^\ast\) was calculated for each experimental condition using the minimum FPT among three tests. The minimum FPT gave the value closest to the intrinsic propagation rate because longer full penetration time could be due to either a weak tortuosity or a shift in initiation time.

For the same applied potential, the APR\(^\ast\) decreased as function of the apparent thickness of the specimen. This means that the instantaneous propagation rate was decreasing as function of the IG depth. This was consistent with the work of Frankel and coworkers\(^*\) and will be discussed in section Validation of a propagation law.

The effect of the potential on the APR\(^\ast\) was dependent of the potential range. For potentials higher than the breakdown potential, a slight increase of the propagation rate as function of the potential was observed whereas there was a drastic change of propagation scheme when the potential decreases below the breakdown potential. The scattering of the data was higher especially for the 520-μm thick foil. The APR\(^\ast\) at −600 mV was much lower than the APR\(^\ast\) defined for potentials higher than the breakdown potential.

Regarding the morphology of the induced intergranular corrosion damages which were studied by analyzing metallographic cross sections (Figure 5) the same transition was found. For potentials higher than the AA2024 breakdown potential, sharp “fissures” were observed (Figure 5a). For potentials lower than the AA2024 breakdown potential, the alloy was still sensitive to IG corrosion but there was also dissolution of the grain boundary walls leading to a blunting of the IG paths, whereas some pits could appear at the surface of the alloy (Figure 5b). Zhang and Frankel\(^*\) discussed the existence of a critical potential corresponding to the transition between pitting and IGC. However, in our case, it seemed to be an effect of time rather than a “potential transition” as illustrated in Figure 5b. Indeed, the alloy was still sensitive to IGC at −600 mV as shown by the thin filaments ahead the pre-corroded grain boundaries which widened at long exposures.

Figure 4. Metallographic cross section showing sharp “fissures” after the pre-corrosion step (E = −480 mV during for 5 minutes).

**IG propagation kinetics on AA2024 under free corrosion conditions.—**Variation of the average propagation rate as function of apparent thickness.—In immersion conditions, the same experimental procedure including a pre-corrosion step was applied for tests under free corrosion conditions. FPTs measured for 210 and 350-μm thick foils are presented in Table I. The APR\(^\ast\) calculated for the 210-μm thick foil was close to that calculated at −600 mV for the corresponding apparent thickness. However, the results were scattered, even more for the 350-μm thick foil. Experiments were also carried out on a 520-μm thick foil but the specimens remained unpenetrated (for an exposure time up to 360h), so it was impossible to define a FPT.

The localized corrosion morphologies were examined by metallographic cross sections. Some IG defects with a depth lower than 60 μm, formed during the pre-corrosion step, did not propagate under free corrosion conditions (Figure 6a) whereas some defects propagated and perforated the foil (Figure 6b) confirming the results presented in Table I.

Under free corrosion conditions, results confirmed the random nature of IGC in these conditions, which has been discussed in numerous studies.\(^1,3,6\) In section Theoretical part results and discussion, it will be shown that the results provided by the numerical models allow the proposal of a reliable hypothesis to explain the random nature of IGC under free corrosion conditions.

**Influence of the exposure conditions.—**IGC propagation under free corrosion conditions was also studied under 3 mm diameter droplets which were closer to the atmospheric corrosive conditions encountered by real structures. In this case, as no pre-corrosion step was applied, the time considered to calculate the APR corresponded to the time elapsed for the fastest full penetrating intergranular defect to perforate the entire nominal thickness. The measured values were compared to foil penetration experiments carried out under immersion conditions following the same experimental procedure (Table I).

APR\(^\ast\) was much higher for a 3 mm diameter droplet. This could be explained by the increase of the cathodic kinetics inside the droplet due to the higher oxygen concentration at the surface of the alloy. Indeed, the oxygen flux toward the surface was much higher inside a droplet.
Validation of a propagation law.—Effect of the depth of IG path on the IGC propagation rate.—Results obtained from foil penetration experiments (Table I) were post-treated to retrieve the relation between the propagation time and the IG depth. Even if penetration experiments generated FPTs for foils of varying thicknesses, results could be plotted as the thickness or depth of the fastest IG path versus propagation time. As shown in Figure 7a for a potential of $-480$ mV, by fitting a power law to these experimental data points, it was possible to plot a virtual curve representing the time variation of the depth of an intergranular defect. The individual data points were matching with an equation of the already discussed form:

$$d = a \cdot t^n$$

with, in this work, $a = 350$ and $n = 0.67$ for an imposed potential of $-480$ mV ($d$ and $t$ are expressed respectively in $\mu m$ and $h$).

This confirmed the findings of Zhang and Frankel, who introduced this type of equation to describe IGC kinetics. It must be kept in mind that this type of law was validated for an IGC mechanism based on continuous dissolution of the pfz (for AA $2xxx$ or AA $7xxx$ series) but was still not valid for example for AA $5xxx$ because IGC propagation was not controlled by pfz dissolution.

The time dependent propagation law (relation 1) was derived to yield an instantaneous propagation rate ($v_{inst}$), which was plotted as function of the depth ($d$) of the IG path (Figure 7b).

$$v_{inst} = an \left[ \frac{d}{a} \right]^{n-1}$$

It is worth noting that this latter relation represents the intrinsic propagation rate due to the choice of the propagation direction. This implies that the decrease cannot be attributed to the branching of IG defects within the microstructure. The decay of $v_{inst}$ (Figure 7) explained why the APR was decreasing as a function of the apparent thickness of the specimen. This was more pronounced for a small IG depth.

In a previous paper, simulating the IG path by a dissolving pore-shape electrode consisting in a pure Al wire, it was also found that the propagation rate for the 1D-artificial pit electrode decreased as a function of the depth of the defect. It was concluded that IGC was under ohmic control explaining the decrease of the propagation rate as function of the polarization time or depth of IG path on specimens tested in the L direction. Nevertheless, it was impossible to validate this assumption on thin foil specimens by analysing the recorded current to find a relationship between the net current and the time of the APR.

Effect of potential conditions (imposed or OCP).—The same methodology was applied to determine the influence of the potential on the propagation rate. Relation 1 was used to fit the experimental data obtained for each potential (Figure 8). The values of the coefficient $a$ and $n$ can be found in Figure 8b. For potentials higher than the breakdown potential, it seemed there was a slight effect of the potential on the propagation law which could be taken into account by only varying the value of $a$. The influence on the exponent, $n$, was limited in this range of potential. It could be related to the fact that the tested potentials were close each other and that the dissolution of the pfz occurred at the same rate.

In Figure 9, propagation rates obtained on AA2024 foils were compared to the propagation rate found for a 1D-artificial pit pure aluminum electrode mimicking an IG path as appearing on metallographic cross section showing clearly sharp “fissures” (see for...
example Figure 5a). The propagation rate for the “1D-artificial pit” was obtained from the current density using the Faraday law.

In order to normalize the curve fitting, the results were presented considering the value of the imposed potential versus the breakdown potential of the metal electrode. A good agreement was found between the dissolution rate of the 1D-artificial pit electrode and the propagation rate of IGC on AA2024 for a potential 100 mV higher than the breakdown potential. These results confirmed the assumption that the IGC propagation was controlled by the anodic dissolution of the pfz which had the same dissolution rate as pure aluminum. It also validated the assumption of the pore geometry to represent an IG path as function of the potential.

It was clear from the data presented in Figure 8 that there was a change of propagation scheme when the imposed potential was below the breakdown potential. The values of both coefficients $a$ and $n$ in the propagation law decreased in agreement with the lower propagation rate of IGC. Consequently at potentials below the breakdown potential, as propagation in depth was slow down, the grain boundary walls were dissolved during the IGC propagation leading to the blunting of the IG defect (Figure 5b). A recent study has shown it was possible to quantify the porosity induced by the dissolution of the grain boundary walls by recording the apparent conductivity with an eddy current probe. At potentials higher than the breakdown potential, the dissolution rate of the grain boundary walls was much lower than the dissolution rate of the tip of the defect. This explains why the blunting of the IG path was not observed on metallographic cross sections during the reduced full penetration time.

Under free corrosion conditions, it was impossible to define a propagation law under immersion conditions due to the high amount of scattering of the data, especially for thicker foils. The observations on metallographic cross sections showed that the IG defects did not grow identically; some of them propagated whereas others repassivated. As under free corrosion conditions the question of the location of the cathodic reactions is still under debate in the literature, several configurations will be tested with mass transport models as proposed by Abodi and co-workers. In the theoretical section, it will be shown that one of the configurations well describes the experimental findings suggesting an explanation for the scattering of data under free corrosion conditions.

**Determination of the pH value of the electrolyte trapped in the “IG crevice”:**—Although chemical analysis have been reported for stress corrosion cracking or artificial crevices on aluminum alloys, chemical analyses of the electrolyte trapped in corroded grain boundaries have never been reported to our knowledge. As already discussed in the experimental section, the filter paper of the initial version of the foil penetration technique was replaced by a pH-indicator paper. pH measurement on the rear side of the foils was repeated for several electrochemical conditions (potentiostatic and OCP) and different nominal thicknesses (between 210 and 520 μm). Irrespective of test conditions, the pH paper turned pink (Figure 10) indicating that the pH value of the electrolyte trapped in the “IG crevice” was around 1 and that in particular this value was independent on the depth of the “IG crevice” and the electrochemical conditions.

This acidification resulted from the hydrolisis of Al ions generated at the tip of the “IG crevice” and from the reduced mass transport from the bulk to the confined dissolved grain boundary which helped to maintain the local occluded chemistry. This assumption will be checked in the theoretical section using mass transport models to simulate the chemical evolution of the electrolyte within the “IG crevice” during the propagation.

**Summary of experimental results:**—An alternative detection method applied to the foil penetration technique allowing monitoring of the penetration of IG defects through thin foils by continuous optical video recording of the rear side of the foil was presented. As the rear side of the foil was free during the experiments it was possible to collect and analyze the electrolyte trapped inside the grain boundary network and released by the full penetrating defects. Moreover, the optical detection provides the time distribution of the droplets which was related to all of the full penetrating defects. This parameter remained difficult to interpret but it probably contains information about the initiation regime and the 3D volume propagation of IGC which are not well-documented in the literature.

The results highlighted the importance of the control of IGC initiation to accurately determine the propagation rate. A well-controlled experimental procedure consisting in the generation of short “fissures” was then developed and was used to study the effects of the depth of the “IG crevice” and of the potential on the propagation rate of intergranular corrosion.

On AA2024 foils it was confirmed that the propagation of intergranular corrosion under potentiostatic conditions can be realistically described by a function of the form $d = a \cdot t^n$ (with $n$ value between 0.67 and 0.67).
the grain boundary network was measured for various foil thicknesses and several electrochemical conditions. It was found that the pH value was around 1 and did not depend on the depth of the “IG crevice” and the electrochemical conditions. In this work, only pH measurement of the electrolyte was carried out but it would be interesting to go deeper with finer chemical analyses, as performed during crevice corrosion for ferrous alloys\[^{25}\] in order to obtain more robust validation data for mass transport models.

### Theoretical Part: Results and Discussion

In this section, after the presentation of the theoretical model, results of the simulation of the pH distribution inside the “IG crevice” will be compared to experimental measurements of the pH of the trapped electrolyte released from full penetrating intergranular defects which were described in the previous part (Figure 10). First under potentiostatic conditions, the model specification, especially the definition of the homogeneous reactions occurring inside the “IG crevice” and controlling the expected hydrolysis of $\text{Al}^{+++}$ cations, was validated. This was possible by converting the propagation rate determined experimentally in a flux boundary condition for the dissolution of the pfz. Secondly under free corrosion conditions, the same mass transport simulation was applied to clarify the location of cathodic areas which remains an open question. Moreover we discussed the relevance of this numerical model regarding the difference in propagation rates observed in immersion versus droplet conditions.

**Model and governing equations.**—Using COMSOL Multiphysics software to solve the basic differential equations (Nernst-Planck equation) describing the mass transport and electrochemical and chemical reactions occurring inside the “IG crevice”, simulations were performed to calculate the chemical changes inside a pore-shape electrode representing a dissolving grain boundary. Simulations were made for various electrochemical (potentiostatic and OCP) and environmental (full immersion and droplet) conditions. Mass transport and reaction models were solved for both the steady and time dependent states using Finite Element Method (FEM) analysis. In this modelling approach it was assumed that the Nernst-Planck equation describing the mass transport control (migration, diffusion) and the mass conservation of chemical species was still valid at the reduced scale of the “IG crevice”. The construction of these models were mainly validated using the measurement of the pH of the electrolyte trapped in the IG full penetrating paths which could be easily collected in the revisited foil penetration experiments.

**Mathematical background.**—In the electrolyte, the motion of the species can be described using the Nernst-Planck equation at steady state and for time dependent simulations. The mass conservation for any chemical species considered in the medium is given by:

$$\frac{\partial C_i}{\partial t} = R_i \cdot \nabla N_i$$

\(N_i\) stands for the flux of species \(i\) \((\text{mol.m}^{-2}.\text{s}^{-1})\), \(C_i\) the concentration of species \(i\) \((\text{mol.m}^{-3})\) and \(R_i\) \((\text{mol.m}^{-1}.\text{s}^{-1})\) the production/consumption rate of species \(i\) due to chemical reactions.

Excluding the convection term, the flux can be expressed as follows:

$$N_i = -D_i \nabla C_i - z_i u_i F C_i \nabla \phi$$

Consequently the governing equation, i.e. Nernst-Planck equation, dealing with transport of species by diffusion and migration and reaction processes, can be written:

$$\frac{\partial C_i}{\partial t} = R_i + D_i \nabla^2 C_i + z_i u_i F \nabla (C_i \nabla \phi)$$

where \(D_i\), \(z_i\), \(u_i\) represent respectively the diffusion coefficient \((\text{m}^2.\text{s}^{-1})\), the charge number and the ionic mobility \((\text{s.mol.kg}^{-1})\) of species \(i\). \(\phi\) is the electric potential in the solution, \(F\) the Faraday

\[
\begin{array}{|c|c|c|}
\hline
\text{pH of test solution} & \text{Observed colouring} & \text{Commercial indication} \\
0 & 5 & \\
1 & 5 & 5 \\
2 & 5 & 5 \\
3 & 5 & 5 \\
7 & 5 & 5 \\
10 & 5 & 5 \\
\hline
\end{array}
\]

**Figure 10.** pH measurement of the electrolyte trapped inside the “IG crevice”. Left: schematic set up; the pH indicator paper was taped on the rear side of the foil; calibration of the pH indicator paper. Right: rear side of 210-μm thick foils covered partially with a pH-indicator paper after full penetration of IG paths: (a) OCP; (b) −480 mV; (c) −600 mV.
constant \((F = 96485 \text{ A.s.mol}^{-1})\). The ionic mobility \(u_i\) can be expressed through the Nernst-Einstein equation: \(u_i = D_i / RT\), where \(T\) is the absolute temperature \((K)\) and \(R\) the universal gas constant \((R = 8.314 \text{ J.mol}^{-1}.K^{-1})\).

One of the unknowns is eliminated by the electroneutrality condition:

\[
\sum_i z_i C_i = 0 \quad [7]
\]

Modeling outputs concerned various chemical and electrochemical parameters; but the main one was the pH gradient inside the dissolved “IG crevice” or filament and specially the pH of the trapped electrolyte which could be collected on the rear side of the specimen.

**Representative geometry for simulation.—**A 2D axisymmetric geometry has been defined (see Figure 11). The active tip (dissolution of the pfz) was placed over a very deep and narrow cylindrical pore with a radius of 50 nm (domain #1). The outer electrolyte (domain #2 in Figure 11) was only described by a limited zone in which the gradient of species could be found (diffusion layer) whereas their concentrations were assumed to be constant in the bulk electrolyte which was not represented in the schematic description presented in Figure 11a. Indeed the electrolyte was considered as stagnant, consequently the concentration of species in the bulk electrolyte were controlled by the natural convection which lead to uniformed concentrations of species (no gradient), whereas this effect was not sensitive at the surface of the electrode where concentrations were under diffusion and migration control. Then boundary #5 (Figure 11a) which defined the transition between the bulk and this region near the surface was fixed by the thickness of the diffusion layer (500 \(\mu\text{m}\)). On boundary #5, the concentrations were those of the 0.1M NaCl solution (neutral pH) used in our experiments (see Table II). The value of the electrical potential in solution, \(\theta\), was fixed to 0 along this boundary #5 (virtual counter electrode).

**Homogeneous solution chemistry in the “IG crevice”.—**Chemical reactions which could occur in solution have been defined considering the already selected chemical species (Table III) and were characterized by the diffusion of species in solution (Table II) and kinetics of the involved homogeneous reactions (Table III). These homogeneous reactions were defined whatever the simulation conditions, i.e. potentiostatic or OCP conditions.

The modelling approach was developed not to predict the IG propagation rate but to validate the model specifications assumed in the previous tables (Tables II and III). Unlike to other modelling approaches which have been applied to localized corrosion processes, robust experimental output data from the foil penetration experiments (Table I) were used as boundary conditions (instantaneous propagation rate) or as validation parameter (pH value of the electrolyte trapped in the “IG crevice”).

**Simulation under potentiostatic conditions and discussion.—**Initial and boundary conditions.—Initial values of the concentration of chemical species were defined in Table II. The main boundary condition which might be defined in details was that at the active tip of the pore. A flux condition was applied at this boundary (boundary #1). The anodic dissolution and also a cathodic contribution were assumed to occur at this location as demonstrated on a previous work on a 1D-artificial pit electrode. The same value of 10% for the ratio between the current related to \(\text{H}^+\) reduction reaction and the anodic current related to Al dissolution was applied to define the ratio between the flux of \(\text{Al}^{3+}\) and \(\text{H}^+\). If from the phenomenological point of view, it was important to consider this consumption of \(\text{H}^+\) in the mass balance inside the pore mimicking the IG path, its effect on the pH gradient inside the pore-shape electrode was found to be very low.

As already mentioned, the derivative of relation (1) which corresponded to the instantaneous propagation rate can be expressed as a function of \(d\), the depth of the IG path:

\[
v_{\text{inst}} = a n \left[ v_0 \right]^{v_1} \quad [8]
\]

and the current density related to the dissolution encountered at the pore tip, \(j_{pfz}\), was obtained from the Faraday law:

\[
j_{pfz} = \frac{3F \rho_{Al} V_{\text{inst}}}{M_{Al}} \quad [9]
\]
The molar flux of $\text{Al}^{3+}$ was easily deduced from $j_{p_{fz}}$:

$$N_{\text{Al}^{3+}} = \frac{j_{p_{fz}}}{3F}$$  \[10\]

On the basis of observations of cross sections of full penetrated foils as shown in Figure 5a, the grain boundary walls (boundary #2) were assumed to be chemically and electrically inactive which means that insululation and null flux conditions were imposed on this boundary. The consumption of the walls was neglected because their dissolution rate was much lower than the dissolution rate of the pfz for potentials higher than the breakdown potential (Figure 5a). This was probably not true for potentials lower than the breakdown potentials because the blunting of the IGC defects during the propagation was obvious on metallographic cross sections (Figure 5b). Therefore, no simulation was made in this range of potential.

Outer parts of the schematic boundary grain (boundary #3 and #4), defining the limits of the domain of resolution of Equation 6, were also assumed to be chemically and electrically inactive.

**Simulation results under potentiostatic conditions.**—Time dependent concentration profiles (not presented here) have been calculated for the following conditions: imposed potential of $-480 \text{ mV}$ and for a $200 \mu\text{m}$ “IG crevice” depth.

Regarding the boundary condition at the tip of the pore, it is reminded that the potentiostatic condition was simulated by imposing a fixed $\text{Al}^{3+}$ flux at the boundary #1 corresponding to the instantaneous propagation rate calculated at a given potential (e.g., Figure 7b for $-480 \text{ mV}$).

It was found that a change in pH occurring very rapidly, a steady-state was reached in less than one minute. Consequently, only the simulated pH at the steady state was considered for comparison with the experimental measurement performed on the leaking electrolyte.

As illustrated in Figure 12a, FEM simulation of mass transport inside a pore with an active tip resulted in a very acidic electrolyte, i.e. pH value around 1, which was in agreement with the experimental measurement made on a 210 $\mu\text{m}$ thick foil.

The effects of potential and “IG crevice” depth on the pH value at the tip of the grain boundary were evaluated from parametric studies. Regarding the boundary conditions, the increase of the “IG crevice” depth lead to a decrease of the pH value inside the crevice because the mass transport with the bulk was reduced. Consequently, the increase of the “IG crevice” depth lead to two antagonistic effects on the pH value inside the crevice.

However, simulation results (Figure 12b) showed that the two effects balanced each other because the pH value slightly varied with the “IG crevice” depth for a given potential. The potential did not much influence the acidity within the “IG crevice”. These findings were in accordance with the experimental results which showed that neither the “IG crevice” depth nor the potential (above the breakdown potential) affected the pH value within the crevice. From the mechanistic point of view, numerical simulation confirmed the acidification was mainly due to the hydrolysis reactions of $\text{Al}^{3+}$ cations emitted by the dissolution of the pfz.

**Simulation under free corrosion conditions and discussion.**—As shown in Figure 10, from the pH value of the collected electrolyte no difference has been found regarding the dissolution mechanism of the pfz under free corroding conditions. In contrary to potentiostatic condition, at OCP, the anodic dissolution must be balanced by a cathodic reaction. As function of its nature and mainly of the location of the cathodes, the change in chemistry inside the “IG crevice” can influence the acidity within the “IG crevice”.
be affected more or less. From a phenomenological point of view, the cathodic reactions, which whatever its nature results in local alkalization, could be located inside the “IG crevice” or on the outer surface. The cathodic reactions can occur, in the first case on re-deposited copper covering walls of the “IG crevice” or in the second case on the selectively dissolved coarse intermetallic particles. It can be expected that as function of their location, the cathodic reactions will affect (if inside) or not (if outside) the chemistry change inside the “IG crevice”.

It must be reminded that the influence of the location of cathodic reaction has been already discussed through numerical simulation in confined media and clearly demonstrated for crevice experiments on AA2024. In these later experiments, it was demonstrated that the electrolyte became alkaline when both the anodic and cathodic reactions occurred inside the crevice whereas it became acidic when the cathodic reactions took place outside the crevice.

In our work, pH measurement under free corrosion conditions were discussed comparing the mass transport simulation for two different configurations for the location of cathodic areas: cathode “in” for which the cathode was located inside the “IG crevice” and cathode “out” for which the cathode was located at the surface of the alloy.

**Initial and boundary conditions.**—Comparing to potentiostatic conditions, under free corrosion conditions, mass transport model was simulated considering the balance of cathodic (Ic) and anodic current (Ia):

\[ I_a + I_c = 0 \] \[ [11] \]

As the current balance (relation 11) was the controlling factor under free corrosion conditions, electrochemical kinetics have been fixed as boundary conditions to test especially the contribution of the cathodic reactions. These cathodic reactions were located along boundaries #2 or #3 as shown in Figure 13a. For “out” geometry, the cathode on boundary #3 was a ring of 1 μm width at a distance of 0.5 μm from the symmetry axis whereas for “in” geometry, the cathode was a cylindrical surface of 20 μm height located at half depth of the pore (domain #1).

Three irreversible electrochemical reactions were considered characterizing the anodic dissolution of the pfz (Al) (Boundary #1) and the cathodic reduction of H⁺ and dissolved O₂ occurring on the cathode:

\[ Al \rightarrow Al^{3+} + 3e^- \] \[ [12] \]
\[ H^+ + e^- \rightarrow \frac{1}{2} H_2 \] \[ [13] \]
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \] \[ [14] \]

Typical Butler-Volmer law (as function of \( \nu_m \phi \), where \( \nu_m \) was the potential of the metal and \( \phi \) the electric potential in solution) have been used to quantify the current density of the electrochemical processes contributing to the anodic and cathodic reactions:

\[ j_{Al} = i_{0Al} \exp \left( \frac{V_m - \phi - E^{0}_{Al}}{b_{Al}} \right) \] \[ [15] \]
\[ j_{H_2O} = -2Fk_{H_2O} \exp \left( -\frac{V_m - \phi - E^{0}_{H_2O}}{b_{H_2O}} \right) \] \[ [16] \]
\[ j_{O_2} = -4Fk_{O_2}C_{O_2} \exp \left( -\frac{V_m - \phi - E^{0}_{O_2}}{b_{O_2}} \right) \] \[ [17] \]

with \( i_{0Al} \) the exchange current density for Al dissolution, \( k_{H_2O} \) and \( k_{O_2} \) the interfacial rate constants, \( E^{0}_{Al}, E^{0}_{O_2} \) and \( E^{0}_{H_2O} \) the standard potentials and \( b_{Al}, b_{H_2O} \) and \( b_{O_2} \) the Tafel parameters. All the constant values deduced from previous work on simulation of localized dissolution of Al were summarized in Table IV.

**Figure 13.** Numerical simulation of the chemistry inside an “IG crevice” under free corrosion conditions. a) Schematic illustration (not at scale) of the boundary conditions for the two different geometries (cathode “in” and cathode “out”) under immersion and droplet exposures (same 2D axisymmetric geometry than in Figure 11). b) pH gradient inside the pore of 200 μm depth as function of the location of the cathode areas.

\( C_{O_2} \) represents the oxygen concentration at the cathode interface and can be deduced from the mass transport calculation affecting the bulk concentration \( C_{O_2} \) as function of selected geometries, i.e. cathode “in” or cathode “out”. As shown in Figure 13a, to distinguish immersion geometry from droplet one, two different values for the thickness of the diffusion layer (boundary #5 where the bulk concentration of dissolved oxygen \( C_{O_2} \) was imposed) were chosen to mimic the increase of mass transport process. The diffusion layer was maintained at 500 μm in immersion whereas it was reduced to 100 μm in the case of a droplet.

Regarding the anodic reaction, the molar flux of \( Al^{3+} \) imposed at the active tip was calculated using Equations 7 and the fluxes on the cathode were deduced from the current densities corresponding to the proton reduction (relation 14) and oxygen reduction (relation 15):

\[ N_{O_2} = \frac{j_{O_2}}{4F} \] \[ [18] \]
\[ N_{H^+} = \frac{j_{O_2} + j_{H_2O}}{F} \] \[ [19] \]
Therefore the head of the “IG crevice” explained the faster propagation rate found side the pore was found. this suggested that the main cathodic reaction APR corresponded to the time elapsed for the fastest full penetrating no pre-corrosion step was applied, the time considered to calculate the condition was compared to the response when the thin foil was covered the observed difference between the APR in the two exposure conditions. Consequently the galvanic current was the same for immer-

Simulations results under free corrosion conditions and discussion.—Under free corrosion conditions, the simulation results were discussed regarding the location of cathode whereas the anode was always located at the head (tip) of the 200-μm depth pore-shape electrode representing an IG path.

As shown in Figure 13b, the cathode “in” geometry was not at all in agreement with the pH measurement of the trapped electrolyte in the foil penetration experiment whereas the cathode “out” geometry is. These results, i.e. evolution toward alkaline values when both anodic and cathodic site were located inside the “IG crevice” and evolution toward acidic values when cathodic reactions took place outside the “IG crevice”, confirmed previous simulations of crevice experiments.

To highlight the validity of the application of modelling into pH distribution prediction, numerical simulation was applied to discuss the observed difference between the APR in the two exposure conditions. It is reminded that the IG propagation regime in immersion condition was compared to the response when the thin foil was covered by 3 mm diameter droplets (Table I). In these exposure conditions, as no pre-corrosion step was applied, the time considered to calculate the APR corresponded to the time elapsed for the fastest full penetrating intergranular defect to perforate the entire nominal thickness.

Regarding the cathode “in” geometry, a strong depletion in O2 inside the pore was found. this suggested that the main cathodic reaction would be the reduction of H+. This depletion occurred also in the case of the droplet in spite of the increase of the oxygen transport toward the surface. The calculated galvanic current was the same for immersion and droplet exposures (Table V), which was not in agreement with the foil penetration experiments (Table I).

For the cathode “out” geometry, the oxygen reduction reaction appears to be the main cathodic reaction. As expected from the results in Table I, in case of exposure under a droplet, the numerical simulation yielded to a cathodic current five times larger than in immersion conditions. Consequently the galvanic coupling between the Cu-enriched coarse intermetallic particles at the metal surface and the anodic head of the “IG crevice” explained the faster propagation rate found in foil penetration experiments under droplet exposure. Therefore simulation results for the cathode “out” geometry were in agreement with the experimental results. This means that the dissolution rate of the pﬁz was mainly dependent on the cathodic sites outside the “IG crevice”. However, these results did not exclude a minor contribution of inner cathodes, corresponding to redeposited Cu generated by the selective dissolution of grain boundary intermetallic precipitates, on which reduction of H+ was contributing to the cathodic current.

The importance of external cathodic areas was already assumed to explain the competitive process for the propagation of multi intergranular corrosion “tissues”, suggesting that stable IGC required a cluster of intermetallic particles. It must be mentioned that the same comparison between immersion and atmospheric (droplet) conditions showed that under free corrosion conditions, for other aluminum alloy series (5xxx), kinetics of cathodic reactions on outer surface of specimens seemed to also control the rate of IGC.

This cathodic control of the propagation resulting from the surface microstructure could be one of the factors explaining the stochastic nature of IG propagation under free corrosion conditions. Indeed, the cathodes (coarse intermetallic particles) were statistically distributed at the surface. Moreover, it exits plenty of types of intermetallic particles on AA2024, as demonstrated by the work of Boag et al., with probably various cathodic reactivities. If the anodic propagation was balanced by cathodic reaction occurring on the grain boundary walls, as suggested by Svenningsen et al. for AA6XXX, the scattering of the experimental data would probably be reduced.

### Table IV. Summary of the constants used in the model (from Ref. 30).

| Constant          | Value          |
|-------------------|----------------|
| $\phi_{Al}$       | 0.1 A. m$^{-2}$|
| $E^0_{H^2O}$      | −1.38 V(SCE)   |
| $b_{Al}$          | 0.095 V(SCE)   |
| $k_{H^2O}$        | 10$^{-5}$ m.s$^{-1}$ |
| $E^{0}_{O_2}$     | 0.16 V(SCE)    |
| $k_{O_2}$         | 10$^{-6}$ m/s  |
| $b_{H_2O}$        | −1 V(SCE)      |
| $b_{O_2}$         | 0.1 V          |
| $b_{H_2}$         | 0.05 V         |
| $C^0_{H_2}$       | 0.26 mol.m$^{-3}$ |

Others boundaries were assumed to be chemically and electrically inactive.

### Table V. Electrode potentials and coupling current as function of exposure conditions (droplet and full immersion) for two modeling geometries (cathode “in” and cathode “out”).

|                | Cathode « in » | Coupling (A) | Cathode « out » | Coupling (A) |
|----------------|----------------|--------------|-----------------|--------------|
|                | $E_{cathode}$ (mV) | $E_{anode}$ (mV) | $I_{coupling}$ (A) | $E_{cathode}$ (mV) | $E_{anode}$ (mV) | $I_{coupling}$ (A) |
| Full Immersion | −831           | −834         | 2.46 $10^{-13}$  | −549          | −583          | 3.47 $10^{-12}$  |
| Droplet        | −831           | −834         | 2.46 $10^{-13}$  | −374          | −438          | 1.59 $10^{-11}$  |

### Conclusions

The main objective of this work was to show that the foil penetration technique could be more easily applied by changing the detection method from a humidity sensing plate to an optical monitoring of the leakage of the electrolyte emerging from the full penetrating intergranular defects on the rear side of the foil. This was clearly achieved under potentiostatic conditions and it was demonstrated that a pre-corrosion step reduced the scattering of the time for full penetration intergranular paths of well oriented thin foils machined on AA2024 plates. It is confirmed that the propagation of intergranular corrosion as function of depth of the propagating defect can be well described by a power law of the following type, $d = a r^p$, where $d$ is the resulting IG path length.

Another advantage of optical detection was to render the collection of the electrolyte trapped in the grain boundaries possible, giving an evaluation of the change in pH value resulting from the continuous dissolution and chemical processes occurring at the head of the intergranular “crevice”.

This pH measurement of the electrolyte trapped inside the grain boundaries was used to validate a mass transport model under poten-

### Acknowledgments

This work was supported by French program ANR-14-CE07-0027-01 M-SCOT: Multi Scale COrosion Testing. The authors thank Hugh Dunlop (FEMS Communications Manager) for his comments.
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Journal of The Electrochemical Society, 165 (9) C502-C514 (2018)