A local electrochemical probe was combined with the thin foil penetration technique to study the corrosion propagation of a reduced number of grain boundary traces (in-plane) propagating inside a 60 μm thick foil of AA2024. This local and “in-volume” approach allowed analysis of the current transient resulting from the full penetration of the selected intergranular paths. By coupling a 2D spatially resolved electrochemistry to digital optical observation on the back side of the foil, it was possible to relate the current transient to the successive steps of the “in-volume” propagation of intergranular corrosion.

Regarding the intergranular corrosion (IGC) mechanism for Al-Cu alloys, the main dissolution process affects the active anodic head at the tip of the grain boundary and for a minor part the faces of the surface of the grain crevice behind the active anodic head. Therefore it could be assumed that the measure of the anodic part of the total current during potentiostatic experiments would be useful to establish a charge balance to evaluate the IGC propagation rate. Nevertheless, electrochemical approaches of IGC on aluminum alloys are not largely widespread. Only a few papers reported the current response during potentiostatic tests inducing IGC of AA2024 alloys in dilute chloride solutions.

In the 80’s, Rota and Boehni discussed the time evolution of the current profiles recorded during IGC on AA2024 thin foils in the ST direction. Current records presented three consecutive steps corresponding to successive type of damages. During the activation step (step I), the current increased because the number of IG defects increased. Then there was a transition stage (stage II), characterized by a low current decay, corresponding to the propagation of grain boundary heads in the volume. Finally, the current stabilized (step III) and a macroscopic dissolution of the grains was put in place.

In one of the papers of the group of Frankel reporting experimental results based on the foil penetration technique, the current densities obtained during potentiostatic experiments were found to be dependent on thermal treatments. It was also suggested that the measured current density may not represent well the metal anodic dissolution kinetics because it would be possible that the local cathodic reaction greatly affects the net current measurement under potentiostatic conditions. This latter point will be discussed in this paper.

More recently on the same type of alloy, other current profiles during imposed IGC were presented for various metallurgical treatments. The current responses were obtained for all samples while potentiostatic experiments using a large scale electrochemical cell (exposed area of 14 mm in diameter) or the droplet cell (exposed area of 0.5 mm in diameter). The study is based on current transients recording but before switching to the desired potential, the open circuit potential (OCP) was measured during five minutes. This droplet cell (Figure 1), derived from a commercial SDC (Scanning Droplet Cell from Sensolytics GmbH) and developed for photoelectrochemical experiments, is movable by stepper motors (Figure 2). A miniaturized reference electrode and a Pt counter electrode are housing in the head. The reproducible droplet formation is controlled by a micro-metering pump. To prevent leakage, the PTFE head (Figure 1) was approached to the substrate until the force reached 200 mN (the force was controlled by a force sensor integrated in the piezo-positioner). In contrast to glass microcapillaries used in electrochemical microcells, the conical shape of the PTFE tip of this droplet cell was very convenient to avoid any contact with the sample.

In the following, from the phenomenological point of view, (i) the “in-volume” IGC trace (as illustrated in Figure 3) is named “fissure” whereas (ii) the sudden crack observed on the backside the thinned foils (Figure 4) is named “crack”.

Materials and Experimental Set Up

Test specimens were machined from thick plates of a 2024-T3 aluminum alloy of which the average grain sizes within the plate were respectively 100, 300 and 700 μm in the short transverse (ST), long transverse (LT) and longitudinal (L) directions. Two types of foils were machined: (i) thick foils (hundreds of μm in thickness) machined in (L) or (LT) direction to induce IGC of a large number of grain boundaries and (ii) some of these thick foils were manually polished to thin them up to 60 μm thick. For these later thin foils, only a reduced surface was exposed to the corrosive solution limiting the segments of the grain boundary traces (in-plane) which could be attacked (under the tip of the droplet cell). With the few hundred μm thick foils, the objective was to induce IGC propagation of a large number a grain boundaries until a limited depth (about 60 μm) to carry out interrupted tests. The resulting current transients obtained during a potential step were compared to the current transients recorded during the perforation of the thinned foils (60 μm thick). In the two configurations the morphology of the IG defects corresponded to sharp “fissures” as was observed in 2D metallographic cross-sections.

Electrochemical experiments were performed in 0.1M NaCl aerated solution using a large scale electrochemical cell (exposed area of 14 mm in diameter) or the droplet cell (exposed area of 0.5 mm in diameter). The study is based on current transients recording but before switching to the desired potential, the open circuit potential (OCP) was measured during five minutes. This droplet cell (Figure 1), derived from a commercial SDC (Scanning Droplet Cell from Sensolytics GmbH) and developed for photoelectrochemical experiments, is movable by stepper motors (Figure 2). A miniaturized reference electrode and a Pt counter electrode are housing in the head. The reproducible droplet formation is controlled by a micro-metering pump. To prevent leakage, the PTFE head (Figure 1) was approached to the substrate until the force reached 200 mN (the force was controlled by a force sensor integrated in the piezo-positioner). In contrast to glass microcapillaries used in electrochemical microcells, the conical shape of the PTFE tip of this droplet cell was very convenient to avoid any...
cutoff of the electrical circuit due to hydrogen bubbles induced by the hydrogen evolution during localized corrosion of the AA 2024 foils.

As mentioned above, the objective was to perform thin foil penetration experiments, but at a reduced scale in order to reduce the grain boundaries associated with the dissolution. As schematized in Figure 2, an optical detection system (digital optical microscope Keyence VHX 5000) was positioned in front of the droplet cell to detect the emergence of full penetrating IG defects in a similar way than in large scale experiments.6,7 As it will be illustrated in the discussion of this paper, the results obtained by digital optical microscopy improved the optical resolution compared to preliminary results8 and allowed the successive steps of the detectable events corresponding to the full penetration of selected grain boundaries to be distinguished.

Experimental Results and Discussion

Large scale experiments.—Interrupted electrochemical experiments were performed on thick foils (210 μm), to record the current transient related to the IGC of numerous exposed grain boundaries until a limited depth, i.e. 60 μm as shown in Figure 3. The propagation was controlled by the imposed potential; by switching the imposed potential from $E_{\text{imp}} = -480 \text{mV (SCE)}$ to $-600 \text{mV (SCE)}$ after five minutes, i.e. a potential below the breakdown potential ($E_b = -580 \text{mV (SCE)}$), it was possible, at short time, to stop or more precisely to reduce drastically the propagation in depth.

The efficiency of this procedure was verified by analysing post-mortem cross sections. After the five minutes at $-480 \text{mV (SCE)}$, SEM observations showed sharp “fissures” which were homogeneously distributed all along the surface with a maximum depth of around 60 μm (Figure 3bI). This very reproducible grooving was used as a “pre-corrosion” procedure to control the initiation of grain boundary dissolution which led to the improvement of the accuracy of the measurement of the IG propagation rate.3

To support the beneficial effect of switching the potential to a value lower than the breakdown potential ($-580 \text{mV (SCE)}$), potential steps at $-480 \text{mV (SCE)}$ were followed by very long maintains at $-600 \text{mV (SCE)}$. As shown in Figure 3b (II), initial short “fissures” initiated at $-480 \text{mV (SCE)}$ widened after long exposures whereas the alloy remained still sensitive to IGC at $-600 \text{mV (SCE)}$ but at a very reduced rate as illustrated by the thin filaments ahead. During the first five minutes at $-480 \text{mV (SCE)}$, the current transient (Figure 3a) is probably related to the dissolution of the anodic heads of the numerous exposed grain boundaries. This hypothesis is supported by the SEM observations (Figure 3bI) of the metallographic cross sections showing very sharp “fissures” without any blunting of which could be related to any current flowing through the flanks of the grain boundaries. The plateau observed after five minutes could be interpreted as a constant dissolution rate of the anodic heads but it would suggest that the active area is constant over time which is probably not the case as it will be highlighted by the local scale experiments (see part Local scale experiments). The current drop observed after the potential switch at
Figure 3. Interrupted potentiostatic experiments on a AA2024 foil (210 μm-thick). (a) Current transient observed for the imposed potential step (the sampling rate was larger after the first 300 s). (b) SEM observation on a cross-section after a 5 minutes polarization step at −480 mV(SCE) followed by a polarization at −600 mV(SCE) during: (I) a short time and (II) a very long time. The breakdown potential was −580 mV(SCE) in 0.1M NaCl solution.

−600 mV(SCE) confirms the drastic reduction of the IGC propagation clearly observed on metallographic cross sections (Figure 3b).

To validate the propagation mechanism, the thin foil penetration experiments were performed using the droplet cell coupled to a digital optical observation of the back side of the foil while maintaining the potential at −480 mV(SCE). It was expected to define, from the current transients recorded for a reduced number of grain boundaries, a more focused value of the electrical charge confirming the anodic dissolution control. In terms of experiments, the expected time profile of elementary current transient cannot be nevertheless strictly compared with a change of scale to the current variation observed in Figure 3a. Indeed at the macro scale, the potential step below the breakdown potential would cutoff the dissolution of the precipitate free zone (pfz) and of the grain boundary flanks, whereas at the micro scale, only a “physical” cutoff can be expected at the perforation of the foil and will concern only the dissolution of the head and not the flanks of the selected grain boundaries. This would induce a smaller drop of the net current. This latter point will be illustrated and discussed in the following.

Local scale experiments.—The droplet cell set up was combined with the optical detection of reduced number of full emerging defects to perform modified thin foil penetration experiments compared to previous large scale conditions.6,7 This was achieved by recording the current response on a polished thin foil (60 μm-thick) imposing the same potential step at −480 mV (SCE) as previously.

The most convenient conditions, i.e. the longest initial grain boundary traces (in-plane), were found for specimens thinned in the LT direction because the L∗ST exposed surface presented very long segments of grain boundary traces which can be attacked under the tip of the droplet cell.

Optical control of the location of the droplet cell was improved compared to preliminary experiments6 allowing to check, before and after electrochemical tests, the exposed surface in contact with the tip of the droplet cell to confirm the initiation of IGC.

The transient current response and optical detection of the emerging defects were recorded in real time. As explained in a previous publication,7 continuous imaging of the rear side of the specimen allowed “cracks” induced by the emergence of any full penetrating IG paths after 60 μm in depth propagation to be located. It was validated that there is not a large risk of branching of the IG path (Figure 3bI) at short times.

The length of this emerging trace was defined as L_{GB}^1 (index i to distinguish the successive emerging traces). A representative experiment is presented in the Figure 4. On the plateau value of the current, no change on the rear side was detected because the propagation was confined in the volume. As expected, the IGC propagation through the 60μm-thick foil ended after around 5 minutes and the emergence of a first “crack” (L_{GB}^1) on the rear side of the foil, related to the full penetration of the corroding grain boundaries, occurred. It corresponded to a sharp drop of the current at time t = t_1 (Figure 4). As already mentioned7 the emergence of these “cracks” was followed by electrolyte leakage through these “cracks”, forming droplets. This phenomenon was observed at time t = t_2 and the volume of electrolyte increased in the following as shown at time t = t_3. At the same time, other “cracks” corresponding to the emergence of L_{GB}^2 and L_{GB}^3 appeared on the rear side (Figures 4d and 4e). In Figure 4a, current drops were always related to the full penetration of a grain boundary (L_{GB}^i), as it was expected. Nevertheless, the perforation of the thin foil resulted from a cumulative process probably because not only one grain boundary was associated with the tip of the droplet cell and an internal increase of the active anodic head of the concerned grain
boundaries during the IG propagation would occur. Indeed only the spatial area on the upper side of the foil was controlled and not the real volume associated with the propagation along the flanks of the concerned grain boundaries which constitute a continuous network. But this latter phenomenon was very difficult to prove (see discussion of Figure 5).

To summarize, the emergence of grain boundary trace or “crack” on the rear side of the thin foil was always related to a drop of the net current (decrease of the anodic current). The droplet formation occurred after these “cracks” and the time lag of the electrolyte leaching varied as function of the experiments.

Discussion.—The net current transient, which was recorded, can be assumed to be the sum of various contributions:

\[
i_{\text{net}} = i_{\text{surf}} + i_{\text{IM}} + i_{\text{H}} + i_{\text{flank}} + i_{\text{head}}
\]  

[1] Regarding Al-Cu alloys, the IG propagation is controlled by the anodic dissolution of the precipitate free zone (pfz). This latter has quite the same dissolution rate as pure aluminum and corresponds to \(i_{\text{head}}\). This was illustrated in a previous work comparing the average propagation rate of IGC on 2024 with the dissolution rate of an Al “one-dimensional artificial pit”. \(i_{\text{H}}\) which is linked to the “negative difference effect” \(^{10}\) named also the “superfluous “ hydrogen evolution, \(^{11}\) induced an accelerated production of hydrogen gas on the dissolving aluminum metal surfaces. In a previous work, \(^{9}\) this latter was estimated to represent around 10% of \(i_{\text{head}}\) (absolute value). \(i_{\text{flank}}\) (dissolution of the Al-Cu solid solution along the flanks of the dissolved grain boundaries) was neglected at short time because no blunting of the IG paths was observed at short time (Figure 3bI). As no change in thickness was observed for the foils whatever the experimental conditions (short or long time), \(i_{\text{surf}}\) (corrosion reactions at the surface of the exposed specimen) was considered to be negligible. It must be mentioned that before switching to the desired potential, the OCP was measured for five minutes before the potentiostatic test. Consequently, following the hierarchy of dealloying of IM particles as reported in the work of Boag et al., \(^{12}\) it can be assumed that the anodic dissolution of IM particles (S-phase) was reduced during the IGC propagation. Indeed, after five minutes of immersion the S-phase particles were Cu-enriched and \(i_{\text{IM}}\) was probably slightly cathodic and did not contribute to much to the total current.

From this brief discussion it was reasonably assumed that the main contributions to the current transient recorded during thin foil experiments were \(i_{\text{head}}\) and \(i_{\text{H}}\).

To analyse these transient current responses, the dissolution was tentatively related to the total length of exposed grain boundaries which can be expressed by the cumulative value of the traces \((L_{\text{GB}})\) observed in the rear side of the thin foil at the end of the current transient. But, to validate this approach, only the first step observed in Figure 4 (until time \((t_1)\)) was selected. First the total charge consumed during the penetration of the IG defect, corresponding to the emergence of \(L_{\text{GB}}^1\), can be deduced from the current drop observed at the perforation. Assuming the perforation corresponded strictly to the end of a continuous dissolution process occurring at the head of the grain boundary, the total charge consumed during the full penetration was estimated to be:

\[
Q_{\text{net}} = \text{current drop} \times \text{full penetration time} = 0.9 \mu \text{A} \times 250 \text{ s} = 225 \mu \text{C}
\]

and taking into account an estimation of \(i_{\text{H}}\), it gives

\[
Q_{\text{diss}} = Q_{\text{net}}/0.9 = 250 \mu \text{C}.
\]
On the other hand, the charge involved during the net current transient before the first current drop (ΔI in Figure 5b) was up to 750 μC; this means that the anodic charge consumed during the transient response was around 825 μC. Even if some crevice effects cannot be neglected (poor contact under the droplet cell), the main discrepancy in the electrical charge value was probably due mainly to the estimation of the total L_{GB} from the optical observation of the rear side. L_{GB} represented a partial view of the internal corroded grain boundary and the real size of the flanks of any dissolving grain boundary was not possible to evaluate. Nevertheless such a difference indicated that other dissolution processes such as selective dissolution of intermetallic particles cannot be neglected but remained difficult to estimate. Probably the actual area associated with the anodic dissolution could not be controlled, as illustrated in Figure 5c, because the grain boundaries constituted a continuous network in volume. Inside the thinned foil volume, this latter could be larger than the length of the emerging trace because lateral spreading can occur, inducing a larger anodic area which was difficult to relate to the apparent L_{GB}. It would be easier to control the anodic area for AA 5xxx series for which the IGC is not based on continuous dissolution of the pfz but on the dissolution of sensitive precipitates at grain boundaries.

Otherwise, this coupling of an electrochemical measurement with the thin foil penetration technique carried on a very reduced area allows for more details in the discussion of the triggering of the droplets of electrolyte which were at the origin of the recorded parameters in the previous versions of the thin foil penetration technique for tests performed at large scale\(^7,13\) whatever the physical nature of the detection of the perforation (electrical or optical). In a recent paper\(^7\), this discussion was launched and it was concluded that the detected droplets could be considered only as apparent indicators resulting from the emergence of the electrolyte trapped inside the dissolved grain boundaries. Working at the local scale (this paper) it was possible to propose some complementary hypothesis concerning the origin of the “crack” itself as was observed in Figure 4. The benefit of digital microscopy was to clearly show that the “crack” (L_{GB} for example) occurred in a very short time and looked like a “pure” mechanical breakdown of the ultimate thickness of the head of the IG path. This phenomenology could be related to the contribution of hydrogen embrittlement to the IG propagation. To tackle this question, a possible sequence was proposed as shown in Figure 6. At the end of a propagation sequence (Figure 6), involving hydrogen diffusion beyond the dissolved anodic head of the grain boundary, the formation of a brittle fracture (“crack”) in Figure 6 on the rear side of the foil could be reasonably expected. The presence of hydrogen along the IG path was confirmed by local analysis with SKPFM\(^14\) and also supported by the chemical analysis of the electrolyte droplet leaking through the full penetrating defects;7 indeed the pH of the electrolyte trapped in the grain boundary network was found to be around 1. It could be assumed that the stress field generated by, for example, the corrosion products (Al(OH)\(_3\)) inside the IG path\(^8\) would be sufficient to promote the perforation of the residual metallic layer at the head of the grain boundary, as schematized in Figure 6. This phenomenon would explain the time delay between the emergence of the “crack” and the leakage of electrolyte (droplet). From a mechanistic point of view, this description would support the continuous role of hydrogen embrittlement at the head of any propagating grain boundary.

Figure 6. Schematic drawing of the effect of a possible hydrogen embrittlement at the moving head of an IG path.

Conclusions

Digital optical microscopy of the detection side improved the description of the perforation sequence during thin foil penetration experiments on a thinned foil when corrosion initiation was induced on a reduced area using a local electrochemical cell. It was then possible to record simultaneously (despite the hydrogen evolution) the current transient resulting from the full penetration of spatially controlled IG paths. As expected, any sharp drop of the anodic current was related qualitatively to a full penetration, but the comparison of the electrical charges involved during transient current responses and deduced from the estimated dissolved volume of pfz along the selected grain boundaries and the real one which was increased by the 3D lateral spreading of the IG paths, even if the contribution of others dissolution processes cannot be excluded.
A contribution of the hydrogen embrittlement beyond the active head at the tip of the selected grain boundaries has been proposed to explain the time lag between the mechanical perforation of the thinned foils and the leakage of the electrolyte trapped inside the corroded grain boundaries. From a mechanistic point of view, this description would support a continuous role of hydrogen embrittlement at the head of any propagating grain boundary.

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