



On the microstructural control of localized corrosion in non-anodized and TSA-anodized AA7475-T761 aluminium alloy[☆]

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ABSTRACT

The corrosion behaviour of the AA7475-T761 alloy in non-anodized and tartaric-sulfuric acid (TSA) anodized conditions in a chloride environment is investigated. In the non-anodized alloy, localized corrosion initiated at constituent intermetallic particles (IMPs) and grain boundary precipitates, leading to trenching and intergranular attack. In contrast, in the anodized alloy, corrosion initiated at defects located at the film/alloy interface, originating from the dissolution of IMPs during anodizing. These defective regions acted as preferential pathways for electrolyte ingress, promoting underfilm corrosion and pit growth beneath the oxide. While the anodic film delayed the onset of corrosion, the highly localized nature of the attack in the anodized sample increased the severity of the damage once initiated.

1. Introduction

The 7XXX series aluminium alloys (Al-Zn-Mg-Cu) are widely used in aerospace applications due to their excellent strength-to-weight ratio, fatigue resistance, and overall mechanical performance [1]. Major producers such as ALCOA France and Aleris have developed several high-strength variants, including 7075, 7475, 7050, 7150, 7055, and 7085 [2]. Despite these advantageous properties, the application of 7XXX series alloys in aerospace structures requires surface treatments to ensure adequate corrosion resistance. Among the various procedures available, anodizing stands out [3]. Therefore, understanding how this process influences the corrosion resistance of aluminium alloys is essential for an accurate assessment of material performance.

Considering anodized alloys, most of the available findings are based on substrates such as AA7075 and AA7175 anodized in sulfuric or tartaric-sulfuric acid electrolytes [4–15]. These investigations revealed that intermetallic particles such as Al₃Cu₂Fe and MgZn₂ exhibit distinct behaviours during anodizing, including selective dissolution, occlusion, and O₂ evolution, which in turn influence the uniformity, porosity, and

mechanical properties of the anodic film [3]. A commonly adopted experimental approach involves preparing samples in the so-called 'bare' condition (non-anodized), corresponding to a polished surface without any alkaline or acidic desmutting treatment. This condition is frequently employed to isolate the influence of microstructure on anodizing behaviour and to better elucidate the role of intermetallic particles in anodic film formation.

Although the growth and morphology of anodic films are well documented, the relationship between microstructural features and corrosion behaviour after anodizing remains insufficiently understood [16]. Most investigations focus predominantly on the formation of the anodic film, while the influence of microstructure on corrosion initiation and propagation is still not comprehensively characterized in the current literature [3].

Araujo et al. [17] conducted corrosion tests on anodized AA7475 alloy and reported variation in the assessed depth of corrosive attack depending on the characterization technique employed. Their findings highlighted the importance of accounting for microstructural features to adequately investigate the corrosion behaviour of anodized alloys. The

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study proposed a comparison between non-anodized and anodized surfaces under identical exposure conditions to more accurately assess the impact of anodizing on corrosion mechanisms.

Other researchers have raised similar concerns. For instance, Jude Mary Runge [18–20] emphasized the need for a deeper understanding of the corrosion mechanisms in both anodized and non-anodized states to assess the impact of anodizing. While many studies employ electrochemical impedance spectroscopy (EIS) to quantify improvements in corrosion resistance after anodizing and sealing, such analyses often rely on generalized electrochemical parameters. Furthermore, they frequently lack complementary microstructural evaluation, thereby limiting the ability to elucidate how anodizing alters corrosion pathways [21–36].

Although anodizing is a standard requirement for aerospace-grade 7XXX series alloys exposed to aggressive environments, studying non-anodized surfaces remains essential for scientific and comparative purposes [16]. This is because, regardless of the surface condition, after its onset, corrosion progresses by deteriorating the base metal. However, as anodizing changes the surface condition, the onset and spread of corrosion can likely follow entirely different mechanisms compared to the non-anodized surface [17,25,32,34,37–40]. Therefore, comparing both conditions under identical exposure circumstances must enable researchers to isolate the effects of the anodic film on corrosion behaviour and to better understand how final surface finishes influence degradation processes.

Recently, Araujo et al. [38] investigated the role of constituent intermetallic particles in the development of defects in the anodic films and their influence on localized corrosion. The authors advised that evaluating corrosion performance exclusively under anodized conditions may lead to incomplete or even misleading interpretations, particularly regarding underfilm corrosion. Similar concerns were previously raised by Queiroz et al. [24] and Ma et al. [41], who highlighted the importance of directly comparing the non-anodized and anodized conditions of the same alloy to obtain a more comprehensive understanding of corrosion initiation and propagation beneath anodic films. Nevertheless, comprehensive studies correlating microstructural features with electrochemical behaviour remain scarce, especially for TSA-anodized surfaces. This lack of systematic comparison underscores the need to clarify how microstructure affects corrosion under different surface conditions. To address this gap, the present study examines the impact of surface condition and microstructure on the corrosion of AA7475-T761, aiming to answer the central question: What role does microstructure play in determining the differences in corrosion mechanisms between non-anodized and TSA-anodized AA7475-T761 aluminium alloy?

2. Experimental

2.1. Material

The AA7475-T761 aluminium alloy used in this study was in plate form, 1.6 mm thick. Its chemical composition, determined by inductively coupled plasma optical emission spectrometry (ICP-OES), is (wt %): 2.34% Cu, 2.64% Zn, 0.85% Mg, 0.009% Cr, 0.006% Fe, and 0.002% Si, with aluminium as the balance. The T761 temper condition comprises solution heat treatment, cold working, stress relief, and artificial aging [42].

2.2. Methods

2.2.1. Microstructural characterization and analysis

The surface of the alloy sample was ground with silicon carbide paper up to #P4000 and then polished with diamond suspensions of 3 μm and 1 μm . Prior to microstructural observation, the samples were chemically etched in a solution containing 2 (v/v)% hydrofluoric acid and 25 (v/v)% nitric acid in order to reveal the grain structure [43].

Microstructural characterization and analysis were conducted by means of scanning electron microscopy (SEM) using a JSM-6701F microscope equipped with energy-dispersive X-ray spectroscopy (EDX) detectors. Statistical analyses regarding microstructural parameters and phases were performed using ImageJ® software. To identify all phases, the nanometric phases in the alloy were analyzed by transmission electron microscopy (TEM) using a JEM-2100 microscope operating at 200 kV. The samples were 2 mm diameter disks, prepared by grinding with SiC #1200 until an average thickness of 100 μm . Electrolytic etching was then performed using TenuPol equipment with a stainless-steel plate as the cathode. The etching electrolyte consisted of 20% nitric acid in methanol, with a voltage of 25 V and at $-30\text{ }^{\circ}\text{C}$.

2.2.2. Anodizing procedure

Anodizing was carried out in an aqueous solution containing 0.46 mol L⁻¹ sulfuric acid and 0.53 mol L⁻¹ tartaric acid (TSA) at $(37 \pm 1)\text{ }^{\circ}\text{C}$, using an SP-300 Biologic® potentiostat. The samples, with an exposed area of 1 cm², were used as working electrodes, while a platinum mesh served as the cathode. The anodizing process was performed using potentiostatic polarization at 14 V for 20 min. Surface images, before and after anodizing, were acquired using a JSM-6701F SEM equipped with a backscattered electron (BSE) detector and an EDX system.

2.2.3. Corrosion tests

The corrosion resistance of non-anodized and anodized AA7475-T761 samples was evaluated starting with immersion tests in a 0.1 mol L⁻¹ NaCl solution. The non-anodized samples, representing the alloy without surface treatment, were previously ground and polished with diamond suspension down to 1 μm . Electrochemical measurements were also performed using a Biologic® SP-200 potentiostat in a conventional three-electrode setup, with the alloy samples (exposed area of 1 cm²) as working electrodes, an Ag|AgCl|KCl 3 mol L⁻¹ electrode as reference, and a platinum wire (5 cm² exposed area) as the counter electrode. Open-circuit potential (OCP) measurements were recorded continuously for 70 h to monitor the electrochemical stability of the surfaces. Anodic potentiodynamic polarization tests were acquired after 5 min immersion at a scan rate of 0.5 mV s⁻¹, starting from -10 mV vs. OCP and progressing to 1 V vs. the reference electrode. Polarization experiments were performed on at least six specimens per condition (non-anodized and anodized) to ensure reproducibility.

After the electrochemical tests, surface analysis of both non-anodized and anodized samples was conducted by SEM on a JEOL JSM-6010 LA microscope equipped with an EDX detector, with image acquisition in BSE mode. High-resolution imaging was additionally performed using a Zeiss Ultra 55 microscope operating at 1.5 kV to minimize charging effects and improve the observation of fine surface features. Additionally, the morphology and depth of the corrosion pits were quantified by optical profilometry (Zygo ZeGage). Furthermore, to assess pit morphology independently of the oxide, corrosion products and the anodic film were removed by film stripping using a chromic acid–phosphoric acid desmutting solution (20 g CrO₃ + 30 mL H₃PO₄ in 1 L deionized water; 60 $^{\circ}\text{C}$, 3 min), followed by immersion in distilled water in an ultrasonic bath for 20 min and air drying.

Cross-sectional preparation was performed using two different approaches. In the first method, the procedure followed is that described in previous works [44], in which the specimens were sectioned using a precision diamond saw, successively ground with silicon-carbide papers up to P4000 grit, and finally polished using a 0.05 μm colloidal silica suspension. In the second approach, cross-sections were prepared by ultramicrotomy using a Leica Ultracut instrument equipped with a diamond knife, allowing high-precision sectioning for detailed microstructural analysis. Corrosion sites were first identified by surface inspection and marked prior to sectioning. The selected regions were initially trimmed using a glass knife at a cutting speed of 3 mm s⁻¹ with a slice thickness of 3 μm . Subsequently, the region containing the

corrosion pit was sectioned using a diamond knife at a cutting speed of 1 mm s^{-1} , producing slices with thicknesses between 500 nm and $1 \text{ }\mu\text{m}$.

3. Results

3.1. Microstructure characterization

The surface of the AA7475-T761 alloy, after mechanical polishing, was examined by SEM, as shown in Fig. 1.

In the lower-magnification image (Fig. 1(a)), small, bright spots scattered across the surface correspond to micrometric constituent intermetallic particles (IMPs). These features appear with higher contrast due to their chemical composition, which differs from the surrounding aluminium matrix and reflects the presence of elements with higher atomic numbers [45,46]. EDX analysis of 50 particles revealed an average composition of $57.3 \pm 9.3 \text{ wt\% Al}$, $27.5 \pm 2.6 \text{ wt\% Cu}$, and $15.2 \pm 4.4 \text{ wt\% Fe}$. The average particle size was $3.7 \pm 2.1 \text{ }\mu\text{m}$, likely influenced by thermomechanical processing such as rolling, which can fracture or fragment larger IMPs formed during solidification. The corresponding particle size distribution is presented in Fig. 1(a1), which indicates that the IMP population spans a range of sizes. Most particles are distributed within the micrometric range, although smaller particles close to $\sim 1\text{--}2 \text{ }\mu\text{m}$ and larger ones reaching $\sim 8\text{--}10 \text{ }\mu\text{m}$ are also observed. This distribution indicates that the alloy contains particles both significantly smaller and of the same order of magnitude as the typical thickness of anodic oxide films reported for aluminium alloys, which may influence the density and nature of defects generated during anodizing [47]. In agreement with the literature [45,46,48], these are typical IMPs, which form during casting due to the limited solid solubility of certain alloying elements and the incorporation of impurities such as Fe and Si originating from bauxite extraction and/or alloy recycling [49]. Since the removal of IMPs is economically or technically impractical, these particles are considered inherent to aluminium alloys and are commonly observed across most alloy families, particularly those developed for structural applications that require significant alloying additions [18].

At higher magnification (Fig. 1(b)), the particles appear either isolated or clustered, as indicated by the red arrows, and exhibit irregular morphologies. A closer view of one cluster is shown in Fig. 1(c), highlighting a local tendency toward coalescence. In addition to the micrometric particles, nanometric precipitates can be identified along the grain boundaries (Fig. 1(d)), as indicated by the white arrow. At even higher magnification (Fig. 1(e)), the alignment of these nanometric precipitates along grain interfaces becomes more evident. The grain morphology of the alloy is illustrated in the SEM micrographs of etched samples, shown in Fig. 2.

The surface view (Fig. 2(a)) reveals a polycrystalline microstructure with well-defined grain boundaries, indicated by the red arrows. Voids

distributed along some grain boundaries, marked by white arrows, correspond to the dissolution of IMPs during metallographic etching. The grain size distribution obtained from image analysis is shown in Fig. 2(a1), with an average grain size of approximately $23.1 \pm 6.6 \text{ }\mu\text{m}$. The relatively equiaxed grain morphology observed at the surface suggests that the alloy underwent partial recrystallization during thermomechanical processing [43,50]. The transverse cross-section (Fig. 2(b)) reveals elongated grains aligned along the deformation direction, highlighted by the yellow arrow, indicating the influence of the rolling process used to produce the alloy sheet. This morphology indicates that although some recrystallization may have occurred, the microstructure still retains features aligned with the rolling direction. Such microstructure is consistent with the T761 temper condition of AA7475 sheets, in which solution heat treatment, stress relief by stretching, and artificial overaging can lead to a partially recrystallized microstructure while preserving deformation-induced grain elongation [42]. In addition, the preferential dissolution of nanometric precipitates during metallographic etching reveals grain-boundary regions containing second-phase particles. The presence and distribution of these nanometric precipitates along grain boundaries are further confirmed by TEM, as shown in Fig. 3.

In Fig. 3(a), several nanoscale features are clearly aligned along the grain boundary, as indicated by the white arrow. A higher magnification image of the selected region in Fig. 3(a), shown in Fig. 3(b), reveals that they are elongated ($100\text{--}200 \text{ nm}$) and densely packed. These features are not merely associated with segregation but correspond to actual precipitates, as widely reported in the literature for 7XXX series aluminium alloys [51,52]. In 7XXX alloys, the dominant hardening mechanism arises from fine, coherent or semi-coherent intragranular clusters and precipitates (GP zones and η') that hinder dislocation motion. In contrast, MgZn_2 precipitates are commonly found at grain boundaries [53–55]. Their direct contribution to overall strengthening is limited, but they strongly influence electrochemical behaviour by acting as preferential sites for localized corrosion [56,57]. Although EDX mapping of the region shown in Fig. 2(b) was not feasible due to the spatial resolution limitations of the equipment used in this study, point analysis was performed in the area, as shown in Fig. 3(c). The intense Mg and Zn peaks confirm that the nanoscale precipitates are mainly composed of magnesium and zinc, consistent with the composition of MgZn_2 precipitates. The spectrum also displays peaks ascribed to aluminium and copper, both of which are present in the alloy matrix. A previous investigation by Cassell et al. [58] showed that copper segregates at the broad faces of η' and η precipitates in 7XXX-series aluminium alloys; therefore, the combined microstructural and compositional evidence indicates the presence of grain boundary Cu-containing MgZn_2 precipitates in the AA7475-T761 alloy, as suggested in the literature.

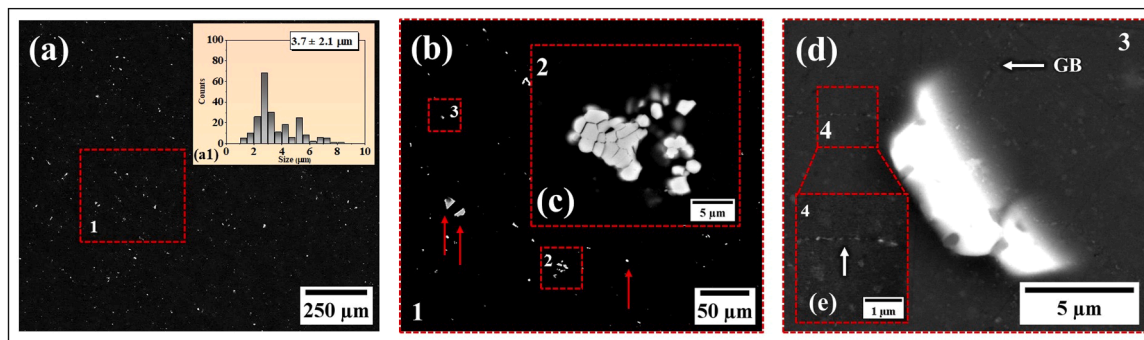


Fig. 1. Scanning electron micrographs of the AA7475-T761 alloy surface after polishing, showing constituent intermetallic particles (IMPs): (a) lower magnification; (b) higher magnification of the dashed region 1 shown in (a); (c) higher magnification of the dashed region 2 shown in (b); (d) higher magnification of the dashed region 3 shown in (b); and (e) higher magnification of the dashed region 4 shown in (d). Red and white arrows in images (b) and (e) indicate IMPs and nanometric precipitates at grain boundaries (GB), respectively. All images were acquired using backscattered electrons (BSE) at an accelerating voltage of 20 kV.

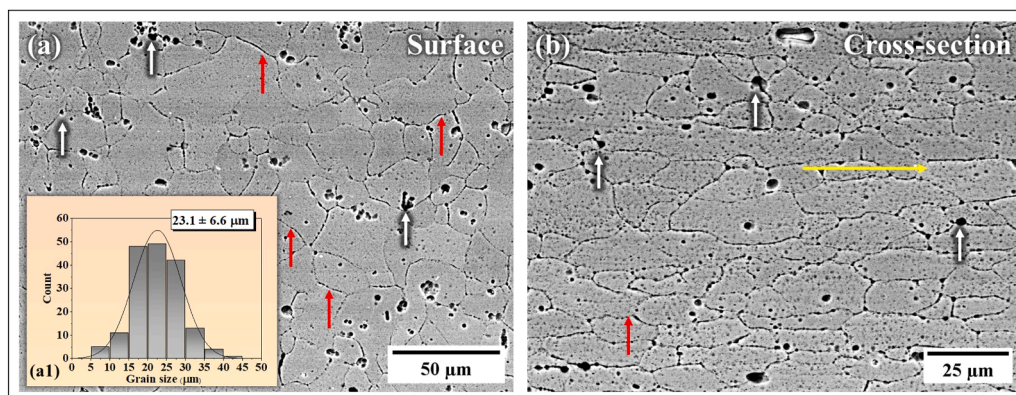


Fig. 2. Scanning electron micrographs of the AA7475-T761 alloy microstructure: (a) surface; (a1) grain size distribution obtained from image analysis; and (b) transverse cross-section. Red arrows in images (a) and (b) indicate grain boundaries (GB). White arrows indicate voids formed by the dissolution of intermetallic particles during metallographic etching. The yellow arrow in image (b) indicates the rolling direction. All images were acquired using backscattered electrons (BSE) at an accelerating voltage of 20 kV.

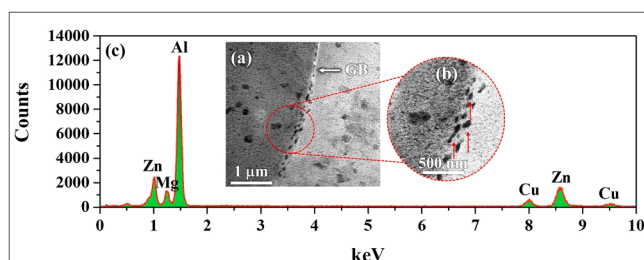


Fig. 3. (a) Bright-field TEM image of the AA7475-T761 alloy showing nanometric precipitates along grain boundaries; (b) higher magnification of the dashed region shown in (a); and (c) EDX spectrum of the precipitates highlighted in (b). Red arrows in (b) indicate nanometric precipitates located at grain boundaries.

3.2. Anodizing behaviour

Morphological features of the AA7475-T761 alloy after anodizing were investigated, as shown in Fig. 4.

The formation of the anodic film and its porous morphology, typical of anodizing in acidic electrolytes such as TSA [59], are evident in the micrographs in Fig. 4(a) and 4(a1), respectively. The cross-sectional image, Fig. 4(a), reveals a uniform film with an average thickness of $4.1 \pm 0.1 \mu\text{m}$. In contrast, the top-view image, Fig. 4(a1), shows nanoscale pores regularly distributed, as indicated by the red arrows.

As reported in Section 3.1, the microstructure of the AA7475-T761 alloy contains IMPs that are exposed on the surface and therefore interact directly with the anodizing electrolyte. Fig. 4(b) shows a surface region containing an IMP prior to anodizing, while Fig. 4(b1) presents the same region after the process. The formation of a cavity in the area where the IMP was located is evident and is attributed to its preferential

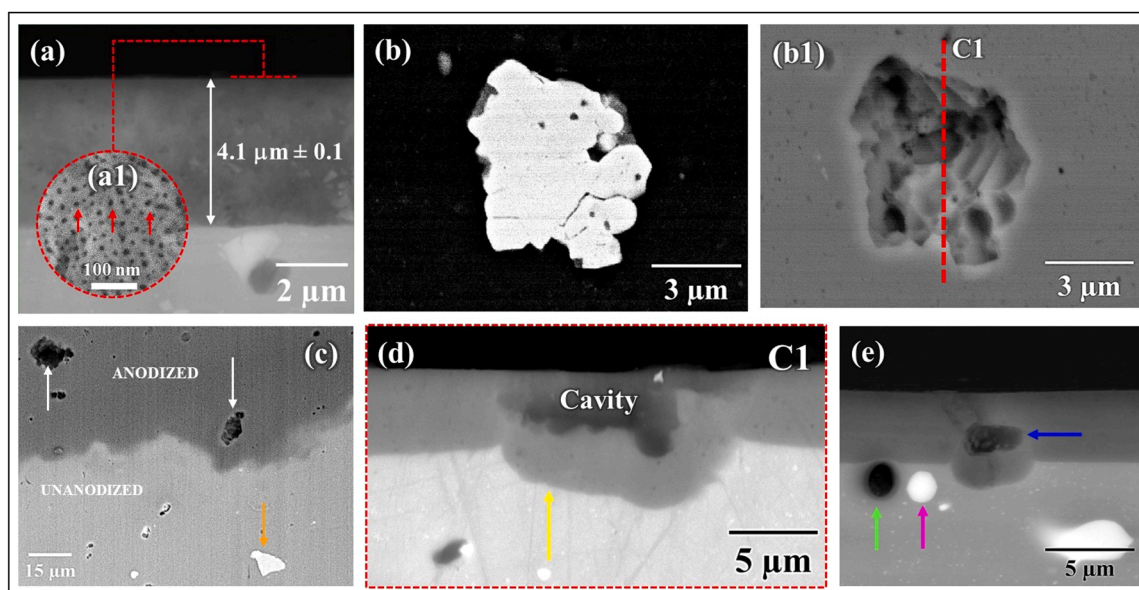


Fig. 4. Scanning electron micrographs: (a) cross-sectional view of the anodic film; (a1) surface of the anodic film evidencing its porous structure (red arrows); (b) region containing a micrometric constituent intermetallic particle (IMP) before anodizing; (b1) the same region as (b) after anodizing; (c) interface between anodized and non-anodized regions of the alloy surface; (d) cross-section along the dashed line C1 in (b1), showing the anodic film, including a region with cavities. White and orange arrows in (c) indicate cavities formed in the film due to dissolution of IMPs during anodizing, and an IMP that was not in contact with the anodizing electrolyte, respectively. The yellow arrow in (d) shows the anodic film growing at the bottom of a cavity. In (e), blue and green arrows indicate anodic film cavities and an IMP beneath the film, respectively, while the pink arrow highlights an IMP that was not in contact with the anodizing electrolyte. All images were acquired using backscattered electrons (BSE); images (a, b–e) were obtained at an accelerating voltage of 20 kV, while image (a1) was acquired at 5 kV.

dissolution during anodizing. This phenomenon has been extensively documented in the literature for Cu- and Fe-rich IMPs, which exhibit high reactivity in acidic electrolytes and low stability of their respective oxides, resulting in rapid dissolution during the early stages of anodic film growth [38,59,60].

The reactivity of IMPs toward the electrolyte is further illustrated in Fig. 4(c), where two distinct surface conditions are displayed: one exposed to the anodizing process and another that remained unexposed to the anodizing bath. In the anodized region (top side), cavities are observed at sites where IMPs existed, as indicated by white arrows. In contrast, an IMP that was not exposed to the electrolyte remains unaltered, as marked by the orange arrow (lower side). This confirms the

understanding that IMP dissolution and cavity formation are localized at the interface where anodic oxidation occurs.

The extent of such cavities can be examined in detail in Fig. 4(d), which presents a cross-sectional view along the C1 line indicated in Fig. 4(b1). The image confirms the cavity resulting from the faster IMP dissolution, inside which the anodic film is formed, as indicated by the yellow arrow. Prada-Ramirez et al. [61] reported similar features for an AA2024-T3 alloy anodized in TSA; they evidenced the presence of cracks within the oxide film and claimed that these defects, associated with the occluded geometry, may constitute preferential sites for the onset of localized corrosion. It is also worth mentioning that, because the anodic film growth consumes part of the aluminium substrate, IMPs located just

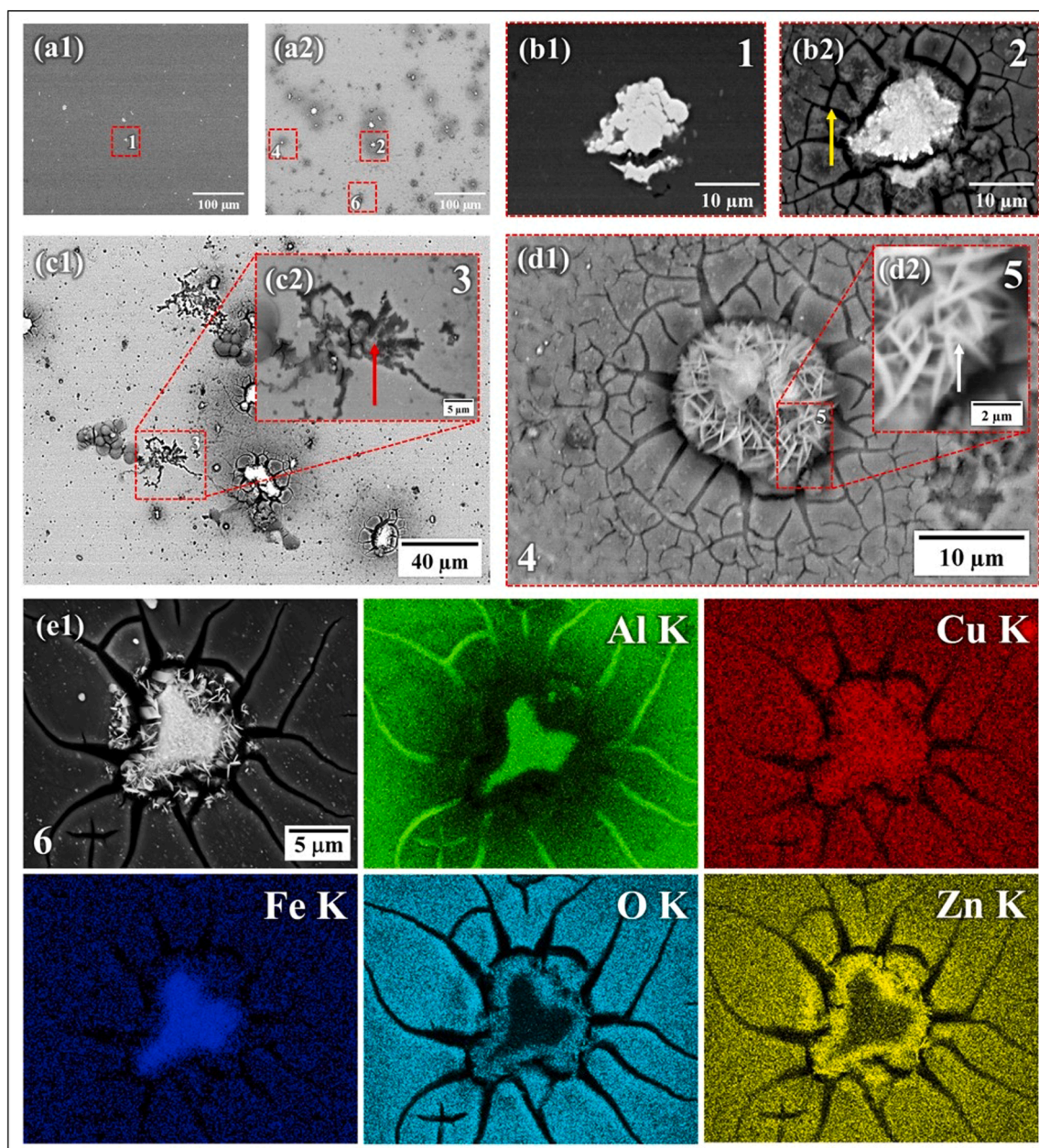


Fig. 5. Scanning electron micrographs of the non-anodized AA7475-T761 alloy surface after immersion in 0.1 mol L⁻¹ NaCl solution for 24 h: (a1) low-magnification image of the region before immersion; (a2) the same region as (a1) after immersion; (b1) higher magnification of dashed region 1 in (a1); (b2) higher magnification of dashed region 2 shown in (a2); (c1) another area of the alloy surface after immersion; (c2) higher magnification of dashed region 3 shown in (c1); (d1) higher magnification of dashed region 4 shown in (a2); (d2) higher magnification of dashed region 5 shown in (d1); (e1) higher magnification of dashed region 6 shown in (a2), along with corresponding EDX maps. The yellow arrow in (b2), the red arrow in (c2), and the white arrow in (d1) indicate, respectively, a crack in the corrosion products adjacent to the IMP, intergranular corrosion (IGC), and the deposition of zinc aluminium hydroxide (AlZn(OH)₄). All images were acquired using back-scattered electrons (BSE) at an accelerating voltage of 20 kV.

beneath the original exposed surface may also be exposed to the electrolyte; therefore, film defects are not restricted to the surface but can extend into the film interior or along the film/alloy interface [37]. Fig. 4 (e) illustrates a representative micrograph of such features: a cavity within the film thickness (blue arrow), another located at the film/alloy interface (green arrow), and an intact IMP beneath the film (pink arrow), which remained undissolved due to the lack of contact with the anodizing bath. It is noteworthy that the defect indicated by the green arrow evidences dissolution of an IMP in the absence of visible surface perforations. It indicates the passage of current through a confined electrolyte pathway, likely enclosed within the anodic film or at the nanoscale, enabling localized dissolution even in the absence of visible surface perforations.

3.3. Corrosion behaviour: non-anodized alloy vs. anodized alloy

The corrosion behaviour of the non-anodized AA7475-T761 alloy was evaluated by immersion tests in a 0.1 mol L⁻¹ NaCl solution for 24 h. Representative micrographs are shown in Fig. 5.

Fig. 5 (a1) shows the polished surface of the alloy before the immersion test, while Fig. 5 (a2) presents the same region after 24 h exposure to the chloride-containing medium. The micrographs in Fig. 5 (b1, b2) are magnified views of the marked areas in Fig. 5 (a1, a2), respectively, revealing the presence of an IMP before and after the corrosion attack. As discussed in Section 3.1, these particles are primarily composed of Al, Cu, and Fe, and have a more noble electrochemical potential than the Al matrix, thus exhibiting cathodic behaviour [62,63]. As a result, they act as preferential sites for the cathodic reaction, promoting localized trenching corrosion in the surrounding Al matrix—a type of attack widely reported for 7XXX series Al alloys [4,5]. The extensive electrochemical activity between the particle and the matrix leads to the precipitation of corrosion products, as evidenced in Fig. 5 (b2), where cracks in the corrosion products on the adjacent matrix (indicated by the yellow arrow) result from drying of the precipitated products.

In addition to corrosion around micrometric particles, intergranular corrosion (IGC) was also identified, as shown in Fig. 5 (c1). At higher magnification, Fig. 5 (c2) highlights the attack along the grain boundaries, as indicated by the red arrows. This behaviour is typical of 7XXX series alloys. It is associated with the precipitation of the MgZn₂ phase along grain boundaries, as shown earlier in Fig. 3. However, in the present case, IGC was observed only in regions adjacent to the sites where IMP-induced trenching occurred. This suggests that the local galvanic coupling induced by IMP dissolution increases the anodic driving force in the surrounding regions, promoting intergranular attack along precipitate-decorated grain boundaries. Previous studies have reported similar behaviour, indicating that the electrochemical influence of IMPs can extend beyond their immediate vicinity, promoting localized IGC propagation [52,56,57,64].

Another relevant feature observed after the immersion test was the presence of a deposit on some particles, as evidenced in Fig. 5 (d1). Fig. 5 (d2) shows this structure at higher magnification, revealing a lamellar-like morphology, as indicated by the white arrow. The chemical composition of the particle and the corrosion products was analysed by EDX, as shown in the image sequence in Fig. 5 (e1). The elemental maps of Al, Cu, and Fe confirm the composition of the IMP, while the oxygen (O K) map indicates the presence of a corrosion product formed around the particle, on the Al matrix. Notably, the zinc (Zn K) map reveals Zn enrichment at the deposited region, suggesting the precipitation of zinc hydroxide (Zn(OH)₂). This hydroxide forms due to the dissolution of Zn from the matrix during corrosion, followed by its redeposition under locally alkaline conditions around the particle, typical of cathodic zones [65,66]. Interestingly, the geometry of the IMP combined with the radial deposition of Zn(OH)₂ results in a morphology that visually resembles a “heart,” as illustrated in Fig. 5 (e1).

To better understand the influence of anodizing on corrosion

behaviour, surface modifications before and after the immersion test in 0.1 mol L⁻¹ NaCl were examined, as shown in Fig. 6.

Fig. 6(a) displays the alloy surface prior to anodizing, where several IMPs are observed (red arrows in dashed region 1). Fig. 6(b) shows the same area after anodizing, revealing the formation of cavities due to the dissolution/oxidation of IMPs (green arrows in dashed region 2). Fig. 6 (c) presents the same area after exposure to a chloride-containing medium for 24 h (0.1 mol L⁻¹). In this latter image, white arrows indicate cracks in the anodic film, suggesting localized corrosion. However, as indicated by the white arrows in Fig. 6(b), these areas were defect-free in the pristine anodic film. Conversely, after immersion, no significant morphological changes or increased surface damage were observed at the defective sites associated with the IMPs, as evidenced by comparing the dashed regions in Fig. 6(b) and Fig. 6(c). Therefore, the presence of surface defects is not the sole reason for localized corrosion susceptibility of the anodized alloy; rather, it also depends on defect morphology, depth, and connectivity to the electrolyte. This interpretation is consistent with our previous observations [38].

A quantitative survey of the defects was performed based on four SEM images covering an analysed area of approximately 490 × 366 μm. In the anodized condition, the anodic film exhibited on average 181 ± 61 surface defects. After immersion in the chloride-containing electrolyte, 35 ± 8 circular cracks were observed on the surface of the anodic film. It is important to emphasize that these circular cracks are not directly related to the population of surface defects observed after anodizing.

Higher-magnification views of the corroded regions A and B in Fig. 6 (c) are presented in Fig. 6(d–e). Cracks are visible on the surface of the anodic film (yellow arrows), as a consequence of film degradation. According to the literature [38,67], regions of the anodic film adjacent to such cracks often appear darker due to the absorption of corrosion products. These areas, referred to as modified anodic film, are indicated by blue arrows. In the center of such areas, brighter features were detected within the cracked regions (pink arrows), indicating increased interaction between the incident electron beam and heavier chemical elements [68–70]. As shown previously, defective films form at sites where IMPs exist. Moreover, as previously shown, these particles become rich in heavier elements either due to interaction with the anodizing bath or with the aggressive electrolyte (selective dissolution/oxidation of more active elements). In the literature [38] for anodized copper-containing alloys, copper enrichment can occur at the film/alloy interface during anodizing, followed by coalescence into nanoparticles that, under corrosive conditions, protrude into the corrosion products. Similar enrichment of Cu within cracks of anodized aluminium alloys exposed to chloride-containing media has been confirmed by EDX mapping in the literature [37], supporting this interpretation.

Fig. 6 (d1, e1), acquired in BSE mode, show micrographs, after film stripping, of the two corroded regions represented in Fig. 6(d) and 6 (e). They reveal cavities (dashed circles) with diameters of approximately 15 μm (Fig. 6 (d2)), and 7 μm and 2 μm (Fig. 6 (e2)), indicating the progression of corrosion beneath the anodic film. Similar features have been found in the anodized alloy, where cavities originated from defects developed at the film/alloy interface, as indicated by the green arrow in Fig. 4(e). The presence of such features may facilitate electrolyte penetration, promoting corrosion propagation through the alloy matrix underneath the oxide layer [38,67]. To further support the proposed mechanism for the cracked defects, detailed microstructural and compositional analyses of a representative circular crack site are presented in Fig. 7.

The detailed characterization of a representative circular crack site is presented in Fig. 7. The surface morphology of the defect is shown in Fig. 7(a), where circular cracks surrounding the corrosion site are clearly observed, exhibiting morphological characteristics similar to those previously shown in Fig. 6(d) and (e). The yellow arrow highlights cracks formed in the anodic film, while the blue arrow indicates the

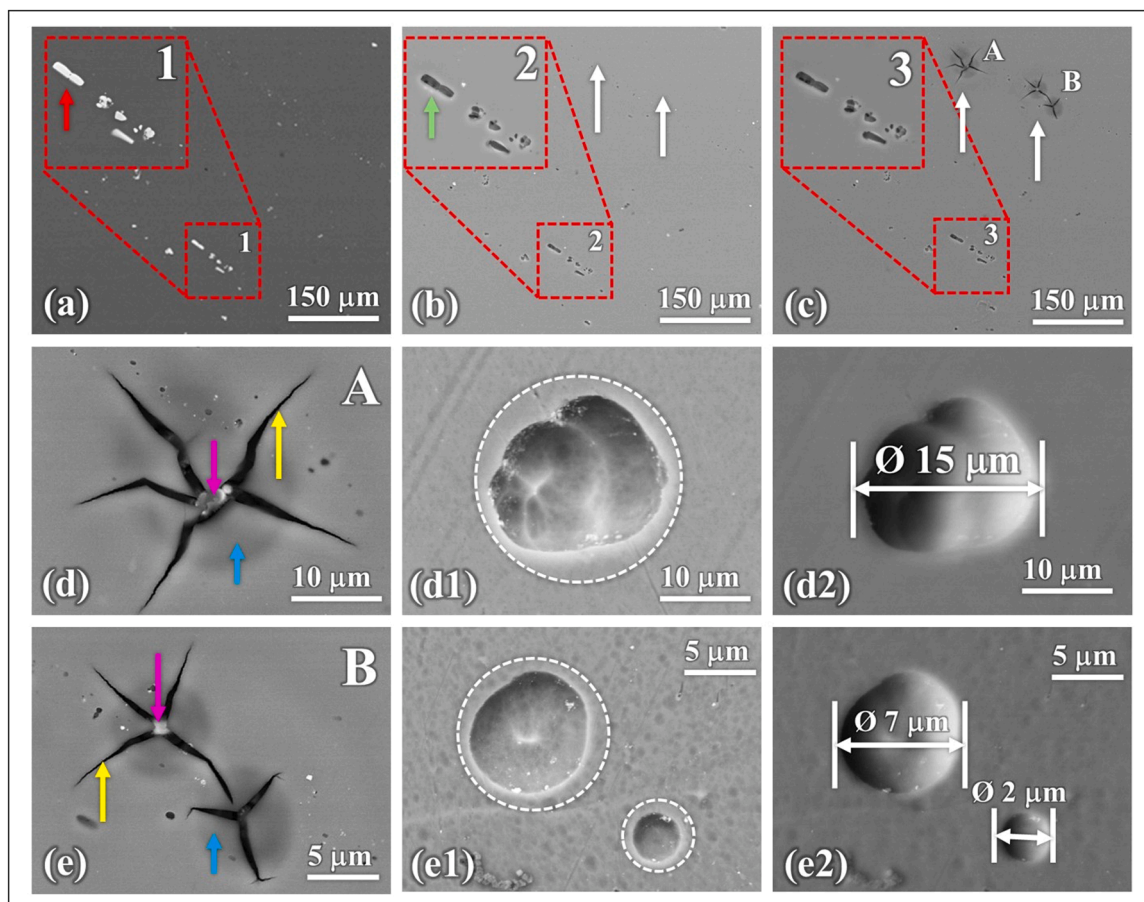


Fig. 6. Scanning electron micrographs of aluminium alloy: (a) surface before anodizing; the same region as in (a) after anodizing: (b) before and (c) after immersion in 0.1 mol L⁻¹ NaCl solution for 24 h; (d–e) higher magnification of regions A and B in (c); and (d1–e2) corresponding surfaces from (d–e) after film stripping. Red, green, and white arrows in (a), (b), and (c), respectively, indicate constituent intermetallic particles (IMPs) on the alloy surface prior to anodizing, cavities caused by IMP dissolution during anodizing, and corrosion sites that developed at defect-free regions after the immersion test. Yellow arrows in (d–e) indicate cracks formed in the anodic oxide, while blue arrows highlight modified regions of the anodic film, and pink arrows point to brighter features that may be associated with copper-enriched particles beneath the oxide layer. Dashed white circles in (d1–e1) indicate cavities formed beneath the anodic film revealed after film stripping. Images (a), (b), (c), (d), (e), (d1), and (e1) were acquired using backscattered electrons (BSE), while images (d2) and (e2) were obtained using secondary electrons (SE), all at an accelerating voltage of 15 kV.

surrounding region of modified anodic film, which appears darker due to the absorption of corrosion products, as previously discussed. Such circular features are typically associated with localized corrosion sites that develop beneath the anodic film.

A tilted view of the same region is presented in Fig. 7 (a1), acquired in secondary electron mode at a tilt angle of 35°. In this image, the cracks can be clearly seen propagating into the anodic film. In contrast to the BSE image in Fig. 7 (a), the modified anodic film surrounding the crack is less evident in this image due to the lower interaction volume and reduced compositional contrast associated with SE imaging at low accelerating voltage.

The corresponding EDX elemental maps of the circular crack region are presented in Fig. 7 (a2). As expected, strong signals of Al and O are observed, corresponding to the anodic oxide. However, particular attention should be given to the presence of Cl within the crack region, which provides clear evidence of localized corrosion processes occurring at this site. Additionally, a localized enrichment of Cu is observed, which may be associated with copper-rich nanoparticles formed at the film/alloy interface, as previously discussed in relation to the cracked regions shown in Fig. 6(d) and (e).

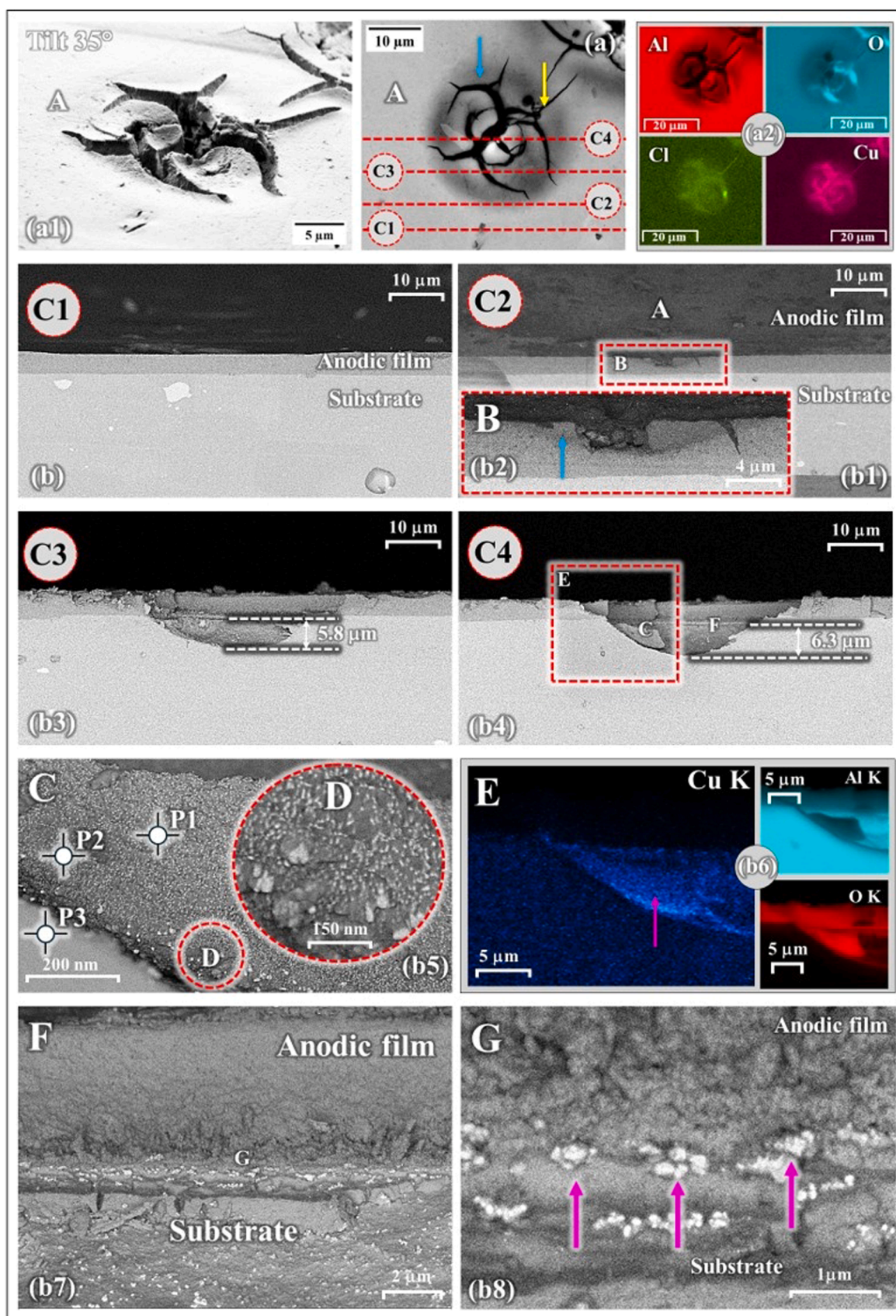
To further investigate the internal morphology of the defect, precise cross-sectional cuts were performed across the circular crack site, as indicated by the dashed lines C1–C4 in Fig. 7(a). The corresponding cross-sectional micrographs are presented in Fig. 7(b–b4). The cross-

section corresponding to cut C1 (Fig. 7(b)) shows the anodic film and substrate in a region far from the corrosion site, where no evidence of corrosion attack is observed.

As the cross-sections approach the circular defect, morphological changes become evident. In the cross-section corresponding to C2 (Fig. 7 (b1)), a contrast variation within the anodic film can be observed, indicating the presence of a modified anodic film. A higher magnification of the dashed region B is presented in Fig. 7 (b2), where a crack within the anodic film becomes clearly visible, together with the darker contrast region associated with the modified anodic film, indicated by the blue arrow. This observation agrees with the mechanism previously discussed in Fig. 6, where corrosion processes occurring beneath the film lead to modification of the anodic oxide.

Closer to the centre of the corrosion site, the cross-section corresponding to C3 (Fig. 7 (b3)) reveals a circular cavity beneath the anodic film with a depth of approximately 5.8 μm. This morphology is consistent with the cavities observed after film stripping in Fig. 6 (d1–d2) and (e1–e2), confirming that corrosion progresses beneath the anodic film. The absence of oxide above the cavity is attributed to detachment of the weakened anodic film during ultramicrotomy cutting, which commonly occurs due to the accumulation of corrosion products weakening the oxide layer.

At the centre of the corrosion site, cut C4 (Fig. 7 (b4)), the attack becomes more pronounced, with a cavity depth of approximately 6.3



(caption on next page)

Fig. 7. Scanning electron micrographs of anodized AA7475-T761 alloy after immersion in 0.1 mol L⁻¹ NaCl solution for 24 h: (a) surface showing a region associated with localized corrosion; (a1) same region shown in (a) tilted at 35°; (a2) EDX maps corresponding to the region presented in (a) and (a1). (b–b4) cross-sectional images corresponding to the dashed red lines C1–C4 indicated in (a), respectively. (b2) higher magnification of region B highlighted in (b1); (b5) higher magnification of region C shown in (b4); (b6) EDX maps corresponding to region E highlighted in (b4); (b7) higher magnification of region G; and (b8) higher magnification of the same region showing nanometric particles along the film/alloy interface. Yellow arrows in (a) indicate cracks formed in the anodic film, while blue arrows in (a) and (b2) highlight modified regions of the anodic film. Pink arrows in (b6) and (b8) indicate copper-enriched particles. Images (a), (b), (c), (d), (e), (d1), and (e1) were acquired using backscattered electron imaging (BSE), while images (d2) and (e2) were obtained using secondary electron imaging (SE), all at an accelerating voltage of 1.5 kV.

μm. A higher magnification of region C, indicated in Fig. 7 (b4), is shown in Fig. 7 (b5). In this region, numerous bright nanoscale features can be observed within the corrosion products. These particles appear as bright spots in BSE images due to their higher atomic number contrast, suggesting the presence of copper-rich nanoparticles.

To further confirm this hypothesis, EDX analyses were performed at points P1, P2, and P3, as indicated in Fig. 7 (b5). Points P1 and P2 show Cu contents of approximately 7.5 wt% and 6.1 wt%, respectively, whereas the surrounding matrix (P3) shows only about 1.1 wt% Cu. Although point analysis provides some indication of Cu enrichment, the small size of these features limits the accuracy of such measurements. Therefore, elemental mapping was performed in the region indicated by E in Fig. 7 (b4), and the result is shown in Fig. 7 (b6). The map clearly shows a strong Cu signal concentrated within the cavity, as indicated by the arrow. This observation confirms that copper-rich nanoparticles accumulate within the corrosion products formed beneath the anodic film. Such enrichment is consistent with the mechanism proposed in the literature, in which copper enrichment occurs at the film/alloy interface during anodizing, followed by the formation and coalescence of copper nanoparticles during corrosion.

Further evidence of this mechanism is provided by the higher magnification image of region F (Fig. 7 (b7)), where numerous bright particles are distributed within the cavity. In the even higher magnification image of region G (Fig. 7 (b8)), these nanoparticles can be seen coalescing along the film/alloy interface. This finding is consistent with the mechanism previously discussed for the cracked defects in Fig. 6 and reported in the literature [38], where copper-rich nanoparticles form and accumulate beneath the anodic film, promoting localized corrosion propagation.

The cross-sectional morphology of defects formed at the alloy surface during anodizing due to the dissolution of IMPS was further investigated

after immersion testing. These defects, previously observed in Fig. 6 (a–c), are shown in detail in Fig. 8.

In Fig. 8(a), a circular crack associated with localized corrosion is observed and indicated by region A. The morphology and propagation of this feature were previously described in Figs. 6 and 7. Adjacent to this corrosion site, another defect is observed (region B), which originates from the dissolution of an IMP during anodizing. In contrast to region A, this defect does not present a surrounding circular crack. Instead, it appears as a bright region, indicated by the orange arrow, which is attributed to charging effects during SEM observation [71]. Such contrast arises because electrons accumulate at the cavity edges, where local electrical conductivity is reduced.

To gather a better insight into the internal morphology of this defect, cross-sectional cuts were performed along line C1 indicated in Fig. 8(a). The corresponding images acquired in secondary (SE) and backscattered (BSE) electron modes are presented in Fig. 8 (a1) and (a2), respectively. Both images show that no corrosion attack occurs at the film/alloy interface, as indicated by the green arrow. Instead, discontinuity is observed at the surface of the anodic film, which is attributed to the preferential dissolution of the intermetallic particle during anodizing.

As reported in the literature [47], the rapid dissolution of Cu-rich IMP during anodizing may generate cavities while the anodic film continues to grow around the defect. In such cases, oxide growth proceeds beneath the dissolved particle, thereby locally preserving portions of the barrier layer at the film/alloy interface. This process often leads to the formation of hemispherical or spherical morphological features beneath the cavity, associated with the continued oxide growth below the dissolved particle site. Such features are indicated by the green arrow at the film/alloy interface (Fig. 8 (a1, and a2)).

It is also important to highlight the presence of fragmented oxide material accumulated above the cavity. These features are most likely

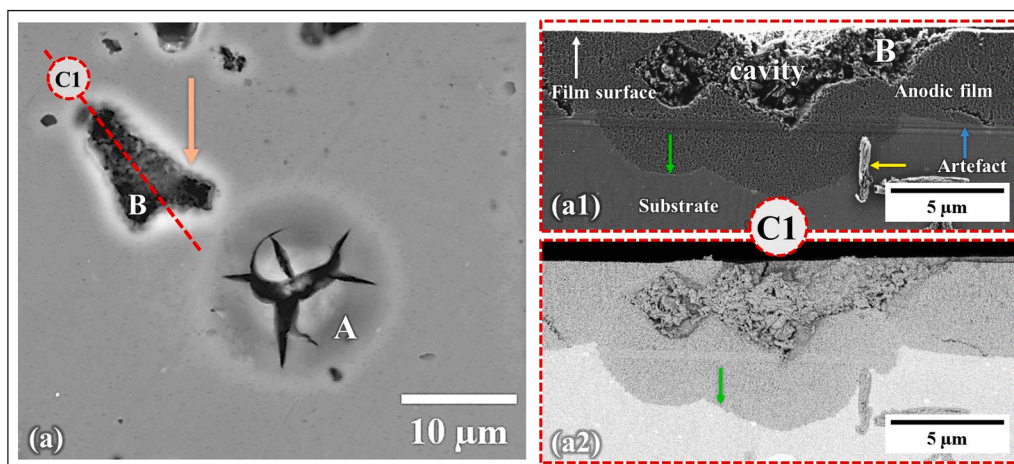


Fig. 8. Scanning electron micrographs of anodized AA7475-T761 alloy after immersion in 0.1 mol L⁻¹ NaCl solution for 24 h: (a) surface after immersion; (a1) and (a2) cross-sectional images corresponding to the cut along line C1 indicated in (a). Regions A and B in (a) correspond to defects originating from the dissolution of intermetallic particles (IMPs) during anodizing. Region A shows a characteristic circular crack surrounding the defect, while region B corresponds to a corrosion site associated with a previously formed circular crack. The orange arrow in (a) indicates charging effects during SEM observation. White, green, yellow, and blue arrows in (a1) and (a2) indicate the film surface, film/alloy interface, detached anodic oxide, and an artefact produced during diamond cutting, respectively. Image (a) was acquired using backscattered electrons (BSE) at 20 kV, while images (a1) and (a2) were obtained at 1.5 kV using secondary electrons (SE) and backscattered electrons (BSE), respectively.

associated with the upper portion of the anodic film that becomes detached during ultramicrotomy cutting. This behaviour is commonly reported when hydrated anodic oxides are sectioned [38,41,72–74], since the oxide film becomes mechanically fragile and may partially delaminate during sample preparation. In this case, small fragments of the anodic oxide remain at the surface of the cavity, as indicated by the yellow arrow, and may also be displaced into the cavity during sectioning. Additionally, mechanical artefacts associated with diamond-knife cutting can be observed, as indicated by the blue arrow. Such artefacts appear as linear scratches produced during ultramicrotomy and should not be interpreted as corrosion features. The observation of the same structural features in both SE and BSE imaging modes further supports this interpretation, indicating that these features are related to sample preparation rather than to actual corrosion processes. This interpretation also explains why, in the cross-sectional images of circular crack sites shown in Fig. 7 (b3) and (b4), the anodic oxide is absent above the cavity region. In those cases, the oxide film becomes significantly weakened due to corrosion beneath the film, making it prone to detachment during sectioning.

The morphological features observed in Figs. 5 and 6 highlight the distinct corrosion behaviours of the alloy in non-anodized and anodized conditions. In the non-anodized alloy (Fig. 5), trenching corrosion, intergranular attack, and localized deposition of corrosion products were predominant, particularly around cathodic IMPs. In contrast, the anodized surface (Fig. 6) exhibited cracks and modified regions in the anodic film, while subsurface cavities became evident after film removal. This shows that, although the anodic film acts as a protective barrier, its effectiveness can be compromised by interfacial defects and localized degradation. These observations demonstrate that the presence of the anodic film not only alters the corrosion morphology but also affects the intensity of the local corrosion process. The following section, therefore, compares the electrochemical behaviour and overall corrosion resistance of the non-anodized and TSA-anodized surfaces after polarization experiments, corresponding to a harsher anodic stress imposed on the samples.

3.4. Electrochemical behaviour and corrosion resistance: non-anodized vs. anodized alloy

Fig. 9 shows the open circuit potential (OCP) curves of the non-anodized and anodized AA7475-T761 alloy during 70 h of immersion in a 0.1 mol L⁻¹ NaCl solution. The non-anodized alloy (blue curve) exhibited a continuous decrease in potential from approximately -0.66 V (Ag/AgCl) to -0.82 V (Ag/AgCl) during the immersion period.

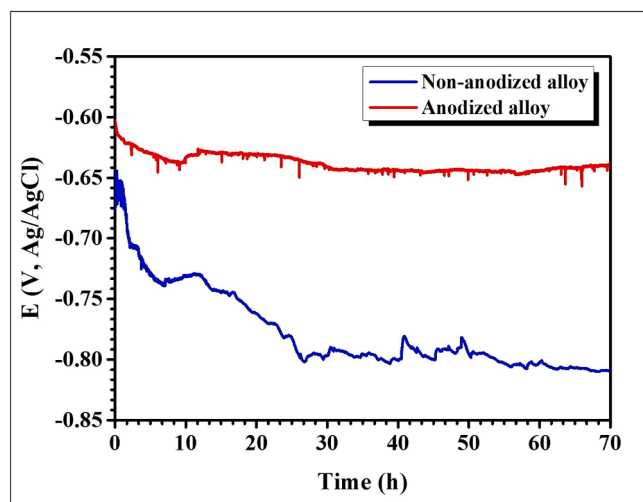


Fig. 9. Open circuit potential (OCP) curves of non-anodized and anodized AA7475-T761 alloy during 70 h of immersion in 0.1 mol L⁻¹ NaCl solution.

This trend indicates active dissolution and progressive corrosion without the formation of a stable passive film. The absence of a plateau region and the increasingly negative OCP values suggest the initiation and propagation of localized corrosion, likely associated with galvanic interactions between the aluminium matrix and cathodic IMPs, as discussed previously in Fig. 5.

In contrast, the anodized alloy (red curve) maintained a nobler and more stable potential, fluctuating mildly between -0.61 V (Ag/AgCl) and -0.66 V (Ag/AgCl). The limited amplitude of these fluctuations reflects a delayed corrosion process, suggesting that the anodic film acts as a physical barrier, restricting direct electrolyte access to the metallic substrate. The lack of sharp potential drops further confirms that no aggressive localized corrosion occurred during the test period.

The minor but repeated fluctuations observed in the OCP of the anodized sample can be attributed to localized interactions at film defects or thinner regions. However, the anodic film prevents stabilization of anodic sites, commonly associated with severe pitting or trenching corrosion. The more noble potential exhibited by the anodized sample (~150–200 mV more positive than the non-anodized alloy) is in accordance with previous results and the morphological observations presented in Figs. 5 and 6, confirming that anodizing enhances both the stability and durability of the alloy in corrosive environments.

Fig. 10 displays the potentiodynamic polarization curves and post-test surface morphologies for the AA7475-T761 alloy in non-anodized and anodized conditions.

In Fig. 10 (a), a representative anodic polarization curve of the non-anodized AA7475-T761 sample after 5 min immersion in the NaCl 0.1 mol L⁻¹ is shown. The results were highly reproducible, as confirmed by the consistent behaviour observed across all replicates. The alloy reaches high current densities at low anodic overpotentials, indicating that the corrosion potential (E_{corr}) is very close to the pitting potential (E_{pit}), even considering a short immersion period, with no clear evidence of a stable passive region. Consequently, the metallic surface is highly susceptible to rapid passivity breakdown and early initiation of localized corrosion.

In contrast, the anodized samples, shown in Fig. 10 (b), exhibit distinctly more variable electrochemical behaviour. The polarization curves display significant scatter in both the potential at which the anodic film breaks down and the current densities of the passive regime. In some samples, film breakdown occurs at potentials below +0.1 V (Ag/AgCl), whereas in others, the anodic film remains passivated at higher potentials. Similarly, the passive current density plateau ranges from approximately 10⁻⁵ mA cm⁻² to nearly ten times higher in some instances. Although this dispersion primarily reflects the non-uniformity of the anodic film, the limited electrode area also contributes to the apparent variability observed [17,44]. Nonetheless, despite the dispersion, a well-defined passive region is observed for the anodized alloy, attributed to the formation of a protective oxide film that promotes and stabilizes passivity. Conversely, the non-anodized alloy exhibits passive behaviour only in deaerated media (Fig. 10 (c)), where a significant negative shift of the corrosion potential, from approximately -0.63 V (Ag/AgCl) (aerated) to -1.13 V (Ag/AgCl), occurs, accompanied by the onset of a distinct passive region.

The potentiodynamic polarization curves in Fig. 10 further evidence the differences in electrochemical activity between the two conditions. For the non-anodized alloy (Fig. 10 (a)), the current density rapidly reaches very high values, on the order of mA cm⁻², at potentials only slightly above E_{corr} , suggesting that corrosion initiates and propagates readily. By contrast, in the anodized condition (Fig. 10 (b)), the current density increases at potentials significantly above E_{corr} , clearly confirming that anodizing enhances the alloy's corrosion resistance. These differences are more clearly highlighted in Fig. 10 (d), further proving that under aerated conditions, the non-anodized alloy remains near or at its pitting potential, confirming its high susceptibility to localized attack.

The potentiodynamic curves displayed in Fig. 10 show that the

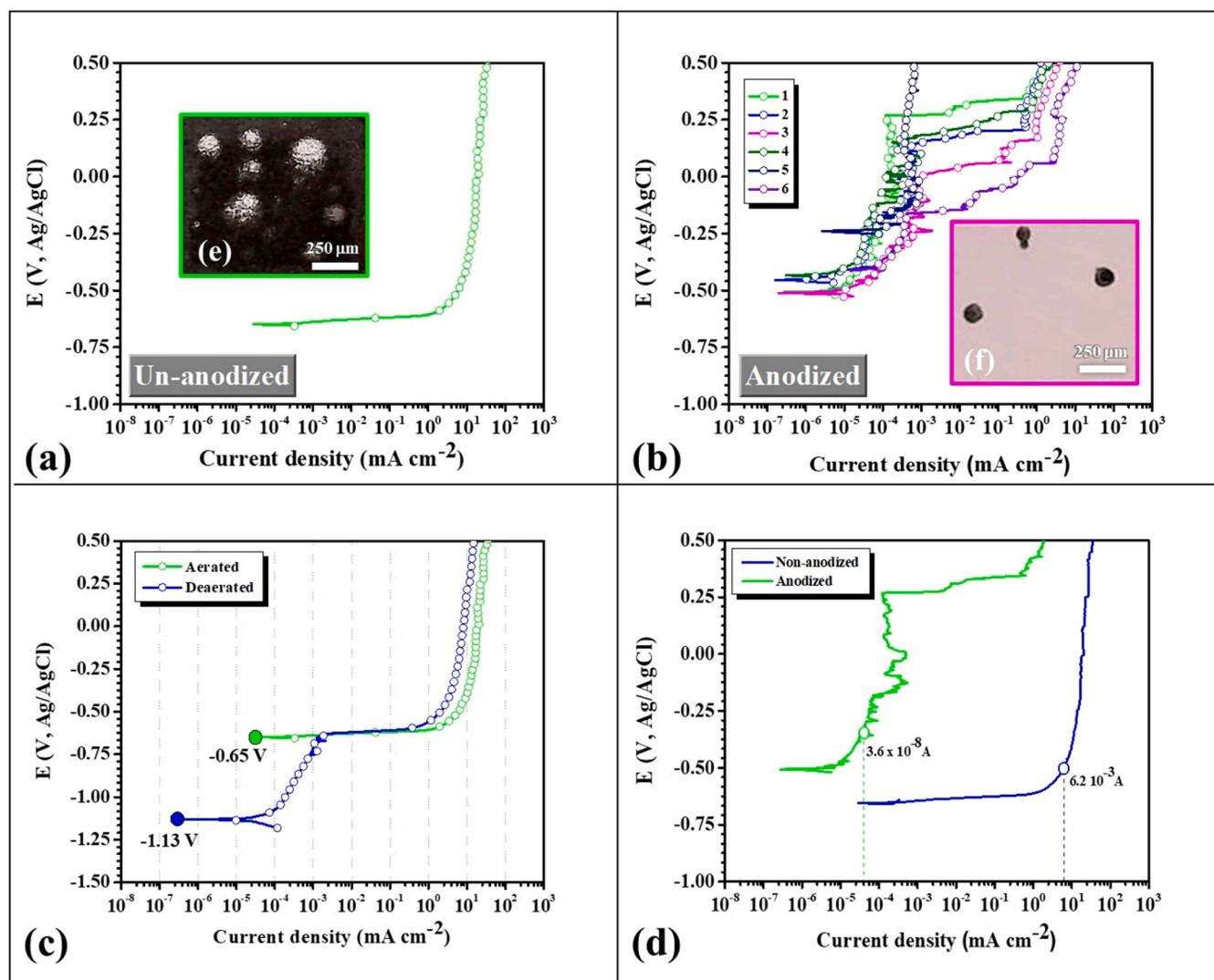


Fig. 10. Anodic potentiodynamic polarization curves of the AA7475-T761 aluminium alloy after 5 min of immersion in 0.1 mol L⁻¹ NaCl solution: (a) non-anodized; (b) anodized; (c) Anodic potentiodynamic polarization curves for the non-anodized surface in aerated and deaerated 0.1 mol L⁻¹ NaCl solution; (d) comparative polarization curves of the alloy in non-anodized and anodized conditions. Surface macrographs of the AA7475-T761 alloy after the polarization test in the non-anodized (e) and anodized (f) conditions.

corrosion potential (E_{corr}) of the anodized surface was approximately 190 mV nobler than that of the non-anodized alloy. This is in accordance with findings of several studies reporting the ennoblement of E_{corr} of anodized aluminium alloys in different media [32,34,40,44], and is also consistent with the results reported by Zuo et al. [75], who showed that anodizing, followed by appropriate sealing, yields more noble E_{corr} values and improved passivation stability in chloride solutions. In addition, the anodized samples exhibited a well-defined pitting potential (E_{pit}), at which a sharp transition from passive to active behaviour was observed, even though the passive ranges varied across the different tested regions. With that in mind, a mean value of + 0.101 V (Ag/AgCl), and a passive range ($\Delta E = E_{\text{pit}} - E_{\text{corr}}$) of about 0.555 V was calculated for the set of anodized samples presented in Fig. 10(b), indicating good resistance to pit initiation; however, it is important to emphasize that these values may change if another set of samples is considered. In contrast, the non-anodized samples displayed a stable E_{corr} and a sharp increase in the anodic current density, indicating the growth of stable pits, thereby confirming their high susceptibility to localized corrosion.

The differences in the corrosion resistance of the two samples are further illustrated in Fig. 10 (d), at which the current densities at an overpotential of + 100 mV relative to E_{corr} are indicated: the non-

anodized sample exhibits a current density approximately five orders of magnitude higher than that of the anodized surface, highlighting the significant decrease in electrochemical activity promoted by the anodic film. Consistent with these observations, the total charge (C), estimated from the integrated area under the polarization curves, was significantly lower for the anodized surface (17.1 ± 8.8 A.s) compared to the non-anodized samples (49.3 ± 6 A.s). This reduction in electrochemical charge supports the enhanced protectiveness of the anodic film and is indicative of lower overall surface electrochemical activity, which is an expected outcome, since corrosion of the anodized alloy is highly localized, restricted to a few sites; however, it can be more severe at each individual location [47], as will be shown later. These features are relevant to comparative corrosion behaviour, as the polarization curves were halted at the same potential and collectively demonstrate improved overall and localized corrosion resistance for the anodized sample.

The polarization experiments were complemented by the macroscopic examination of the tested surfaces, and representative macrographs are shown in Fig. 10 (e, f). The non-anodized specimen (Fig. 10 (e)) exhibits extensive surface damage and corrosion product precipitation, consistent with the higher current densities and poor corrosion

resistance. In contrast, the anodized sample (Fig. 10 (f)) displays a mostly intact surface and isolated pitting sites, consistent with improved passive behaviour.

A more detailed assessment of the resistance of both samples to localized attack was performed by SEM analysis, as shown in Fig. 11.

Fig. 11 (a) shows the surface of the non-anodized sample after the full anodic polarization test, highlighting areas with distinct contrast. The brighter regions exhibit a smoother morphology, with no apparent precipitation of corrosion products, whereas the darker zones appear rougher and are covered with corrosion products; Fig. 11 (a1), an enlarged view of the dashed square 1 in Fig. 11 (a), provides clearer evidence of this feature. In Fig. 11 (a2), an enlargement of the square 2 in Fig. 11 (a1), severe localized corrosion becomes evident in the brighter areas. The high magnification micrograph in Fig. 11 (a3) reveals pronounced intergranular corrosion (IGC), as indicated by the red arrow. The morphology and dimensions of the attacked region closely follow the grain structure of the alloy, with a characteristic size of approximately 21.1 μm , which is in good agreement with the grain size observed in the microstructural analysis presented in Fig. 2. The corrosion path clearly propagates along grain boundaries, rather than through the grain interior. Such behaviour is commonly reported for 7XXX series aluminium alloys and is associated with galvanic coupling involving MgZn_2 precipitates distributed along grain boundaries, as previously discussed in Fig. 4. The absence of corrosion products surrounding this severely attacked region suggests local cathodic protection promoted by the intense anodic activity within the IGC crevice. This observation is consistent with the findings of Boag et al. [76,77] who reported similar corrosion product distribution in 2024 Al alloys exposed to chloride solution, at which precipitation occurred far from pit openings, whereas areas adjacent to the openings remained relatively

free of corrosion products.

A cross-sectional analysis of the interface zone was carried out along line C1, indicated in Fig. 11 (a2). The tilted image Fig. 11 (a4) shows the attack depth, $\sim 22 \mu\text{m}$, indicated by the white arrow, as well as the direction of corrosion propagation. These micrographs show that the darker attacked regions did not evolve from intergranular corrosion fronts. Instead, under intense anodic polarization, the progression of corrosion may be more reasonably attributed to the heterogeneous dissolution of the alloy surface due to passive film instability, or to subsurface attacks initiated at localized corrosion sites, such as those associated with IMPs. Similar interpretations have been reported in literature, where surface heterogeneities and passive film breakdown were shown to drive localized attack in AA2024 alloys [76–80]. Although in some cases, crystallographic pits have been shown to develop from intergranular corrosion fronts [81], such an evolution is not directly evident in the micrographs displayed in Fig. 11 (a).

In the anodized condition, spherical cavities developed on the surface during polarization tests (Fig. 11 (b)). Fig. 11 (b1) presents a higher-magnification image of the dashed square 1, indicated in Fig. 11 (b), showing a representative pit. The actual extent of the attack was revealed only after the anodic film was stripped, as shown in Fig. 11 (b2). The pit diameter, 68 μm before stripping (Fig. 11 (b1)), reached 504 μm after the oxide removal (Fig. 11 (b2)), indicating that the anodic film concealed the full extent of the localized attack. A higher magnification micrograph of the area marked by the letter A in Fig. 11 (b2) is presented in Fig. 11 (b3), where a rougher surface is observed, indicative of aggressive corrosion in this region. At even higher magnification, crystallographic corrosion features become evident at the pit bottom (indicated by the yellow arrow), as shown in detail in Fig. 11 (b4). In Fig. 11 (b1), the presence of swollen regions farther away from the

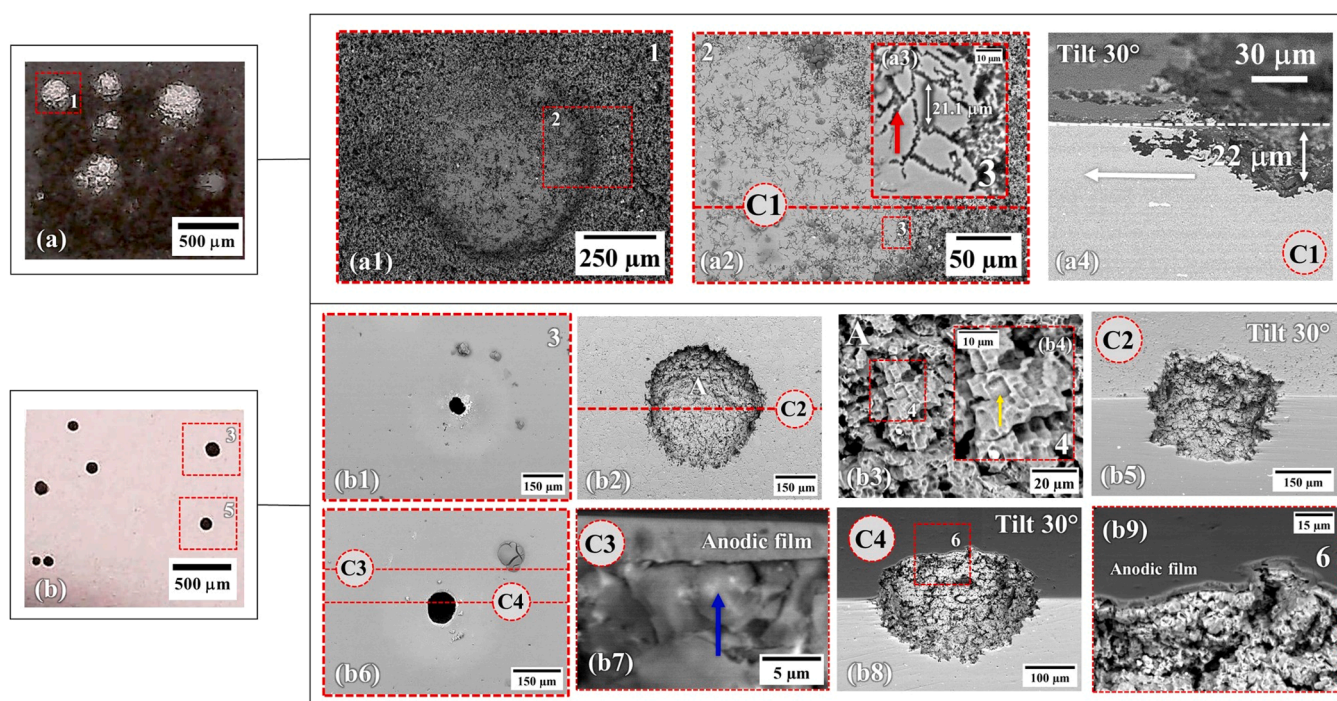


Fig. 11. Analyses of the AA7475-T761 alloy surface after the anodic polarization tests. (a) Macroscopic optical image of the non-anodized surface after polarization; (a1) micrograph at higher magnification of region 1 in (a); (a2) micrograph at higher magnification of region 2 in (a1); (a3) higher magnification of region 3 in (a2); (a4) cross-sectional view corresponding to dashed line C1 in (a2). (b) Macroscopic optical image of the anodized surface after the polarization test; (b1) before and (b2) after film stripping; (b3) higher magnification of region A indicated in (b2); (b4) higher magnification of the dashed area in (b3); (b5) cross-sectional view corresponding to dashed line C2 in (b2); (b6) low-magnification image of a pitted region; (b7) cross-sectional view corresponding to dashed line C3 in (b5); (b8) cross-sectional view corresponding to dashed line C4 in (b5); and (b9) higher magnification of region 6 in (b8). The red, white, yellow, and blue arrows in (a3), (a4), (b4), and (b7) indicate intergranular corrosion, the direction of corrosion propagation, crystallographic corrosion, and the accumulation of corrosion products beneath the anodic film, respectively. Images (a) and (b) were obtained by optical microscopy, whereas all remaining micrographs were acquired by scanning electron microscopy using backscattered electrons (BSE) at an accelerating voltage of 20 kV.

opening of the pit is evident. They appear to correspond to the limit of the pit cavity after the oxide layer has been removed (Fig. 11 (b1)). This finding indicates that swollen regions on the surface of the anodized samples correspond to the eruption of corrosion points from beneath the oxide layer, a process assisted by the aggressive electrolyte confined within the pit, which is partially covered by the anodic film.

Fig. 11 (b5) presents a cross-sectional view of the pit in Fig. 11 (b2) at a 30° tilt angle, corresponding to the C2 line cut, highlighting the depth and propagation characteristics of the localized attack. The depth reached $\sim 175 \mu\text{m}$, consistent with the average depth of $170 \pm 35 \mu\text{m}$ obtained from analysis of 30 pits. In addition, to evaluate the progression of the attack underneath the anodic film, pits formed after polarization were also sectioned without stripping the anodic layer, as shown in Fig. 11 (b6), which presents a higher-magnification image of the dashed square 2 indicated in Fig. 11 (b), together with the indication of the cross-sectional cuts, which were performed along C3 and C4 lines.

The cross-section along the C3 line, shown in Fig. 11 (b7), reveals a region where the anodic film is in contact with corrosion products accumulating beneath the film (indicated by the blue arrow). However, distinguishing modified anodic film from unmodified regions using SEM-EDX is challenging, as the porous anodic film undergoes hydration after immersion, changing its composition from Al_2O_3 (Al:O ratio of 2:3) to $\text{Al}(\text{OH})_3$ or $\text{AlO}(\text{OH})$ (Al:O ratio of approximately 1:2–3), which resembles the composition of corrosion products [82]. Consequently, the aluminium ratio cannot be used to differentiate between these two regions. In addition, corrosion products may incorporate elements such as Cl, which EDX cannot detect at concentrations below 0.1%. The limited spatial resolution of EDX in SEM ($1\text{--}3 \mu\text{m}^3$) limits compositional analysis, as the signal represents an average over the entire sampled volume [69,83,84]. In this context, contrast differences in BSE images resulting from interactions of the electron beam with corrosion products containing higher atomic-number elements make the modified anodic film more distinguishable (as shown in Fig. 6(d, e)). Therefore, SEM in BSE mode remains the most reliable approach for identifying regions of the anodic film affected by corrosion.

The cross-section along the C4 line, passing through the centre of the pit shown in Fig. 11 (b6), is presented in Fig. 11 (b8). In this region, the anodic film above the cavity collapsed during sample preparation, as shown in Fig. 11 (b8) and (b9), due to compromised adhesion to the substrate. As a result, only the portion of the pit adjacent to the anodic film remained visible, as shown at higher magnification in Fig. 11 (b9).

4. Discussion

Corrosion is fundamentally a surface-mediated phenomenon; however, the factors defining the surface condition of an alloy play a key role in determining its overall corrosion resistance and propagation. In the non-anodized AA7475-T761 alloy, localized corrosion initiates at constituent intermetallic particles (IMPs) and nanoscale precipitates (Figs. 1 and 3). These phases establish micro- and nano-galvanic cells with the aluminium matrix, where cathodic IMPs promote trench formation (Fig. 5 (b2)) and anodic grain-boundary precipitates drive intergranular attack (Fig. 5 (c1, c2)). In regions adjacent to cathodic IMPs, intergranular corrosion may also intensify due to increased electrolyte aggressiveness within the trenches. Thus, the widespread occurrence of microstructural heterogeneities results in corrosion propagation across the surface.

In contrast, in the anodized alloy, corrosion initiation is confined to defects formed at the film/alloy interface during anodizing. These defects arise mostly from the selective dissolution of IMPs and are observed as discontinuities in the anodic film (Fig. 4(e)). Electrolyte penetration through these defective regions enables the onset of underfilm corrosion (Fig. 11). As corrosion progresses, accumulation of corrosion products and Cu enrichment beneath the film (Fig. 6(d, e) and Fig. 7) modify the oxide morphology, promoting local cathodic sites and further enhancing underfilm propagation. This mechanism explains the severe, yet highly

localized, attack observed after the polarization tests.

It should be noted that establishing a direct one-to-one correlation between a specific dissolved IMP and the subsequent corrosion cavity is experimentally challenging. Once corrosion initiates beneath the porous anodic film, the process evolves rapidly, and the original dissolution site may no longer be preserved in the final morphology. For this reason, the present interpretation relies on consistent observation of corrosion cavities and cracked defects associated with interfacial discontinuities rather than on a single micrograph capturing the earliest stage of the process. Similar challenges have been discussed in literature, where defects induced by intermetallic particles located beneath anodic oxide layers were shown to influence post-anodizing corrosion behaviour. For example, Raffin et al. [85] reported that IMPs buried under the oxide may promote localized degradation through subsurface electrochemical interactions. In contrast, the mechanism discussed in the present study involves defects generated during anodizing by IMP dissolution at the film/alloy interface. These differences highlight that the influence of microstructure on post-anodizing corrosion cannot be generalized and strongly depends on the characteristics of the alloy, including its IMP population and composition. Consequently, each alloy system and surface condition must be investigated individually to properly understand the mechanisms governing corrosion initiation and propagation.

It is also important to emphasize that defects observed at the anodic film surface do not necessarily represent the full geometry of the defect within the oxide layer. In many cases, the visible surface feature corresponds only to the upper portion of a bigger subsurface cavity formed due to the dissolution of IMPs [47,86]. Consequently, the presence of a surface defect does not necessarily imply that the cavity extends down to the film/alloy interface. In the alloy investigated in the present study, corrosion sites were not directly associated with the surface defects (Fig. 4(d) and 6 (a-c)), suggesting that the cavities generated during anodizing did not extend through the entire thickness of the anodic film (Fig. 8). However, this behaviour may vary depending on the alloy composition, the size and protrusion of the IMPs, as well as the anodizing parameters. If the particle size or its projection above the matrix exceeds the thickness of the growing oxide film, the resulting defect may extend to the substrate and act as a preferential site for corrosion initiation. Therefore, a three-dimensional characterization would be required to fully resolve the true geometry of these defects and their relationship with corrosion initiation. These considerations also highlight that the influence of microstructure on defect formation and corrosion behaviour cannot be generalized, and that each alloy system requires a dedicated and carefully designed investigation to properly understand the role of intermetallic particles and anodizing parameters in controlling corrosion initiation.

Although the mechanisms differ, corrosion initiation in both conditions stems from loss of passivity. In the non-anodized alloy, the natural passive film is thin and locally disrupted by microstructural heterogeneities. In contrast, the anodized alloy is protected by a thicker oxide formed under non-equilibrium conditions, which fails locally at defect sites where barrier layer is absent (Fig. 11). Therefore, corrosion in both systems is governed by passivity loss, regardless of whether the oxide is natural or anodically formed. Still, the extent, localization, and propagation of the damage differ markedly.

Electrochemical analyses support this interpretation. The anodized surface displays a nobler E_{corr} and a well-defined passive range, while the non-anodized alloy shows immediate breakdown with no distinct E_{pit} (Fig. 10 (a-c)). Despite its lower total anodic charge ($17.1 \pm 8.8 \text{ A}\cdot\text{s}$ vs. $49.3 \pm 6 \text{ A}\cdot\text{s}$), the anodized alloy exhibits deeper pits ($170 \pm 35 \mu\text{m}$) confined to a few defective sites (Fig. 11 (b5, b8)). In contrast, the non-anodized condition displays shallower pits ($25 \pm 8 \mu\text{m}$) but more widespread corrosion (Fig. 11 (a4)). This difference arises because current flow in the anodized alloy is concentrated at a limited number of defects, producing intense local attack even though the overall electrochemical activity is lower.

Therefore, anodizing plays a dual role. It enhances general and

localized corrosion resistance by increasing E_{corr} and delaying the attack, yet once the film is breached, the confined electrolyte beneath the oxide accelerates localized propagation underneath the oxide layer [75,87–91]. Consequently, corrosion becomes highly localized and may progress aggressively beneath the anodic film even though the overall electrochemical activity of the surface is reduced. These findings highlight that the corrosion resistance of anodized aluminium alloys cannot be evaluated solely through electrochemical parameters such as E_{corr} or passive current density. Microstructural features and anodizing-induced defects must also be considered to fully understand corrosion initiation and propagation mechanisms.

It is worth emphasizing that the influence of the initial surface condition is often underestimated in corrosion studies of aluminium alloys. Many investigations evaluate corrosion behaviour primarily through electrochemical parameters [32,34,40,92–94], frequently without a detailed assessment of the microstructural features present at the surface prior to exposure. However, features such as intermetallic particles, grain-boundary precipitates, and defects generated during surface treatments can fundamentally alter corrosion initiation pathways. As a result, electrochemical responses alone may not fully reflect the mechanisms governing localized corrosion. The present results highlight that understanding corrosion behaviour requires careful consideration of surface condition, since the distribution and nature of microstructural heterogeneities can significantly modify both the initiation and propagation of corrosion.

5. Conclusion

The results of the study conducted allow to draw the following conclusions:

- In the non-anodized alloy, localized corrosion initiates through micro and nano galvanic cells between constituent intermetallic particles (IMPs), grain-boundary precipitates, and the aluminium matrix, leading to trenching, intergranular, and crystallographic attack.
- In the anodized alloy, corrosion initiation is confined to defects at the film/alloy interface, originating from the dissolution of Cu-rich IMPs during anodizing, and these sites promote underfilm propagation.
- Corrosion initiation mechanisms differ fundamentally between the two conditions, with microstructural heterogeneities dominating in the non-anodized alloy and film/interface defects governing the anodized one.
- In the anodized alloy, localized corrosion is confined to a few defective sites. Once initiated, corrosion progresses beneath the anodic film, forming broader and deeper pits compared to the non-anodized condition, underscoring the need to couple microstructural control with optimized anodizing for long-term protection.

CRediT authorship contribution statement

Isolda Costa: Writing – review & editing, Funding acquisition. **Xiaorong Zhou:** Writing – review & editing, Validation, Supervision, Funding acquisition. **Izabel Fernanda Machado:** Resources. **Woraphan Intaphan:** Formal analysis. **Hercílio G. de Melo:** Writing – review & editing, Formal analysis. **Araujo João Victor:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

- [1] D.K. Koli, G. Agnihotri, R. Purohit, Advanced aluminium matrix composites: the critical need of automotive and aerospace engineering fields, *Mater. Today Proc.* 2 (2015) 3032–3041, <https://doi.org/10.1016/j.matpr.2015.07.290>.
- [2] R. Guan, H. Lou, H. Huang, X. Liang, X. Xiao, H. Li, F. Li, J. Wang, X. Yun, L. Zeng, Development of aluminum alloy materials: Current status, trend, and prospects, *Chin. J. Eng. Sci.* 22 (2020) 68–79, <https://doi.org/10.15302/J-SSCAE-2020.05.013>.
- [3] J.V. de, S. Araujo, M. Milagre, I. Costa, A historical, statistical and electrochemical approach on the effect of microstructure in the anodizing of Al alloys: a review, *Crit. Rev. Solid State Mater. Sci.* 49 (2024) 521–581, <https://doi.org/10.1080/10408436.2023.2230250>.
- [4] J. Tardelli, E. Rocca, Electrochemical behaviour of inter-metallic phases in sulfuric acid at high voltage—anodization of Al_7Cu_2Fe and $MgZn_2$ phase, 10th Symp. Electrochem. Methods Corros. Res. Maragogi (2012).
- [5] D. Nickel, D. Dietrich, R. Morgenstern, I. Scharf, H. Podlesak, T. Lampke, Anodisation of aluminium alloys by micro-capillary technique as a tool for reliable, cost-efficient, and quick process parameter determination, *Adv. Mater. Sci. Eng.* 2016 (2016) 1374897, <https://doi.org/10.1155/2016/1374897>.
- [6] Y.S. Huang, T.S. Shih, J.H. Chou, Electrochemical behavior of anodized AA7075-T73 alloys as affected by the matrix structure, *Appl. Surf. Sci.* 283 (2013) 249–257, <https://doi.org/10.1016/j.apsusc.2013.06.094>.
- [7] H.A. Elkilany, M.A. Shoeib, O.E. Abdel-Salam, Influence of hard anodizing on the mechanical and corrosion properties of different aluminum alloys, *Metallogr. Microstruct. Anal.* 8 (2019) 861–870, <https://doi.org/10.1007/s13632-019-00594-5>.
- [8] J.M. Runge, T. Hossain, Interfacial phenomena in 7000 series alloys and their impact on the anodic oxide, *Mater. Today Proc.* 2 (2015) 5055–5062, <https://doi.org/10.1016/j.matpr.2015.10.096>.
- [9] F. Zhang, C. Örnek, J.O. Nilsson, J. Pan, Anodisation of aluminium alloy AA7075: influence of intermetallic particles on anodic oxide growth, *Corros. Sci.* 164 (2020) 108319, <https://doi.org/10.1016/j.corsci.2019.108319>.
- [10] S.U. Okene, M. Abdullahi, A. Gana, Corrosion improvement of AA7075 through precipitation hardening and anodization, *Mater. Today Proc.* 38 (2021) 729–736, <https://doi.org/10.1016/j.matpr.2020.04.084>.
- [11] D. Veys-Renaux, N. Chahboun, E. Rocca, Anodizing of multiphase aluminium alloys in sulfuric acid: In-situ electrochemical behaviour and oxide properties, *Electrochim. Acta* 211 (2016) 1056–1065, <https://doi.org/10.1016/j.electacta.2016.06.131>.
- [12] P. Atz Dick, G.H. Knörnschild, L.F.P. Dick, Anodising and corrosion resistance of AA7050 friction stir welds, *Corros. Sci.* 114 (2017) 28–36, <https://doi.org/10.1016/j.corsci.2016.10.015>.
- [13] J.H. Liu, M. Li, S.M. Li, M. Huang, Effect of the microstructure of Al 7050-T7451 on anodic oxide formation in sulfuric acid, *Int. J. Miner. Metall. Mater.* 16 (2009) 432–438, [https://doi.org/10.1016/S1674-4799\(09\)60076-5](https://doi.org/10.1016/S1674-4799(09)60076-5).
- [14] M. Mokaddem, J. Tardelli, K. Ogle, E. Rocca, P. Volovitch, Atomic emission spectroelectrochemical investigation of the anodization of AA7050T74 aluminum alloy, *Electrochem. Commun.* 13 (2011) 42–45, <https://doi.org/10.1016/j.elecom.2010.11.008>.
- [15] M. Schneider, W. Fürbeth, Anodizing—The pore makes the difference, *Mater. Corros.* 73 (2022) 1752–1765, <https://doi.org/10.1002/maco.202213324>.
- [16] M.P. Martínez-Viademonte, S.T. Abrahami, T. Hack, M. Burchardt, H. Terryn, A review on anodizing of aerospace aluminum alloys for corrosion protection, *Coatings* 10 (2020) 1106, <https://doi.org/10.3390/coatings10111106>.
- [17] J.V. Araujo, M.X. Milagre, A.D. Gabbardo, R.E. Klumpp, I. Costa, The effect of tartaric-sulfuric acid (TSA) anodizing on the corrosion resistance of the AA7475-T761, ECS, Meet. Abstr. MA2022-02 (2022) 2475, <https://doi.org/10.1149/MA2022-02142475mtgabs>.
- [18] J.M. Runge, Trace elements and their impact on surface finishing characteristics of aluminum extrusions, in: 15th Annu. Anodizing Conf. Expo, Aluminum Anodizers Council, 2013, pp. 1–11.
- [19] J.M. Runge, Base metal microstructural considerations for anodizing aluminum extrusions, *Proc. Elev. Int. Alum. Extrus. Technol. Semin. Chic.* (2016).
- [20] J.M. Runge, Anodizing complex 7000 series, *Light Met. Age* 74 (2016) 52–56.

- [21] I. Tsangaraki-Kaplanoglou, S. Theohari, T. Dimogerontakis, Y.M. Wang, H.H. Kuo, S. Kia, Effect of alloy types on the anodizing process of aluminum, *Surf. Coat. Technol.* 200 (2006) 2634–2641, <https://doi.org/10.1016/j.surfcoat.2005.07.065>.
- [22] V.R. Capelossi, M. Poelman, I. Recloux, R.P.B. Hernandez, H.G. de Melo, M. G. Olivier, Corrosion protection of clad 2024 aluminum alloy anodized in tartaric-sulfuric acid bath and protected with hybrid sol-gel coating, *Electrochim. Acta* 124 (2014) 69–79, <https://doi.org/10.1016/j.electacta.2013.09.004>.
- [23] O.M.P. Ramirez, T.M. Kremmer, T.F. de Almeida, J.H. Marin, C.L. Rodrigues, T. F. da Silva, R.A. Ando, S. Pogatscher, H.G. de Melo, Direct cerium-doped hybrid sol-gel sealing of TSA-anodized AA2024-T3 for corrosion protection, *Prog. Org. Coat.* 215 (2026) 110085, <https://doi.org/10.1016/j.porgcoat.2026.110085>.
- [24] F.M. Queiroz, A.F.S. Bugarin, N.P. Hammel, V.R. Capelossi, M. Terada, I. Costa, EIS behavior of anodized and primer coated AA2198-T851 compared to AA2024-T3 exposed to salt spray CASS test, *Surf. Interface Anal.* 48 (2016) 755–766, <https://doi.org/10.1002/sia.5982>.
- [25] O.M. Prada Ramirez, F.M. Queiroz, M. Terada, U. Donatus, I. Costa, M.G. Olivier, H.G. de Melo, EIS investigation of a Ce-based posttreatment step on the corrosion behaviour of Alclad AA2024 anodized in TSA, *Surf. Interface Anal.* 51 (2019) 1260–1275, <https://doi.org/10.1002/sia.6633>.
- [26] O.M. Prada Ramirez, F.M. Queiroz, M.A. Tunes, R.A. Antunes, C.L. Rodrigues, A. Lanzutti, S. Pogatscher, M.G. Olivier, H.G. de Melo, Tartaric-sulphuric acid anodized clad AA2024-T3 post-treated in Ce-containing solutions at different temperatures: corrosion behaviour and Ce ions distribution, *Appl. Surf. Sci.* 534 (2020) 147634, <https://doi.org/10.1016/j.apsusc.2020.147634>.
- [27] H. Costenaro, F.M. Queiroz, M. Terada, M.G. Olivier, I. Costa, H.G. de Melo, Corrosion protection of AA2524-T3 anodized in tartaric-sulfuric acid bath and protected with hybrid sol-gel coating, *Key Eng. Mater.* 710 (2016) 210–215, <https://doi.org/10.4028/www.scientific.net/KEM.710.210>.
- [28] H. Costenaro, A. Lanzutti, Y. Paint, L. Fedrizzi, M. Terada, H.G. de Melo, M. G. Olivier, Corrosion resistance of 2524 Al alloy anodized in tartaric-sulphuric acid at different voltages and protected with a TEOS-GPTMS hybrid sol-gel coating, *Surf. Coat. Technol.* 324 (2017) 438–450, <https://doi.org/10.1016/j.surfcoat.2017.05.090>.
- [29] M. Terada, F.M. Queiroz, H. Costenaro, V.H. Ayusso, M. Olivier, I. Costa, H.G. de Melo, Effect of cerium addition to a hydrothermal treatment on the corrosion protection of the tartaric-sulfuric acid anodized AA2524-T3, *Corrosion* 75 (2019) 1110–1117, <https://doi.org/10.5006/3063>.
- [30] M. Terada, F.M. Queiroz, D.B.S. Aguiar, V.H. Ayusso, H. Costenaro, M.G. Olivier, H.G. de Melo, I. Costa, Corrosion resistance of tartaric-sulfuric acid anodized AA2024-T3 sealed with Ce and protected with hybrid sol-gel coating, *Surf. Coat. Technol.* 372 (2019) 422–426, <https://doi.org/10.1016/j.surfcoat.2019.05.028>.
- [31] T.V. Machado, P. Atz Dick, G.H. Knörnschild, L.F.P. Dick, The effect of different carboxylic acids on the sulfuric acid anodizing of AA2024, *Surf. Coat. Technol.* 383 (2020) 125283, <https://doi.org/10.1016/j.surfcoat.2019.125283>.
- [32] P.O. Samaniego-Gómez, F. Almeraya-Calderon, E. Maldonado-Bandala, J. Cabral-Miramontes, D. Nieves-Mendoza, J. Olguin-Coca, L.D. Lopez-Leon, L.G. Silva Vidaurri, P. Zambrano-Robledo, C. Gaona-Tiburcio, Corrosion behavior of AA2055 aluminum-lithium alloys anodized in the presence of sulfuric acid solution, *Coatings* 11 (2021) 1278, <https://doi.org/10.3390/coatings11111278>.
- [33] X. Yu, G. Zhang, Z. Zhang, Y. Wang, Research on corrosion resistance of anodized and sealed 6061 aluminum alloy in 3.5% sodium chloride solution, *Int. J. Electrochem. Sci.* 18 (2023) 100092, <https://doi.org/10.1016/j.ijeecs.2023.100092>.
- [34] J. Cabral-Miramontes, F. Almeraya-Calderon, C.T. Méndez-Ramírez, J.P. Flores-De los Rios, E. Maldonado-Bandala, M.A. Baltazar-Zamora, D. Nieves-Mendoza, M. Lara-Banda, G. Pedraza-Basulto, C. Gaona-Tiburcio, Effect of citric acid hard anodizing on the mechanical properties and corrosion resistance of different aluminum alloys, *Materials* 17 (2024) 4285, <https://doi.org/10.3390/ma17174285>.
- [35] R. Fabris, G. Masi, M.C. Bignozzi, Corrosion behavior of aluminum alloys in different alkaline environments: Effect of alloying elements and anodization treatments, *Coatings* 14 (2024) 240, <https://doi.org/10.3390/coatings14020240>.
- [36] R. del Olmo, M. Moledano, P. Visser, A. Rodriguez, E. Matykina, R. Arrabal, Effect of cerium (IV) on thin sulfuric acid anodizing of 2024-T3 alloy, *J. Mater. Res. Technol.* 15 (2021) 3240–3254, <https://doi.org/10.1016/j.jmrt.2021.09.117>.
- [37] J.V. de S. Araujo, Microstructural influence on anodic film formation and corrosion resistance in anodized high-strength aluminium alloys, PhD thesis, Universidade de São Paulo, São Paulo, 2025, <https://doi.org/10.11606/T.85.2025.tde-19022025-161436>.
- [38] J.V. de S. Araujo, J. Chen, I. Costa, X. Zhou, Localized corrosion in anodized aluminium alloys: The role of constituent particle-induced defects in anodic films, *Corros. Sci.* 252 (2025) 112961, <https://doi.org/10.1016/j.corsci.2025.112961>.
- [39] J.M. Runge, The metallurgy of anodizing aluminum, Springer Int. Publ, Cham, 2018, <https://doi.org/10.1007/978-3-319-72177-4>.
- [40] J.A. Cabral Miramontes, B.S. Martínez-Aparicio, F.J. Olguín-Coca, L.D. López León, F. Estupiñán-Lopez, C.G. Tiburcio, P. Zambrano, F. Almeraya-Calderón, Corrosion resistance of alloy 2024 anodized on sulfuric-citric acid, *ECS Trans.* 94 (2019) 73–80, <https://doi.org/10.1149/09401.0073ecst>.
- [41] Y. Ma, X. Zhou, G.E. Thompson, M. Curioni, X. Zhong, E. Koroleva, P. Skeldon, P. Thomson, M. Fowles, Discontinuities in the porous anodic film formed on AA2099-T8 aluminium alloy, *Corros. Sci.* 53 (2011) 4141–4151, <https://doi.org/10.1016/j.corsci.2011.08.023>.
- [42] J.C. Benedyk, International temper designation systems for wrought aluminium alloys: Part II—Thermally treated (T temper) aluminium alloys, *Light Met. Age* (2010) 16–22.
- [43] J.V. de Sousa Araujo, A. de, F. Santos Bugarin, U. Donatus, C. de, S.C. Machado, F. M. Queiroz, M. Terada, A. Astarita, I. Costa, Thermomechanical treatment and corrosion resistance correlation in the AA2198 Al–Cu–Li alloy, *Corros. Eng. Sci. Technol.* 54 (2019) 575–586, <https://doi.org/10.1080/1478422X.2019.1637077>.
- [44] J.V. de Sousa Araujo, M.X. Milagre, X. Zhou, I. Costa, An assessment of pitting corrosion in anodized aluminium alloys: It might not be what it seems, *Mater. Corros.* 75 (2024) 599–613, <https://doi.org/10.1002/maco.202313977>.
- [45] J.V. de Sousa Araujo, I. Costa, X. Zhou, Comparison of constituent intermetallic particles in different aluminium alloys, *Metallogr. Microstruct. Anal.* 14 (2025) 106–119, <https://doi.org/10.1007/s13632-025-01170-w>.
- [46] Y. Ma, X. Zhou, G.E. Thompson, T. Hashimoto, P. Thomson, M. Fowles, Distribution of intermetallics in an AA2099-T8 aluminium alloy extrusion, *Mater. Chem. Phys.* 126 (2011) 46–53, <https://doi.org/10.1016/j.matchemphys.2010.12.014>.
- [47] J.V. de S. Araujo, J. Chen, I. Costa, X. Zhou, Anodic film formation on aluminium alloys: Analysis of defects induced by constituent intermetallic particles, *Mater. Chem. Phys.* 350 (2026) 131803, <https://doi.org/10.1016/j.matchemphys.2025.131803>.
- [48] J.V. de Sousa Araujo, M.X. Milagre, R.O. Ferreira, C. de Souza Carvalho Machado, C.P. de Abreu, I. Costa, Microstructural characteristics of the Al alloys: The dissimilarities among the 2XXX alloys series used in aircraft structures, *Metallogr. Microstruct. Anal.* 9 (2020) 744–758, <https://doi.org/10.1007/s13632-020-00688-5>.
- [49] C. Vargel, M. Jacques, M.P. Schmidt, The most common wrought aluminium alloys, in: *Corrosion of Aluminium*, 2004, pp. 61–69, <https://doi.org/10.1016/B978-008044495-6/50009-4>.
- [50] C. Gao, Y. Luan, J.C. Yu, Y. Ma, Effect of thermo-mechanical treatment process on microstructure and mechanical properties of 2A97 Al–Li alloy, *Trans. Nonferrous Met. Soc. China* 24 (2014) 2196–2202, [https://doi.org/10.1016/S1003-6326\(14\)63332-X](https://doi.org/10.1016/S1003-6326(14)63332-X).
- [51] P.A. Rometsch, Y. Zhang, S. Knight, Heat treatment of 7xxx series aluminium alloys—Some recent developments, *Trans. Nonferrous Met. Soc. China* 24 (2014) 2003–2017, [https://doi.org/10.1016/S1003-6326\(14\)63306-9](https://doi.org/10.1016/S1003-6326(14)63306-9).
- [52] A.C.U. Rao, V. Vasu, M. Govindaraju, K.V.S. Srinadh, Stress corrosion cracking behaviour of 7xxx aluminium alloys: A literature review, *Trans. Nonferrous Met. Soc. China* 26 (2016) 1447–1471, [https://doi.org/10.1016/S1003-6326\(16\)64220-6](https://doi.org/10.1016/S1003-6326(16)64220-6).
- [53] J.Q. Su, T.W. Nelson, R. Mishra, M. Mahoney, Microstructural investigation of friction stir welded 7050-T651 aluminium, *Acta Mater.* 51 (2003) 713–729, [https://doi.org/10.1016/S1359-6454\(02\)00449-4](https://doi.org/10.1016/S1359-6454(02)00449-4).
- [54] E. Nizery, J.Y. Buffière, H. Proudhon, A. Daniélou, S. Forest, Influence of particles on short fatigue crack initiation in 2050-T8 and 7050-T74, *Mater. Sci. Forum* 794796 (2014) 296–301, <https://doi.org/10.4028/www.scientific.net/MSF.794-796.296>.
- [55] J.A.M. de Camargo, H.J. Cornelis, V.M.O.H. Cioffi, M.Y.P. Costa, Coating residual stress effects on fatigue performance of 7050-T7451 aluminium alloy, *Surf. Coat. Technol.* 201 (2007) 9448–9455, <https://doi.org/10.1016/j.surfcoat.2007.03.032>.
- [56] T.A. Huang, G.S. Frankel, Kinetics of sharp intergranular corrosion fissures in AA7178, *Corros. Sci.* 49 (2007) 858–876, <https://doi.org/10.1016/j.corsci.2006.04.015>.
- [57] J.B. Lumsden, M.W. Mahoney, G. Pollock, G.G. Rhodes, Intergranular corrosion following friction stir welding of aluminum alloy 7075-T651, *Corrosion* 55 (1999) 1127–1135, <https://doi.org/10.5006/1.3283950>.
- [58] A.M. Cassell, J.D. Robson, X. Zhou, T. Hashimoto, M. Besel, The direct observation of copper segregation at the broad faces of η' and η precipitates in AA7010 aluminium alloy, *Mater. Charact.* 163 (2020) 110232, <https://doi.org/10.1016/j.matchar.2020.110232>.
- [59] J.V. de Sousa Araujo, M.X. Milagre, R.E. Klumpp, V.H. Ayusso, U. Donatus, I. Costa, TSA anodising voltage effects on the near-surface coarse intermetallic particles in the AA2024-T3 and AA2198-T8 alloys, *Corros. Eng. Sci. Technol.* 57 (2022) 380–396, <https://doi.org/10.1080/1478422X.2022.2071666>.
- [60] G.E. Thompson, H. Habazaki, K. Shimizu, M. Sakairi, G.C. Wood, Anodizing of aluminium alloys, *Aircr. Eng. Aerosp. Technol.* 71 (3) (1999) 228–238, <https://doi.org/10.1108/00022669910270709>.
- [61] O.M.P. Ramirez, M.A. Tunes, M.M. Mennucci, M. Starykevich, C. Neves, M.G. S. Ferreira, S. Pogatscher, H.G. de Melo, Ce post-treatment for increased corrosion resistance of AA2024-T3 anodized in tartaric-sulfuric acid, *Corros. Sci.* 204 (2022) 110371, <https://doi.org/10.1016/j.corsci.2022.110371>.
- [62] N. Birbilis, R.G. Buchheit, Electrochemical characteristics of intermetallic phases in aluminium alloys: An experimental survey and discussion, *J. Electrochem. Soc.* 152 (4) (2005) B140–B151, <https://doi.org/10.1149/1.1869984>.
- [63] D.K. Xu, N. Birbilis, P.A. Rometsch, The effect of pre-ageing temperature and retrogression heating rate on the strength and corrosion behaviour of AA7150, *Corros. Sci.* 54 (2012) 17–25, <https://doi.org/10.1016/j.corsci.2011.08.042>.
- [64] B. Zhou, B. Liu, S. Zhang, The advancement of 7XXX series aluminium alloys for aircraft structures: A review, *Metals* 11 (2021) 718, <https://doi.org/10.3390/met11050718>.
- [65] B. Beverskog, I. Puigdomenech, Revised Pourbaix diagrams for zinc at 25–300 °C, *Corros. Sci.* 39 (1997) 107–114, [https://doi.org/10.1016/S0010-938X\(97\)89246-3](https://doi.org/10.1016/S0010-938X(97)89246-3).
- [66] T. Yu, J. Fu, R. Cai, A. Yu, Z. Chen, Nonprecious electrocatalysts for Li-air and Zn-air batteries: Fundamentals and recent advances, *IEEE Nanotechnol. Mag.* 11 (2017) 29–55, <https://doi.org/10.1109/MNANO.2017.2710380>.
- [67] Y. Ma, X. Zhou, W. Huang, G.E. Thompson, X. Zhang, C. Luo, Z. Sun, Localized corrosion in AA2099-T83 aluminum-lithium alloy: The role of intermetallic

- particles, *Mater. Chem. Phys.* 161 (2015) 201–210, <https://doi.org/10.1016/j.matchemphys.2015.05.037>.
- [68] C. Luo, M. Gao, Z. Sun, X. Zhang, Z. Tang, X. Zhou, FIB-SEM investigation on corrosion propagation of aluminium-lithium alloy in sodium chloride solution, *Corros. Eng. Sci. Technol.* 50 (2015) 390–396, <https://doi.org/10.1179/1743278214Y.0000000235>.
- [69] A.J. Bard, F.R.F. Fan, J. Kwak, O. Lev, Scanning electrochemical microscopy: Introduction and principles, *Anal. Chem.* 61 (1989) 132–138, <https://doi.org/10.1021/ac00177a011>.
- [70] W. Zhou, Z.L. Wang (Eds.), *Scanning microscopy for nanotechnology*, Springer, New York, 2007, <https://doi.org/10.1007/978-0-387-39620-0>.
- [71] T.J. Shaffner, R.D. Van Veld, Charging” effects in the scanning electron microscope, *J. Phys. E* 4 (1971) 633–637, <https://doi.org/10.1088/0022-3735/4/9/002>.
- [72] Y. Ma, H. Wu, X. Zhou, K. Li, Y. Liao, Z. Liang, L. Liu, Corrosion behavior of anodized Al-Cu-Li alloy: The role of intermetallic particle-introduced film defects, *Corros. Sci.* 158 (2019) 108110, <https://doi.org/10.1016/j.corsci.2019.108110>.
- [73] Y. Ma, X. Chen, X. Zhou, Y. Yi, Y. Liao, W. Huang, Microstructural origin of localized corrosion in anodized AA2099-T8 aluminium-lithium alloy, *Surf. Interface Anal.* 48 (2016) 739–744, <https://doi.org/10.1002/sia.5856>.
- [74] Y. Ma, X. Zhou, G.E. Thompson, M. Curioni, P. Skeldon, X. Zhang, Z. Sun, C. Luo, Z. Tang, F. Lu, Anodic film growth on Al-Li-Cu alloy AA2099-T8, *Electrochim. Acta* 80 (2012) 148–159, <https://doi.org/10.1016/j.electacta.2012.06.126>.
- [75] Y. Zuo, P.H. Zhao, J.M. Mao, The influences of sealing methods on corrosion behavior of anodized aluminum alloys in NaCl solutions, *Surf. Coat. Technol.* 166 (2003) 237–242, [https://doi.org/10.1016/S0257-8972\(02\)00779-X](https://doi.org/10.1016/S0257-8972(02)00779-X).
- [76] A. Boag, R.J. Taylor, T.H. Muster, N. Goodman, D. McCulloch, C. Ryan, B. Rout, D. Jamieson, A.E. Hughes, Stable pit formation on AA2024-T3 in a NaCl environment, *Corros. Sci.* 52 (2010) 90–103, <https://doi.org/10.1016/j.corsci.2009.08.043>.
- [77] A. Boag, A.E. Hughes, A.M. Glenn, T.H. Muster, D. McCulloch, Corrosion of AA2024-T3 Part I: Localised corrosion of isolated IM particles, *Corros. Sci.* 53 (2011) 17–26, <https://doi.org/10.1016/j.corsci.2010.09.009>.
- [78] A.E. Hughes, A. Boag, A.M. Glenn, D. McCulloch, T.H. Muster, C. Ryan, C. Luo, X. Zhou, G.E. Thompson, Corrosion of AA2024-T3 Part II: Co-operative corrosion, *Corros. Sci.* 53 (2011) 27–39, <https://doi.org/10.1016/j.corsci.2010.09.030>.
- [79] A.M. Glenn, T.H. Muster, C. Luo, X. Zhou, G.E. Thompson, A. Boag, A.E. Hughes, Corrosion of AA2024-T3 Part III: Propagation, *Corros. Sci.* 53 (2011) 40–50, <https://doi.org/10.1016/j.corsci.2010.09.035>.
- [80] F.M. Queiroz, U. Donatus, O.M. Prada Ramirez, J.V. de Sousa Araujo, B. V. Gonçalves de Viveiros, S. Lamaka, M. Zheludkevich, M. Masoumi, V. Vivier, I. Costa, H.G. de Melo, Effect of unequal levels of deformation and fragmentation on the electrochemical response of friction stir welded AA2024-T3 alloy, *Electrochim. Acta* 313 (2019) 271–281, <https://doi.org/10.1016/j.electacta.2019.04.137>.
- [81] W. Zhang, G.S. Frankel, Transitions between pitting and intergranular corrosion in AA2024, *Electrochim. Acta* 48 (2003) 1193–1210, [https://doi.org/10.1016/S0013-4686\(02\)00828-9](https://doi.org/10.1016/S0013-4686(02)00828-9).
- [82] H. Akahori, Electron microscopic study of growing mechanism of aluminium anodic oxide film, *J. Electron Microsc.* (Tokyo) 10 (3) (1961) 175–185, <https://doi.org/10.1093/oxfordjournals.jmicro.a049304>.
- [83] A. Ul-Hamid, A beginners’ guide to scanning electron microscopy, Springer Int. Publ, Cham, 2018, <https://doi.org/10.1007/978-3-319-98482-7>.
- [84] K. Shimizu, T. Mitani, New horizons of applied scanning electron microscopy, Springer, Berlin, Heidelberg, 2010, <https://doi.org/10.1007/978-3-642-03160-1>.
- [85] F. Raffin, A. Makogon, F. Kanoufi, J. Echouard, V. Shkirskiy, P. Volovitch, Initial cathodic reactivity of intermetallic particles in 7175 aluminum alloy buried under 6 μm thick anodized oxide layer revealed by in-situ reflective microscopy, *Electrochim. Acta* 492 (2024) 144155, <https://doi.org/10.1016/j.electacta.2024.144155>.
- [86] B. Nogueira Pereira, J.V. de Sousa Araujo, R.E. Klumpp, R.A. Antunes, I. Costa, Effects of surface preparation on the corrosion resistance of TSA anodized aluminum alloys, *Mater. Res.* 28 (2025) e20250452, <https://doi.org/10.1590/1980-5373-MR-2025-0452>.
- [87] H. Takahashi, M. Chiba, Role of anodic oxide films in the corrosion of aluminum and its alloys, *Corros. Rev.* 36 (2018) 35–54, <https://doi.org/10.1515/corrrev-2017-0048>.
- [88] H. Takahashi, K. Fujiwara, M. Seo, The cathodic polarization of aluminum covered with anodic oxide films in a neutral borate solution—II. Film breakdown and pit formation, *Corros. Sci.* 36 (1994) 689–705, [https://doi.org/10.1016/0010-938X\(94\)90074-4](https://doi.org/10.1016/0010-938X(94)90074-4).
- [89] J. Ren, Y. Zuo, The growth mechanism of pits in NaCl solution under anodic films on aluminum, *Surf. Coat. Technol.* 191 (2005) 311–316, <https://doi.org/10.1016/j.surfcoat.2004.04.054>.
- [90] V. Moutarlier, M.P. Gigandet, J. Pagetti, Characterisation of pitting corrosion in sealed anodic films formed in sulphuric, sulphuric/molybdate and chromic media, *Appl. Surf. Sci.* 206 (2003) 237–249, [https://doi.org/10.1016/S0169-4332\(02\)01240-0](https://doi.org/10.1016/S0169-4332(02)01240-0).
- [91] V. Moutarlier, M.P. Gigandet, J. Pagetti, L. Ricq, Molybdate/sulfuric acid anodising of 2024-aluminium alloy: Influence of inhibitor concentration on film growth and on corrosion resistance, *Surf. Coat. Technol.* 173 (2003) 87–95, [https://doi.org/10.1016/S0257-8972\(03\)00511-5](https://doi.org/10.1016/S0257-8972(03)00511-5).
- [92] S.U. Ofoegbu, F.A.O. Fernandes, A.B. Pereira, The sealing step in aluminum anodizing: A focus on sustainable strategies for enhancing both energy efficiency and corrosion resistance, *Coatings* 10 (3) (2020) 226, <https://doi.org/10.3390/coatings10030226>.
- [93] C. Cabral, C. Gaona Tiburcio, F. Estupiñán López, P. Zambrano Robledo, F. Olguín Coca, L. López León, F. Almeraya Calderon, J.A. Cabral Miramontes, Citric acid as an alternative to sulfuric acid for hard anodizing in aluminum alloys used in the aeronautical industry, *ECS Trans.* 110 (2023) 225–236, <https://doi.org/10.1149/11001.0225ecst>.
- [94] J.C. Miramontes, C. Gaona Tiburcio, E. García Mata, M.Á. Esneider Alcála, E. Maldonado-Bandala, M. Lara-Banda, D. Nieves-Mendoza, J. Olguín-Coca, P. Zambrano-Robledo, L.D. López-León, F. Almeraya Calderón, Corrosion resistance of aluminum alloy AA2024 with hard anodizing in sulfuric acid-free solution, *Materials* 15 (18) (2022) 6401, <https://doi.org/10.3390/ma15186401>.