Stress-corrosion cracking characterisation of the advanced aerospace Al–Li 2099-T86 alloy

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Abstract

New alloy developments driven by aircraft industry have identified aluminium lithium (Al–Li) alloys as potential candidates for substitution of incumbent high strength aluminium alloys used for manufacturing spacecraft and launchers. Whereas properties like specific stiffness, strength and toughness are proven as superior when compared to those of currently adopted Al alloys, the Stress Corrosion Cracking (SCC) characteristics are still an open aspect if advanced Al–Li alloys are considered for space structural applications. The present paper provides a comprehensive characterisation of the Al–Li 2099-T86 SCC performances.

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1. Introduction

In the last 30 years, the leading aircraft manufacturers have been posing severe demands on the aluminium suppliers to deliver alloys with improved performances in terms of mechanical properties, high specific strength, and high specific stiffness for a wide spectrum of airframe structural applications. Even earlier, from the period of 1930s to 1980s, a number of key aluminium alloys were developed which provided the backbone to aircraft production. These alloys included AA7075 and AA7050 which were predominantly used for thick plate applications such as wing spar and ribs, and AA2024 used for fuselage sheets, lower wing covers and various extrusions. For aluminium alloys used in current spacecraft and launchers applications the situation is no different. The alloys of choice for the space industry are still limited to a small number of materials including AA7075, AA2024, AA6061, and AA6082 which were mainly developed in the 1930–1950s.

Further tuning of these alloys focused mainly on strength, toughness and damage tolerance as well as stress-corrosion or corrosion performances (for the 7xxx series), but little was achieved to enhance density or elastic modulus. Promising improvements regarding these properties were found already in 1920 by adding lithium as alloying element. Being the lightest metallic element (with an atomic number of three) and having a solid solubility in aluminium (with a maximum of approximately 4% at 610 °C) lithium contributes reducing the density by 3% and enhancing the elastic modulus nearly 6% for every added weight % Li with a significant increase of strength [1]. Al–Li alloys have been found to exhibit superior mechanical properties when compared to conventional Al alloys [2–4], in terms of higher specific strength, enhanced resistance to high cycle fatigue, fatigue crack growth and fracture toughness also at cryogenic temperatures. [5–7]. The property evolution over the different Al–Li generations has been reviewed in [8–10]. After decades of poor performance issues during the implementation of the first and second generation of Al–Li alloys, the third generation could overcome many of the identified problems, including property anisotropy, low tensile elongation, poor fracture toughness, low corrosion resistance and poor thermal stability. [8]. With dropping the Li content, the first grade developed was the weldable ultra-high strength alloy Weldalite 049° [11], which is currently widely adopted in aeronautical and aerospace applications. Similar to this alloy, but with a lower copper content, the AA2195 has been used for manufacturing the NASA’s Space Shuttle external fuel tank, implementing the Friction Stir Welding (FSW) process [12–14], and will be used for the Space Launch System (SLS) external tanks, currently under development. The more recent AA2050 and AA2196 alloys, considered as direct replacement without any redesign [3], have been adopted for Airbus aircraft structural parts [2], while the AA2198 is used for the Falcon 9 launcher walls and domes, also combined with FSW [14,15].

The current advanced Al–Li alloys were established at the...
beginning of the 21st century by Alcoa and Alcan separately. In particular AA2099, has been recently developed by Alcoa for use in aerospace and high performance applications requiring high strength, low density, superior damage tolerance, excellent corrosion resistance and good weldability [16]. AA2099 has a high lithium content of 1.8% which improves the specific properties. Subsequent development of controlling and refining the composition, temper, and microstructure took place in cooperation with Bombardier from 2005 onwards [1]. AA2099 was made commercially available in accordance with AMS 4458 and can already be found in the fuselage and floor structure of Airbus’ A380 aircraft [17]. The manufacturer offers two tempers of the AA2099 alloy: T83 and T86 of which the high fracture toughness T86 temper is used in the present study.

If the AA2099 is considered for spacecraft and launcher structural applications, it shall comply with European ECSS standards for materials selection. Whilst strength and toughness are driving properties for aircraft industry, excellent corrosion and especially stress-corrosion resistance are key criteria for space applications. Stress Corrosion Cracking (SCC) is a critical failure phenomenon and has been investigated for more than half a century. A significant amount of work has been carried out to understand SCC behaviour of Al-alloys [18]. SCC behaviour of high strength aluminium alloys is treated in [19–23]. It can be stated that SCC generally correlates to chemistry and morphology of Grain Boundary Precipitations (GBP) [24,25], among all proposed mechanisms in aluminium alloys the most cited are two: Anodic dissolution initiated cracking [19,20,26] and Hydrogen induced cracking [27,28]. Burleigh [26] related the latter mechanism rather to effect 7xxx series, whilst anodic dissolution was observed on 2xxx series alloys.

Often related to aqueous environment it is less known that stress-corrosion cracking is also an insidious failure mechanism in aircraft [20,29] and even spacecraft applications [30–32]. Water condensation, either atmospheric or in inhabited modules, exposure to coastal environments, typically at launch sites, and the presence of aggressive chemical substances such as cleaning solvents and hydraulic fluids or rocket propellants can promote stress-corrosion cracking on space hardware. In order to prevent the occurrence of SCC failures in space programs, the European Space Agency has developed advanced testing methodologies [33] as well as dedicated standards in collaboration with the European space industry, for the determination of the susceptibility of materials to SCC and the selection of suitable alloys for space hardware manufacturing, [34,35]. Due to their inaccessibility during service and high sustained stress levels, only materials with excellent resistance to SCC can be used for spacecraft and launchers structural applications. Initial internal SCC tests have shown poor results for AA2099 according to the standard [35] and further investigations towards SCC have been performed, including alternate immersion SCC tests, Slow Strain Rate Testing (SSRT) as well as electrochemical and X-Ray Diffraction analysis. The results of this extensive test campaign are presented in the current study.

### 2. Material and specimens

All test specimens used in the laboratory investigations were machined from a 37 mm thick plate of aluminium Alloy AA2099 in T86 state (solution heat treated, cold-worked by thickness reduction of 6% and artificially aged). Chemical composition and mechanical properties [7] are given in Tables 1 and 2 respectively. The dimensions of the samples used for performing the whole experimental test program are shown in Fig. 1. Different samples proportions (W, B, t), reported in the table of Fig. 1, have been used as presented in the separate test descriptions.

### 3. Experimental program

#### 3.1. Stress Corrosion Cracking (SCC) test and subsequent Four Point Bending test

As general procedure materials for spacecraft and launchers structural applications are first tested at 75% of the yield strength under alternate immersion in 3.5% NaCl water solution according to [35] and classified in three tables based on the susceptibility to SCC, [34].
Fig. 2. An overview of the sample shows total amount of pitting. Detail pictures in Fig. 3 (two columns).

Fig. 3. Selective-grain pitting of AA2099-T86 under tensile (a) and compressive (b) load.

Fig. 4. AA7075-T651 with SCC attack stressed (a) and unstressed (b); AA2099-T86 stressed (c) and unstressed (d) with no traces of SCC but non stress dependent pitting attack.
In this work SCC testing was conducted tailoring the requirements of the ECSS Standard [35]. Specimens from both alloys introduced in Section 2 have been flat ground with sandpaper to 1200 grit, rinsed with deionised water and dried before exposing. Samples were loaded with constant 60% of Yield Strength in short transverse direction. Subsequent but limited tests have been performed at 75%. The loading was applied by imposing a fixed deflection on the sample with a custom built 3-point bending fixture. This is called and described Constant Total-Deflection Test by Parkins [36]. All performed experiments followed a continuous ten minutes immersion phase and 50 min drying phase throughout 21 and 30 days in 3.5% NaCl water solution (alternate immersion). The water solution was held constant at 3.5% sodium chloride, with a pH of 6.4–7.2 and was renewed on day 7, 14 and 21. The sample was electrically isolated from the stainless steel fixture by means of covering the contact areas with non-conductive tape. In parallel to the stressed AA2099-T86 and AA7075-T651 samples, one unstressed control specimen per material and testing duration has been exposed to the same cycling.

Due to the limitations of the plate thickness, specimens were re-sized to produce a smaller sample than specified in the standard. The effect of specimen size on the testing procedure and results was evaluated by testing specimens of different dimensions (WxBxT in Fig. 1). In particular, 37 x 10 x 2, 63 x 15 x 2, 37 x 10 x 4 and 63 x 15 x 4 mm$^3$ samples have been submitted to the same test campaign.

Subsequent to the 21 and 30 days SCC test exposure, AA2099-T86 samples (both stressed and unstressed) have been subjected to Four Point Bending testing until rupture in order to determine remaining flexural strength and fracture location. Bending testing has been performed using a Zwick Z100 machine. Moreover, pristine AA2099-T86 samples (i.e. not pre-corroded neither pre-stressed) have been subjected to Four Point Bending testing until rupture for comparison purposes.

All tested specimen have been subjected to fracture surfaces analysis in a ZeissEVO SEM as well as metallographic preparation. For microscopic imaging samples have been subjected to a stepwise polishing routine up to 0.25 µm OPS followed by etching in Keller’s reagent (95 mL water, 2.5 mL HNO$_3$, 1.5 mL HCl, 1.0 mL HF) for 20 s.

### 3.2. Slow Strain Rate Testing (SSRT)

SSRT tests were performed as constant extension rate tests (CERT) using a 3-point bending mount on an Instron Electropuls™ E10000 machine. 37 x 10 x 2 mm$^3$ samples have been constant extension rate tested while exposed to 3.5% NaCl water solution and subsequent alternate immersion technique described in Section 3.1 (ten minutes immersion, fifty minutes drying) using a custom configured environmental chamber. Load and displacement data were recorded periodically by a 2.5 kN loadcell and the contactless GOM ARAMIS strain measurement system was used to...
observe the local stress distribution. The strain rate was calculated from materials data and validated by pre trials.

Prior to the testing plan the cross head speed was determined by conducting CERT in bending on the AA7075 material samples over a range of $10^{-5}$–$10^{-8}$ s$^{-1}$ strain rates (corresponding to $10^{-6}$–$0$–$9$ ms$^{-1}$). Based on the observations, strain rates of $10^{-6}$ s$^{-1}$ and $10^{-7}$ s$^{-1}$ were further determined as suitable to show corrosion attack and therefore applied to the AA2099-T86 samples.

3.3. X-Ray diffraction (XRD)

To investigate the microstructure and phase evolution during corrosion XRD analyses were conducted on pristine material as well as after-corrosion state. The X-ray pattern of processed samples was measured at a step width of 0.01°. For calibration of the instrumental line broadening, a pristine specimen was tested in the same condition. Scans were obtained from 10° to 90° 2Theta using a Bruker D8 Discover with a Cu-source and Lynxeye XE detector at a scanning rate of two seconds and increment of 0.01° for each step.

3.4. Electrochemical analysis

Polarisation curves were conducted to determine the potentiodynamic response as well as the corrosion rates using the Tafel interpolation. The aim was finding the difference in corrosion response of stressed and unstressed material. The testing was performed using a three-electrode glass cell (a saturated calomel reference electrode (SCE), a Pt plate counter electrode and a working electrode connected to the sample), and the

<table>
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<tr>
<th>Table 5</th>
<th>Detected phases in XRD analysis.</th>
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<tr>
<td>As received</td>
<td>corroded</td>
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<tr>
<td>Main phases</td>
<td>Al, Al$_2$Li($\delta'$)</td>
</tr>
<tr>
<td>Characteristic phases</td>
<td>Al$_2$Li($\delta'$)</td>
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<td>$\theta'$ (Al$_2$Cu)</td>
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<td>T1 (Al$_2$CuLi)</td>
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Fig. 8. a-c) Fracture surface of AA2099-T86 after SSRT. Fractographic view reveals quasi cleavage structures with ductile behaving areas; d) shows the fracture surface of pristine material tested in air.

Fig. 9. Potentiodynamic polarisation of AA2099-T86 unstressed and stressed in 3.5% NaCl solution (75% and 95% of YS). (one column).
electrochemical tests were carried out using a potentiostat type Parstat 2273. The electrochemical measurements were performed in the test solution after reaching the open-circuit potential. The polarisation test was conducted at a scan rate of 0.167 mV s⁻¹. As electrolyte a 3.5% NaCl solution was used. Prior to exposure to testing environment each AA2099-T86 specimen has been ground with P1200 grit paper and rinsed with deionized water. Samples were taken as bulk material covered with non-conductive tape exposing only 1 cm² of blank metal to the electrolyte and were spot welded to high purity nickel wires.

The 37 × 10 × 2 mm³ samples were tested unstressed and stressed at 55%, 75% and 95% of Yield Strength using the custom built 3-point bending fixture described in Section 3.1.

4. Results and discussion

4.1. Stress Corrosion Cracking Test (SCC) and subsequent Four Point Bending test

The summary of the results obtained with the AA2099-T86 samples is presented in Tables 3 and 4. No failure occurred during the SCC testing in any of the stressed as well as un-stressed (control) specimens (Table 3) after neither 21 nor 30 days of exposure. Pitting occurred on both compressive and tensile sides of the stressed samples showing increased pit depth on the tensile side of the specimens, as reported in Table 4. Moreover, a significant difference of pits dimensions was documented between stressed and un-stressed samples, revealing a correlation between stress and pitting attack. No evidence of SCC was found by metallographic or fractographic analysis. Fig. 2 shows an overview of a AA2099-T86 stressed sample with very limited pitting corrosion attack, present both in the compression (upper side in the picture) as well as tension (lower side in the picture) areas. Selective grain pitting occurred both under tensile (Fig. 3a) as well as compressive (Fig. 3b) loads. Observed pitting occurred in an elongated scheme following affected grains. Grain boundaries appear to inhibit pit propagation between grains. Due to the elongated texture in longitudinal (rolling) direction the pitting attack propagates into the material as shown in Fig. 3a and b. In Fig. 3a three pits are visible. While the top one is surface connected the other two are blind ones. Top and middle pit are connected by a crack. The thickness reduction due to pitting increased the local stress concentration and led to mechanical breaking of the ligament between the pits. This pure mechanical failure occurred resulted from the pit appearance and not related to SCC mechanisms. No evidence of SCC is observed.

As expected, microscopic investigations on the AA7075-T651 specimens revealed stress driven corrosion attack including intergranular cracks to a depth of 1000 μm and general pitting on the surface layers.

In Fig. 4a comparison between stressed and un-stressed samples of AA7075-T651 and AA2099-T86 alloys is presented. In particular, Fig. 4a shows SCC cracking on a stressed AA7075-T651 specimen, while in Fig. 4b the corresponding un-stressed sample is presented, showing non-stress dependent pitting attack. The behaviour of the stressed AA2099-T86 samples is exemplary reported in Fig. 4c, where no indication of SCC damage is present, whereas Fig. 4d shows the behaviour of the alloy in un-stressed conditions. Non-stress dependent pitting is shown. The thickness of the samples had no effect on the observed corrosion behaviour in any of the tested specimens.

The Four Point Bending test results are summarised in Fig. 5, where pre-corroded AA2099-T86 samples both stressed (red line) and un-stressed (blue line) are compared with pristine (un-corroded and un-stressed) specimens (dashed black line).

When compared to the pristine material, the pre-corroded specimens (both in stressed and unstressed conditions) showed a drop of approximately 25% in the flexure strength, whereas the elongation to break was reduced by approximately 70%. Stressed and un-stressed pre-corroded samples show similar elongation as well as similar flexural strength. No preferred failure location could be observed in the specimens.

4.2. Slow Strain Rate Testing (SSRT)

The Slow Strain Rate Test results obtained during alternate immersion are reported in Fig. 6, in which the comparison between the samples tested at 10⁻⁷ s⁻¹ (red lines) and 10⁻⁸ s⁻¹ (dashed black lines) strain rates are presented. Samples tested at the slower testing rate were exposed 10 times longer to the corrosive environment. The samples tested with slower testing rate show a drop in ductility with significantly lower elongation at fracture, while the strength remains at similar values. This behaviour has been observed in previous SCC tests of aluminium alloys and it may be linked to the uptake of hydrogen during the exposure [37]. Microscopic evaluation revealed similar pitting as the SCC testing. In particular, Fig. 7 shows pitting attack propagating into the material. Since the Slow Strain Rate continues until failure is reached, it was not possible to assess the maximum pit depth which is usually the fracture surface.

The pit initiation always took place in one grain and dissolved the homogeneous grain material. As shown in Fig. 7, no intergranular propagation is visible although the corrosion process proceeds very close to the grain boundaries. Although under this loading condition the elongated grain structures associated with these corrosion products provide a preferential path for stress concentration, this could never been observed as initiation area for cracking. This is related to the high toughness properties of AA2099.

SEM evaluations on the fracture surfaces of all tested specimens showed no SCC evidence but classical quasi cleavage fracture surface with areas of ductile fracture artefacts, as shown in Fig. 8. Here mechanical crack initiation location can be seen at the middle-top. In Fig. 8d a fracture surface of pristine material is given for comparison. The structure shows similar fracture mode. The flexure strength results of the mechanical testing indicate that the observed pitting is not impacting the mechanical properties (flexural strength), confirming its limited nature. The pit distribution peaks towards the stressed area, mainly on the specimen side of tensile stress. This was determined by an analogue use of the ARAMIS photogrammetry system, where the specimen could be monitored in-situ in terms of stress distribution and amount.

Warner-Lock proposed [38] and then refuted that pitting of the AA2099 initiates on nascent SCC cracks. No evidence of any SCC was found during the present investigation. The limited size of the specimens used has resulted in inhibiting of most of the pitting in the region of the failure; while the main pit was growing, it polarised the surface and draw the current away from other sites. This issue could have been mitigated by the use of larger specimens which were however not compatible with the experimental configuration used.

The asymmetric shape of the pits may be a result of the described mechanism: these pits, initially growing, have been stifled as the main pit drawn there current and then they continued to open as the mechanical effect of the loading plasticity deformed the stifled pits.

To find out about the pitting on selected grains XRD, electrochemical and optical strain measurements were also conducted.
4.3. Electrochemical analysis

The AA2099-T86 material was used material was used stressed at different strain levels and are presented in Fig. 9. Data shows typical polarisation curve response, the interpolated Tafel slope reveals corrosion potential of -690 mV ± 10 mV for all stress levels. This data was given as plot data and does not appear in the graph. Corresponding current can be found on higher levels when stress is applied. The Tafel interpolation shows a higher activity (corrosion rate) when stress is applied which can result in pitting.

4.4. XRD analysis

Resulting XRD curves gave good matches for aluminium and the strengthening δ' phase (Al₃Li) for both testing conditions: corroded and not corroded. Strong peaks were found at 38.5°, 44.7°, 65.1°, 78.2° and 82.5° 2θ angles. As further phases, θ' (Al₃Cu) and traces of T1 (Al₂CuLi) could be detected. A more detailed overview of detected phases is given in Table 5.

The XRD curves showed δ' phase (Al₃Li), θ' (Al₃Cu) and traces of T1 (Al₂CuLi). These phases first identified by [39] are known as strengthening phases within the matrix [40–42]. Comparing intensities the δ' phase is the strongest due to the high atomic amount of lithium, which is about six times higher than Copper. This has been reported for high Li alloys (> 1.5%) [42]. Regarding the corroding state, a clear raise in several oxide products like Bayerite (Al(OH)₃) or AlLiO₂ as a result of the oxidation process with Al and Li is observed. As disappearing phases a reduction of the δ' phase is detected which forms into Alumina, hydrated oxides and AlLiO₂ corrosion products. This can be explained by the two main corrosion driving causes in Al-Li-Cu alloys, precipitation of copper resulting in a lack of copper in solid solution and the presence of active lithium in precipitates. While the θ' phase is susceptible itself. Cu-containing phases promote surrounding precipitation free zone (PFZ) into a localised galvanic coupling. Phases which were reported to act as local cathodic elements are Copper containing phases like T1 or θ'. This leads to dissolution of Copper-depleted zones which are usually situated in the matrix material where lighter elements like Al, Li or Mg can be found. Phases are known to settle down at microstructural boundaries forming preferential pathways for anodic dissolution [43]. The behaviour of the T1 phase has been studied by Li et al. [44]. The corrosion potential difference between the phase and the surrounding matrix was found to be 0.18 V and assumed to drive the dissolution of the anodic acting part, here the PFZ.

5. Conclusions and outlook

In the present study the new third generation Al-Li alloy AA2099-T86 has been submitted to a comprehensive SCC and SSRT test campaign combined with detail metallurgical and electrochemical assessment. The following can be summarised:

- SCC and SSRT testing did not show any evidence of stress-corrosion cracking in the ST direction at 60% Yield.
- Pitting corrosion occurred on selective grains in the stressed samples both during SCC as well as SSRT testing, showing similar morphology for both testing conditions.
- Pitting occurred on both compressive and tensile load sides of the stressed samples showing increased pit depth on the tensile side of the specimens.
- A significant difference of pits dimensions was documented between stressed and un-stressed samples, where pitting was of significantly smaller nature.
- Electrochemical analysis revealed higher corrosion activity with higher stress levels (electrochemical activity being promoted by stress).
- XRD investigations showed δ' phase as dominating phase besides other age hardening θ and T1 phases. It also indicated a strong contribution in corrosion morphology of δ' phase (Al₃Li).

A pitting morphology appeared which was so far only reported by Warner-Locke [38]. Throughout all performed testing pitting had no influence on crack initiation or propagation. Though, once grain was 'selected' for pitting attack, the process propagated rapidly and led to deep elongated (grain shaped) fissures in short transverse direction.

Regarding the SCC and SSRT testing results AA2099-T86 is considered as an improvement with respect to incumbent standard AA7075 or AA2024 high strength aluminium alloys for aerospace structural applications. The authors recommend further work to ensure results are more statistically significant.

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