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EXFOLIATION CORROSION AND STRESS CORROSION CRACKING BEHAVIOUR OF 8090-T81 SHEET

R. Braun

DLR - Deutsche Forschungsanstalt für Luft- und Raumfahrt, Institut für Werkstoff-Forschung, D-51140 Köln, Germany

Abstract

Accelerated tests have been carried out to investigate the exfoliation corrosion and stress corrosion cracking (SCC) behaviour of 8090-T81 sheet. Blistering was observed on coupons exposed to the EXCO solution and to an intermittent acidified salt spray fog. Slow strain rate (SSR) tests were performed on long transverse tensile specimens using various synthetic environments. Fracture energy data obtained from SSR tests in substitute ocean water revealed a big scatter. The degradation of specimens dynamically strained in this synthetic environment was largely related to corrosion processes independent of stress. Immersed in an aqueous solution of 0.5 M NaCl + 0.1 M LiCl + 0.05 M NaHCO₃ + 0.05 M Na₂CO₃, 8090-T81 sheet was found to be sensitive to stress corrosion cracking. The SSR testing technique also indicated SCC susceptibility when an aqueous solution of 0.6 M NaCl + 0.06 M NaNO₃ was used. However, 0.6 M NaCl solutions with a reduced inhibitor concentration of 0.03 M NaNO₃ or 0.03 M Na₂SO₄ were not conducive to environmentally assisted cracking, neither promoted additions of 0.05 M NaHCO₃ + 0.05 M Na₂CO₃ stress corrosion cracking on 8090-T81 specimens exposed to the inhibited chloride solutions.

Introduction

Due to the higher costs of aluminium-lithium alloys, the fly-to-buy ratio has to be considered when semi-fabricated products of conventional aluminium alloys should be replaced by the stiffer and lighter newly developed materials. This ratio is high for sheet and extruded profiles. Therefore, these product forms have a great potential for applications in aircraft structures [1]. However, recrystallized lithium bearing aluminium sheet in underaged tempers exhibits considerable shortcomings compared with the standard damage tolerant alloy 2024-T3, including lower crack resistance, an unusual crack deviation behaviour and a lower stress corrosion cracking (SCC) resistance [2,3]. The sensitivity to environmentally assisted cracking may be related to the particular solution chemistry at the crack tip in Al-Li alloys which is controlled by lithium dissolution [4]. Absorption of carbon dioxide leads to an alkaline chloride-carbonate electrolyte which provides a critical balance between activity and passivity promoting cracking [5]. The aim of the present work was to study the exfoliation and, in particular, the stress corrosion cracking behaviour of damage tolerant 8090-T81 sheet. Several synthetic environments were used to investigate the effect of different ions on SCC susceptibility of Al-Li alloys.

Experimental

The material studied was an 1.6 mm thick 8090 sheet in the underaged temper T81 supplied by British Alcan Aluminium. Flat tensile specimens with 16 mm gauge length and a cross section of 10 mm² were machined with loading axis in the long transverse direction. Tensile properties measured in long transverse direction were: 0.2% proof stress = (286 ± 4) MPa, ultimate tensile strength = (432 ± 7) MPa, fracture elongation = (16.3 ± 0.6) %.

The exfoliation corrosion behaviour was investigated performing EXCO tests (ASTM G34) and intermittent acidified salt spray (MASTMAASIS) tests [6]. Sizes of coupons used in EXCO and MASTMAASIS tests were 100×50 mm² and 30×25 mm², respectively. Corrosion attack was rated according to ASTM G34 by visual inspection. Weight loss measurements and metallographic work were carried out on specimens exposed to the intermittent acidified salt spray fog. To remove corrosion products, the coupons were cleaned in an aqueous solution of chromic and phosphoric acids as recommended in ASTM Standard Practice G1.

The SCC behaviour was studied in the long transverse direction using the slow strain rate (SSR) testing technique. Strain rates ranged from 10⁻⁷ to 5·10⁻⁴ s⁻¹. The SSR tests were performed at free corrosion potential under permanent immersion conditions in the following aerated corrosive media: substitute ocean water without heavy metals according to ASTM D1141 (pH=8.2), an aqueous solution of 0.5 M NaCl + 0.1 M LiCl + 0.05 M NaHCO₃ + 0.05 M Na₂CO₃ (pH=9.7), aqueous 0.6 M NaCl solutions without (pH=6.0) and with additions of 0.03 M Na₂SO₄ (pH=6.0), 0.03 M NaNO₃ (pH=5.5) and 0.06 M NaNO₃ (pH=5.5). Furthermore, 0.05 M NaHCO₃ + 0.05 M Na₂CO₃ were added to the chloride-sulfate and chloride-sulfate-nitrate solutions (pH=9.8). Reference tests were carried out in dry laboratory air (inert environment), generated by embedding the specimens in Mg(ClO₄)₂-powder. The fracture energy was used to assess sensitivity to stress corrosion cracking. Pre-exposure tests were carried out to evaluate the degradation of the specimens caused by immersion in the corrosive environment in the absence of applied strain. Details of the SSR testing technique are described elsewhere [7]. Before testing, the specimens were ultrasonically cleaned in ethanol and degreased in acetone vapour.

Results and discussion

After 48 h exposure to the EXCO solution, 8090-T81 coupons revealed slight blistering. The corrosion attack became more severe with longer exposure time. After 96 h immersion, the blisters broke open. For coupons of unclad 2024-T3 sheet, the EXCO test promoted pitting. Slight blistering was observed after 96 immersion with the latter alloy, too.

Results of the intermittent acidified salt spray tests are summarized in Table I and Figure 1. Unclad sheet of the Al-Li alloys 8090-T81 and 2091 CPHK-T8X and of the conventional alloys 2024-T3 and 6013-T6 have been tested. The visual assessment of corrosion attack after different exposure times is listed in Table I. Alloy 8090-T81 coupons exhibited slight blistering after two weeks. Blisters broke open after three weeks and a noticeable damage was observed, but it seemed that the severity of corrosion attack did not increase with longer testing time. 2091 CPHK-T8X sheet revealed slight pitting after two weeks exposure. Blistering occurred after

Table I. Corrosion ratings for aluminium alloy sheet exposed to an intermittent acidified salt spray fog

	2 weeks	3 weeks	4 weeks	5 weeks
8090-T81	B-	B/EA	B/EA	B/EA
2091 CPHK-T8X	N/P	B-	B	B/EA
2024-T3	P	P	P	P
6013-T6	U	U/P	U/P	U/P

Abbreviations of ratings: N = no appreciable attack; U = uniform corrosion; P = pitting; B = blistering; EA = superficial exfoliation corrosion according to ASTM G34; - slight attack

three weeks which became more severe with longer testing time. Some of the blisters broke open. After five weeks exposure, surface degradation was similar with 2091 CPHK-T8X and 8090-T81 coupons. For unclad 2024-T3 sheet, only pitting was observed which became more severe with longer exposure times. Uniform corrosion and pitting were found with 6013-T6 sheet. Corrosion increased moderately with increasing immersion times.

Figure 1 shows the weight loss and the maximum depth of corrosion attack measured on coupons after different intermittent acidified salt spray times. A similar weight loss was found for both Al-Li alloys. It was moderately and considerably higher for the control alloys 6013-T6 and 2024-T3, respectively. In accordance with visual inspection, weight loss of the latter alloys

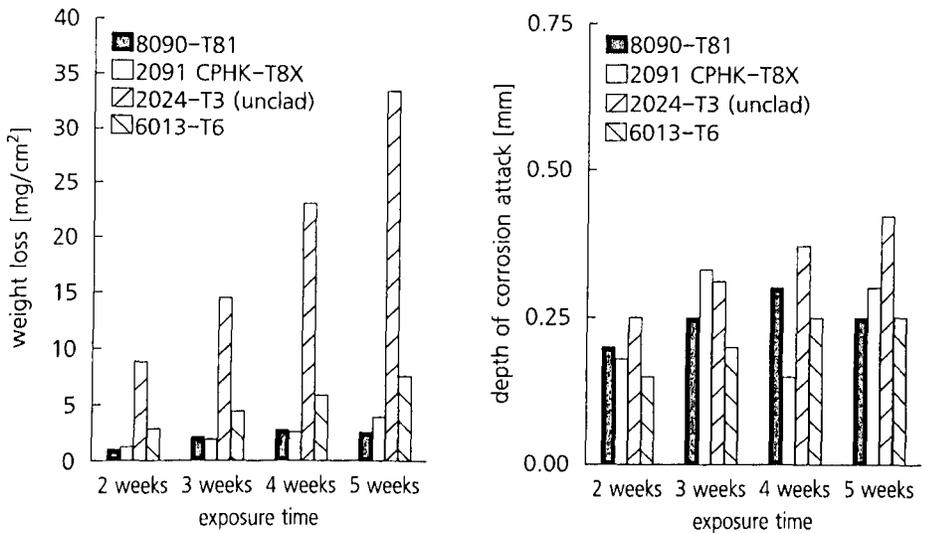


Figure 1. Weight loss and maximum depth of corrosion attack measured on coupons of unclad aluminium alloy sheet after different intermittent acidified salt spray testing times

increased with increasing exposure time. Metallographic sections of 8090-T81 and 2091 CPHK-T8X coupons revealed exfoliation corrosion, whereas pitting and intergranular corrosion were observed with the alloys 2024-T3 and 6013-T6, respectively. For the conventional alloys, the depth of corrosion attack increased with exposure length, whilst corrosion did not apparently penetrate further into the Al-Li alloy coupons after 3 weeks. The results of these accelerated tests correlate with outdoor exposure tests. Exposed to a marine environment, recrystallized damage tolerant Al-Li alloy sheet materials were susceptible to exfoliation corrosion [8]. Well defined blisters were observed.

Figure 2 shows the results of the SSR tests for 8090-T81 sheet using substitute ocean water. At strain rates below $1 \cdot 10^{-6} \text{ s}^{-1}$, a large scatter is observed in the fracture energy data of both dynamically strained SCC and pre-exposed specimens. Pre-exposure tests indicate that the degradation of specimens strained in substitute ocean water is largely related to corrosion processes independent of applied stress, such as pitting, intergranular corrosion or hydrogen absorption. On the fracture surfaces of pre-exposed specimens, intergranular corrosion and pitting were observed. Besides a transgranular ductile overload fracture, fractographic examinations of the dynamically strained SCC specimens revealed also intergranular fracture with dissolved grain boundaries (Figure 3). The dissolution of the grain boundaries was slight and might result from a post-fracture attack. The proportion of intergranular fracture was greater than the area on fracture surfaces of pre-exposed specimens showing intergranular corrosion. Thus, stress corrosion cracking or stress assisted intergranular corrosion might also contribute to the degradation of dynamically strained specimens. Similar results of SSR tests performed in substitute ocean water have been found for 2091 CPHK-T8X sheet and 2091-T8X51 plate when tested in long transverse direction [9,10]. Again, degradation during pre-exposure and a big scatter in data were observed. The reasons of the scatter are not understood. It may be related to heterogeneities in the microstructure of the specimens or to changes of the artificial seawater.

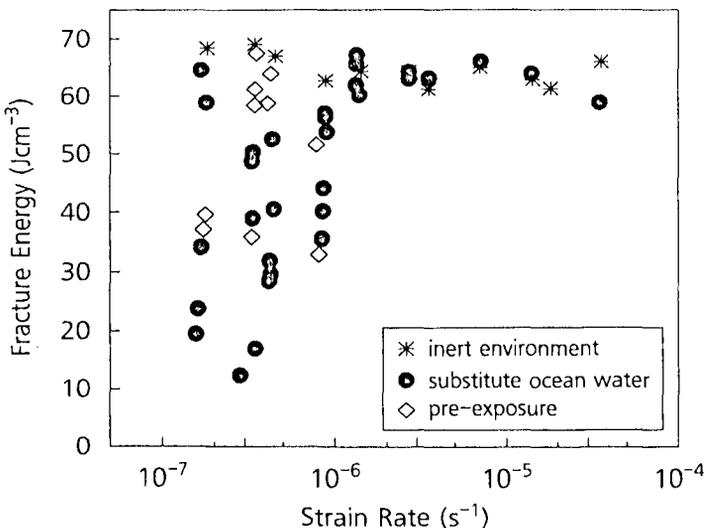


Figure 2. Results of slow strain rate tests for 8090-T81 sheet using substitute ocean water.

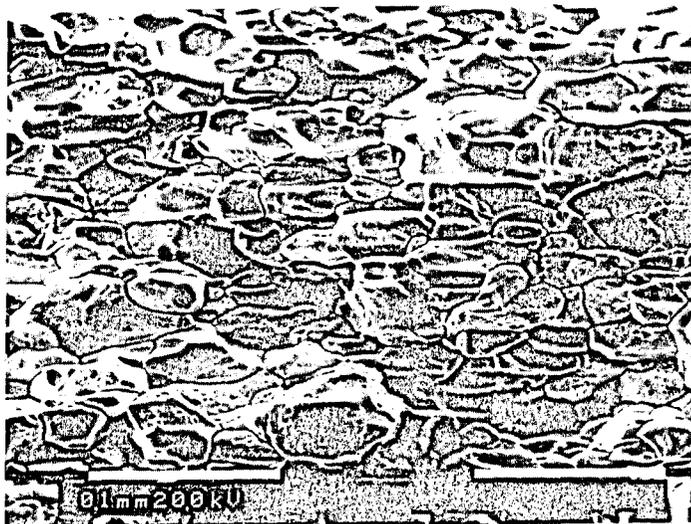


Figure 3. Scanning electron fractograph of an 8090-T81 specimen which was dynamically strained in substitute ocean water at a strain rate of $3.5 \cdot 10^{-7} \text{ s}^{-1}$.

Figure 4 illustrates the fracture energy vs strain rate curve obtained from SSR tests using an aqueous solution of $0.5 \text{ M NaCl} + 0.1 \text{ M LiCl} + 0.05 \text{ M NaHCO}_3 + 0.05 \text{ M Na}_2\text{CO}_3$. The fracture energy decreases at strain rates below $5 \cdot 10^{-7} \text{ s}^{-1}$. The reduction is shifted to slower strain rates when the specimens were tensile tested in an aqueous 0.6 M NaCl solution with equal additions of carbonate-bicarbonate but without lithium ions. As demonstrated in subsequent tensile tests, specimens which were pre-exposed to these synthetic environments were not deteriorated in tensile properties. Therefore, chloride-carbonate-bicarbonate solutions promote stress corrosion cracking with recrystallized 8090-T81 sheet. Lithium ions added to the bulk electrolyte seem to force the occurrence of stress corrosion cracking, facilitating the buildup of a local environment in which crack initiation is favoured. Using this synthetic environment, the SSR testing technique also indicates SCC susceptibility for damage tolerant sheet of the alloy 2091 and for 8090-T81 sheet when tested in longitudinal direction [9,11].

Results of SSR tests carried out in chloride-nitrate solutions are plotted in Figure 5. Sensitivity to stress corrosion cracking is not observed in pure 0.6 M NaCl solution and in $0.6 \text{ M NaCl} + 0.03 \text{ M NaNO}_3$. However, the addition of 0.06 M NaNO_3 results in a deterioration of specimens which is associated with environmentally assisted cracking, as demonstrated by pre-exposure tests in the latter environment. In near neutral chloride solution, stress corrosion cracking does not occur in Al-Li alloys under permanent immersion conditions [4]. This electrolyte is too aggressive to sustain sharp cracks [5]. In chloride-carbonate-bicarbonate solutions, crack blunting can be prevented by precipitation of lithium compounds causing crack wall passivation. Inhibition of intergranular corrosion might also hinder the dissolution of crack walls. As shown in Figure 5, the addition of 0.06 M NaNO_3 promotes stress corrosion cracking in chloride solutions, whereas the reduced amount of 0.03 M NaNO_3 is apparently not

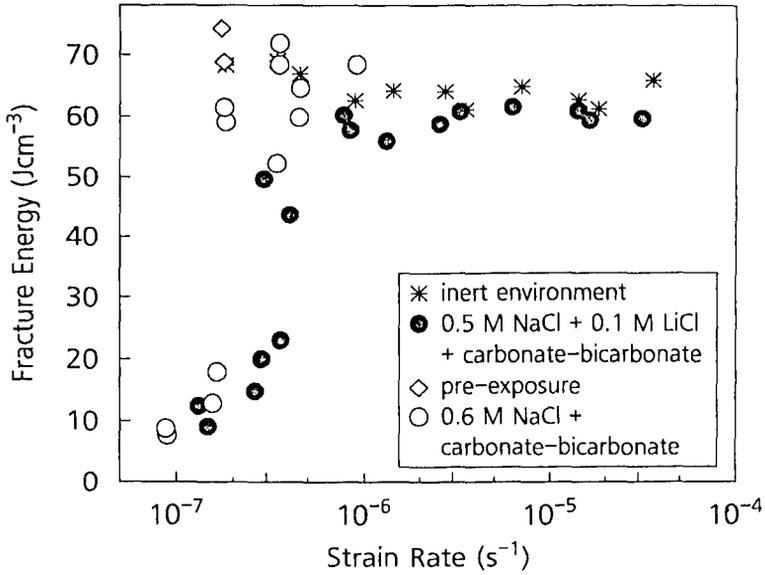


Figure 4. Results of slow strain rate tests for 8090-T81 sheet using an aqueous solution of 0.5 M NaCl + 0.1 M LiCl + 0.05 M NaHCO₃ + 0.05 M Na₂CO₃.

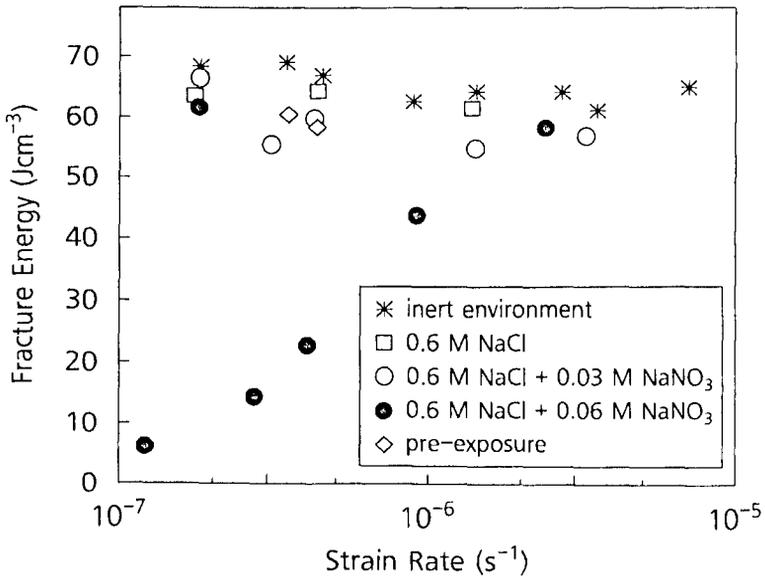


Figure 5. Results of slow strain rate tests with 8090-T81 sheet using chloride-nitrate solutions.

sufficient to impede crack blunting. On the fracture surfaces of specimens dynamically strained in 0.6 M NaCl + 0.06 M NaNO₃, areas of intergranular fracture were observed with considerably attacked grain boundaries, supporting SCC failure via an anodic dissolution mechanism. Similar results were found by Marsac et al. [12]. These authors observed SCC sensitivity with Al-Li alloy 2091-T8X when exposed to an aqueous solution of 0.6 M NaCl + 0.06 M NaNO₃. Failure did not occur when lower or higher inhibitor concentrations were used. The better SCC resistance at higher nitrate contents was attributed to inhibitive effects reducing stress assisted intergranular corrosion [12].

Figure 6 shows results of SSR tests using inhibited chloride solutions with and without carbonate-bicarbonate additions. Environmentally assisted cracking is not observed in an 0.6 M NaCl solution containing 0.03 M Na₂SO₄. The concentration of chloride and sulfate ions is similar in the latter electrolyte and in substitute ocean water. The degradation observed for specimens exposed to substitute ocean water (Figure 2) might be attributed to other species in this environment or to its slightly alkaline pH value. The addition of 0.05 M NaHCO₃ + 0.05 M Na₂CO₃ to the chloride-sulfate solution which leads to an alkaline pH of 9.8 does not promote stress corrosion cracking. SCC sensitivity is not either observed when the total inhibitor concentration in the chloride-carbonate-bicarbonate solution is increased to 0.06 M by the addition of nitrate. Because the latter bulk electrolytes do not contain lithium ions, the applied strain rates may be not slow enough to initiate stress corrosion cracking. A similar effect is observed performing SSR tests in an aqueous solution of 0.6 M NaCl + 0.05 M NaHCO₃ + 0.05 M Na₂CO₃, as mentioned above (Figure 4).

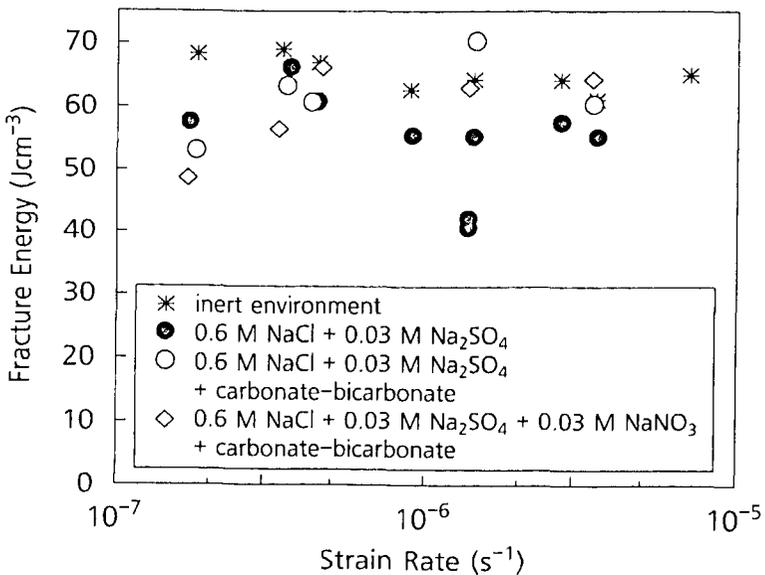


Figure 6. Results of slow strain rate tests for 8090-T8171 sheet using inhibited chloride solutions with and without carbonate-bicarbonate additions.

Conclusions

1. 8090-T81 sheet is susceptible to exfoliation corrosion. The EXCO solution and the intermittent acidified salt spray fog promote blistering.
2. Fracture energy data obtained from SSR tests in substitute ocean water reveal a large scatter. The degradation of specimens results mainly from corrosion processes independent of stress.
3. Using an aqueous solution of 0.5 M NaCl + 0.1 M LiCl + 0.05 M NaHCO₃ + 0.05 M Na₂CO₃, the SSR testing technique indicates sensitivity to stress corrosion cracking for 8090-T81 sheet.
4. An aqueous solution of 0.6 M NaCl + 0.06 M NaNO₃ is also conducive to environmentally assisted cracking. Stress corrosion cracking does not occur in an 0.6 M NaCl solution with a reduced inhibitor addition of 0.03 M NaNO₃.
5. Environment-induced failure of 8090-T81 specimens is not observed using an aqueous solution of 0.6 M NaCl + 0.03 M Na₂SO₄. In the strain rate range investigated, carbonate-bicarbonate additions to the latter synthetic environment do not promote stress corrosion cracking.

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