ENVIRONMENTALLY ASSISTED CRACKING OF ALUMINIUM ALLOYS IN CHLORIDE SOLUTIONS

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ABSTRACT A short review of the stress corrosion cracking behaviour of aluminium alloys is given. Mechanisms of environmentally assisted cracking are outlined. For aluminium alloys, in which stress corrosion cracks propagate predominantly along grain boundaries, anodic dissolution and hydrogen embrittlement have been proposed. Transgranular stress corrosion cracking has found particular interest concerning localised corrosion-deformation interactions. Accelerated test methods for assessing the SCC behaviour are described, including the Slow Strain Rate Testing Technique and the Breaking Load Method. Results of recent studies on environmentally assisted cracking of aluminium alloys are summarised. Most of the work published in the last years was on aluminium-lithium based alloys and modern high strength Al-Zn-Mg-Cu alloys in corrosion resistant retrogressed and reaged tempers.

Keywords: aluminium alloys, stress corrosion cracking, anodic dissolution, hydrogen embrittlement mechanisms, testing methods, 7XXX series alloys, Al-Li alloys

1. INTRODUCTION

Aluminium alloys will remain the predominant structural material in the aircraft industry and are selected to an increasing extent for structural applications in transportation by road, rail or sea [1]. The emphasis on weight savings has forced the development of aluminium-lithium alloys with reduced density and the improvement of conventional alloys and tempers to meet the increased performance requirements for damage tolerance, fatigue behaviour and stress corrosion cracking (SCC). Another concept to save weight and cost is based on new fuselage constructions incorporating integral structures using laser beam welding or extruded panels [2]. This has drawn attention to weldable and/or extrudable high performance aluminium alloys.

For structural materials, high corrosion resistance is crucial since corrosion causes considerable maintenance costs and prevents the exploitation of the potential of mechanical properties. When exposed to chloride containing environments, high strength aluminium alloys can be sensitive to environment-induced cracking. There are several excellent reviews related to stress corrosion cracking of aluminium alloys [3-6]. In this paper being not exhaustive, results of investigations on the SCC behaviour of aluminium alloys reported recently in the literature will be summarised, supplemented by a short description of mechanisms of environmentally assisted cracking and new SCC testing techniques for aluminium alloys.

2. MECHANISMS OF STRESS CORROSION CRACKING

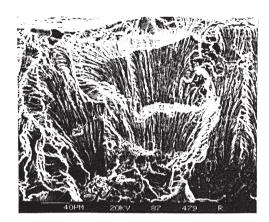
Many different mechanisms have been proposed to explain environment-induced cracking, including slip-dissolution model, film-induced cleavage, surface mobility model and different hydrogen embrittlement mechanisms, being commented and evaluated in reviews published recently [7-9]. For aluminium alloys, in which stress corrosion cracking is characteristically intergranular, two mechanisms are proposed; anodic dissolution and hydrogen embrittlement.

Anodic dissolution is a highly localised process assuming that cracking extends as a result of preferential corrosion along grain boundaries [4,7]. This requires electrochemically active paths in the grain boundary regions. Grain boundary precipitates, being anodic or cathodic to the matrix, and regions adjoining them, such as precipitate-free zones or solute depleted zones, have been considered to contribute to intergranular stress corrosion cracking as well as grain boundary segregation of copper [4,10]. To keep corrosion attack localised, repassivation of the crack walls and at the crack tip is of critical importance, preventing crack blunting and delimiting stress corrosion cracking and intergranular corrosion [11]. The protective film is disrupted by the imposed stress, exposing the pre-existing path to the corrosive environment. Restarting dissolution and subsequent reforming of the passive film can result in a discontinuous SCC propagation. Owing to their effects on repassivation, grain boundary segregation of solutes, such as zinc, magnesium or copper, can influence environmentally assisted cracking.

The exact interaction between hydrogen and a metal resulting in fracture is still unclear despite extensive studies in the last years [4,9]. The various hydrogen embrittlement mechanisms fall broadly in three classifications: (i) hydrogen induced decohesion, (ii) hydrogen enhanced localised plasticity and (iii) hydride formation and cleavage [7,9]. The latter mechanism is suggested to be operative in metals which form stable hydrides, or in which the formation of hydride is assisted by the stress field at the crack tip. In aluminium alloys, hydride formation has been discussed in relation to magnesium segregated on grain boundaries [12]. Magnesium is considered to promote local activity at grain boundaries and to be responsible for hydrogen entry into grain boundaries and its enhanced grain boundary diffusion. However, stress corrosion cracking is not caused by magnesium itself, but results from grain boundary precipitation which facilitates crack nucleation possibly due to the formation of magnesium hydrides on the incoherent interface of grain boundary precipitates. Prolonged aging changes the grain boundary precipitation promoting hydrogen discharge rather than hydride formation.

In the model of hydrogen enhanced localised plasticity, fracture occurs due to plastic processes in localised regions softened by hydrogen present in solid solution [9]. The presence of hydrogen decreases the resistance to dislocation motion resulting in localised deformation processes. These effects are pronounced at the crack tip because there the hydrogen concentration is increased by the stress field and the entry of hydrogen is facilitated by slip processes. The hydrogen enhanced localised plasticity mechanism can be applied to transgranular and intergranular failure. In the latter case, hydrogen enrichment near the grain boundaries is associated with segregation localising ductile fracture in these regions.

Although environment-induced failure of aluminium alloys is almost exclusively intergranular in service, transgranular stress corrosion cracking has been observed when severe loading conditions were applied [3]. Figure 1 shows typical features of transgranular stress corrosion cracking in the alloy 7010-T7651. Metallographic and fractographic examinations revealed discontinuous cleavagelike fractures macroscopically parallel to {100} planes, with crack growth in <110> directions [13]. Transgranular cleavage-like cracking in aluminium alloys has been analysed recently in relation to investigations of corrosion-deformation interactions. An adsorption-induced localised-slip process was proposed by Lynch [13,14]. Interatomic bonds at the crack tips are weakened by adsorbed hydrogen, resulting in injection of dislocations. The crack grows by alternate slip process and coalesces with voids formed by dislocation activity ahead of the crack. These voids reduce the crack-tip opening angles, thus maintaining the crack sharp. The corrosion enhanced plasticity model developed by Magnin can also be applied to transgranular stress corrosion cracking in aluminium alloys [15,16]. It is based on the corrosion-deformation interactions at the stress corrosion crack tip. Localised anodic dissolution on {111} slip planes and hydrogen entry result in an enhanced plasticity at the crack tip. Mobile dislocations can be injected owing to stress concentration, vacancy production, adsorption and absorption of hydrogen. These dislocations emitted by the crack tip will then interact with obstacles, and zig-zag microcracking assisted by hydrogen absorption can occur on {111} facets.



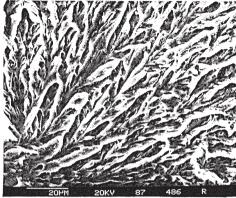


Figure 1: Transgranular stress corrosion cracking in alloy 7010-T7651

3. STRESS CORROSION CRACKING TEST METHODS

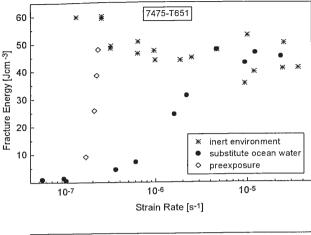
The majority of SCC tests applied in quality assurance and materials research are pass-fail tests, performed under alternate immersion conditions in 3.5% NaCl solution according to ASTM G44. However, alternate immersion pass-fail procedures require relative long test duration and seem to be inadequate to discriminate amongst aluminium alloys with relatively high SCC resistance [17]. Hence accelerated SCC testing techniques have been developed, such as the Slow Strain Rate Technique [18], the Breaking Load Method [19], or the Automated Stress Corrosion Ring (ASCOR) Test [20].

The slow strain rate testing (SSRT) technique was developed by R.N. Parkins in the 1970s [18]. Uniaxially loaded tensile specimens (smooth or notched) are strained until fracture at very low crosshead speeds under controlled environmental conditions. For a particular metal/environment system, a critical strain rate range exists within which stress corrosion cracking occurs. For aluminium alloys, the strain rates range from 10⁻⁸ to 10⁻³ s⁻¹. Sensitivity to environment-induced cracking is indicated by a reduction of parameters of the stress-strain curve obtained in a corrosive medium as compared to reference values determined in an inert environment. Typical SSRT results are plotted in Figure 2, showing curves of fracture energy vs strain rate for 7475 in the T651 and T7351 tempers [21]. Low and high SCC resistances of the alloy 7475 in the tempers T651 and T7351, respectively, are clearly indicated. Because specimens can also be deteriorated by pitting or intergranular corrosion, preexposure tests have to be carried out. The action of stress can be determined by comparison with specimens that were exposed to the corrosive medium without applied stress and subsequently tensile tested in an inert environment [22]. The most attractive benefits of the SSRT technique over static loading SCC tests are the relatively short period of time within which results can be obtained and the definite end when specimens have failed either by environmentally assisted cracking or by ductile fracture.

Extensive work was done in our laboratory to assess the applicability of the SSRT technique to evaluate the SCC behaviour of aluminium alloys in service [22-28]. The tests were performed under continuous immersion conditions in various synthetic environments and at free corrosion potential. Using an aqueous solution of 3% NaCl + 0.3% H₂O₂ and substitute ocean water (ASTM D1141), the SSRT technique was found a useful tool to sort out aluminium alloys being highly sensitive to environmentally assisted cracking. However, it failed to distinguish SCC behaviour of more resistant alloys. When specimens of these materials were dynamically strained in the chloride-peroxide solution, the degradation was associated with corrosion independent of stress, as proved by preexposure

The chloride-peroxide solution is very corrosive promoting pitting and intergranular corrosion. Due to crack blunting, sharp stress corrosion cracks might not be retained with more resistant alloys. Data obtained from SSR tests in substitute ocean water revealed a large scatter related primarily to degradation in ductility caused by corrosion independent stress. An aqueous perchlorate solution as well as mixed salt solutions containing chloride, sulfate and nitrate, which should simulate industrial polluted environments, were found to be unsuitable electrolytes to be used for predicting service behaviour of 7050 alloy in different tempers [28]. Owing to the local chemistry within cracks and fissures of aluminium-lithium based alloys. aqueous chloride solutions with carbonatebicarbonate additions seem to be effective synthetic environments to investigate the SCC behaviour of the latter alloys [27].

The Breaking Load Method was developed and examined at Alcoa Laboratories as an improved technique for evaluating the SCC performance of relatively resistant aluminium alloys



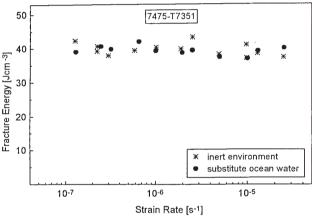


Figure 2: Curves of fracture energy vs strain rate for alloy 7475 in the tempers T651 and T7351. Short transverse specimens were strained in an inert environment and in substitute ocean water. Data for preexposed specimens are included [21].

[19,29]. In this method smooth specimens are exposed to a corrosive environment (usually alternate immersion in 3.5% NaCl solution) under sustained tensile stress for various lengths of time (4 to 10 days for 7XXX series alloys). After exposure, the fracture strength of the specimens is determined and compared with the original strength of not exposed material. In general, the residual strength decreases with increasing SCC sensitivity. Degradation related to pits, intergranular or general corrosion can be measured by comparing the strengths of specimens exposed with and without stress. Compared with conventional pass-fail testing procedures, the Breaking Load Method was found to assess the SCC behaviour using fewer specimens and shorter exposure times [19]. Analysing the data by statistical procedures, estimation of threshold stress and survival probabilities can be obtained. Results of a round robin program organised by the ASTM Subcommittee have confirmed the capability of this testing technique to discriminate between close SCC ratings of more

resistant alloys [17]. Data of the Breaking Load Method can also be interpreted using fracture mechanics concepts, thus avoiding difficulties in SCC ranking associated with specimen geometry and mechanical property variations [29].

The SCC behaviour of aluminium alloys is also evaluated using the damage tolerant approach taking into account the possibility of cracks or flaws already existing in structures. Most of these tests based on fracture mechanics are carried out under constant load or constant displacement conditions. Bolt loaded double cantilever beam (DCB) specimens are widely used [30]. Applying linear elastic fracture mechanics, a threshold value of the stress intensity factor K_{ISCC} is determined below which stress corrosion cracking should not occur in precracked specimens. At intermediate stress intensities (region II), the velocity of subcritical crack growth is independent of K_I, and this plateau velocity is also used for ranking the SCC resistance of aluminium alloys. However, the static loading fracture mechanics based SCC tests require long testing times (10.000 h for aluminium alloys), and, with extended exposure, corrosion product wedging can enhance the mechanical driving force at the crack tip, thereby preventing crack arrest. To reduce the test duration, a dynamic testing procedure is applied. Using precracked fracture mechanics specimens which are exposed to a corrosive environment at constant displacement rates, the Rising Displacement Technique provides results in shorter times, and the results can be evaluated applying elastic-plastic fracture parameters, such as J-integral and crack tip opening displacement [31].

4. STRESS CORROSION CRACKING BEHAVIOUR OF ALUMINIUM ALLOYS 4.1 2XXX series alloys

It is generally proposed, that the SCC mechanism being operative in 2XXX aluminium alloys is intergranular corrosion accelerated and localised by the applied stress [3-6,10]. A copper depleted zone along the grain boundaries forms an anodic path resulting in a potential difference between grain boundary and grain interior. With further aging, hardening phases precipitate in the matrix, thereby lowering the copper content in solid solution and reducing the potential difference. Measuring the pitting potentials of the grains and the grain boundaries for alloy 2024 in different heat treatments, the highest SCC susceptibility was observed when the potential difference was maximum [32]. In recent investigations on aged Al-Cu alloy and on alloy 2214 aged using a complex two-step heat treatment, a strong dependence was found between SCC resistance and intergranular corrosion sensitivity, supporting the assumption that stress corrosion cracking can be interpreted as intergranular corrosion accelerated by mechanical stress [33,34].

Hydrogen embrittlement was observed in 2X24 alloys under severe entry conditions [35,36]. When plastically deformed and cathodically charged, tensile specimens of alloy 2124 strained in longitudinal direction were deteriorated in ductility [35]. The degradation was most severe in the underaged microstructure. The transgranular ductile dimple fracture mode observed with uncharged specimens was not altered by hydrogen. Similar results were obtained for alloy 2024 [36]. Again, hydrogen embrittlement was indicated by a reduction in the extent of plastic elongation, whereas fracture morphology was not changed.

4.2 5XXX series alloys

In Al-Mg alloys with magnesium contents exceeding about 3-4 wt%, grain boundary precipitation of the β phase (Al₈Mg₅) can occur, resulting in sensitivity to intergranular corrosion and stress corrosion cracking [10]. Precipitation of the β phase, which is highly anodic to the matrix, is stimulated by exposure to elevated temperature (60 to 180°C) and enhanced by cold work. A continuous grain boundary precipitate structure is most detrimental to the SCC resistance of these alloys. When exposed to temperatures down to 100°C for 4000 h, cold worked and stretched sheet of the alloy 5182, a candidate for automotive applications, was quite susceptible to stress corrosion cracking, as found in alternate immersion tests in 3.5% NaCl solution under static loading conditions [37].

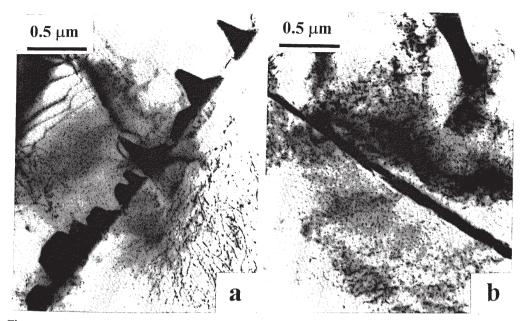


Figure 3: Transmission electron micrographs of an annealed (a) and a cold rolled (b) 5182 sheet, which was heat treated at 150°C for 297 h

Sensitisation to environment-induced cracking was also indicated by the SSRT technique using an aqueous chloride-peroxide solution [37,38]. Transmission electron microscopy revealed grain boundary precipitation in both annealed and deformed 5182 sheet after thermal exposure at 150°C for 297 h (Figure 3). In the cold worked material, precipitates formed an almost continuous structure.

4.3 6XXX series alloys

Service problems with environment-induced cracking are not known for 6XXX series alloys [10]. Naturally aged 6061-T4 was found to be susceptible to stress corrosion cracking in laboratory tests when exposed to relatively high solution heat treatment temperatures followed by slow quenching. SCC failure was only observed with highly stressed preformed specimens. The sensitivity was eliminated by aging to peak strength [10]. Similar results were obtained from SSR tests using an aqueous solution of 3% NaCl + 0.3% H₂O₂ [25]. SCC susceptibility was found for 6061-T4 sheet, whereas 6013 sheet in the peak-aged T6 temper was immune to intergranular stress corrosion cracking. In recrystallised products of copper containing alloys 6013 and 6056, SCC failure can occur, as found in laboratory SCC tests [5]. This SCC susceptibility could not be explained by intergranular corrosion accelerated by an applied stress.

4.4 7XXX series alloys

7XXX series alloys provide the highest strength among the heat treatable aluminium alloys. However, sensitivity to environmentally assisted cracking prevents the exploitation of their potential in strength. Underaged microstructures exhibit the lowest SCC resistance [4]. Stress corrosion cracking was also observed in 7XXX series alloys in the W51 condition when exposed to corrosive environments in the interval between quenching and elevated temperature aging [39]. This sensitivity was related to near grain boundary regions depleted in copper and possibly enriched in magnesium.

Thereby, these regions became anodic relative to the grain interior, resulting in susceptibility to intergranular stress corrosion cracking. The SCC behaviour of Al-Zn-Mg-(Cu) alloys improves with artificial aging [4]. In short transverse direction, however, peak-aged wrought products are still quite susceptible. Environmentally assisted failure in service has not occurred with Al-Zn-Mg-Cu alloys in overaged T73 tempers. For 7XXX series alloys containing more than 1 wt% copper, duplex overaging practices result in immunity to stress corrosion cracking with concomitant sacrifice in strength. However, similar heat treatments are not effective with copper lean Al-Zn-Mg alloys. Thus, stress corrosion cracking resistant tempers do not exist for such alloys [40].

7XXX aluminium alloys can be sensitive to hydrogen embrittlement, as convincingly proved by Ratke and Gruhl [41]. A hollow tube of an Al-5Zn-3Mg alloy with a circumferential notch at the outer surface was filled inside with a corrosive solution and loaded in tension. Fractographic examinations revealed that intergranular stress corrosion cracks initiated at the base of the notch associated with the accumulation of hydrogen in the regions ahead of the notch. Hydrogen embrittlement can also be induced by cathodic charging with concurrent plastic strain. Longitudinal specimens of a 7050-type alloy charged under these hydrogen-entry conditions revealed loss in ductility [42]. The alloy was susceptible to hydrogen embrittlement in the underaged temper, but not in the peakaged temper. Degradation caused by cathodic charging was more severe for a copper-free alloy with similar Zn and Mg content, being sensitive in both underaged and peak-aged conditions. Hydrogen is also involved in the mechanism of white zone cracking occurring in the heat affected zone of welded Al-Zn-Mg alloys [43,44]. A complete re-heat treatment after welding, including solutionising, quenching and artificial aging, could render the material immune to stress corrosion cracking. For Al-Zn-Mg alloys, hydrogen embrittlement is the dominant environment-induced failure mechanism, whereas both anodic dissolution and hydrogen embrittlement are considered being operative in 7XXX alloys containing higher copper content [3-6,45]. However, the metallurgical parameters and microstructural features which control the SCC behaviour are still not clear.

Many efforts have concentrated on the development of tempers exhibiting high SCC resistance without sacrifice in strength. The most successful procedure to achieve an optimum combination of strength and corrosion properties is the retrogression and reaging (RRA) heat treatment which provide strength of a T6 temper and SCC resistance equivalent to that of the overaged T73 temper [46]. Most of the authors who studied microstructural changes associated with the RRA treatment believe that the enhanced SCC resistance is associated with a change in the grain boundary precipitate structure [47,48,49]. Size and spacing of the grain boundary η particles increased during retrogression. This coarsening improved the corrosion properties, while η ' precipitation in the matrix restored the high strength in the subsequent reaging step. As demonstrated by chemical analysis with high spatial resolution, the grain boundary segregation profiles of alloying elements were changed by aging, indicating that reduced grain boundary copper levels observed in T73 and RRA tempers can significantly influence the SCC behaviour [50]. Using transmission electron microscopy, Talianker and Cina observed a decreased density of dislocations near grain boundaries after retrogression and reaging [51]. The authors concluded that the SCC behaviour is related to density of dislocation rather than to the grain boundary precipitate structure. Apparently, the microstructural factors contributing to the improved SCC resistance provided by the RRA treatment are not yet understood.

Most recent developments in high strength aluminium alloys are products of the alloys 7X50 and 7055 produced by Alcoa [52]. Process and the heat treatment T77 are proprietary. These alloys provide a range of strength-corrosion resistance combinations. Both η ' and η precipitates were found in the microstructure of 7150-T77, being more similar to that of the T6 than the T74 temper.

4.5 Al-Li alloys

Because of their reduced density, aluminium-lithium base alloys were developed for substitution of established 2XXX and 7XXX series alloys used in aircraft and space vehicle structures. Whereas

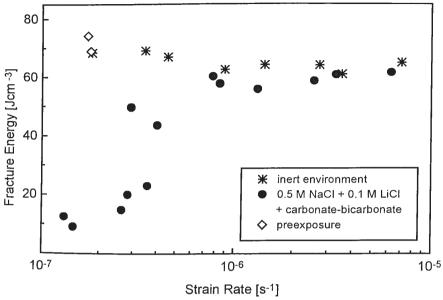


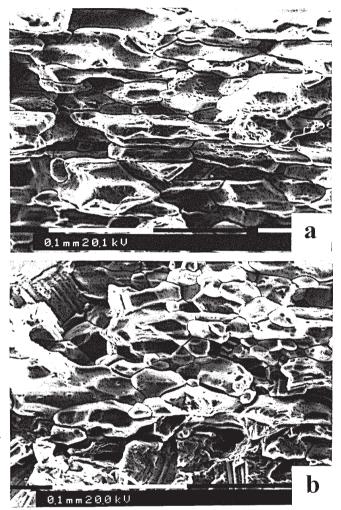
Figure 4: Curves of fracture energy vs strain rate for 8090-T81 sheet. Long transverse specimen, were strained in an inert environment and in an aqueous solution of 0.5 M NaCl + 0.1 M LiCl \pm 0.05 M NaHCO₃ + 0.05 M Na₂CO₃. Date for preexposed specimens are included [57].

service problems with environment-induced cracking are not known for 2024-T3 sheet, damage tolerant sheet of the alloys 2091 and 8090 was found to be susceptible to stress corrosion cracking [20,27,53-58]. The SCC resistance of sheet material depended on the grain structure. Unrecrystal. lised medium-strength 8090-T6 alloy was found to be immune [59], whereas recrystallised 8090-T81 sheet was prone to environmentally assisted cracking, as indicated by the results of the SSR tests shown in Figure 4 [57]. Similar results were obtained for alloy 2091 in the underaged T8X temper Material with a fully recrystallised equiaxed grain structure revealed a very low SCC resistance, which increased with further aging [53]. Improved SCC behaviour was observed for 2091-T8X sheet exhibiting microstructure with grains flattened in the rolling direction and a partially recrystallised layer in the centre of the sheet [27,56]. Results of SSR tests performed in various electrolytes and thorough examinations of the fracture surfaces supported an anodic dissolution mechanism dominating in environmentally assisted cracking of damage tolerant aluminium-lithium based sheet (Figure 5) [27,57]. The SCC behaviour of plate materials of Al-Li alloys is similar to that of high strength alloys which should be substituted, such as 2014-T651, 2024-T351 or 7075-T651, revealing a low resistance in short transverse direction [60-63]. The SCC sensitivity depended upon the heat treatment, decreasing from underaged to peak-aged and further to overaged tempers [60]. However, the influence of isothermal aging was moderate compared to improvements achieved by overaging practices with 7XXX series alloys.

The SCC resistance of Al-Li-Cu-Mg-Zr alloys could be enhanced using more complex heat treatments, however, at sacrifice of strength, or by modifying the alloy composition by adding zinc [60,64]. The SCC initiation behaviour of Al-Li-Cu-Mg-Zr alloys was related to the potential difference between matrix and grain boundary regions, which depended upon type and distribution of the precipitates both within the matrix and on grain boundaries, suggesting an anodic dissolution mechanism. As demonstrated by reversion and reaging heat treatments, grain boundary precipitates play a

significant role in the SCC behaviour of Al-Li-Cu alloys [65]. Using this thermal treatment, the microstructure of the alloy was varied being underaged in the matrix and peak-aged on grain boundaries. The environment-induced crack growth behaviour observed with such a microstructure was similar to material in the peak aged temper rather than in the underaged temper.

Studies have focused on the different SCC behaviour observed when specimens of Al-Li alloys were immersed continuously or alternately in neutral sodium chloride solutions [66-68]. Aerated aqueous chloride do not promote environmentally assisted cracking under continuous immersion. Sharp cracks cannot be sustained because the environment within the fissures is too aggressive towards grain boundaries, causing crack blunting. When removed from the NaCl solution. the fissures become alkaline owing to the dissolution of lithium, which does not readily hydrolyse, and to the displacement of external sides for cathodic reactions, which take place more and more within the fissures. Absorption of atmospheric carbon dioxide results in a local environment providing a critical balance between active dissolution and passivation by the



<u>Figure 5:</u> Scanning electron fractographs of 8090-T81 specimens which were strained in an aqueous solution of 0.5 M NaCl + 0.1 M LiCl + 0.05 M NaHCO₃ + 0.05 M Na₂CO₃ (a) and in substitute ocean water (b), showing attacked grain boundaries.

formation of AlLiO₂ or Li₂[Al₂(OH)₆]₂·CO₃·3H₂O. Thus, cracks initiate and propagate. For the alloy 2090, two key features were proposed: stress-assisted anodic dissolution of T₁ phase being active with respect to the region near subgrain boundaries and the formation of passive films along crack walls [68]. In a recent study using potentiodynamic polarisation measurements and scratching electrode techniques, similar results were obtained for Al-Li-Cu and Al-Cu-Mg alloys, supporting the assumption that the electrochemistry of the copper depleted region along grain boundaries is the active path in an anodic dissolution mechanism [69].

Sensitivity to hydrogen embrittlement of Al-Li alloys was indicated by loss of ductility when longitudinal specimens were tensile tested at low strain rates with simultaneous cathodic charging or

subsequent to cathodic charging or to pre-exposure [70-72]. After a re-heat treatment, preexposed specimens recovered their original ductility, showing that hydrogen was involved in the preexposure degradation [70]. Susceptibility to hydrogen embrittlement of Al-Li-Cu alloys was attributed to the T_1 phase. Using the SSRT technique at applied cathodic potential, the plastic strain of specimens was severely deteriorated, when arsenic, a hydrogen recombination poison, was added to the chloride solution [71]. A brittle AlLiH₄ phase was found in an Al-Li-Cu alloy electrochemically charged with hydrogen [73]. This hydride formed from the grain boundary δ (AlLi) phase.

The influence of RRA treatments on environmentally assisted cracking was also investigated for the alloy 8090 [72,74]. As with 7XXX series alloys, retrogression and reaging decreased the density of dislocations, resulting in a substantial improvement of the SCC resistance. Near the grain boundaries of retrogressed and reaged material, δ ' precipitate free zones were observed, which might affect the SCC behaviour too [74]. Similar effects were observed in hydrogen embrittlement studies [72]. Loss in plastic elongation of cathodically charged specimens tensile tested in longitudinal direction was reduced after RRA treatments

5. CONCLUSION

Despite progress in modelling of environment induced cracking, the exact stress corrosion cracking mechanism(s) being operative in aluminium alloys is still not clear, and microstructal features controlling stress corrosion cracking remain to be elucidated. For the different alloy systems, anodic dissolution or hydrogen embrittlement or both are favoured. Although both mechanisms are supported by experimental evidence, there is no unambiguous experiment until now to identify the one mechanism and exclude the other. Nevertheless, problems with stress corrosion cracking can be surmounted, as proved with 7XXX series aluminium alloys in tempers produced using optimised thermal heat treatments. Further investigations should concentrate on the crack tip chemistry and on the local concentration of alloying elements near grain boundaries.

REFERENCES

- [1] J.T. Staley and D.J. Lege, Journal de Physique IV, Colloque C7, supplément au Journal de Physique III, vol. 3 (1993), 179.
- [2] K.-H. Rendigs, Materials Science Forum, vol. 242 (1997), 11.
- [3] N.J.H. Holroyd, Environment-Induced Cracking of Metals, R.P. Gangloff and M.B.Ives, Eds., National Association of Corrosion Engineers, Houston, 1990, p.311.
- [4] N.J.H. Holroyd, A.K. Vasudevan and L. Christodoulou, Aluminum Alloys Contemporary Research and Applications, A.K. Vasudevan and R.D. Doherty, Eds., Treatise on Materials Science and Technology, vol. 31, Academic Press, 1989, p.463.
- [5] M.C. Reboul, T. Magnin and T.J. Warner, Aluminium Alloys Their Physical and Mechanical Properties (ICAA3), Vol. II, L. Arnberg, O. Lohne, E. Nes and N. Ryum, Eds., Trondheim, 1992, p.453.
- [6] T.D. Burleigh, Corrosion, 47 (1991), 89.
- [7] R.N. Parkins, Parkins Symposium on Fundamental Aspects of Stress Corrosion Cracking, S.M. Bruemmer, E.I. Meletis, R.H. Jones, W.W. Gerberich, F.P. Ford and R.W. Staehle, Eds., The Minerals, Metals, & Materials Society, Warrendale, 1992, p.3.
- [8] A. Turnbull, Corros. Sci., 34 (1993), 921.
- [9] H.K. Birnbaum, I.M. Robertson, P. Sofronis and D. Teter, Corrosion-Deformation Interactions CDI' 96, T. Magnin, Ed., The Institute of Materials, London, 1997, p.172
- [10] D.O. Sprowls and R.H. Brown, Fundamental Aspects of Stress Corrosion Cracking, R.W. Staehle, Ed., National Association of Corrosion Engineers, Houston, 1969, p.466.
- [11] J.C. Scully, Treatise on Materials Science and Technology, vol. 23, Corrosion: aqueous processes and passive films, J.C. Scully, Ed., Academic Press, 1983, p.103.

- [12] G.M. Scamans, N.J.H. Holroyd and C.D.S. Tuck, Corros. Sci., 27 (1987), 329.
- [13] S.P. Lynch, Metallography, 23 (1989), 147
- [14] S.P. Lynch, Acta metall., 36 (1988), 2639.
- [15] T. Magnin, A. Chambreuil and J.P. Chateau, International Journal of Fracture, 79 (1996), 147.
- [16] T. Magnin, Materials Science Forum, 217-222 (1996), 83.
- [17] E.L. Colvin and M.R. Emptage, New Methods for Corrosion Testing of Aluminum Alloys, ASTM STP 1134, V.S. Agarwala and G.M. Ugiansky, Eds., American Society for Testing and Materials, Philadelphia, 1992, p. 82.
- [18] R.N. Parkins, Stress Corrosion Cracking The Slow Strain-Rate Technique, ASTM STP 665, G.M. Ugiansky and J.H. Payer, Eds., American Society for Testing and Materials, Philadelphia, 1979, p.5.
- [19] R.J. Bucci, R.L. Brazill, D.O. Sprowls, B.M. Ponchel and P.E. Bretz, Corrosion Cracking, Conference Proceedings, V.S. Goel, Ed., American Society for Metals, 1986, p. 267.
- [20] L. Schra and F.F. Groep, Journal of Testing and Evaluation, 21 (1993), 44.
- [21] R. Braun, Corrosion-Deformation Interactions CDI '92, T. Magnin and J.M. Gras, Eds., Les Editions de Physique, Paris, 1993, p. 163.
- [22] R. Braun and H. Buhl, Advanced Aerospace Materials, H. Buhl, Ed., Springer-Verlag, Berlin, 1992, p.296.
- [23] R. Braun, Werkst. Korros., 43 (1992), 453.
- [24] R. Braun, Werkst. Korros., 44 (1993), 73.
- [25] R. Braun, Werkst. Korros., 45 (1994), 255.
- [26] R. Braun, Werkst. Korros., 45 (1994), 369.
- [27] R. Braun, Mater. Sci. Eng., A190 (1995), 143.
- [28] R. Braun, Corrosion, 53 (1997), 467.
- [29] D.A. Lukasak, R.J. Bucci, E.L. Colvin and B.W. Lifka, New Methods for Corrosion Testing of Aluminum Alloys, ASTM STP 1134, V.S. Agarwala and G.M. Ugiansky, Eds., American Society for Testing and Materials, Philadelphia, 1992, p. 101.
- [30] M.O. Speidel, Metall. Trans. A, 6A (1975), 631.
- [31] W. Dietzel and K.-H. Schwalbe, Slow Strain Rate Testing for the Evaluation of Environmentally Induced Cracking: Research and Engineering Applications, ASTM STP 1210, R.D. Kane, Ed., American Society for Testing and Materials, Philadelphia, 1993, p. 134.
- [32] K. Urushino and K. Sugimoto, Corros. Sci., 19 (1979), 225.
- [33] G. Wenzel, G. Knörnschild and H. Kaesche, Werkst. Korros., 42 (1991), 449.
- [34] B. Dubost, J. Bouvaist and M. Reboul, Aluminum Alloys Their Physical and Mechanical Properties, E.A. Starke and T.H. Sanders, Eds., EMAS, Cradley Heath, 1986, p. 1109.
- [35] D.A. Hardwick, M. Taheri, A.W. Thompson and I.M. Bernstein, Metall. Trans. A, 13A (1982), 235.
- [36] F. Zeides and I. Roman, Mater. Sci. Eng., A125 (1990), 21.
- [37] R. Braun and T. Hack, Materials Science Forum, 217-222 (1996), 1635.
- [38] K.M. Gatenby, G.J. Marshall and R.A. Ricks, Aluminum Alloys Their Physical and Mechanical Properties (ICAA4), Vol. I, T.H. Sanders and E.A. Starke, Eds., The Georgia Institute of Technology, Atlanta, 1994, p. 378.
- [39] J.T. Staley, S.C. Byrne, E.L. Colvin and K.P. Kinnear, Materials Science Forum, 217-222 (1996), 1587.
- [40] T.J. Summerson and D.O. Sprowls, Aluminum Alloys Their Physical and Mechanical Properties, E.A. Starke and T.H. Sanders, Eds., EMAS, Cradley Heath, 1986, p. 1575.
- [41] L. Ratke and W. Gruhl, Werkst. Korros., 31 (1980), 768.
- [42] D.A. Hardwick, A.W. Thompson and I.M. Bernstein, Corros. Sci. 28 (1988), 1127.
- [43] B. Grzemba, H. Cordier, W. Gruhl, Aluminium, 63 (1987), 496.
- [44] M.C. Reboul, B. Dubost and M. Lashermes, Corros. Sci., 25 (1985), 999.

- [45] W. Gruhl, Z. Metallkde., 75 (1984), 819.
- [46] B.Cina, U.S. Patent 3856584, Dec. 24, 1974.
- [47] J.J. Thompson, E.S. Tankins and V.S. Agarwala, Materials Performance, 26 (1987), 45
- [48] J.K. Park, Mater. Sci. Eng., A103 (1988), 233.
- [49] M.B. Hall and J.W. Martin, Z. Metallkde., 85 (1994), 134.
- [50] W. Hepples, M.R. Jarrett, J.S. Crompton and N.J.H. Holroyd, Environment-Induced Cracking of Metals, R.P. Gangloff and M.B.Ives, Eds., National Association of Corrosion Engineers, Houston, 1990, p.383.
- [51] M. Talianker and B. Cina, Metall. Trans. A, 20A (1989) 2087.
- [52] W.H. Hunt and J.T. Staley, Light-Weight Alloys for Aerospace Applications, E.W. Lee, E.H. Chia, and N.J. Kim, Eds., The Minerals, Metals & Materials Society, Warrendale, 1989, p.111.
- [53] K. Welpmann, H. Buhl, R. Braun and M. Peters, Journal de Physique, Colloque C3, supplément au n° 9, 48 (1987), C3-677.
- [54] R. Braun, Werkst. Korros. 41 (1990), 547.
- [55] R. Braun, Werkst. Korros. 43 (1992), 106.
- [56] R. Braun and H. Buhl, Aluminium-Lithium, M. Peters and P.-J. Winkler, Eds., DGM, Oberursel, 1992, p. 807.
- [57] R. Braun, Aluminum Alloys Their Physical and Mechanical Properties (ICAA4), Vol.II, T.H. Sanders and E.A. Starke, Eds., The Georgia Institute of Technology, Atlanta, 1994, p. 511.
- [58] M. Doudeau, P. Meyer and D. Constant, AGARD Conference Proceedings 444, Neuilly sur Seine, 1989, paper 2.
- [59] R. Braun, Werkst. Korros. 40 (1989), 661.
- [60] A. Gray, Journal de Physique, Colloque C3, supplément au n° 9, 48 (1987), C3-891.
- [61] R. Braun, Aluminium-Lithium, M. Peters and P.-J. Winkler, Eds., DGM, Oberursel, 1992, p.697.
- [62] R. Braun, Aluminum Alloys Their Physical and Mechanical Properties (ICAA4), Vol.II, T.H. Sanders and E.A. Starke, Eds., The Georgia Institute of Technology, Atlanta, 1994, p. 519.
- [63] R. Braun, AGARD Conference Proceedings 565, Neuilly sur Seine, 1995, paper 2.
- [64] A. Gray, N.J.H. Holroyd, J. White, Aluminum-Lithium Alloys, T.H. Sanders and E.A. Starke, MCE Publications, Birmingham, 1989, p. 1175.
- [65] A.K. Vasudevan, J. Liu, R.E. Ricker, Environmental Degradation of Engineering Materials III, Pennsylvania State University, 1987, p. 321.
- [66] J.G. Craig, R.C. Newman, M.R. Jarrett, N.J.H. Holroyd, Journal de Physique, Colloque C3, supplément au n° 9, 48 (1987), p. 825.
- [67] R.G. Buchheit, J.P. Moran, F.D. Wall, G.E. Stoner, Parkins Symposium on Fundamental Aspects of Stress Corrosion Cracking, S.M. Bruemmer, E.I. Meletis, R.H. Jones, W.W. Gerberich, F.P. Ford and R.W. Staehle, Eds., The Minerals, Metals, & Materials Society, Warrendale, 1992, p. 141.
- [68] J.P. Moran, R.G. Buchheit, G.E. Stoner, Parkins Symposium on Fundamental Aspects of Stress Corrosion Cracking, S.M. Bruemmer, E.I. Meletis, R.H. Jones, W.W. Gerberich, F.P. Ford and R.W. Staehle, Eds., The Minerals, Metals, & Materials Society, Warrendale, 1992, p. 159.
- [69] F.D. Wall and G.E. Stoner, Corros. Sci., 39 (1997), 835.
- [70] E.I. Meletis and W. Huang, Mater. Sci. Eng., A148 (1991), 197.
- [71] R. Balasubramaniam, D.J. Duquette, K. Rajan, Acta metall. mater., 39 (1991), 2597.
- [72] C. Thakur and R. Balasubramaniam, Acta mater., 45 (1997), 1323.
- [73] R. Balasubramaniam, D.J. Duquette, K. Rajan, Acta metall. mater., 39 (1991), 2607.
- [74] V. Komisarov, M. Talianker, B. Cina, Mater. Sci. Eng., A221 (1996), 113.

