Environment-Induced Cracking of High-Strength Al-Zn-Mg-Cu Aluminum Alloys - Past, Present and Future

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ABSTRACT

Environment induced cracking (EIC) during commercial use of aluminum alloys started over 125 years ago (mid-1890's), some 45 years earlier than previously documented, with earliest failures for Al-Zn-Mg-Cu, 7xxx series alloys occurring a decade later. Needs for lighter, thicker and stronger alloy products, firstly driven by WW1 and WW2 militaristic requirements and subsequently by relentless demands from modern aircraft industry designers, resulted in major in-service EIC in commercial high strength Al-Zn-Mg-Cu alloys in the US and UK during the 1950's, 1960's and 1970's. These were avoidable had research findings from France, Germany and Japan from the 1930's and 1940's been implemented. Unprecedented US Government R&D funding during the late 1960's, 1970's and early 1980's led to AA7050 and similar alloys, that essentially eliminated EIC issues during commercial usage for several decades. EIC assessment for the following 'new-generation' high-strength alloys relied totally on standard ASTM Test Methods, incapable of providing data directly relatable to the service conditions. Although EIC service issues for the latest generation of 7xxx series alloys remains manageable, the premature appearance of EIC requires a quantitative understanding of EIC initiation under environmental and mechanical conditions directly relatable to intended use, to prevent un-expected failures for future alloys. Directions for future high-strength 7xxx series aluminum alloy development and EIC assessment to provide quantitative date relatable to service conditions and input for structural design and for service life prediction are discussed.

KEY WORDS: Al-Zn-Mg-Cu aluminum alloys, alloy development history, environment induced cracking, stress corrosion cracking, service performance and laboratory test prediction, next generation high strength alloys.

INTRODUCTION

The historic reviews of the environment-induced cracking (EIC) of metals over the last twenty years have paid limited attention to aluminum alloys [1-3]. Hence, we have reviewed the history of EIC in commercial Al-Zn-Mg-Cu high-strength 7xxx series aluminum alloys, including un-cited instances from well before 1940, and have developed this overview for this Special Issue of Corrosion on 'Environment-Induced Crack Initiation and Early Stages of Crack Growth in Aluminum Alloys'.

The lack of EIC references from aluminum alloy usage pre-1940 results from the use of alternate descriptors, including: 'Spontaneous disintegration' [4,5], 'Brittleness' [6,7], 'Season Cracking of Aluminium' [8-12] (due to the apparent similarities to season cracking of brass [13]), 'Intergranular fracture under prolonged application of stress' [14-16], 'Stress cracking' [17,18], and 'Acceleration of corrosion under stress' [18].

Rosenhain [16] in 1921, declared it inappropriate to collectively categorize the cracking phenomena in metals as 'season cracking', as was common in England at the time, or 'Stress Cracking' as was also used in the US. From the early 1930's, researchers in Germany consistently used the term 'Spannungskorrosion' (Stress Corrosion) to describe EIC in aluminum alloys [19-26]. Webber's [17] depiction of a 'peculiar' cracking mode promoting structural failure in high zinc containing Al-Zn-Mg-Cu alloys exposed to corrosive conditions while under high stress, as 'stress cracking' in 1933 was further complicated in 1941 when Nock [18] noted that these alloys were also potentially susceptibility to another cracking phenomenon he called 'Accelerated Corrosion under Stress'. Meanwhile, in Japan during the late 1930's, Igarashi and Kithara having observed EIC in high-zinc content (8-10 wt.%) Al-Zn-Mg-Cu alloys also used the term 'Season Cracking' adding that the cracking could occur in water vapour [8]. In 1940 Dix [27] advocated use of the terms 'stress corrosion' or 'stress corrosion cracking (SCC)' to describe the spontaneous failure of metals under the combined action of high stress and corrosion, and during the 1944 ASTM/AIME Symposium on the Stress Corrosion of Metals held in Philadelphia proposed these terms should supersede 'season cracking' [28].Wassermann [22] also confirmed the early Japanese findings that water vapor alone promoted rapid crack growth in Al-Zn-Mg-Cu alloys. He also showed that a lower zinc containing, copper-free, Al-6Zn-3Mg alloy, could initiate in vacuum due to retained moisture within surface oxide layers. In addition, researches in France proposed that sub-critical intergranular cracking in naturally-aged aluminum-zinc solid solutions, with and without magnesium and other additions, such as copper, silver, chromium, zirconium, manganese, iron and silicon was a mechanically driven process, where any associated intergranular corrosion was resultant as opposed to causal [29].

We include all previous descriptors in our broad definition of the EIC phenomena, along with a more recent variant, hydrogen-environmentally-assisted-cracking (HEAC), where the role of anodic dissolution during crack initiation and/or propagation may be simply the provision of a local hydrogen generation source. Few examples of EIC in aluminum alloys are quoted in the literature pre-1940, or following the 1944 ASTM/AIME Symposium [28] in the later major reviews, e.g., Haynie and Boyd 1966 [30], Sprowls and Brown, 1969 [31], Speidel, 1975 [32], Holroyd, 1989 [33], Burleigh, 1991 [34] or Zhou et al, 2021 [35].

Our overview of the initiation and propagation of EIC of in aluminum alloys has focused on Al-Zn-Mg-Cu (7xxx series) alloys because most EIC issues occurring during commercial usage involve these alloys, with instances starting around 1910 and then consistently through several generations of commercial alloys, including today's 3rd Generation of high-strength 7xxx series alloys.

EIC IN EARLY COMMERCIAL ALUMINUM ALLOYS, PRE-MID-1940'S

There are examples of EIC in unalloyed aluminum [7, 36-39] and aluminum alloys [6,7,12,14,15,27,36,39-44] from the mid-1890's onwards. The earliest of these are contemporaneous with Roberts-Austin's 1886 ('Uri Geller' [45] style) demonstration of the sudden local fracture of stressed hard-drawn 13-carat gold (Au-33.3Cu-12.5Ag) thick-wire, two minutes after local exposure to a small volume of ferric chloride [5]. The earliest documented service failures in commercially pure aluminum was in 1894 [36,37] and in an aluminum alloy (Al-2Cu) in 1899 [40]. The EIC of aluminum alloys during commercial usage has at least 125 years of history.

2.1 Early Aluminum EIC Failures

Gavey [38] in 1907 found that when 8ft lengths of 3.2 mm diameter aluminum telegraph-wire (UTS 195 MPa) were exposed to humid air under a range of stresses using dead-weight loading that failure, plotted here in Figure 1 as a function of the initial applied stress, resulted from sudden 'brittle' premature fracture with no significant evidence of corrosion, creep or overloading. These fractures closely resembled those found within a few months of service of similar telegraph wire in the English Potteries [38] and in North Africa [37].

The absence in these failures over the next few years (Gavey [38] and Wilson [41,42]) was probably due to improved 'material cleanliness' and 'surface quality control' during manufacture [42,46]. The early cracking issues were more likely due to solid-metal embrittlement associated with the high lead (Pb) and bismuth (Bi) 'tramp' element concentrations, which dropped following the aluminum industries adoption of an 'electrolytic', as opposed to a 'chemical' manufacturing process route [47].

2.2 The First Aluminum Alloys EIC failures

In 1899, single-strand Al-2 wt. % Cu hard-drawn wire used for power-transmission lines in the USA suffered frequent and sudden catastrophic breakages [40]. These failures were later shown to readily initiate and propagate in Al-2% Cu alloy wires exposed to relatively benign environments [41]. Experimental evidence of EIC in an Al-9.4Zn-0.39Mg-0.32Cu alloy (as used in many of the early German Zeppelin Airship's [6]) followed similar service failures of overhead power lines in the Ore Mountain region of Germany [39] as reported by Cohn in 1913 [7]. Cohn showed that extruded sections of a high-zinc containing aluminum alloy suffered embrittlement when tensile samples pre-exposed to water for short periods at 70 ^{O}C. were Strength and ductility losses increased with longer pre-exposure times, Figure 2.

Cohn's contribution in 1913, partially recognized in 1945 [48], demonstrated the use of high zinc containing alloys in structural applications before WW1, that aluminum alloys were potentially susceptible to hydrogen embrittlement and that EIC was involved in the failure of these alloys used in early Zeppelin Airships [6,43,44].

Rosenhain and Archbutt [14] in 1919 and Rosenhain et al [15] and Rosenhain [16] in 1921 reported mechanical property degradation for several high-zinc containing age-hardened aluminum alloys, including Al-18Zn-2.5Cu-0.35Mg-0.35Mn alloy (UTS 534 MPa, Yield Stress 473 MPa), held under tensile stress while exposed to sea-water or dilute saline solutions, such a tap water. The resultant cracking phenomenon called 'Intercrystalline Fracture under prolonged application of Stress' [14] was likened to the 'Season Cracking' of brass [8,13]. Then in 1939 Grogan and Pleasance [49] applied constant-load tests to similar alloys,(including Al-Zn binary alloys in laboratory air and 5% NaCl, and found reduced susceptibility with lower quench rates after solution-heat-treatment (SHT) and increased susceptibility with exposure to more aggressive test environments, Figure 3. They described this EIC behavior as 'Inter-crystalline Cracking'. French research during the late 1930's and early 1940's on the deformation and fracture of naturally aged aluminum-zinc alloys, found that intergranular decohesion could initiate under strain in vacuum when fully isolated from the test environment. This lead to the proposition that intergranular cracking in these high-Zn alloys was a mechanically driven process [29].

In the US Al-Zn-Mg-Cu alloy development started in during the late 1920's [50] with experimental alloy compositions, X70S and X71S for sheet, extruded and forged products established in 1931-32 (see Table 1) although these alloys were never commercialized due to their high EIC susceptibility. Alloy development intensified during the 1930's, stimulated by the military need for higher strength and the announcement of the high strength wrought alloy, DTD 363 in the UK in 1937, Table 1, marketed under the trade name Hiduminium RR77. This alloy (4-6%Zn, 2-4%Mg, 1-3%Cu, Mn <1%) developed by High Duty Alloys when water quenched and aged exhibited good mechanical properties (UTS 510-587 MPa with 10-16% elongation) [51]. However, this alloy was found to be prone to intergranular cracking stimulated by quenched-in residual stresses even at low operational stresses [52].

Al-Zn-Mg-Cu alloy development in Japan, starting in 1935, resulted in patent applications for high-strength aluminum alloys containing up to 14% Zn, 2-5% Mg, and 1% Cu that had maximum strengths of up to 560 MPa with a 10% elongation [53]. Igarashi and Kitahara [8] based on studies at Sumitomo Light Metals restricted the claimed chemical compositional range to 8-10% Zn, 1.5% Mg, 2.5% Cu, 0.25% Cr, and 0.5-1.5% Mn, where suitable heat-treatment could provide enhance resistance to 'Season Cracking', along with excellent forgeability and maximum tensile strengths up to 598 MPa with around 14% elongation. Alloy compositions designated as Extra Special Duralumin (ESD) were patented [9] and during 1938 introduced into the wings of the Japanese 'Zero Fighter' plane [10,54]. 'Season Cracking' was used in Japan to describe EIC until at least the mid 1940's [10,11].

Al-Zn-Mg-Cu alloys were rejected for structural use in the US Navy Zeppelin's [50] due to EIC concerns. Webber's 1933 US patent [17] disclosed EIC issues, termed 'Stress Cracking' for Al-Zn-Mg-Cu alloy compositions containing 7-15% zinc, 0.2 to 2.5% magnesium and 0.5% to 2.5 wt.% copper. In mid-1938, following extensive laboratory testing, Alcoa selected an alloy composition, X74S (see Table 1) that was considered to provide an optimum balance of strength, SCC resistance and mechanical properties. Dix [27] in 1940 reported EIC problems within a few months few X74S sheet-based components due to to plastic deformation and fit-up stresses. This ended the supply of X74S, and initiated several years of extensive R&D efforts to establish the influence of small addition of high-melting point element (Cr, Zr, V, Mo and W) additions, and the development of more predictive SCC test procedures [50].

Nock [18] in 1941 confirmed Webber's [17] claim that high-zinc containing Al-Zn-Mg-Cu alloys could be made more resistant to 'Stress Cracking' and also identified potential susceptibility to another cracking phenomenon, he described as 'Accelerated Corrosion under Stress', which closely resembled the 'Inter-crystalline Cracking', described by Grogan and Pleasance [49]. By 1943, Alcoa, based on analysis of Al-Zn-Mg-Cu Extra Super Duralumin (ESD) alloy extrusions [51,52] from the wings of the Japanese Zero Fighter planes [54] and Japanese Patents [9], coupled with extensive in-house testing and plant trials, showed that replacement of manganese in X74S with 0.2 to 0.35% Cr could significantly enhance EIC performance. After the alloy's Zn, Mg and Cu levels were slightly increased alloy 75S was created, essentially a derivative of ESD [55-57] (see Table 1) which became AA7075. During its early usage in military applications in the T6 temper, as sheet and then as extrusions and forgings, it became obvious that the chromium addition had a negative impact due to quench sensitivity on the maximum strength for thicker sections [50]. This restricted product section thicknesses to below 75 mm and the alloy also had poor short-transverse SCC resistance, even in moderately thick sections [50].

Table 1. Chemical compositions and typical mechanical properties of early Al-Zn-Mg-Cu Alloys.

Alloy #	Year	Zn	Mg	Cu	Mn	Cr	UTS (MPa)	YS (MPa)	% Elong	Envisaged Product*
X70S	1931	10.0	0.4	1.0	0.7	--	400	310	18	F
X71S	1932	10.0	2.0	2.0	1.0	--	585	560	10	S, E
XB71S	1932	9.0	2.7	2.0	1.0	--	595	565	10	S
X73S	1935	5.2	0.9	0.5	--	--	370	290	20	F
DTD 363A	1937	5.5	2.8	1.3	0.7	0.5	586	510	5	F, E

ESD	1937	8.0	1.5	2.0	0.5	0.2	585	--	15	E, S
X7C70S	1938	8.0	1.1	0.5	0.8	--	480	420	17	F
X74S	1939	5.2	2.1	1.5	0.4	--	510	440	12	S
75S	1943	5.6	2.5	1.6	--	0.25	570	500	11	S, P, F, E

*F = Forging, S = Sheet, P = Plate, E = Extrusion

EIC IN 1ST GENERATION COMMERCIAL 7xxx Series ALUNIMUM ALLOYS, MID-1940'S TO MID-1960'S

WW2 had a major impact on the aluminum industry's global development:
a) The demand for aluminum in the US, grew from 130,000 tons in 1938 to 790,000 tons in 1944, and the US Government mandated that the Reynolds Metals Company and the Kaiser Aluminum and Chemical Corporation should manufacture aluminum alloys to supplement Alcoa's production capability. This significantly modified Alcoa's 'monopolist' position in the marketplace [58],
b) Following WW2 global aluminum over-production, the aluminum industry was forced to develop new high-volume market opportunities [59],
c) EIC issues became sufficiently recognized to justify two full-sessions at the International Symposium on the Stress-Corrosion Cracking of Metals, held in Philadelphia in 1944. In two previous conferences, discussion was restricted to brass in 1913 [60] and reference to aluminum in 1921 was limited to comments Rosenhain made during his opening address [16].

The recovery and global growth of the Aluminum Industry following WW2 is well documented [61-63] and the history of aluminum-magnesium based marine alloys has recently been reviewed [64-66].

Al-Zn-Mg alloy development in Germany differed from that in UK, US or Japan [67, 68], with compositions that had a minimal or zero copper content, due to its limited availability in Germany, despite their earlier negative experience with higher zinc-containing alloys [6,7,39,43,44]. The favored alloy compositions in Germany during WW2 were: Fliegwerkstoff (Aircraft Material) 3415 and 3425, with nominal compositions based on a 4.5% Zn, 3% Mg with additions of Cr, Mn and V. Table 2, shows the mechanical properties and the dependence on alloy composition, product form, temper and level of cold work. Usage as forgings, extrusions and unclad sheet was restricted during the latter part of WW2 [67,68] by a limited availability of sufficiently high-grade aluminum [67] and EIC issues.

Table 2: Chemical compositions and peak-aged mechanical properties of 1st Generation Al-Zn-Mg-Cu Alloys.

Alloy #	Year		Zn	Mg	Cu	Mn	Cr	other	UTS	YS	% Elong	Product*
FLW 3415	1942	Germany	4.5-5.5	2.0-2.8	0.5	0.2-0.3	0.2	0.08 V	451	354	3-8	S, E, W
FLW 3425 (HY43)	1942	Germany	4.0-4.5	3-3.5	--	0.2-0.6	0.15-0.25		--	--	--	E
DTD363 (RR77)	1937	UK	4.5-6.5	2.0-3.5	1.1-1.5	0.25-1.0	0.5		586	510	5	S, F, E
DTD683		UK	5.2-6.2	2.2-3.20	0.3-0.7	0.18-0.7	0.08-0.25		541	463	7	S, F, E
AA7079§	1954	USA	3.8-4.8	2.9 - 3.7	0.4 -0.8	0.1-0.3	0.10-0.25		540	470	14	S, P, F, E
X7080-T7	1965	USA	5.0-7.0	1.5-3.0	0.5-1.5	0.1-0.7	0.25		448	393	6	F

AA7075	1954	USA	5.1-6.1	2.1-2.9	1.2-2.0	0.3	0.18-0.4		570	500	11	S, P, F, E
AZ74		Germany	5.5-6.5	2.1-2.5	0.7-1.0	<0.1	0.15-0.25	0.3-0.5 Ag	590	539	9.8	F, P, E
AA7178	1951	USA	6.3-7.3	2.4-3.1	1.6-2.4	0.3	0.18-0.28		600	540	10	S, P, E
AA7001	1955	USA	6.8-8.0	2.6-3.4	1.6-2.6	0.2	0.18-0.35		675	625	9	E

*F = Forging, S = Sheet, P = Plate, E = Extrusion W = Wire

§ AA7079 added to 'Inactive' alloy List March 1989

Following WW2, aluminum had almost totally replaced wood in aeroplane structures although the fastest and most successful British WW2 fighter plane, the 'Mosquito', had been constructed entirely of wood [69].

Sutton in 1948, stated that "A leading development in the aluminium alloy field is the very high-strength type of alloy containing aluminium, zinc, magnesium and usually a small amount of copper" and "Alloys of this class are coming into use for primary aircraft structures in the US and the British aircraft industries" [68].

Use of the high strength Al-Zn-Mg-Cu alloy, DTD 683 (next generation from DTD 363) (see Table 2) in several UK military aircraft began during the late 1940's and grew during the 1950's to include application in several UK aircraft manufactured by Vickers, including the Varsity, Valiant and Viscount. However, the early service experience of the Viscount involved numerous EIC failures in forgings and inter-rivet cracking of extrusions with minimal evidence of any associated corrosion. This according to James [70] led to 'stress-cracking' being preferred to 'stress corrosion cracking' as a descriptive term. EIC of the DTD 683 alloy was detected in many aircraft structures during the 1950's [71] including the intergranular cracking (referenced as 'Crystalline Corrosion') [52,71] found in 1963 in the rear spar attachment forgings in the wings of the British high-altitude jet bomber the Vickers Valiant [70,72,73] that was designed to carry nuclear weapons. These service experiences remained a concern over several decades in the UK [70].

The Metal Division of Imperial Chemical Industries (ICI), in Birmingham, England began their major Al-Zn-Mg-Cu alloy development program during the late 1940's. They explored the mechanical properties and corrosion resistance (with and without applied stress) for alloys containing up to 12% Zn, 3.5% Mg and 3% Cu. The effects of Zn, Mg, Cu, Cr, Mn, Fe and Si additions were assessed for each elemental addition. A summary report was published in 1951 [74] and in 1956-57 Chadwick et al [75] provided their EIC results. Turner [76], Champion [77], Doyle [78] and Farmery [79], all questioned the relevance of EIC data derived from sheet material without the influence of grain size and shape of thick products, e.g., extrusions, plate or forgings, loaded in the short-transverse direction, known to be significantly more prone to EIC [31-34].

The Chadwick et al [75] EIC studies involved: Commercially cast, rolled and heat-treated, 1.27 mm thick sheet material with alloys cast using two purity bases: high-purity (HP) with Fe (0.013 ± 0.006), Si (0.025 ± 0.015) and commercial purity (CP) with Fe (0.185 ± 0.085), Si (0.133 ± 0.026). Custom built constant-load test equipment was designed to tightly control the mechanical and environmental test conditions for smooth tensile test specimens exposed at 30°C and sprayed three times a day with 3% NaCl, while maintained at 85% RH.

Chadwick et al's findings [75] for the influence of manganese and/or chromium additions on the EIC for the alloy composition, Al-7.2Zn-2.2Mg with and without 1.25Cu has a zinc-content well exceeding maximum levels of both 1st Generation (e.g. AA7075) and 2nd Generation (e.g. AA7050) alloys is representative of the 3rd Generation Al-Zn-Mg-Cu alloys commercialized some 50 years later [80,81].Constant load EIC failure times for Al-7.2Zn-2.2Mg base alloys, with and without 1.25% copper and various Mn, Cr or (Mn + Cr) additions after heat treatment for 18 hours at 125°C are shown in Figures 4a and b, for alloys cast on both the HP and CP base. The atypical non-overlapping stress-time curves obtained for individual alloy compositions during constant load EIC testing confirm the excellent control of the mechanical and environmental conditions during testing.

Replotting the Chadwick et al [75] constant-load failure time data in terms of the reciprocal square root of alloy grain size to normalize the EIC data with respect to grain size separates the observed EIC behavior into three distinct compositional groupings, as shown in Figure 5.

By 1950 AA7075-T6 alloy was 20% of Alcoa's total shipment of heat-treatable aircraft products [59]. However, peak-aged AA7075-T6 has inadequate EIC resistance in the short-transverse loading direction [50,82,83]. Smooth tensile samples in 0.6M NaCl under alternate immersion conditions showed EIC failures at stresses as low as 70 MPa [82] at only 15% of the yield stress. Alcoa introduced a duplex heat-treatment process, -T73 [84] which effectively eliminated EIC issues for AA7075 sheet material, although this was at the expense of a 15% strength loss penalty. This treatment underpinned alloy development programs for the next-generation higher-strength commercial Al-Zn-Mg-Cu alloys for sheet and thicker products.

The aircraft industry continued using AA7075-T73 in significant quantities [59], although the demand for weight-reduction led Alcoa to introduce AA7178-T6 in 1951 and AA7001 in 1955 with slightly higher Zn, Mg and Cu additions to provide strength advantages of 35 and 50 MPa, respectively, over AA7075-T6 (see Table 2). AA7178-T6 was used as sheet and extrusions in several commercial and military aircraft [83]. However its use was restricted by EIC service issues and AA7001's demise was due to inadequate toughness and damage tolerance. Alcoa then introduced the alloy, AA7079 (Al-4.3Zn-3.3Mg-0.6Cu-0.2Mn-0.2Cr) in 1954, that was similar to a German WW2 forging alloy [78].

Mechanical test data and results for AA7079-T6 smooth tensile tests specimens subjected to alternate immersion to 0.6M NaCl suggested it would provide higher short-transverse ductility and strength properties in thick sections than any other commercial aluminum alloy, with an improved EIC performance relative to AA7075-T6, with cracking rarely initiating at stresses below 138 MPa [85].

AA7079 was specified for aircraft designs during the late 1950's and early 1960's, and it became the most used alloy for large high-strength forgings in the US [85]. Unfortunately, EIC service failures in AA7079-T6 forgings and thick extrusions started during the late 1950's and this rapidly escalated into numerous failures during the 1960's [32,83,85]. This created major issues for the US aluminum industry and its customers, as there was no awareness of the pre-WW2 experiences in Germany of EIC with similar aluminum alloy compositions.

The next alloy developments were a slight increase of the Zn and Mg content and replacement of the Cr addition with an increased Mn content to reduce quench-sensitivity. This resulted in the experimental alloy, X7080-T7, with a nominal composition Al-6Zn-2.5Mg-1%Cu with laboratory test data, suggesting a

EIC resistance at high stress for smooth tensile specimens under standard alternate immersion 0.6M NaCl testing. Alcoa hesitated launching X7080-T7, not wanting a repeat of the AA7079 experience, and following premature EIC test failures under outdoor exposure conditions withdrew the alloy's registration [83].

Lifka and Sprowls [85] in 1966 during an ASTM conference on 'Stress Corrosion Testing' suggested that the choice of EIC test environment used during alloy development had created an optimistic expectation that AA7079 would outperform AA7075-T6 during commercial usage. This was demonstrated with EIC data for AA7079-T6 showing a reduced EIC resistance in less aggressive environments (industrial or marine atmosphere) than observed in the saline environment used during standard EIC testing, and the reverse trend for AA7075-T6, Figure 6. Lifka and Sprowls successfully argued the case for using an 'alternate-immersion' saline environment for all higher-strength aluminum alloys, other than AA7079 and low copper-containing alloys, e.g., AA7039, which were called a 'special case' requiring an alternate ASTM test method, subsequently developed as ASTM G103-97 [86].

EIC issues with AA7079-T6 and X7080-T7 could have been avoided had alloy developers been aware of German [20-26], French [29] and Japanese [8,10] publications and the work of Chadwick et al [75] (Figures 4 and 5) that showed the replacement of chromium with manganese could not provide alloys with an adequate EIC performance [63].

EIC IN 2ND GENERATION COMMERCIAL ALUMINUM ALLOYS, MID-1960'S TO EARLY-1990'S

The many EIC issues in aircraft structures during the 1960's and early 1970's [32,82] led to unprecedented levels of R&D funding from US Government Agencies during the mid-1960's, through the 1970's and into the early 1980's for the aluminum industry, aircraft manufactures and various research laboratories to study and develop commercial high strength aluminum alloys, focusing on thick-gauge forgings and extrusions.
A compilation of US Government Agency funded R&D programs with a significant EIC component is provided in the Appendix. These programs were designed to address several alloy property requirements, including EIC. The aspirational objectives targeting EIC performance were to fully characterize the phenomena [87-96], to provide reliable accelerated test methods [97-102] and to establish chemical compositions and manufacturing process routes to provide adequate EIC resistance under the expected service conditions [103-111].

The specific targets were:
a) Longitudinal tensile yield stress > 496 MPa for 76 mm thick plate and > 434 MPa for 203 mm thick forgings,
b) Short-transverse EIC threshold stress > 241 MPa in an alternate immersion salt solution test,
c) Fracture Toughness, $K_{IC} > 38.5\ MNm^{-3/2}$, and
d) Minimum fatigue strength equivalent to AA7075-T6.

Experimental work conducted at Boeing in 1967 [93] suggested aluminum alloys with: Al-(5.9-6.9) Zn, (2.2-2.9) Mg, (0.7-1.5) Cu, (0.10-0.25), (0.05-0.15) Zr, Fe <0.20, Si <0.2, Mn <0.05, Cr<0.1 should match the target properties [103,104] and this was reflected in alloy compositions subsequently developed by others (see Table 3).

Table 3: Chemical compositions and typical mechanical properties of 2nd Generation Al-Zn-Mg-Cu Alloys for various tempers.

Alloy # Year	Zn	Mg	Cu	Mn	Cr	Zr	UTS (MPa)	YS (MPa)	% Elong	Fracture Toughness** K_{IC} ($MNm^{-3/2}$)	Product*
X-7080[§] (1965)	5.0-7.0	1.5-3.0	0.5-1.5	0.1-0.7	0.25	--	448	393	6	25	F
7049-T73 (1968)	7.2-8.2	2.0-2.9	1.2-1.9	0.20	0.10-0.22	--	540	470	11	19-25	F,E
7475-T6 (1969)	5.2-6.2	1.9-2.6	1.2-1.9	0.06	0.18-0.25	--	560	490	12	27 - 32	S,P,E
7050-T74 (1971)	5.7-6.7	1.9-2.6	2.0-2.6	0.10	0.04	0.08-0.15	530	460	11	21-29	P,F,E
7010-T6 (1975)	5.7-6.7	2.1-2.6	1.5-2.0	0.10	0.05	0.10-0.16	560	530	10	20-23	P, F
7150-T6 (1978)	5.9-6.9	2.0-2.7	1.9-2.5	0.10	0.04	0.08-0.15	613	575	11	27	P,F,E

*F = Forging, S = Sheet, P = Plate, E = Extrusion

** Short Transverse K_{IC} for thick plate material

[§]Experimental Alloy Registration Application Withdrawn

These detailed studies undertaken at Alcoa and Boeing during the mid- and late-1960's providing an understanding how the toughness and tearing resistance of wrought high-strength aluminum alloys [112-114] led to the progressive reduction of the maximum allowable iron and silicon content over the following years, Table 4.

Table 4. Maximum Iron and Silicon contents in Al-Zn-Mg-Cu 7xxx series Aluminum alloys.

Year	Alloy	Maximum % wt.	
		Fe	Si
1954	7075	0.5	0.5
1971	7050	0.15	0.12
2002	7085	0.08	0.06

Alcoa initially focused on mechanistic studies [89, 91, 92, 96] (1963-1968) and EIC test method development [98,101,102] (1968 to 1982). Having evaluated the influence of various minor elemental additions (Zr, Mn, Cr, Ag, V and Ni) on the relative EIC susceptibility [96], Alcoa realized achievement of a short-transverse EIC threshold stress > 241 MPa in an alternate immersion salt solution test required a slightly overaged temper, as opposed to a -T6 temper [96] and concentrated on the development of alloy AA7050. Details of the R&D programs are provided in a series of detailed reports [106,108-111], summarized by Staley [83] (see Appendix).

During its development AA7050 was subjected to many hundreds of EIC tests [50,106,108,109-111], significantly more than for any other commercial aluminum alloy in history, to ensure the EIC performance during commercial usage would differ from AA7079, AA7075-T6 and DTD 683. Staley applied Probit statistical numerical analysis [106] to ASTM G47 test data for several alloys overaged to a range of short transverse yield stresses and developed the concept of the 'critical yield stress', below which failure does not occur [106]. EIC test data showing 'critical yield stress' estimations for AA7049-

T7X loaded to a stress of 172 MPa after 30 and 84 days exposure are provided in Figure 7. The 'critical yield stress' for AA7049 and AA7050-T76X at various applied stresses, Figure 8, showed that differentiation in EIC resistance using ASTM G47 testing in 0.6M NaCl requires 84 days as opposed to the more commonly used 30 days [106].

Staley's analysis [106] showed that the stress corrosion performance of AA7050 at a given strength level would exceed the performance of other similar alloys, despite it not always ranking highest in test data from conventional 30-day alternate immersion testing. These findings question the use of the current ASTM G47 test method as the 'go/no-go' assessment of EIC resistance. The critical short-transverse yield stress data for AA7050, AA7049 and other alloys after exposure to outdoor conditions in New Kensington, Pittsburgh for 365 and 500 days, provided further evidence of AA7050's superior EIC resistance at higher stress levels [106].

Staley also provided detailed statistical analysis of alloy compositions that revealed a subtle dependence on alloy composition [115], that was associated with S-phase precipitation, now known to degrade AA7050's EIC performance [80,116].

Government Funded programs using pre-cracked DCB test specimens for a range of 7xxx series alloys exposed to 0.6M NaCl [98,117], mainly reported EIC data as crack growth rate as a function of the imposed stress intensity factor, K. The published data for commercial AA7050 [118,119] and AA7075 [80] thick plate in various tempers, Figure 9, demonstrates the aluminum industries extensive successful R&D effort (alloy composition and heat treatment practice developments) to provide high strength 2nd Generation AA7xxx alloys, confirmed by many years of service without issue [63].

EIC IN 3RD GENERATION COMMERCIAL ALUMINUM ALLOYS, EARLY 1990'S TO 2022

In the 1990's the aviation industry focused on heavier payloads and extended flight ranges and the design and manufacture of significantly larger aircraft. Hence, the aluminum industry was again under pressure to develop higher strength EIC resistant alloys to retain competitiveness with other candidate aerospace materials, such as non-metallic composites. Aircraft designers employed damage-tolerant designs, 'fail-safe' structural concepts and regulated periodic inspection together with the selection of specific aluminum alloy/tempers for individual parts. For instance, the selection of AA7055-T77 provided 10% improvement in compressive yield stress over AA7050 [83,120] was an ideal choice for upper wing skins. It was not a suitable choice for thicker sections used in wing spars that required a less quench-sensitive alloy.

The use of thick aluminum alloy plates and forgings for the fabrication of wing upper spar, web and lower spars structures from a single section, referred to as 'integrated-spars' was necessary for the required for weight saving. The specific challenge for the aluminum industry was to provide thick-gauged aluminum alloy products with low quench-sensitivity, mechanical property variation and EIC and exfoliation susceptibility.

This required a compromise of the localized corrosion and EIC performance requirements for 3rd Generation 7xxx series alloys (e.g., AA7085, AA7449, AA7037) relative to 2nd Generation alloys, such as AA7050. This is shown from a comparison of the stress below which EIC failure does not occur, $\sigma_{EIC,}$ the stress intensity factor below which cracks propagate at sufficiently slow rates, K_{IEIC} and the exfoliation resistance with those typical of earlier alloys, as provided by Sprowls et al in 1973 [98] and Hunt et al in 1993 [120].

Table 5: Experienced based EIC susceptibility ratings for aluminum alloys suggested by Sprowls et al in 1973, using smooth and pre-crack test specimen test data [98].

EIC Rating Susceptibility	EIC Threshold		EIC K-Insensitive Growth Rate (m/s)	Typical Alloy	Exfoliation Rating (ASTM G34)
	б$_{EIC}$ (MPa) % Yield Stress (ASTM G47)	K_{IEIC} % K_{IC} (DCB)			
A– Very Low	>90	>95	< 7×10^{-11}	6061-T6	P
B– Low	>75	>80	7×10^{-11} to 3×10^{-10}	7075-T73, 7050-T73	P/EA
C–Moderate	>40	>50	3×10^{-10} to 3×10^{-9}	7075-T76, 7050-T76	EA/EB
D-Appreciable	<40	<50	> 3×10^{-9}	7055-T77, 7085-T76	EB/EC

Table 6: 1990's EIC and exfoliation resistance rating for AA7075, AA7050 and AA7150 in T73, T74, T76 and T6 tempers, provided by Hunt et al [120].

Alloy Temper	б$_{EIC}$, EIC Stress Threshold (MPa)	Exfoliation Requirement (EXCO Test ASTM G34-01) [121]
-T73	≥ 290	P – pitting; little or no exfoliation
-T74	≥ 241	EA – Slight or superficial exfoliation
-T76	≥ 121 – 172	EB – moderate – more than EA
-T6	No Standard (maybe <7)	No Standard – typically EC to ED – more than EB

The EIC and exfoliation susceptibility ratings for the 3rd Generation alloys match the lowest category, 'D – Appreciable' of the 1973 criteria, Table 5,and for the -T76 type tempers just meet the 1990's ratings, Table 6, with the exfoliation Corrosion ratings [121] downgraded from EA to EB and in some cases as low as EC.

The main factor driving the compromise on EIC and Exfoliation performance was the reduced effectiveness of over-aging, used previously for 2nd Generation alloys [118,122,123]. Such treatments were progressively less effective for 3rd Generation alloys as the Zn concentration increased above 7.5 wt%, and became almost ineffective when Zn contents exceeded around 9.0 wt%. This implies a process other than the manipulation of grain-boundary precipitate copper content (generally accepted as how overaging improves EIC susceptibility [124]), control the EIC susceptibility of these higher Zn content alloys.

The development of 3rd Generation 7xxx series alloys was mainly focused on quench sensitivity minimization [125-127]. EIC and localized corrosion evaluations were limited to standard ASTM EIC, exfoliation and other localized corrosion tests [121,128,129] and it was assumed that the results from these tests were relatable to expected service performance during use in structurally demanding engineering applications. The alloys with reduced quench-sensitivity in thick sections relative to AA7050, emerged during the early 2000's, e.g., AA7085 [125,127], with increased Zn and reduced Mg and Cu contents that led to 'excess Cu', as opposed to the 'excess Mg' alloys of the earlier generation alloys, Table 7, where the 'excess' Cu and Mg levels are calculated using stoichiometric relationships defined previously [80].

Table 7: 2nd and 3rd Generation Al-Zn-Mg-Cu alloys Mid-Range Zn, Mg and Cu contents and calculated % excess %wt. of Cu or Mg.

Alloy (Registration, yr)	Mid-Range %wt			% wt Excess	
	Zn	Mg	Cu	Mg	Cu
Mid-1950's – 1st Generation 7xxx series Alloys					
7075 (1954)	5.6	2.5	1.6	0.90	--
7079 (1954)§	3.9	3.3	0.6	2.44	--
7178 (1955)	6.8	2.75	2.0	0.72	--
X-7080 (Never)	6.0	2.0	1.0	0.99	--
7049 (1968)	7.7	2.45	1.55	0.41	--
7475 (1969)	5.7	2.25	1.55	0.64	--
1970's – 2nd Generation 7xxx series Alloys					
7050 (1971)	6.2	2.25	2.3	0.22	--
7010 (1975)	6.2	2.35	1.8	0.52	--
7150 (1978)	6.4	2.35	2.2	0.36	--
1990's – 3rd Generation 7xxx series Alloys					
7055 (1991)	8.0	2.05	2.3	--	0.87
7449 (1994)	8.1	2.25	1.75	0.11	--
7032 (1995)	6.0	2.0	2.0	0.12	
7040 (1996)	6.2	2.1	1.9	0.22	
7085 (2002)	7.5	1.5	1.65	--	1.58
7056 (2004)	9.1	1.9	1.55	--	2.09
7037 (2006)	8.4	1.7	0.85	--	0.57
7099 (2011)	7.9	1.85	1.75	--	0.81
7065 (2012)	7.7	1.65	2.1	--	1.59
7097 (2015)	7.9	2.1	1.2	0.15	--

§AA7079 added to 'Inactive' alloy List March 1989

EIC performance data for these 3rd Generation high strength 7xxx series alloys within the patent literature, typically are presented as the minimum stress levels for survival after conventional ASTM G47 EIC testing under alternate immersion in 0.6M NaCl [127,130], and further testing to outdoor marine environments [127,130] and high humidity at 80 °C [131]. The slow strain rate testing (SSRT) method used to characterize the influences of homogenization, solution heat-treatment, thermal aging and alloy microstructure, strength and toughness on EIC performance typically employ nominal strain rates well above the ~10^{-7}/s, needed to provide information on EIC initiation and initial growth behavior [132,133]. High nominal strain rates during SSRT provides insufficient time at stresses around the yield stress (Region 1 in Figure 10) for EIC incubation/initiation processes to activate and promote crack growth before plastic deformation processes trigger local inhomogeneous deformation and the onset of mechanical failure (Region 2 in Figure 10).

The results presented by Chiba et al [134] in 2019, summarized here in Table 8 for three peak-aged 7xxx series alloys, (commercial AA7075-T6 containing 5.4 Zn and two experimental alloys containing 8.5 and 10.5 % Zn along with slightly higher Mg and Cu contents) subjected to SSRT in five test environments (laboratory air, distilled water, 0.1M Na_2SO_4, 0.1M NaCl and 1M NaCl) without an inert reference test environment (dry air or vacuum). The nominal strain rate used, 6×10^{-6} /s, was at least an order of magnitude too fast and was additionally compromised by the tensile loading not being applied to the through-thickness (short-transverse) direction. It is clear from their results, when assessed in terms of UTS and plastic elongation ratios for tests conducted in the test environments relative to mechanical testing (Table 8), the extreme brittleness of the 10% Zn alloy renders it unsuitable for EIC assessment using SSRT, no evidence of EIC initiation is provided for AA7075-T6 in any of the test environments, and EIC had initiated in the 8.5% Zn alloy strained in the chloride containing environments and may have in all the other test environments. Using conventional SSRT to assess the EIC propensity of commercial aluminum alloys is not recommended and ideally should only be conducted on tensile samples strained in the through-thickness (short-transverse) direction, using extremely low nominal strain rates ($\leq \sim 10^{-7}$ /s) and for particularly resistant tempers should involve pre-exposure to an appropriate environment ahead of testing [132].

Table 8: UTS and % plastic elongation to failure for SSRT in various test environments for three Al-Zn-Mg-Cu alloys with various zinc contents using data provided or calculated from that provided by Chiba et al [134] using a nominal strain rate of 6×10^{-6} /s.

	Alloy Zn Content, %Wt.			Alloy Zn Content, %Wt.		
SSRT Test Environment	5.54	8.5	10.5	5.54	8.5	10.5
	UTS (MPa)			Plastic Elongation (%)		
Lab Air	604	666	640	12.2	10.0	1.0
Distilled Water	612	670	651	12.4	11.2	1.2
0.1M Na_2SO_4	609	674	619*	12.2	9.0	1.1
0.1M NaCl	612	655	646	11.4	3.6	1.0
1M NaCl	608	675	648	11.4	4.7	1.0
Average (All 5 Tests)	609 (±3.3)	668 (±8.1)	646 (±4.7)	11.9 (±0.5)	7.7 (±3.3)	1.1 (±0.1)
Average (Non Cl^- tests)	608 (±4.0)	670 (±4.0)	646 (±7.8)	12.3 (±0.1)	10.0 (±1.1)	1.1 (±0.1)
Average (Cl^- tests)	610 (±2.8)	665 (±14.1)	647 (±1.4)	11.4	4.2 (±0.8)	1.1
Tensile test (10^{-6} /s)	605	698	632	12.0	11.1	1.8
SSRT/Tensile Ratio	>1.0	0.96 0.95**	>1.0	>1.0 0.95**	0.9 0.38**	--

*This result is most likely a statistical outlier.

** Test in environments containing chloride ions.

SSRT (135,136) can be used as a 'screening test', like other current ASTM Standard EIC Test methods. However, the method is incapable of either consistently differentiating between the EIC performance of relatively resistant aluminum alloys and tempers or providing quantitative data to predict service life performance or provide quantitative input for product design purposes.

Use of pre-cracked fracture mechanics type test specimens during EIC studies on 3rd Generation 7xxx series alloys has increased during the last decade, particularly in China using DCB test specimens [138] and a test method very similar to ASTM G139 [137], Table 9 and Figure 11.The reduced EIC performance for 3rd versus 2nd Generation alloys is shown by minimum mechanical driving forces (K_{IEIC}) to sustain EIC crack growth rates above around 10^{-11} m/s being consistently lower for 3rd Generation alloys, and crack propagation rates for alloys in equivalent tempers under similar mechanical driving forces being consistently higher for 3rd Generation alloys, Figure 11b, Table 9.

Table 9: Comparison of published data for the EIC threshold Stress Intensity Factors, K_{IEIC} and K-insensitive Crack Growth rates obtained from conventional DCB testing for 1st, 2nd and 3rd Generation Commercial Al-Zn-Mg-Cu alloys exposed under freely corroding conditions to 0.6M NaCl at room temperature. All ASTM G47 testing conducted using alternate immersion and DCB testing as indicated in the Table.

Alloy (Registration, yr)	Mid-Zn (%wt)	$б_{TH}$, Threshold Stress, (MPa) ASTM G47	K_{IEIC} ($MNm^{-3/2}$)	K-Insensitive Crack Growth Rate, (m/s)	DCB Test Conditions* Ref. [xxx]
7075 (1954)	5.3	< 55 (T6) 172 (T76) 276 (T73)	7 (T6) 12 (T76) 24 (T73)	1.2×10^{-8} (T6) 1.9×10^{-9} (T76) 8×10^{-10} (T73)	A [32,98,192]
7079 (1954)§	3.9	< 55 (T6) <41* (T6)	11 (T651) 12.5 (T7)	2.5×10^{-6} (T6) 2.5×10^{-6} (T7)	A [32,98,192]
7178 (1955)	6.8	< 55 (T6) -- ~172 (T76)	6 (T651) 9.3 (T651) <20 (T76)	1.1×10^{-8} (T6) 1.0×10^{-9} (T651) 8×10^{-11} (T76)	B [193] C [200] B [193]
X-7080 (Never)	6.0	< 103 (T7)	-- 21.1 (T751)	3×10^{-10} (T7X) 5.6×10^{-10} (T751)	B [193] D [200]
7049 (1968)	7.7	<222 (T6) 310 (T73)	<12 (T6) 19 (T73)	4.6×10^{-8} 6×10^{-10} (T73)	C [194]
7475 (1969)	5.7	>296 (T7)	24 (T73)	6×10^{-9} (T6) 4×10^{-10} (T73)	D [117]
7050 (1971)	6.2	241 (T74) 172 (T76)	8.4 (T651) 9.3 (T6) 14.5 (T76) 15.6 (T6) 16.9 (T74) 22 (T73)	2×10^{-8} (T651) 3×10^{-8} (T6)3.3×10^{-9} (T7651) 1.0×10^{-9} (RRA) 2.9×10^{-9} (T7451) 4.2×10^{-10} (T73)	A [118,192] C [195] A [118,192] C [195] A [118,192] A [118,192]
7010 (1975)	6.2	241 (T74)	5.5 (T651) 8.0 (T6) 19 (T74] 30 (T73)	5×10^{-9} (T651) 2×10^{-8} (T6) 3×10^{-10} (T74) 2×10^{-10} (T73)	E [196] D[199] D[199] E [196]
7150 (1978)	6.4		7-9.5 (T6) 15 (T76) 23 (T73)	4×10^{-9} (T651) 1.2×10^{-9} (T76) 2×10^{-10} (T73)	C [197]
7055 (1991)	8.0	103 (T7751)	13 (T6) 15 (RRA) 11 (T7751)	6×10^{-8} (T6) 1.2×10^{-9} (RRA) 10^{-9} (T7751)	C [195] C [195] C [197]
7449 (1994)	8.1		7 (T6 Lab) 11 (T6 Lab) 8.5 (T7 Lab)	9×10^{-8} (T6 Lab) 2×10^{-8} (T6 Lab) 1.1×10^{-9} (T7x Lab)	F [198]

			11 (T79)	5×10^{-10} (T79)	C [197]
7085 (2002)	7.5	180 (T76) 241 (T74)	14.0 (T7x)	1.1×10^{-8} (T7x)	F [138]
7056 (2004)	9.1		1.8 (T6) 2.8 (T77) 9.0 (T7x)	2×10^{-7} (T6) 6×10^{-8} (T77) 1.5×10^{-8} (T7x)	F [138]
7037 (2006)	8.4		3.6 (T7x) 4.3 (T7x)	7.5×10^{-8} (T7x) 1.3×10^{-7} (T7x)	F [138]
7099 (2011)	7.9	170 (T76) 240 (T74)			
7065 (2012)	7.7	172 (T76) 241 (T74)			
7097 (2015)	7.9		3.8 (T6) 5.8 (T74) 7.0 (T7x)	10^{-7} (T6) 10^{-7} (T74) 3×10^{-8} (T7x)	F [138]

§AA7079 added to 'Inactive' alloy List March 1989

*DCB Test Conditions: A: 0.6M NaCl at RT, dropwise, 3 times a day
B: Saturated Aqueous NaCl, 23 ^{O}C, Total Immersion
C: 0.6M NaCl at RT, Full Immersion
D: Artificial Seawater at RT, Alternate Immersion
E: Artificial Seawater at RT, Full Immersion
F: 0.6M NaCl at 35 ^{o}C, Full Immersion

EIC IN FUTURE COMMERCIAL 7XXX SERIES ALUMINUM ALLOYS

The successful development of a 4th Generation of Al-Zn-Mg-Cu 7xxx series aluminum alloys will necessitate a 'step-change', as opposed to an 'incremental' innovation, simply involving an alloy compositional optimization with a modified multi-step heat treatment [35].

The lack of any significant EIC related issues for AA7050 or other 2nd Generation alloys during structural use in the aviation industry led to an overreliance that standard ASTM EIC testing [121,128,129] would provide an adequate 'fitness-for-purpose' criteria for the 3rd Generation of higher strength 7xxx series alloys. Recent premature in-service EIC issues reported for 3rd Generation high-strength Al-Zn-Mg-Cu alloys in less aggressive environments [139] are reminiscent of experiences 50 years earlier for 1st Generation alloys, where EIC susceptibility only became apparent following introduction into structural use. It is not possible to rely on current ASTM standard EIC test methods using either smooth or pre-cracked test specimens to provide go/no-go assessments of the EIC performances of candidate 4th Generation high strength aluminum alloys during structural use.

The various EIC ASTM tests are described in detail by R H Jones in a chapter in a classic text [140], who concludes that: "One of the toughest problems for SCC investigators is that of convincing the decision makers that service life cannot be predicted in hard numbers because materials traditionally have been evaluated by comparisons."

The ASTM test methods, e.g., G47 [128], G103 [86], G139 [129], G168 [137], G129 [136], are unable to reliably differentiate between the EIC susceptibility of relatively resistant alloy tempers [122,141].

Dix in 1940 [27] and 1949 [142] summarized the situation:

“While it is relatively easy to determine if a product is susceptible to stress-corrosion cracking it is far more difficult to determine if it possesses a degree of susceptibility that will hamper its general usefulness” [142] and

“Correlation between laboratory stress-corrosion testing and service performance is difficult to obtain and often requires many years.” [27]. He suggested that:

“If the test conditions are intelligently selected, accelerated stress-corrosion tests are useful in the development of new alloys”.

The 4th Generation high strength Al-Zn-Mg-Cu aluminum alloy thick plate developers require quantitative information characterizing EIC initiation and early growth from various initial surface conditions exposed to a range of environmental conditions, to enable:
a) Go/no-go assessment for candidate new alloy and tempers,
b) Differentiation between relatively EIC resistant alloys and tempers and
c) Input data for structural engineering design and product service-life prediction.

A computer designed double-tapered four-point bend test specimens, machined from thick plate with their long axis aligned in the short-transverse direction and width in the rolling direction, Figure 12, could provide this information. The specimen would be constant displacement tested in various controlled environments to enable evaluation of its ability to arrest growing EIC at K’s below the K_{IEIC}, threshold obtained under decreasing K conditions generated during conventional DCB testing [137].

The surface conditions evaluated would include: a) a controlled mechanical polishing procedure, e.g., see [143,144], to remove the influence of the deformed layer, always present on rolled and machined aluminum plate surfaces [145,146], b) simulation of the alloys as-supplied mill-finish and possibly c) one agreed between alloy supplier and customer/user. Test environments to be strongly considered would be: a) water vapor at 70 ^{O}C, b) total immersion in a dilute NaCl solution at RT with concentration above ~0.03M to ensure local acidification to pH’s below 3 occurs within restricted geometries during EIC initiation [80] and c) one agreed between alloy supplier and customer/user, representative of the ‘worst-case’ in-service condition.

The double-tapered 4 point bend test specimen has been adapted from previous specimen designs to provide constant K test specimens [147,148], with EIC initiating at their external surfaces near the mid-point of test specimen, see Figure 12. The initial 10-15 mm of EIC growth occurs under rising K conditions, after which the next ~ 10-15 mm of potential EIC growth occurs under a fixed K, controlled by the specimen’s increasing cross-sectional volume due to the taper, which only happens if the EIC propensity is sufficient to prevent crack arrest, see Figure 12, with the applied K exceeding the K_{IEIC} threshold under rising K loading conditions. Confidence EIC will initiate during such testing is provided by recently reported EIC initiation and crack growth data in conventional four-point bend test specimens taken from thick plate AA7449-T7651 [149] and AA7085-T7651 [143,144] exposed to water vapor at 70 ^{O}C. Euesden et al [143], used high resolution in-situ automated optical monitoring in real-time to enable the unambiguous detection of EIC initiation sites and the characterization of early crack growth behavior during four-point bend tests.

Further extensive experimental studies are needed to fully validate this approach, which if successful will provide product design engineers quantitative data for service life predictions as opposed to the qualitative data currently provided based on historical 'comparisons' [140].

6.1 EIC minimization for 4th Generation 7xxx series Aluminum Alloys

Zhou et al [35] in 2021, following a detailed review of the literature of the advancement of 7xxx series aluminum alloys for use in aircraft structures, have proposed the next generation of 7xxx series alloys will have: Zn contents above 10%, lower magnesium and copper contents, further reduced Fe and Si impurity levels, along with alloy microstructures manipulated using optimized/modified heat-treatment practices.

This approach fails to address several known adverse issues, namely:

a) Inherent alloy 'brittleness' with low-ductility intergranular (LDIG) fracture occurring in inert environments as zinc contents approach 10 wt.% [17,29,74,150],
b) EIC benefits from optimized/modified heat-treatment practices becoming increasingly less effective as alloy zinc content rises above 7.5 wt.%, despite the clear benefits for alloys with lower Zn contents (compare data in Figure 9 and 13),
c) EIC growth rates in relatively benign environments such as water vapor increase significantly for alloys containing Zn above 7.5 wt.% [81,139,150,151].

The increased tendency for Al-Zn-Mg-Cu alloys to suffer low ductility intergranular (LDIG) fracture with increasing zinc content is shown in Figure 13, using UTS and % elongation to failure data provide by Herenguel [29] for peak-aged Al-Zn-Mg alloys with a fixed 2 wt.% Mg content and zinc varying from zero to 11 wt.%. The sudden loss of alloy ductility (elongation decrease) when a high-purity alloy's zinc content exceeds around 6 wt.% (see Figure 13) is associated with a fracture mode transition from ductile transgranular microvoid coalescence to a LDIG fracture mode that Herenguel and others describe as 'Intergranular decohesion' [29]. The use of minor alloy additions such as Cr, Cu and Zr to suppress the LDIG fracture mode transition has enabled the aluminum industry to provide higher strength commercial 7xxx series aluminum alloys with zinc contents up to around 8 wt.% (see Figure 13).

The patents issued claiming improved EIC for 7xxx series aluminum alloys over the last several decades typically have upper-bound claimed Zn content below 8.5 wt.%, and rarely if ever provide actual examples demonstrating good EIC resistance in alloys with zinc contents above 8 wt.% [17, 84, 122,127].

The reduced EIC benefits obtained from optimized/modified heat-treatment practices applied to alloy's with zinc content above around 7.5 wt.% indicates the process controlling EIC for lower zinc levels is transitioning from process associated with the copper contents of grain boundary precipitates and most likely 'electrochemically' influenced to a 'mechanical' process associated with the onset of LDIG. Crack growth rates for the LDIG process, while not directly dependent on the local environmental conditions can be enhanced by the local environment. Experimental evidence supporting this 'mechanically' dominated process and environmental enhancement is provided by the experimental crack propagation data Kovacs and Low [151] reported for a commercially cast high-purity peak-aged Al-14.8Zn alloy, supplied as plate material by Alcoa, subjected to DCB testing while exposed to: a) 0.5M NaCl, b) distilled water and c) laboratory air (RH <40%), Figure 14. The observed crack growth rates generated during DCB testing for the high zinc-containing alloy exceed those reported for lower zinc-containing alloys, $< 10^{-7}$ m/s (see Figures 10 and 12) by at least an order of magnitude for all three test environments, and are consistently $> 10^{-7}$ m/s (see Figure 14).

Kovacs and Low's [151] crack growth rates scaled linearly with the elastic strain energy release rate, G, and the square of the imposed stress intensity factor, K, for all three environmental conditions used, suggesting that the observed sub-critical crack growth rate dependence on alloy microstructure was associated with the blocking of inhomogeneous plastic flow in the matrix by grain boundaries, resulting in local severe stress concentrations at the boundaries, i.e. a slip-induce intergranular fracture process, that could be accelerated by the presence of distilled water or a saline solution. These findings are consistent with earlier studies conducted in Japan during the 1930's [8,10,55-57], France during the late 1930's [29] ('intergranular decohesion') and in England in the 1950's [150].

6.2 4th Generation Al-Zn-Mg-Cu Alloys

Successful 4th Generation alloy development will necessitate acquisition of a significantly improved understanding of the factors controlling and limiting:
a) The maximum Zn contents in commercial alloys to avoid the onset of the LDIG fracture mode,
b) the multi-step EIC initiation process [140,143,144,152,153] for a range of initial surface conditions relatable to expected service conditions, including those involving various types of 'disturbed' layers' immediately below external surfaces [145, 146] and
c) How 'micro' EIC cracks develop and then either arrest, or continue to propagate to become 'macro' cracks.
The most likely route will necessitate acceptance of EIC propagation rates similar to those of 2nd Generation alloys (see Table 9), counter-balanced by an inherent high and robust resistance to localized corrosion and the multi-step EIC initiation process, with a threshold K_{IEIC} >25 $MNm^{-3/2}$ under decreasing K conditions and one exceeding 15-20 $MNm^{-3/2}$ under rising K conditions.

The majority of academic and commercial studies over the last 50 years have only addressed EIC propagation, with very few studies of the EIC initiation process from conditions representative of service applications. It is interesting K_{IEIC} threshold and K-insensitive crack growth rates obtained from conventional DCB testing [137] (see Figure 15) are rarely used as indicators of EIC susceptibility in material specifications for commercial usage. K_{IEIC} being a measure of the minimum mechanical driving force to either enable local equilibrium H decohesion [154] and/or to prevent crack arrest induced by uncracked ligaments [155].

There are two EIC thresholds, one for 'micro' cracks, K_{IEIC} (Micro), where cracks 'arrest' if the local crack tip process zone conditions fail to satisfy the second and more demanding EIC threshold, K_{IEIC} (Macro) required for growth, Figure 16. This means that maximum depth of arresting microcracks will be both, alloy and temper dependent, scaling with the K_{IEIC}, and typically ranging from 10 to 100 µm for highly susceptible compositions and tempers and up to a few mm's for highly EIC resistant microstructures. Short 'arrested' EIC cracks will be found in test specimens surviving long-term EIC testing under loading conditions close to threshold conditions and in commercial 7xxx series aluminum alloys after their use in structural applications for many years, especially under challenging service conditions.

Short 'arrested' EIC cracks were reported by Schra and Wanhill [156,157] during their development of an Automated Method for Stress Corrosion Testing of Aluminum Alloys (ASCOR), which involved continuously monitoring the strain developed in smooth tensile test specimens during exposure to 0.6M NaCl under well-controlled ASTM alternate immersion conditions. They proposed two EIC thresholds for AA7010-T651 thick plate, one for the threshold for 'macro' cracks (equivalent to the K_{IEIC} threshold obtained from conventional DCB testing) and a second, lower threshold associated with 'micro' cracks.

Schra and Wanhill's predicted EIC initiation times for test specimens failing within 720 hours, and the maximum intergranular EIC depths detected in both failed and non-failed samples are shown in Figure 17, with two designated EIC threshold stresses of 60 and 140 MPa, for 'Micro' and 'Macro' cracks, respectively.

The stress intensity factors, K's, associated with these two EIC thresholds, K_{IEIC} (Micro) and K_{IEIC} (Macro), calculated here using an approach reported before [158,159] assuming an half-penny shaped elliptical profile, are 1.3 and 5.3 $MNm^{-3/2}$, respectively. This 'Macro' threshold K from ASCOR testing, closely matches K_{IEIC} threshold values of 5-6 $MNm^{-3/2}$, quoted in the literature for AA7010-T651 plate subjected to conventional DCB testing [161]. The estimated K_{IC} for the final overload fracture of ASCOR tensile samples containing various shaped intergranular cracks are close to the short-transverse fracture toughness, K_{IC} of 23 $MNm^{-3/2}$ quoted by Schra and Wanhill for the as-received AA7010-T651 material [156,157], Table 10.

Table 10: Estimated Stress Intensity Factors, K, associated with smooth AA7010-T651 tensile specimens containing EIC generated during ASCOR testing conducted by Schra and Wanhill [156,157].

Applied Stress (MPa)	Test Time (hr)	EIC Depth (µm)	EIC Crack Profile	Implied K_I ($MNm^{-3/2}$)
40	Removed after 720 hr without failure	None	--	--
60		~200	Elliptical Half-Penny	1.3
120		~500	Elliptical Half-Penny	3.9
140		~620	Elliptical Half-Penny	5.3
170	434	~700	Peripheral Ring	23.5
170	543	~1430	Chord	24.2
230	36	~1200	Elliptical Half-Penny	22

Arrested EIC growth has been found in both a magnesium-7% aluminum alloy [162-164] and a 0.05% carbon steel [164,165], where it was argued for both materials, 'The threshold stress from constant-load testing is not that stress below which cracks do not form but rather the stress above which they continue to propagate' [164]. Arrested EIC cracks (described then as 'non-propagating cracks') of increasing length were detected as the applied stress under constant load conditions increased up to a threshold stress for EIC propagation, above which cracks no longer arrested, Figure 18a. Estimated stress intensity factors for the arrested EIC of various crack lengths reported by Parkins and Greenwell [165], for a 0.05% carbon steel stressed held under potentiostatic control in a carbonate-bicarbonate environment at 90 °C, are shown in Figure 18b The correspondence between the K_{IEIC} threshold of 21 $MNm^{-3/2}$ obtained from tests conducted using pre-cracked fracture mechanics test specimens and the K_{IEIC} threshold for 'Macro' cracks, from constant load testing of smooth tensile test specimens, Figure 18b, provides strong support that crack arrest has an important role in assessing EIC resistance.

The key opportunity for 4th Generation alloy development is to significantly improve the inherent resistance to EIC initiation, whilst restricting EIC propagation rates to those associated with 2nd Generation alloys, Figure 19 This requires a detailed understanding of the EIC initiation process [91,92,95,97,162-170].

Work involving 'rare-earth' additions conducted over the last 15 years at the Central South University, Changsha, China [171-177] has made some interesting progress, despite several previous issues using this approach. This included unsuccessful attempts with minor additions (0.1-0.25 %wt.) of cerium (Ce) or Yttrium (Y) to AA7075 type alloys in the mid-1960's [93] and to Al-4.4Zn-1.6Mg-0.15Mn extrusion alloys during the late 1970's and early 1980's [178]. Improved EIC performances for peak-aged thin gauge (3 x 3 mm) extruded Al-Zn-Mg-Cu products with a wide range of Zn (4.4 – 10.5 wt.%), Mg (2.7-3.6 %wt.) and Cu (0-2.1 %wt.) containing various rare-earth additions of 2-to-8 %wt. (Y, La, Ce, Nd, Sm and Pr) [179] reported in the late 1980's, with similar findings for larger rectangular extrusions up to 5 x 45 mm for an Al-8Zn-Mg-2.5Mg-4La alloy [180,181]. However, the alloy's maximum strength levels, despite being in a -T6 temper did not exceed 570 MPa. An evaluation of separate 0.1 %wt. Ce, 0.1 %wt. Ni and 0.2 %wt. Sc additions to a wrought Al-8.6Zn-2.6Mg-2.5Cu (Fe and Si <0.005 %wt) alloy during the late 1990's showed the alloy variant containing Ce had the highest EIC susceptibility [182].

The mechanical properties, EIC and localized corrosion performance for Al-8.55Zn-2.3Mg-2.3Cu-0.16Zr base alloy used by the Chinese researchers, along with the various rare-earth and chromium additions is provided in Table 11 [171-177].

Table 11: A summary of mechanical (UTS, YS, % Elongation and Fracture Toughness), EIC (K_{IEIC} and K-Independent Crack Growth Rate immersed in 0.6M NaCl at 35 ^{O}C) and Localized Corrosion (EXCO and IGC) experimental data for an extruded Al-8.6Zn-2.3Mg-2.3Cu-0.16Zr base alloy with various alloying additions, provided over the last 15 years by a group of Chinese research workers base at Central South University, Changsha [154-160].

Alloy Addition wt. %				UTS	YS	Elong (%)	K_{IC} (ST)	K_{IEIC} (ST)	K-Independent Crack Growth Rate	EXCO Rating	ICG Depth	REF. [xxx]
Cr	Yb	Pr	Er	(MNm^{-2})			(MNm$^{-3/2}$)		(m/s)		(µm)	
None	--	--	--	710	684	8.9	21.6	9.8	2.00E-08	EB+	150	[171,172]
None	--	--	--	704	684	8.9	24.8	11	1.50E-08	EB+	147	[173]
None	--	--	--	719	701	8.5	23.7	7.8	9.00E-09	EB	146	[177]
None	--	--	--	706	680	8.9	21.2	9.2	3.00E-08	--	--	[175]
None	0.21	--	--	711	691	7.1	22.2	10.9	1.00E-08	--	294	[176]
0.09	0.21	--	--	721	699	8.1	29.4	13.7	9.00E-09	--	114	[176]
0.18	0.2	--	--	747	726	9.3	32.4	17	2.50E-09	--	32	[176]
0.22	0.21	--	--	749	738	8.5	28.1	15	Rising	--	65	[176]
0.2	0.3	--	--	752	747	9.3	29.3	17	3.00E-09	EA	54	[171,172]
0.1	--	0.14	--	743	708	10.1	29.7	17.6	5.00E-09	EA	104	[177]
0.18	--	0.26	--	732	721	10.8	33.2	25.4	1.20E-09	EA	47	[173]
0.17	--	--	0.28	736	720	9.2	30.8	22.4	1.50E-09	EA	??	[175]
0.16 (No Zr)	--	0.26	--	674	659	8.1	17.8	13.1	1.00E-08	EC	310	[173]

Best efforts were taken to simulate commercial production, with the use of multi-stage hominization, temperature control during extrusion while using of a 12.2 extrusion ratio, multi-stage SHT prior to water quench and one stage final heat treatment of 24 hours at 130 ^{O}C to give a T6 type temper. The mechanical properties (UTS, YS, % Elongation and Fracture Toughness, K_{IC}) and alloy microstructures for the extruded Al-8.6Zn-2.3Mg-2.3Cu-0.16Zr base alloy without chromium or rare-earth additions are equivalent to those expected for similar commercial alloys.

From Table 11, it is clear that EIC benefits from rare-earth additions require alloys to contain both chromium and zirconium (see Figure 20) and that the alloy strength, toughness and EIC resistance are sufficient to satisfy the projected performance expectations for 4th Generation alloy (see Figure 19).

The short-transverse fracture toughness, K_{IC} (ST) increases with the decreases in the EIC growth rates and the threshold stress intensity factor, K_{IEIC} values, Figure 20a, consistent with EIC arrest. The alloy strengths significantly increase with rare-earth addition for alloys containing both Zr and Cr additions, but not when either Zr or Cr addition is absent. The viability of using Zr and Cr additions in 3rd Generation 7xxx series alloy thick-section alloy products is under evaluation, as a Cr addition can provide potential EIC benefits in its own right [52,75,82,183-185]. However, potential 'quench-sensitivity' issues could limit the usefulness of rare-earth additions in thick-section 4th Generation commercial alloys.

The limitation to the maximum achievable strength level in 4th Generation alloys will be dictated by the ability to avoid to onset of LDIG fracture mode and intergranular 'brittleness' when alloy's Zn content exceed around 9 wt.% [17,29,150,186,187].

The use of tapered 4-point bend specimens (Figure 12) to determine the critical 'feature' depths needed to support transitions from 'arresting' to 'propagating' EIC cracks should be informative, especially if these depths are sufficient for meaningful K_{IEIC} thresholds to be obtainable from testing using conventional pre-cracked fracture mechanics specimens under rising K [188-190] and decreasing K loading conditions. This would enable the use of 'Probabilistic Fracture Mechanics Simulation of EIC using Multi-Scale Modeling' [191] to provide service-life predictions.

CONCLUSIONS

- EIC issues during commercial use of high-strength Al-Zn-Mg-Cu alloys dates back to 1913.

- EIC characterization of next generation higher strength alloys must include specific studies on both the initiation and propagation processes in environmental conditions relatable to the expected service conditions, in additional to any assessments using Standard ASTM Test methods.
- Crack arrest after EIC initiation from a free surface from customized double taper 4 point bend test specimens and the implied K_{IEIC} thresholds under increasing and deceasing K loading conditions are the recommended indicators of an alloy/tempers EIC resistance.

- High-strength 7xxx series aluminum alloys with higher Zn contents must: (a) mitigate low-ductility intergranular (LDIG) fracture issues, (b) provide a 'practical' EIC immunity, with EIC growth rates no worse than 2nd Generation alloys, and (c) provide a robust high resistance to EIC initiation under service conditions.

- Development of 4th Generation Commercial Al-Zn-Mg-Cu alloys for structural use will require the use of minor alloy additions (including rare-earths) coupled with enhanced thermomechanical processing.

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APPENDIX

Selected US Government Agency funding R&D programs during the 1960's, 1970's and early 1980's to characterize the EIC/SCC of aluminum alloys.

Date	Tittle	Funding Agency	Recipient	Reports
May 1963 – May 1966	Investigations of the Stress Corrosion Cracking of High Strength Aluminum Alloys	NASA	Alcoa	Sprowls et al, 1966 [89]
Dec 1963 – Feb. 1966	Investigations of the Mechanisms of Stress Corrosion of Aluminum Alloys	Bureau of Naval Weapons	Alcoa	G C English 1965 [87] J McHardy 1966 [88]
1965 – 1966	A Fundamental Investigation of the Nature of Stress-Corrosion Cracking of Aluminum Alloys	American Air Force	Battelle Memorial Institute	F H Haynie et al 1967 [90]
1966 – 1968	Studies of Crack Initiation Phenomena associated with Stress Corrosion of Aluminum Alloys	NASA	Alcoa	M S Hunter et al 1966 [91] M S Hunter & W G Frickle 1969 [92]
March 1966 – March 1969	Development of a Rapid Stress-Corrosion Test for Aluminum Alloys	NASA	Kaiser Aluminum & Chemical Corporation	W J Helfrich 1968 [97]
June 1966 – June 1969	Studies of the General Mechanism of the Stress Corrosion of Aluminum Alloys and Development of Techniques for its detection	NASA	Tyco Laboratories, Inc	S B Brummer et al [95]
1966	Development of Higher Strength Aluminum Alloys with Improved Stress Corrosion Resistance	Air Force Materials Laboratory	The Boeing Company	J C McMillan, M V Hyatt [93]
May 1967 – May 1968	The Role of Dislocations in the Stress-Corrosion Cracking of Aluminum Alloys	Naval Air System Command	Rocketdyne, Rockwell Corporation	A J Jacobs 1968 [94]
1967 – 1969	Investigation to Improve the Stress-Corrosion Resistance of Aluminum Alloys through Alloy Additions and Specialized Heat Treatment	Naval Air System Command	Alcoa	J T Staley 1969 [96]

May 1967 – March 1970	Development of a High-Strength, Stress Corrosion Resistant Aluminum Alloy for use in Thick Sections	Air Force Materials Laboratory	The Boeing Company	J C McMillan, M V Hyatt, 1967 [88], 1968 [103] M V Hyatt, H W Schimmelbusch, 1970 [104]
July 1968- Aug. 1973	Evaluation of Stress-Corrosion Cracking Susceptibility using Fracture Mechanics Techniques	NASA	Alcoa	D O Sprowls et al 1973 [98]
July 1969 -Feb. 1972	Investigation of Smooth Specimen SCC Test Procedure. Variation in Environment, Specimen size, Stressing Frame, and Stress State.	NASA	Alcoa	B F Lifka, D O Sprowls, R A Kelsey [99]
May 1967 – March 1970	Development of a High-Strength, Stress Corrosion Resistant Aluminum Alloy for use in Thick Sections	Air Force Materials Laboratory	The Boeing Company	M V Hyatt, H W Schimmelbusch, 1970 [104]
July 1969 – July 1970	High Strength Aluminum Alloy Development	Air Force Materials Laboratory	Reynolds Metal Co.	D S Thompson, S A Levy, 1970 [105]
1970	Exploratory Development of High-Strength, Stress Corrosion Resistant Aluminum Alloy for use in Thick Section Applications	Air Force Materials Laboratory	Alcoa	J T Staley, H Y Hunsicker [111]
1970	Investigation to Develop a High-Strength Stress-Corrosion Resistant Aluminum Aircraft Alloy	Naval Air Systems Command	Alcoa	J T Staley [110]
Sept. 1970 – Feb. 1972	Further Development of Aluminum Alloy X7050	Naval Air Systems Command	Alcoa	J T Staley, J P Lyle, H Y Hunsicker, 1972 [109]
June 1971 – Dec. 1972	Comparison of Aluminum Alloy 7050, 7049, MA52, and 7175.T736 Die Forgings	Air Force Materials Laboratory	Alcoa	J T Staley, 1972 [106]
May 1972 – Nov. 1974	Design Mechanical Properties, Fracture Toughness, Fatigue Properties, Exfoliation and Stress Corrosion of 7050 Sheet, Plate, Hand Forgings, Dia Forgings and Extrusions	Naval Air Command	Alcoa	RE Davies, G E Nordmark, J D Walsh, 1975 [107]
March 1973 – June 1976	Aluminum Alloy 7050 Extrusions	Air Force Materials Laboratory	Alcoa	J T Staley et al, 1977 [108]
1980	Seacoast Stress Corrosion Cracking of Aluminum Alloys	NASA	NASA	TS Humphries, E E Nelson, 1981 [100]
March 1981 – May 1982	A Study of Environmental Characterization of Conventional and Advanced Aluminum Alloys for Selection and Design Part 1: Literature Review Part 2: The Breaking-Load Test Method	NASA	Alcoa	D O Sprowls, 1984 [101] D O Sprowls et al, 1984 [102]

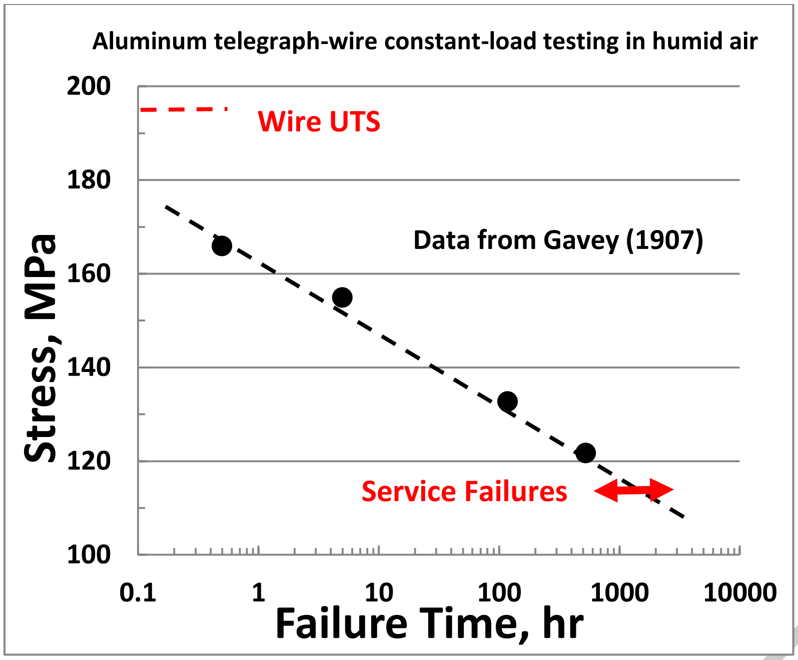

Figure 1. Failure times for 8-foot lengths of aluminum telegraph-wire (3.20mm diameter) dead-weight loaded to various stresses levels in humid air at room temperature [38].

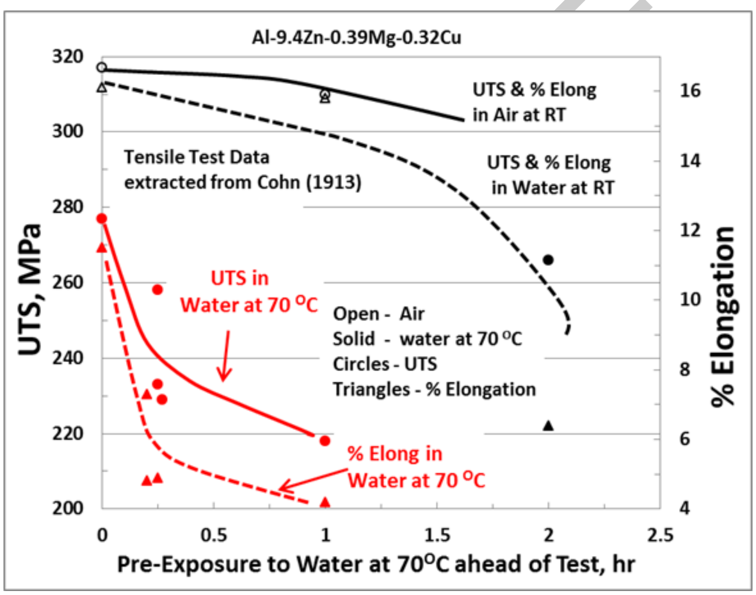

FIGURE 2. Effect of pre-exposure to water at 70°C on subsequent mechanical properties for an Al-Zn-Cu-Mg alloy tensile tested in air or water at RT and 70°C [7].

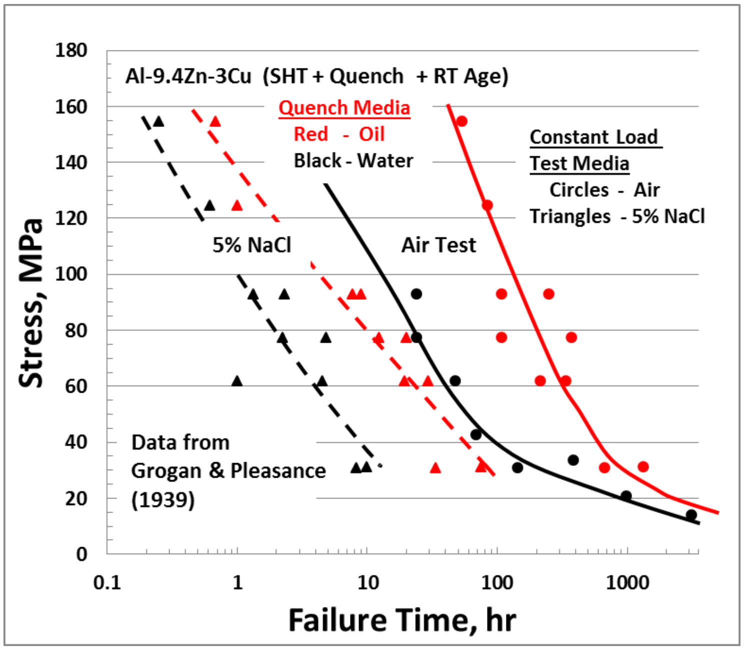

FIGURE 3. Failure time as a function of initial stress for constant-load testing of a high Zn-containing Al-Zn-Mg-Cu alloy exposed to laboratory air and a 5% NaCl solution. Data extracted from Grogan and Pleasence [49].

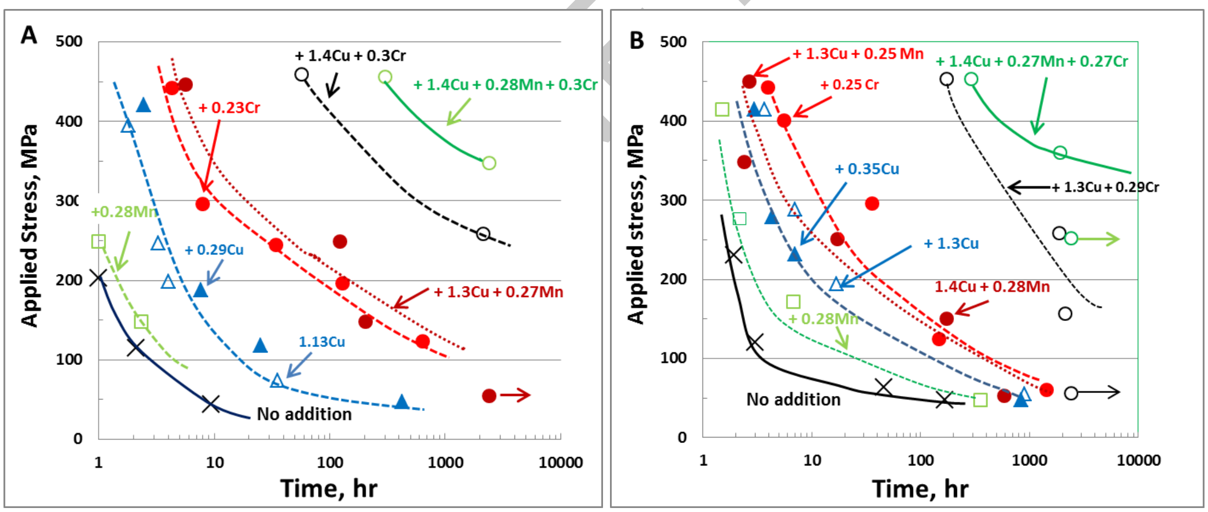

FIGURE 4. Constant-load failure time as a function of applied stress for the various Al-7Zn-2Mg-Cu alloys exposed to 85% RH at 30 ^{O}C while sprayed with 3% NaCl by Chadwick et al [75]. A) Alloys cast on a High-Purity base and B) Alloys cast on a Low-Purity base.

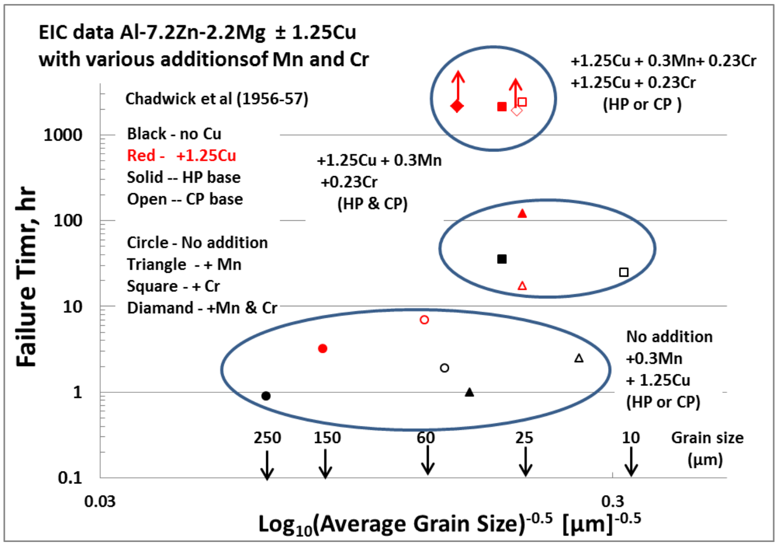

FIGURE 5. Chadwick et al [75] constant-load failure time as a function of the reciprocal square root of grain size.

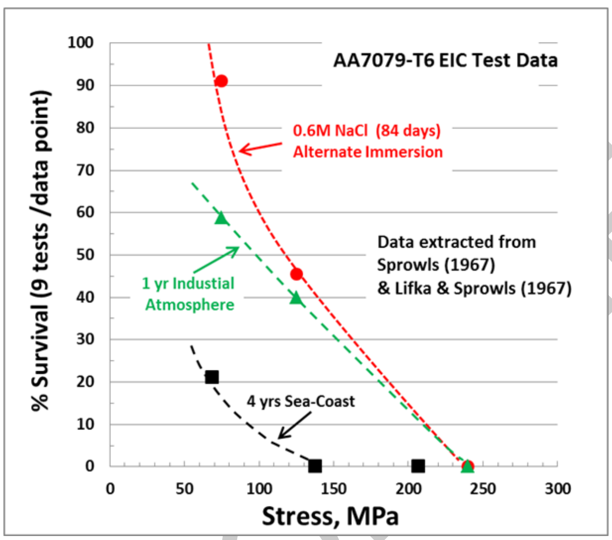

FIGURE 6. EIC data for AA7079-T6 for static load tests under different environmental conditions [85].

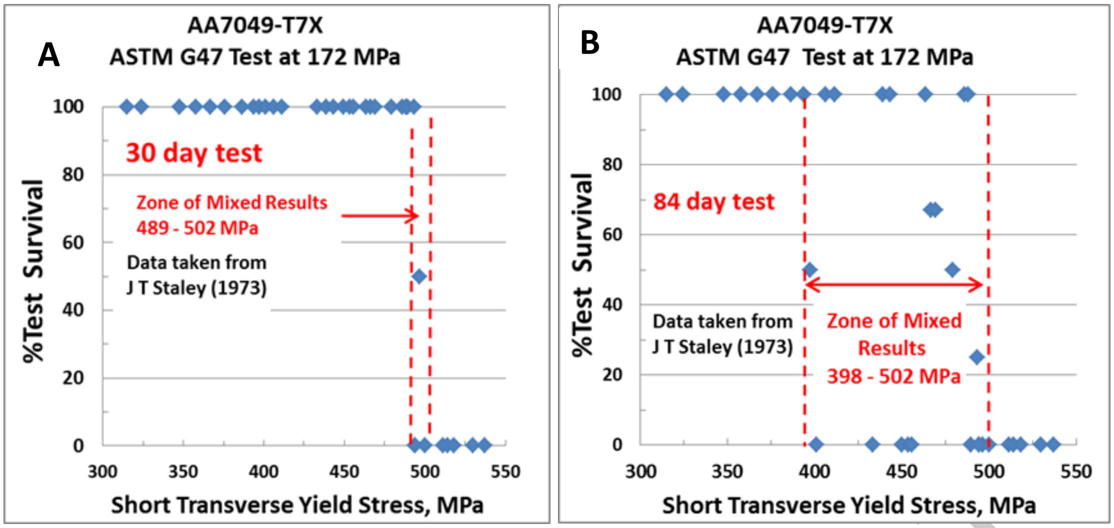

FIGURE 7. EIC test data from a program conducted by Staley [106] to establish the 'critical alloy yield stress' for a thick AA7049-T7X product to survive an ASTM G47 type test.

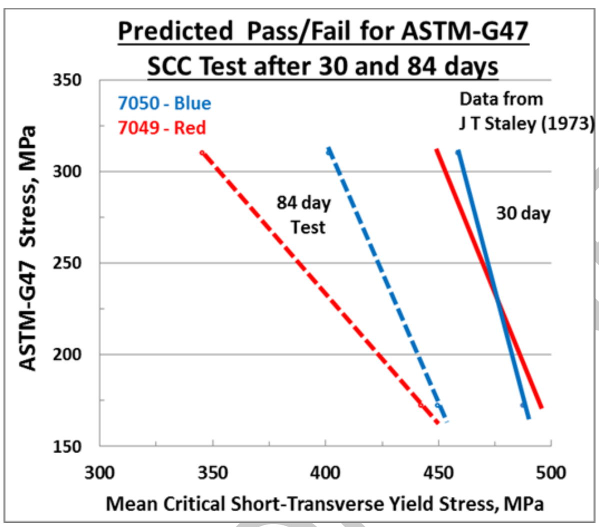

FIGURE 8. Summary of major EIC test program conducted by Staley [106] to establish the 'critical alloy yield stress' for thick AA7049-T7X and AA7050-T7X products to survive ASTM G47 type testing at various stress levels.

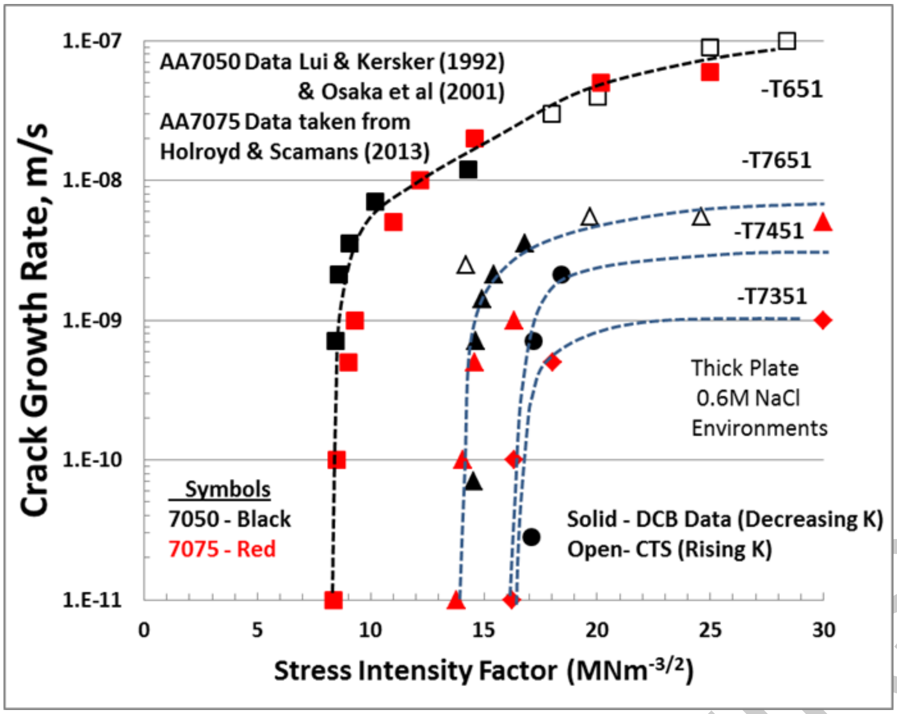

FIGURE 9. Crack Growth data as a function of the imposed stress intensity factor for commercial lots of AA7050 and AA7075 tested in 0.6M NaCl using data for AA7050 provided by Liu and Kerser [118] and Osaka et al [119] and various researchers summarized by Holroyd and Scamans [80].

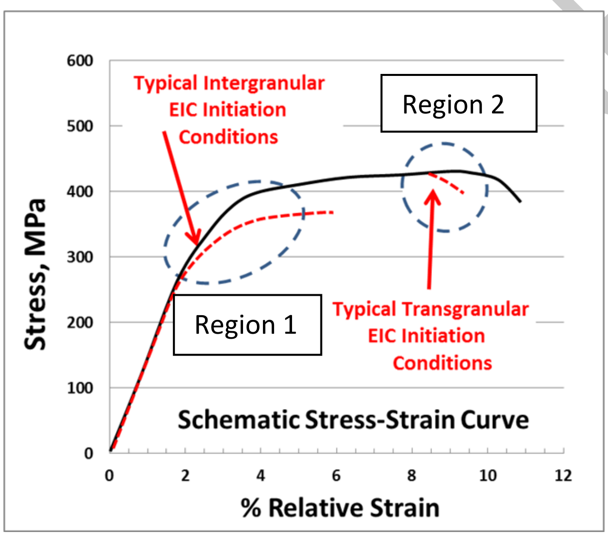

FIGURE 10. Schematic representation of the stress-strain regions for EIC initiation and initial growth in aluminum alloys during SSRT testing of sheet material and/or through-thickness loading of relatively resistant alloy/tempers.

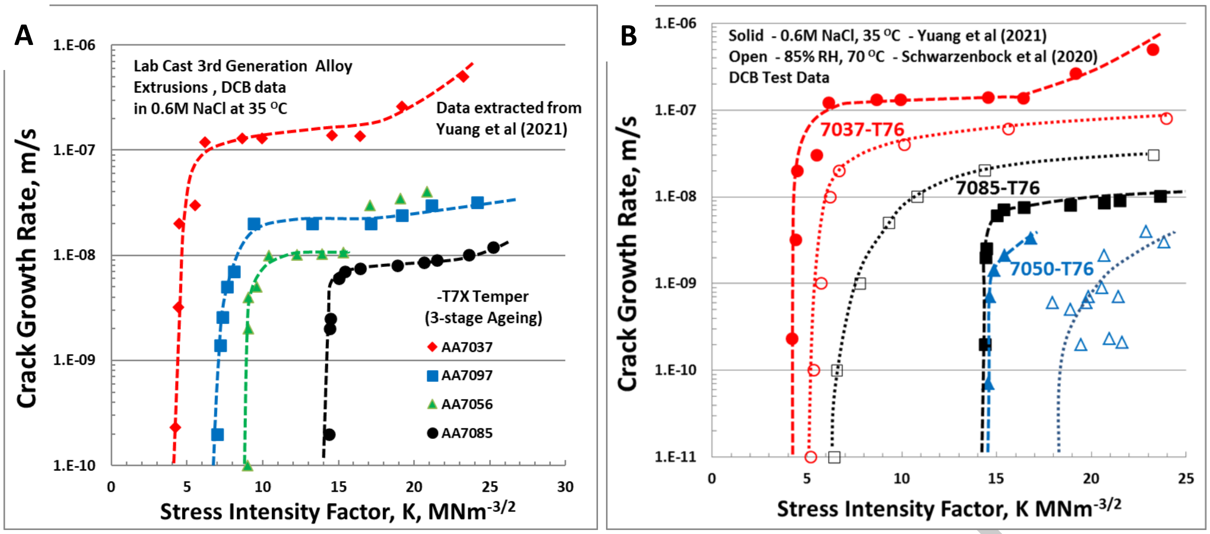

FIGURE 11. EIC Growth rate for 3rd Generation 7xxx alloys in a T7X temper as a function of the applied stress intensity factor for: a) Various laboratory cast alloy thick extrusions immersed in 0.6M NaCl at 35 °C [138] and b) Comparison of a 2nd Generation alloy (AA7050 thick commercial plate [81,118]) and 3rd Generation 7xxx series alloys (AA7037 and AA7085) crack growth rates when exposed to 0.6M NaCl at room temperature and in 85% Humid air at 70 °C [81].

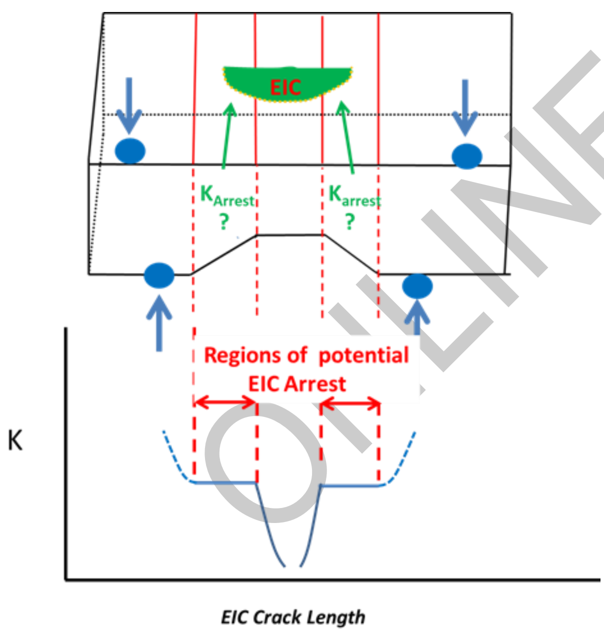

Figure 12: Schematic of a computer designed 4-point tapered Bend Test Specimen to enable EIC initiation from a chosen external surface condition to initially grow with initially increasing applied K and then held at a given K to determine if EIC will arrest.

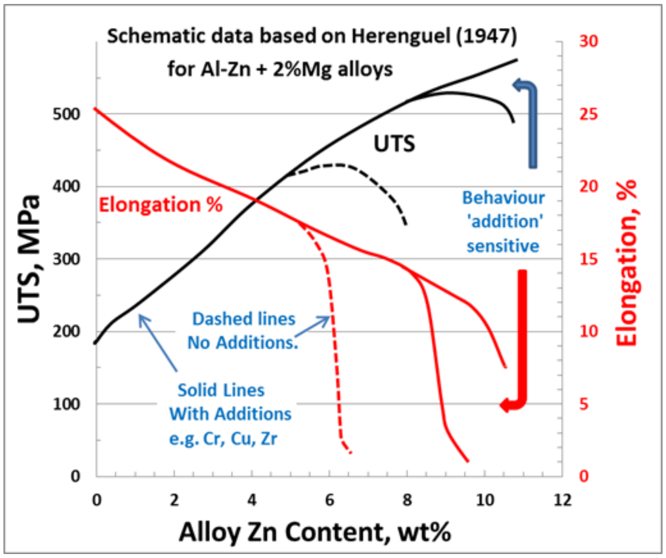

FIGURE 13. Schematic showing UTS and % Elongation data for a series of peak-aged Al-Zn-Mg alloys containing 2wt% Mg and Zn contents from zero to 11 wt%, with and without various minor additions of Cr, Cu and Zr. Data extracted from Herenguel [29].

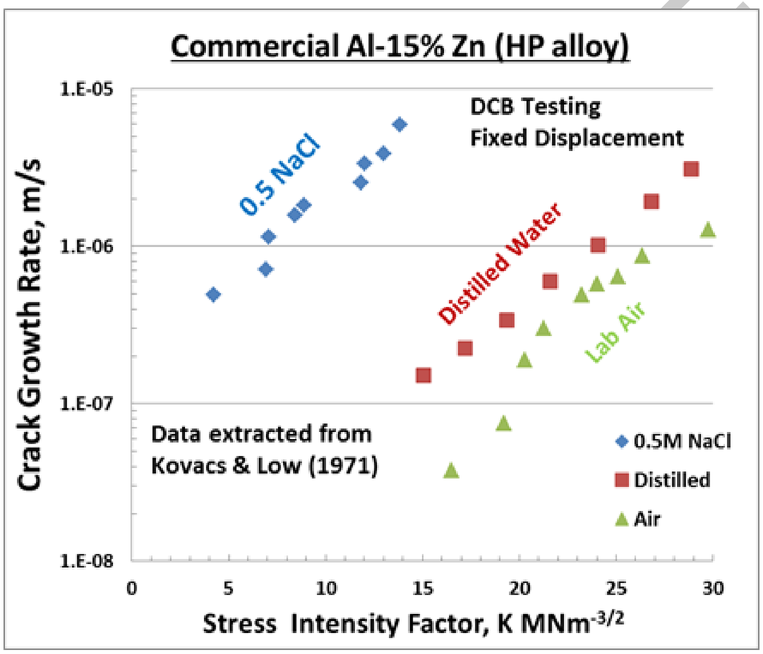

FIGURE 14. Crack growth rate as a function of the stress intensity factor, K imposed during DCB testing of a high-purity commercially cast and peak-aged Al-14.8 Zn alloy under fixed displacement conditions while exposed to 0.5M NaCl, distilled water and laboratory air (<40% RH at 23 ^{O}C) [151].

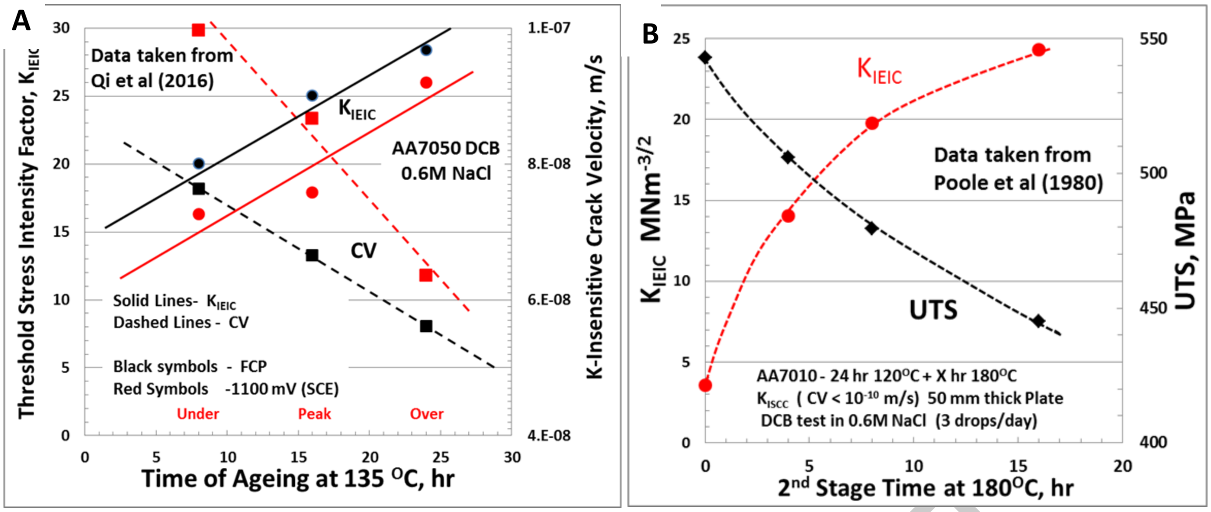

FIGURE 15. Threshold Stress Intensity Factors, K_{IEIC} data as a function of final ageing, extracted from DCB tests exposed to 0.6M NaCl for a) AA7050 along with K-Insensitive crack growth rate [160] and b) AA7010 along with alloy UTS [161]

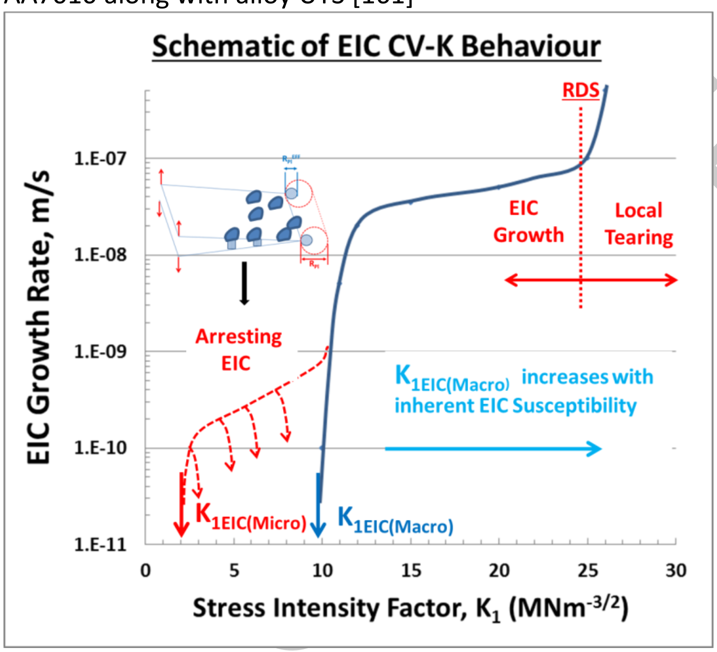

FIGURE 16. Schematic representation of EIC in a high strength Al-Zn-Mg-Cu alloy with short cracks initiating at K's well below the conventional K_{IEIC} obtained from DCB testing, deemed here as K_{IEIC} (Macro), but 'arresting' if the local K's remain below K_{IEIC} (Micro).

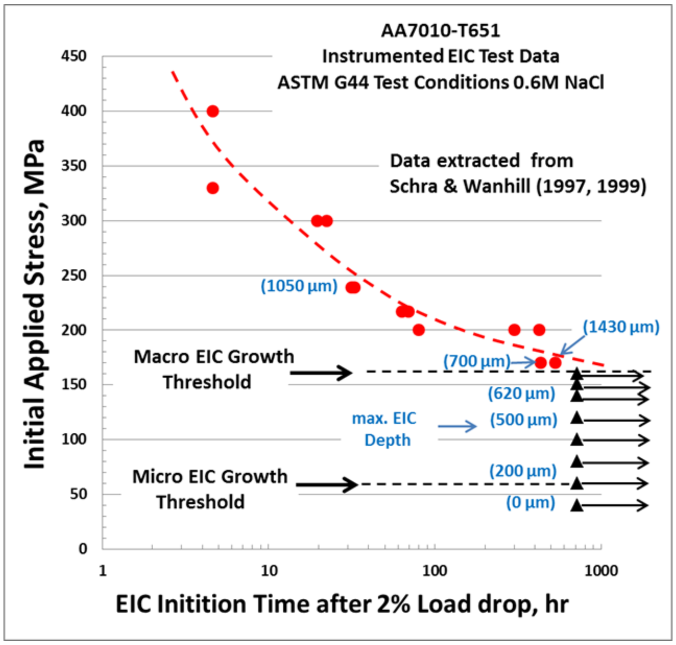

FIGURE 17. EIC test data extracted from Schra and Wanhill [156,157] for tensile samples of AA7010-T7651 plate material exposed to 0.6M NaCl under alternate Immersion test conditions. Predicted EIC initiation times as a function of the initial load applied during ASCOR testing, along with maximum depths of intergranular EIC detected in samples after testing and the implied threshold stresses for the growth of 'Micro' and 'Macro' EIC.

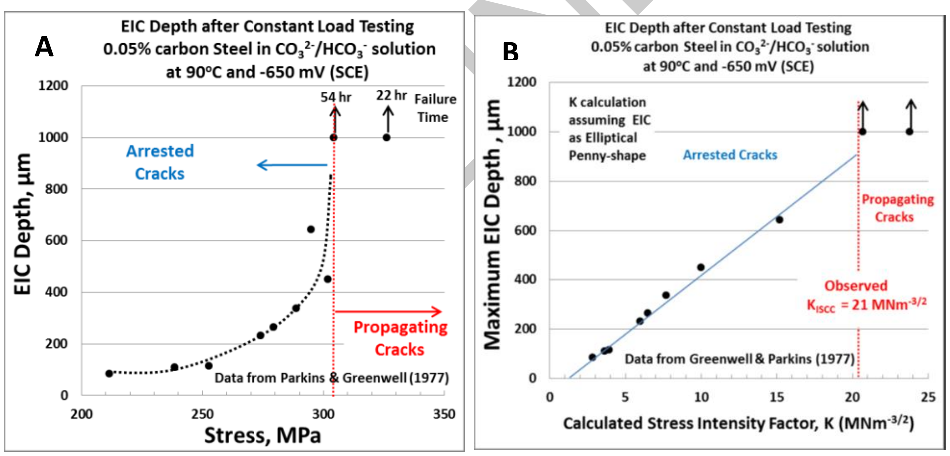

FIGURE 18. EIC depth of cracks arresting during the constant-load testing of a 0.05% carbon steel stressed and held under potentiostatic control in a carbonate-bicarbonate environment at 90 °C: a) EIC depth as a function of applied stress during constant-load testing and b) Estimated stress intensity factors associated with the arrested EIC, assuming a penny-shaped crack profile. (Applied stress and maximum crack depth data is taken from Parkins and Greenwell [165] and the estimated stress intensity factors have been calculated by the authors).

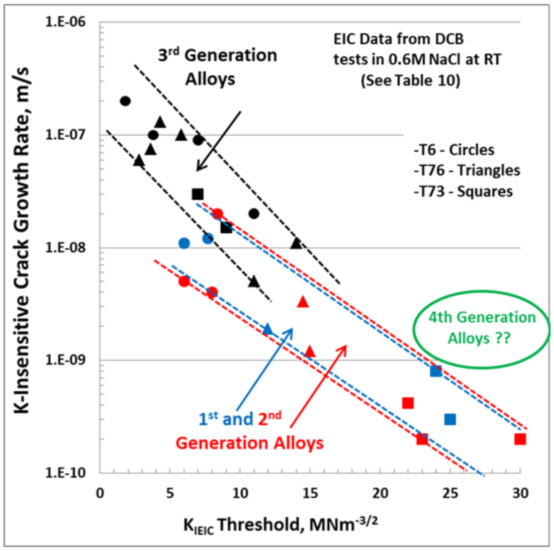

FIGURE 19. K-Independent EIC growth rates as a function of the threshold stress intensity factor for EIC propagation (K_{IEIC}) for commercial Al-Zn-Mg-Cu 7xxx series alloys exposed to 0.6M NaCl environments at room temperature extracted from the DCB results, showing a potential target regime for 4th Generation alloys.

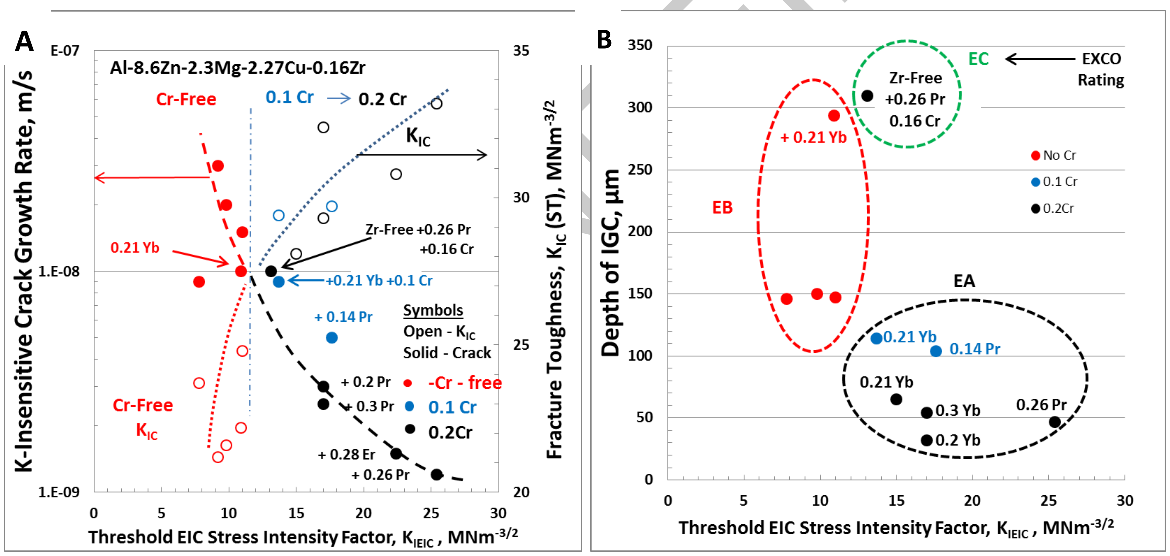

FIGURE 20. EIC and localized corrosion behavior for Al-8.6Zn-2.3Mg-2.3Cu-0.16Zr base alloy with various alloy additions using data provided in Table 12 [171-177]: A) K-Insensitive Crack Growth Rate (EIC propagation) as a function of the threshold Stress Intensity Factor, K_{IEIC} (EIC Initiation) and B) Depth of intergranular corrosion as a function of threshold Stress Intensity Factor, K_{IEIC} and categorized in terms of observed exfoliation corrosion ratings.