Review

N.J. Henry Holroyd*, Timothy L. Burnett, John J. Lewandowski and Geoffrey M. Scamans **Crack initiation during environment-induced** cracking of metals: current status

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Abstract: Environment-induced cracking (EIC) research spanning the last 80 years for ferrous and non-ferrous metals in aqueous environments at ambient and elevated temperatures has concentrated on crack propagation. Studies clearly reveal EIC involves two differentiable processes, one controlling initiation and the other propagation. Utilization of advanced high-resolution electron microscopy over the last 20 years has enabled more focused studies of crack initiation for stainless steel and nickel-based alloys at elevated temperatures exposed to environments associated with the nuclear industry. More recently, when coupled with advanced in-situ experimental techniques such as time-lapse X-ray computed 3D-tomography, progress has also been made for aluminum alloys suffering EIC at ambient temperatures. Conventional wisdom states that chemical processes are typically ratecontrolling during EIC initiation. Additionally, experimental evidence based on primary creep exhaustion ahead of the introduction of an aggressive environment indicates that time-dependent mechanically-driven local microstructural strain accommodation processes (resembling creep-like behavior) often play an important role for many metals, even for temperatures as low as 40 % of their melting points (0.4 T_m). EIC studies reveal initial surface conditions and their associated immediate sub-surface alloy microstructures generated during creation (i.e. disturbed layers) can dictate whether or not EIC initiation occurs under mechanical loading conditions otherwise sufficient to enable initiation and growth. The plethora of quantitative experimental

techniques now available to researchers should enable significant advances towards understanding EIC initiation.

Keywords: crack initiation; metallic alloys; environmentinduced cracking; crack arrest

1 Introduction

Chapter 1, the first chapter of a recently published book that provides an overview of environment induced cracking EIC in metallic alloys, 'Mechanics-Microstructure-Corrosion' Coupling, Blanc and Aubert (2019) confirms that research in this field has focused on crack propagation, paying little attention to the initiation process, which typically originates from an alloys surface layers that often have different microstructure and sometimes different composition compared to the bulk alloy (Combrade 2019). In view of this anomaly, we have carried out a review of the literature on initiation processes for EIC in both ferrous and non-ferrous alloys exposed to aqueous environments at both ambient and elevated temperatures.

Efforts to characterize EIC initiation started during the mid-1950s, continued through the late-1970s (Bakish and Robertson 1956a,b; Eckel 1962; Kohl 1967; Louthan 1965; Pickering and Swann 1963; Silcock and Swann 1977; Smith and Staehle 1967; Sugimoto et al. 1978; Swann 1963; Szklarska-Smialowska and Gust 1979; Tromans and Nutting 1962), but decreased with the introduction of pre-cracked fracture mechanics type test specimens (Brown and Beachem 1965; Novak and Wolfe 1970) and the increased use of slow strain rate testing (Henthorne 2016; Ugiansky and Payer 1979), which modify aspects of the EIC initiation process. Activity continued through the 1980s for non-ferrous (Cassagne et al. 1986; Sieradzki et al. 1987) with a resurgence for ferrous alloys (pipeline, high-strength and stainless steels) beginning during the late-1980s (Blanc et al. 2019; Fairweather et al. 2008; Isaacs 1988; Jones and Simonen 1994; Locci et al. 1987; Maiya 1989; Parkins 1988; Scenini et al. 2019), supported by an increased use of high-resolution electron microscopy (Arioka et al. 2007; Lozano-Perez et al. 2014; Staehle 2010) and in-situ experimentation. Increased activities on nickel-based

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alloys (Bruemmer and Thomas 2008; Le Hong 2001; Moss and Was 2017; Zhai et al. 2017a,b) and austenitic stainless steels (Fairweather et al. 2008; Kamaya and Takumi 2007; Lozano-Perez et al. 2014) were conducted over a decade later in studies at elevated temperatures and environments associated with the nuclear industry, which has continued to date (Fujii et al. 2019; Kuang and Was 2000; Shen et al. 2022; Volpe et al. 2020).

For over 80 years it's been known EIC involves two processes; one controlling initiation and the other propagation (Eckel 1962; Forty 1959; Harwood 1956, 1960; Hines 1961; Hoar and Hines 1956a,b; Lee et al. 1988; Smialowski and Kostanski 1979; Sugimoto et al. 1978).

The lack of research focus on the initiation phase was noted by Hirth (1977) who concluded in his summary of issues arising during a major EIC International Conference, NACE-5 Stress Corrosion Cracking and Hydrogen Embrittlement of Iron based alloys held in France in 1973 that: "It seems that crack initiation is more or less being neglected in comparison to measurements of crack propagation as a function of stress intensity, whereas the incubation time could be a significant fraction of the life in many cases of cracking". More recent publications have confirmed this observation stating that

"On the crack initiation and early-stage crack growth in Stage 1: This is a stage that is less studied and presents many contradictions", Chen (2017) and that "Crack initiation is the least explored stage and is not clearly defined", Hojna (2021).

Our literature review has found that for all metallic alloy/environment systems known to suffer EIC (see subset

provided in Table 1), strain-rate/time dependent metallurgical processes influence the rate-controlling processes during precursor and initiation phases of EIC, irrespective of tests being conducted at temperatures below 0.4 of the melting point (T_m) of an alloy. These findings challenge the current view that chemically-driven processes control the earliest stages of EIC initiation at ambient temperatures that become increasingly less dominant at elevated temperatures where local creep-related processes such as grain boundary cavitation and/or a crystalline ordering become important (Ahn 2021; Arioka 2015, 2020; Shen et al. 2022).

Efforts to quantitatively separate the initiation and propagation stages of EIC have only partially succeeded, although the experimental evidence obtained for various metal/aqueous environments supports different ratedetermining processes controlling crack initiation and crack propagation as the determined activation energies are significantly higher for crack initiation (> 100 kJ/mol) than propagation (< 100 kJ/mol), Table 1.

The comparison of published EIC initiation data is made more complicated by the inter-changeable use of the terms induction, incubation and initiation and the wide range of resolution limits for the experimental techniques used to detect EIC initiation, as shown in Table 2, often yielding different results for a given set of experimental conditions and the absence of an accepted definition for EIC initiation that has prevailed since the 1960s (Eckel 1962).

Table 1: A sub-set of EIC susceptible metal/environment systems with experimental evidence for different processes controlling of initiation and propagation rates.

Alloy Environment		EIC test method	EIC detection method	Temperature (°C)	Apparent activation energy, <i>E_a</i> (kJ/mol)		References
					Initiation	Propagation	
α-Brass (68Cu– 32Cu) annealed	Cu $(NH_4)_n^{2+}$ (CuCO ₃ in NH ₃) at FCP -390 mV (SCE)	Constant load 54 MPa (55 % YS)	Visual and metallographic evaluation of interrupted tests (intergranular)	Room temperature			Sircar and Narsaria (1977)
Al–6Zn–1.2 Mg peak aged	Distilled water	Constant load 98–196 MPa (YS = 333 MPa)	<i>In-situ</i> high-resolution op- tical (intergranular)	0–50 °C	110	37	Abe et al. (1981)
Al-6.2Zn-2.3 Mg		Fixed displace-	Load relaxation	35–100 °C	109 ± 26	-	Pathania 1970;
slightly overaged	0.6M NaCl + 2 wt% K ₂ CrO ₄ , pH = 4	ment (smooth notch K = 14 MNm ^{-3/2})	(intergranular)	0–85 °C	109 ± 9	60	Pathania and Tromans 1981
AZ31B magnesium alloy	0.6M NaCl + 20 g/L K ₂ CrO ₄ ,	Constant load	Extension – time (±10 µm), FCP – time (±1 mV SCE at RT)	30 °C			Logan (1961)
Austenitic stainless	42 wt% MgCl ₂	Constant load	Extension – time (±10 µm)	FCP:	53	84	Kohl (1967)
steel 18.3C r-9.6Ni-	(~154 °C)	412 MPa (> YS,		100–120 °C	66	96	
0.16Mo		70 % UTS)		120–154 °C	34	67	
				(FCP) -360 mV (SCE): 70-120 °C 120-154 °C	29	80	

Table 1: (continued)

Alloy	Environment	EIC test method	EIC detection method	Temperature (°C)	Apparent activation energy, <i>E_a</i> (kJ/mol)		References
					Initiation	Propagation	
Austenitic stainless steel	44 wt% MgCl ₂ (153 °C)	Constant load 180–300 MPa	Extension – time (\pm 10 µm), FCP – time (\pm 1 mV SCE at RT)	153 °C			Desjardins et al. (1980)
Austenitic stainless steel	20 & 35 wt% MgCl ₂ (150 °C)	Constant load (38, 50 & 65 % UTS)	Extension – time (\pm 10 µm), FCP – time (\pm 1 mV SCE at RT)	150 °C			Bleckmann and Zitter (1974)
18.4Cr–9.1Ni annealed	46.4 wt% MgCl ₂ (149 °C)	Constant load 294 MPa (80 % YS)	Extension – time (\pm 10 µm), FCP time (\pm 1 mV SCE at RT) (transgranular)	130–160 °C	163 ± 11	50 ± 3	Sugimoto et al. (1978)
Alloy 600 75Ni–15- Cr–9Fe mill- annealed	Hydrogenated water/steam	Reverse U-bend	>50 % test optical crack detection, (10–160 magni- fication) > 1 mm detected (intergranular)	332-400 °C	183	-	Economy et al. (1987)
		Constant load	<i>In-situ</i> potential-drop (intergranular)		140 ± 25		Richey et al. (2007)
					103 ± 18		Etien et al. (2011)
		Fixed strain via	Metallography (x1000)	320–450 °C	121 ± 13		Moss and Was
		SSRT alloy 600	(intergranular)		(2%)		(2017)
		(3×10^{-7}) , alloy			strain)		Moss and Was
		$\frac{1000}{5 \times 10}$			123 ± 10		(2013)
		dia 20.5 mm Gl			(0 %		
Alloy 690 60Ni–29.5- Cr–10Fe mill- annealed				320-450 °C	92 ± 12		Moss and Was (2017)

Table 2: Experimental methods used to detect EIC initiation in various metallic alloy/environment systems.

EIC initiation detection method	Initial depth of event detected (µm)	Example (reference)
<i>Ex-situ</i> optical ± metallography	~50 µm	18-8 stainless steel in boiling MgCl ₂ (Eckel 1962; Sugimoto et al. 1978)
In-situ optical \pm time-lapse video	(5 ^a —100 ^b) μm	Al–Zn–Mg–Cu alloy 70 °C water vapour (Euesden et al. 2023)
		18-8 stainless steel intermittent boiling MgCl ₂ (Kirk et al. 1959)
In-situ X-ray tomography	~5 µm	AA5083 humid air, RT (Gudla et al. 2020)
<i>Ex-situ</i> surface replica's (acetates)	20 µm	Al–Zn–Mg–Cu alloy in 0.3M NaCl + potassium dichromate
		solution (pH 0.5) at RT (Hilfrich 1968)
Electrode potential during straining	>100 µm	18-8 stainless steel in boiling MgCl ₂ (Bleckmann and Zitter 1974;
		Desjardins et al. 1980; Petit and Desjardins 1977; Hoar and Hines 1954, 1956a;
		Sugimoto et al. 1978)
Resistance-time (potential drop)	~200 µm	Al–Zn–Mg–Cu (McHardy and Hollingsworth 1966)
		Pipeline steel (Wang and Atrens 1996)
		Nickel 600 (Anderson and Chou 2019; Zhia et al. 2017)
Elongation-time, constant-load ^a	>100–1,000 µm	AZ31B magnesium alloy in NaCl/K ₂ CrO ₄ at RT (Logan 1961)
		18-8 stainless steel in boiling MgCl ₂ (Brauns and Ternes 1968; Kohl 1967; Sugimoto et al. 1978)
Load relaxation, constant-	>100–1,000 µm	Stainless steel in water at 289 °C (Wilde 1969)
displacement ^a		
Acoustic emission	~1 mm	304 stainless steel simulated BWR water 288 °C (Hickling et al. 1998)
		316 stainless steel boiling 0.5M NaCl, pH 1.3 (Anita et al. 2006)
Electrochemical noise	200–300 μm's	Sensitized 304 stainless steel water (25 °C) + 100 ppm NaCl or 15 ppm
		sodium thiosulphate (Jones et al. 1991)
Laser light 'speckle'	>200 µm's	AA2024-T3 0.6M NaCl, RT (Shi et al. 2006)
Scanning atomic force microscopy	A few µm's	Al–Zn–Mg in lab air, RT (Komai et al. 1988)

^aSensitive to specimen dimensions. ^bDependent on experimental setup.



Figure 1: Gauge length extension and electrochemical potential as a function of time for an annealed austenitic stainless steel wire exposed to boiling 44 wt% MgCl₂ and an inert environment (oil) under a constant load of 180 MPa. The extension and electrochemical potential are shown as a linear function of time under load. Date taken from Desjardins et al. (1980).

An example of different initiation time predictions for a given set of experimental conditions is provided by the EIC data reported by Desjardins et al. (1980) for 18Cr-10Ni austenitic stainless alloys in boiling 44 wt% MgCl₂ (~154 °C) under constant load testing. Metallographic examination of interrupted constant load tests revealed that EIC microcracks initiated after the sudden electrochemical potential increase but ahead of divergence of the extension-time behavior from that obtained in an inert environment, Figure 1.

Had interrupted testing and off-line metallography not been used to determine when EIC had initiated, three different estimates of crack initiation may be based on: a) the potential-time behavior, b) the initial observation of divergence between extension behavior in an inert and aggressive environment or c) the onset of rapid extension.

Until recently our understanding of the 'how, when and if' for intergranular or transgranular EIC initiation and any subsequent transition to stable crack propagation has been restricted by our inability to consistently reproduce EIC initiation processes in the laboratory representative of service-related mechanical and environmental conditions (Colwell et al. 2008) and a limited availability of suitable high resolution experimental characterization techniques.

Detailed *in-situ* based studies, including use of state-ofthe-art electron microscopy and 3D X-ray computed tomography to characterize EIC initiation are now available for a range of material/environment combinations including the latest generation of high-strength Al–Zn–Mg–Cu alloys exposed to water vapor at ambient temperature (Burnett et al. 2023; Euesden et al. 2023).

2 EIC initiation process

EIC initiation is a complex phenomenon involving several process steps, before, during and after the appearance of initial micro-cracks, which may or may not subsequently undergo self-sustained EIC propagation to become deep cracks.

Our analysis shows that the EIC of metallic alloys involves three process steps, as first suggested in the 1960s for high-strength aluminum alloys in aqueous saline solutions at room temperature (Hunter and Fickle 1968; McHardy and Hollingsworth 1966). As shown in Figure 2A, this was confirmed during the 1970s for austenitic stainless steels in boiling concentrated MgCl₂ solution, Bleckmann and Zitter (1974) and as shown in Figure 2B and reported for nickel 600 type alloys in high temperature water (~360 °C) (Boursier et al. 1992, 1995; Le Hong 2001; Rios et al. 1995).

The three steps are shown in Figure 2B, as: 1) Incubation (Precursor), 2) Micro-crack initiation and early growth and 3) High growth rate EIC after the local mechanical driving force exceeds a minimum, such as a threshold stress intensity factor, K_{IEIC} . These process steps involve an array of overlapping phenomena, depicted in Figure 3, that is based



Figure 2: Experimental data showing the proposed 3 steps for EIC (precursor, initiation/early growth and crack propagation): (A) electrical resistance change during EIC testing AA7075-T651 tensile samples (0.75 % YS) fully immersed in 1M NaCl + 0.21M AlCl₃ (pH = 1) while potentiostatically held at –1100 mV (SCE) at room temperature, McHardy and Hllingsworth (1966) and (B) nominal strain rate estimated from extension-time behavior generated during constant load testing annealed18Cr–8Ni (304) stainless steel immersed in 35 % MgCl₂ at 150 °C reported by Bleckmann and Zitter (1974).

on an amalgamation and extension of proposals by others (Jones and Simonen 1994; Parkins 1988; Persaud et al. 2019; Staehle 2008, 2010).

2.1 Specific adsorption of chemical species

The role of the specific adsorption of chemical species during the precursor period and any subsequent EIC microcrack initiation remains controversial, and was the subject of extensive written discussions between Uhlig and Bockris, Kruger and Pourbaix, Uhlig (1977) and Parkins and Kruger, Pugh and Uhlig, Parkins (1977) following papers presented at a key International Conference in 1973 (NACE-5) in France.

During the late 1930s and following WW2, a group of researches in the USSR (Rehbinder 1947) conducted a series of physico-chemical evaluations of the deformation of various solids (rocks and metals) while surrounded by 'surface-active' species and proposed a 'New physico-chemical phenomena in the deformation and mechanical treatment of solids' (Rehbinder 1947). The phenomena, subsequently known as the 'Rehbinder Effect', was proposed to involve the penetration



Figure 3: A schematic showing potential phenomena during the three phases of EIC.

(adsorption) of 'surface-active' species into ultra-microscopic cracks formed during the strain-hardening of the immediate surface layers during early deformation, that reduced a metals resistance and locally enabled crack extension (Barlow 1966). Another explanation, Andrade and Randell (1949) proposed the adsorption of 'surface-active' species promoted a 'disintegrating action' to the surface oxide film that otherwise would have provided strength.

Subsequent suggestions for the role of specific adsorption a decade or so later, proposed: that a) EIC initiation and propagation in aqueous environments is brittle fracture, where the surface energy associated with crack formation is reduced by the adsorption of specific ions (Coleman et al. 1961) and b) Selective adsorption of specific ions after lowering the surface energy of cracks can operate conjointly with electrochemical action (Uhlig 1959) at potentials above a critical value (Uhlig and Cook 1969) along paths, where defects predominate and where compositional gradients exist.

In more recent times, compelling evidence, based on high-resolution electron microscopy fractography, presented in a series of review articles by Lynch (1977, 1988, 2013) suggest specific adsorption can play a role during EIC propagation for a range of metallic materials including aluminum alloys, nickel, iron-silicon, high-strength steels, magnesium, and titanium alloys when exposed to various aqueous environments. Additionally, similarities were proposed between hydrogen-assisted cracking, stress corrosion cracking, and adsorption-induced liquid-metal embrittlement.

Interest in the role of specific adsorption has continued with further experimental and modelling work to elucidate the role played by mechanochemical and chemomechanical surface effects during the EIC and fracture of metal alloys (Bogdanov et al. 2019; Gutman et al. 1996; Yan et al. 2023; Yin and Yuan 2023).

2.2 Incubation (precursor) process step

Historically the incubation (precursor) step ahead of EIC microcrack initiation has received minimal attention and is the least well understood process step. There has been limited activity for aluminum and magnesium alloys (Cocks et al. 1959; Logan 1961) and copper-based alloys (Pugh 1971) at ambient temperatures, slightly more for carbon steels (Parkins 1988) and somewhat more, for stainless steel and nickel-based alloys at elevated temperatures as used in the fossil and nuclear power generation industries (Arioka et al. 2010, Arioka 2020; Gooch 1984; Lees and Siverns 1978).

Depending on the metallic alloy-environment system involved the incubation (precursor) step can be completed within a few seconds, as shown by sudden failure of stressed hard-drawn 13-carat gold thick-wire exposed to a small volume of ferric chloride, Roberts-Austen (1888), to longer times, from a few hundred to a few thousand hours for austenitic stainless steels in concentrated magnesium chloride solutions at around 150 $^{\circ}$ C (Bleckmann and Zitter 1974; Desjardins et al. 1980). This step can last for up to a decade or more for carbon steels exposed to deoxygenated steam at 360 $^{\circ}$ C in fossil-fueled power plants (Lees and Siverns 1978) to even longer times, up to 40 years, for hydrogenated reactor coolant at 310 $^{\circ}$ C in a pressurized heavy water reactor (PHWR) observed in light-water nuclear reactors (Arioka et al. 2013).

These observations confirm that the critical events during the incubation (precursor) stage differ between metallic alloy-environment systems especially when complications introduced by an alloys initial surface condition and its immediate sub-surface layers with 'disturbed microstructures' (Beilby 1921; Chang et al. 2019; Forsyth 1998; Paxton and Procter 1968; Scamans et al. 2010) generated during manufacture or fabrication for industrial use or during laboratory test specimen preparation.

However, despite of these limitations, we have identified two basic EIC precursor categories:

- Micro-crack initiation following incubation directly from or within a few microns of an external 'smooth' surface exposed to bulk environments and
- Micro-crack initiation from within an occluded geometric feature generated during the precursor process and now containing modified local environmental conditions (solution chemistry and electrochemical potential) from the bulk environment.

We have considered the end-point of these two categories to be equivalent, with the caveat being that the development of an appropriate local environmental and stress raiser conditions needed for EIC micro-crack initiation under full immersion, alternate immersion or thin-electrolyte-layer conditions (e.g. under humid air environments).

Edeleanu and Evans (1951) prediction that local environmental changes should occur within occluded regions was experimentally verified by the measurement of local solution pH changes within unstressed restricted geometries for nonferrous and ferrous alloys exposed to a saline solutions (Alavi and Cottis 1987; Brown et al. 1969; Cooper and Kelly 2007, 2008; Davis 1971a,b; Holroyd et al. 1984, 1987; Kelly 2021; Sandoz et al. 1970). Additionally, extensive modelling has been conducted on the development of electrochemical potential and local solution chemistries with restricted geometries for aluminum alloys under full immersion conditions in aqueous saline environments without the application of load (Edwards 1990; Cooper and Kelly 2007, 2008; Kelly 2021).

For ferrous alloys, Turnbull and coworkers (Turnbull 1993, 2001, 2017, 2021; Turnbull et al. 2009) modelled the complex processes involved during the EIC initiation process that included: electrochemical potential and solution chemistry development within restricted geometries (Turnbull 1990, 2001), the 'pit-crack' transition (Turnbull 2017, 2021; Turnbull and Zhou 2004; Turnbull et al. 2009) and a strain-based rationalization (Horner et al. 2011; Turnbull 2017) as to why EIC initiation can occur towards the open end of pits or occluded regions, rather than at the deepest penetration where the local mechanical stress would be higher. A recent review of the governing factors for pit-to-crack transitions of metallic structures came to similar conclusions (Katona et al. 2023). However, very limited information is available for any metallic alloys under load or for alloys under alternate immersion or thin-electrolyte-layer conditions with or without load.

2.2.1 Influence of deformed surface layers

Deformed surface layers generated during metal processing can control EIC initiation during both in laboratory testing and in commercial applications.

Contrasting responses have been reported for an austenitic stainless steel strained in boiling magnesium chloride at 144 °C (Kohl 1967) and commercial carbon-manganese pipeline steels strained in 0.5 M Na₂CO₃ + 1M NaHCO₃ solution at 70 °C (Wang and Atrens 1996), compared to an Al–Zn–Mg alloy strained in a saline environment at 25 °C (Borchers and Tenckhoff 1969). Significantly longer EIC initiation times resulted after the removal of deformed surface layers generated by machining for both the 18Cr–9Ni austenitic stainless steel, with an electropolished surface following (Table 3) and for carbonmanganese pipeline steels with a lightly machined (Table 4).

Significantly longer EIC initiation times resulted when deformed surface layers were removal from an Al–Zn–Mg alloy subjected to constant load testing in a saline environment at 25 °C, Borchers and Tenckhoff (1969), Figure 4.

Table 3: Effect of deformed surface layer removal on the EIC initiation times for 18Cr–9Ni austenitic stainless steel subjected to constant load testing at 414 MPa (70 % UTS) in boiling 44 % MgCl₂ solution at 144 °C, Kohl (1967).

Surface condition	Time (s)				
	EIC initiation	Crack propagation	Final fracture		
Machined + final light electro- polish (8 tests)	270	1,272	1,542		
Oversized machined + final 250 µm electrochemical surface removal (19 tests)	5,220	1,020	6,240		

Table 4: Effect of surface condition on minimum stress for EIC initiation in X65 pipeline steel (yield stress 446 MPa) in $0.5 \text{ M Na}_2\text{CO}_3 + 1\text{M NaHCO}_3$ solution at 70 °C under potentiostatic control under increasing load.

	EIC minimum stress (MPa)			
Potential (mV, SCE)	Original surface	Polished surface		
-600	452	480		
-1,000	420	437		

Data from Wang and Atrens (1996).



Figure 4: Failure times for an underaged Al–6Zn–3Mg alloy for a range of surface pretreatments prior to constant-load testing at 147 MPa in 0.53M NaCl + 0.1 % H_2O_2 environment held at 25 °C. Data taken from Borchers and Tenckhoff (1969).

Deformed surface layers on the 18Cr–8Ni stainless steel and carbon-manganese pipeline steels are prone to suffer local fracture at relatively low stresses and provide local EIC initiation sites and hence their removal is beneficial, whereas for the Al–Zn–Mg alloy disturbed layers typically are not brittle and their presence prevents or delays environmental access to the underlying alloy bulk microstructure (i.e. removal is detrimental). For aluminum alloys, the deformed layer has a different microstructure with an ultrafine grain size to the bulk material (Beilby 1921; Forsyth 1998; Paxton and Procter 1968; Scamans et al. 2010), that can control EIC initiation behavior, or simply delay the environment having direct access to the underlying bulk alloy.

2.3 Micro-crack initiation and early growth

The transition between incubation (pre-cursor) and microcrack initiation and early crack growth remains a poorly understood aspect of EIC initiation. The local mechanics of micro-crack initiation can be considered as insensitive to





Figure 5: Intergranular EIC initiation: (A) associated with transgranular surface slipsteps generated during the slow strain rate testing 70/30 α-brass in 1M NaNO₂ at RT, while held potentiostatically at -100 mV (SCE) [Image taken from Yu et al. (1984)], and (B) from within localized corrosion sites generated during the early stages of constant load testing a 26Cr-1Mo ferritic stainless steel at 90 YS, while potentiostatically held at -460 mV (SCE) and immersed in boiling 42 % LiCl + 1% thiourea. Localized corrosion site geometry development as a function of test time in minutes. [Images take from Kwon et al. (1992) and Locci et al. (1987) used with permission from ©AMMP 2024].

whether it occurs, near to an external free-surface, involving the bulk environment (Figure 5A) or from within an occluded region (say from 50 μ m up to a few mm deep) that usually contains a locally modified environment different from the bulk, Figure 5B.

Initial EIC crack growth is typically restricted to approximately one grain diameter with cracks terminating on reaching a microstructural barrier. In instances where deeper cracks evolve, sometimes by interacting and coalescence with other cracks (Connolly and Scully 2000; Elboujdaini et al. 2000; Parkins and Singh 1990), growth of these micro-cracks are highly sensitive to and controlled by local EIC susceptibility and microstructure, together with whether a sufficient local mechanical driving force is available to fracture any uncracked ligaments in the cracked regions process zone that otherwise would result in crack arrest.

Processes controlling initial EIC micro-crack growth typically involves either anodic dissolution or a hydrogeninduced process, which for some alloy/environment systems may be controlled potentostatically or by pre-exposure or cathodic pre-charging with hydrogen.

2.3.1 Crack arrest during the initiation process

EIC has been reported to initiate under static loading conditions well below those necessary to enable sustained EIC propagation in magnesium alloys (Wearmouth et al. 1973), carbon-manganese steels (Parkins and Greenwell 1977), aluminum alloys (Holroyd et al. 2015; Liu et al. 2004, 2007; Schra and Wanhill 1997, 1999) and HSLA steel and conventionally quenched and tempered low alloy steel (Kumar 2008) exposed to aqueous saline solutions at ambient temperatures.

A schematic illustration of this behavior under constantload conditions is shown in Figure 6.

Experimental evidence of this behavior is shown in Figure 7, using data for a 0.05 % carbon steel under constant load testing and potentiostatic control in an aqueous carbonate/bicarbonate solution at 90 $^{\circ}$ C (Parkins and



Figure 6: A schematic representation of hypothetical constant-load EIC test behavior showing that EIC can initiate at applied stress levels below the threshold needed to ensure propagation to failure, $\sigma_{Thresshold}$, but subsequently arrest.

Greenwell 1977). EIC cracks can initiate and arrest when the applied stress is below a minimum, $\sigma_{Thresshold}$, Figure 7A. The maximum implied stress intensity factor for the measured 'arrested' cracks (calculated here assuming penny-shaped elliptical cracks) is similar to the experimentally measured threshold stress intensity for EIC, K_{IEIC} , Figure 7B.

Another schematic representation of 'EIC arrest' is provided in Figure 8. Here EIC initiation and its subsequent arrest is superimposed upon crack growth rate – stress intensity factor data from classic double cantilever beam EIC testing of a fatigue pre-cracked test specimen loaded under constant-defection conditions, where the applied stress intensity factor decreases with EIC growth and provides a EIC threshold stress intensity factor, $K_{\rm IEIC(Macro)}$ for a long crack, based on when crack growth rates fall below about 10⁻¹¹ m/s.

Schra and Wanhill (1997, 1999) reported experimental data that confirmed the initiation and arrest of EIC at K levels well below the reported threshold, K_{IEIC} for a high-strength aluminum alloy undergoing EIC in a saline solution, which was analyzed by Holroyd et al. (2023).

The local conditions needed for EIC initiation and whether EIC arrests or continues to propagate are highly sensitive to prevailing local microstructural strainaccommodation characteristics, which is both time and temperature-dependent.

EIC evaluation or the approval/verification testing of metallic alloys rarely assess crack initiation, other than via the assumed relationship with a threshold stress, $\sigma_{\rm EIC}$ or stress intensity factor, $K_{\rm IEIC}$, obtained for arresting 'long cracks' in pre-cracked test specimens. While a higher $K_{\rm IEIC}$ is indicative of an improved EIC resistance to crack propagation, an arrested 'long crack' in a pre-cracked test specimen may not be representative or relatable to EIC initiation where this is no pre-existing crack.



Figure 7: Depth of arrested intergranular EIC in tensile samples developed during constant-load testing of a 0.05 % carbon steel in a carbonate/ bicarbonate environment at 90 °C under potentiostatic control at –650 mV (SCE): (A) EIC depth as a function of applied stress and (B) estimated stress intensity factors for arrested EIC, assuming a half-penny-shaped crack profile. Applied stress and maximum crack depth data taken from Parkins and Greenwell (1977) and estimated stress intensity factors calculated by current authors.



Figure 8: Schematic representation of EIC with micro-crack initiating and arresting at K's below K_{IEIC} , using data for a high-strength aluminum alloy, but applicable to other metallic alloys. Taken from Holroyd et al. (2023); reproduced with permission from © AMMP 2023.

2.4 Role of local microstructural strainaccommodation characteristics

Although it had been considered that strain-accommodation by creep-like processes are unlikely to be relevant for temperatures below $0.4 T_{M}$, experimental evidence for several ferrous and non-ferrous metal/environment systems shows that the exhaustion of primary creep in an inert environment ahead of exposure of a stressed alloys to an EIC environment can either prevent EIC initiation or can significantly increase the minimum mechanical driving force ($\sigma_{Thresshold}$ or K_{IEIC}) required for EIC initiation at ambient and elevated temperatures, Table 5.

Leckie (1967) showed significant differences in EIC initiation behavior for fatigue pre-cracked cantilever beam tests specimens of annealed titanium alloy (Ti–7Al-2Cb-1Ta) loaded in laboratory air (30 % RH) and then exposed to 0.53M NaCl with and without a time delay of a few minutes to enable beam deflection rates to become stable after loading as shown by Kujawski and Krempl (1981). The introduction of a time delay after loading enabled sufficient primary creep exhaustion to prevent EIC initiation at stress levels that would have promoted EIC initiation, Figure 9. These finding suggest that EIC initiation requires a sufficient local strain rate in addition to a mechanical load. Leckie (1967) attributed the local minimum strain rate requirement to that needed to disrupt a thin protective oxide film.

Similar findings by Kwon et al. (1992) have been reported for EIC initiation in a mill-annealed low-interstitial 26Cr–1Mo ferritic steel (E-Brite) subjected to constant load testing in a boiling 42 % LiCl solution, while polarized to potentials above the critical cracking potential, E_{cc} . Uhlig

Alloy	Loading conditions	Environment conditions	Temperature	T _m (T/T _{mp}) °K	References
Ti–7Al-2Cb-1Ta Annealed	Fatigue pre-cracked SEN cantilever bend. constant load	Lab air (30 % RH) or 0.53M NaCl, FCP	RT	0.15	Leckie 1967 (Figure 9)
YS = 706 MPa,					
UTS = 823 MPa, K_{IC} = 121 MNm ^{-3/2}					
Mg–7Al	Constant load, smooth tensile specimen		RT	0.34	Wearmouth et al. (1973)
26Cr–1Mo ferritic stainless steel	Constant load, smooth tensile specimen	42 % LiCl + thiourea, –500 or –460 mV (SCE), de-aerated	140 °C	0.25	Kwon et al. 1992 (Figure 10)
Annealed 304 stainless steel $K_{\rm IC}$ = 86 MNm ^{-3/2}	Constant strain, notched WOL, constant load, SEN both with 0.2 mm notch root radius	42 % MgCl ₂	143 °C	0.25	Gu et al. 1994 (Figure 11)
As-quenched NiCrMoV rotor steel, YS = 1,250 MPa	Double cantilever beam, fatigue pre-cracked, constant load & con- stant strain	Dry air, (silica–gel), distilled water	22 °C	0.17	Rieck et al. 1989 (Figure 12)
As-quenched 4,340 high strength martensitic steel, YS 1700 MPa	Double cantilever beam, fatigue pre-cracked, constant load & con- stant strain	Dry air, (silica–gel or P ₂ O ₅), distilled water	22 °C	0.17	Rieck et al. 1989 (Figure 12)
C–Mn pipeline steel	Constant load fatigue pre-cracked SEN cantilever bend	1M Na ₂ CO ₃ + 1M NaHCO ₃ , -900 or -650 mV (SCE)	75 °C	0.2	Parkins 1979 (Figure 13)

Table 5: Examples of ferrous and non-ferrous metal/environment systems where exhaustion of primary creep ahead of exposure of a stressed sample to the EIC environment can either prevent or significantly increase the minimum mechanical driving force ($\sigma_{\text{Thresshold}}$ or κ_{TEIC}) required for EIC initiation.



Figure 9: Failure time for annealed titanium alloy (Ti–7Al-2Cb-1Ta) fatigue pre-cracked cantilever beam test specimens loaded in laboratory air (30 % RH) and then exposed to 0.53M NaCl or 30 % RH laboratory air. Data from Leckie (1967).



Figure 10: EIC failure time for mill annealed E-Brite ferritic stainless steel subjected to constant-load testing in 42 % LiCl + thiourea polarized at –460 mV (SCE) as a function of initial holding time under load at a 'non-cracking' potential (–500 mV (SCE)) to allow primary creep exhaustion. Data taken from Kwon et al. (1992).

(1959). EIC initiation was prevented by allowing primary creep exhaustion at the corrosion potential ahead of increasing the potential to above E_{cc} , where otherwise EIC would have initiated, Figure 10.

Although similar findings were reported for an annealed 304 stainless steel exposed to boiling $42 \% \text{ MgCl}_2$ under fixed-displacement conditions, Gu et al. (1994), Figure 11, when testing was repeated under a constant load the allowance of 72 h creep under the test load conditions at



Figure 11: Failure time for annealed 304 stainless steel single-edge 0.2 mm notch root diameter test specimens exposed to 42 % boiling MgCl₂. Data extracted from Gu et al. (1994).

Table 6: $K_{\rm ISCC}$ data quoted by Gu et al. (1994) from annealed 304 stainlesssteel notched test specimens subjected to constant strain or constant loadEIC testing in a boiling 42 % MgCl₂ solution, with and without 72 h pre-creep under load prior to the addition of the test environment.

EIC threshold stress intensity factor, $K_{\rm ISCC}$ (MNm ^{-3/2})				
Loading mode	No pre-creep	Pre-creep		
Constant strain	11.8	42.3		
Constant load	8.9	8.9		

either room temperature or 142 °C ahead of adding the aqueous environment had no significant effect on the failure time or the implied EIC threshold stress intensity factor, K_{ISCC} , Table 6.

For austenitized and oil-quenched NiCrMoV Rotor Steel and high-strength 4,340 steel, Rieck et al. (1989) demonstrated EIC initiation was prevented in fatigue pre-cracked double cantilever beam (DCB) test specimens loaded to 40 MNm^{-3/2}, following 10 min creep exhaustion under fixed-displacement conditions in an inert environment (P₂O₅ dried air) after 1 h drying (unloaded) ahead of loading with exposure to distilled water at 22 °C. EIC initiation is prevented, despite the applied K being well above the published K_{IEIC} threshold of 10– 20 MNm^{-3/2} (Magdowski 1987). Similar testing using silica gel dried air was sufficient to prevent EIC initiation for the Rotor Steel but not for the 4,340 steel, Figure 12.

Parkins (1979) demonstrated the importance of local strain rate deformation rates during EIC initiation as shown in Figure 13 for constant load testing of fatigue pre-cracked notched cantilever beam specimens of a carbon-manganese steel exposed to a $0.5M \text{ Na}_2\text{CO}_3 + 1M \text{ NaHCO}_3$ solution at 75 °C, under potentiostatic control.



Figure 12: Use of creep exhaustion in an inert environment to prevent EIC initiation in as-quenched high strength steel (4,340) and 3.3NiCrMoV Rotor steel pre-cracked DCB test specimens load to initial K of 40 MNm^{-3/2}. Data extracted from Rieck et al. (1989).

The unique aspect of these results using two electrochemical potentials during straining is the confirmation that EIC initiation and growth in the system studied requires both an appropriate electrochemical potential, -650 mV (SCE) and an adequate local crack-tip region strain rate.

2.5 Crack arrest and crack coalescence during the initiation process

Characteristic extension-time creep behavior for metal wire or waisted tensile sample subjected to a constant load in an inert environment is shown in Figure 14. The data shown for an austenitic stainless steel strained in an inert oil at 154 °C provided by Desjardins et al. (1980) initially displays characteristic rapid extension (primary creep) followed by a transition to an exponentially decreasing extension rate (secondary creep) Figure 14A, with the overall extension behavior following logarithmic time dependence, Figure 14B.

Nominal strain rates promoted during constant load testing may be estimated as a function of time by using the slope of the extension-time curve, nomalized using the test specimen gauge length. Such estimated are shown in Figure 2B for 304 austenitic stainless steel tensile samples subjected to constant-load testing in oil or 35 % MgCl₂ at 150 ° C by Bleckmann and Zetter (1974). Implied nominal strain rate response in inert environments decease linearly logarithmically with time, whereas any increases in nominal strain rate during testing in the MgCl₂ reflects EIC initiation, and any subsequent decrease are associated with local micro-crack arrest, Figures 2B and 15.



Figure 13: Cantilever beam defections under constant load provided by Parkins (1979) for a C-Mn pipeline steel immersed in a carbonate/ bicarbonate solution at 75 °C as a function of time at the potentials for four test conditions: Curve A: at -650 mV (SCE) throughout the test, shows increasing deflection at a rate increasing with time, especially after the initial stages of testing. EIC initiation and growth, confirmed post-test. Curve B: at -900 mV (SCE) throughout the test, shows a continual decrease in the deflection rate consistent with creep exhaustion and lack of EIC initiation detected post-test. Curve C: at -900 mV (SCE) for the initial 40 h, while the observed deflection rate decreased to a relative steady rate indicative of primary creep exhaustion, and then switched to -650 mV (SCE), which resulted in no significant change to deflection rate behaviour, consistent with the lack of any EIC initiation found after testing. Curve D: at -900 mV (SCE) for the initial 12 h of loading, while the observed deflection rate did not decrease significantly switching to -650 mV (SCE) led to an increasing deflection rate, similar to that found for testing at -650 mV (SCE). EIC initiation and growth was confirmed post-test.

Analysis of the Bleckmann and Zitter (1974) constantload data shows that the implied EIC initiation and subsequent arrest behavior for 304 austenitic stainless steel immersed in a less aggressive environment, 20 % MgCl₂ at 150 °C, Figure 15, is indicative EIC initiation now requires a longer incubation period and additional time for the crack growth needed for onset of rapid EIC as opposed to crack arrest.

2.6 Opportunities/needs for additional research/investigation of EIC in additively manufactured materials

Recent reviews have highlighted the need for EIC research (Lewandowski and Seifi 2016) on selected corrosion-resistant materials (Biserova-Tahchieva et al. 2023) processed via AM



Figure 14: Characteristic extension-time response for a metal alloy under a constant-load in an inert environment. Data taken from Desjardins et al. (1980) for an annealed austenitic steel loaded exposed to an inert oil at 154 °C: (A) extension as a linear function of time, showing an initial high extension rate associated with primary creep followed by an exponentially decreasing rate associated with secondary creep, (B) extension data from (A) replotted as a logarithmic function of time.

techniques. As pointed out by Lewandowsi and Seifi (2016) AM processing has mainly focused on conventional alloys that were not necessarily designed to be processed via AM techniques. This is an important consideration as AM processing may produce a variety of non-equilibrium microstructures (e.g. due to the rapid solidification), nonequilibrium segregation of alloying elements, as well as process-induced defects such as keyholes, lack of fusion, solidification porosity, and as-processed surface roughness. These aspects may completely change the EIC response of as-processed as well as post-processed materials using



Figure 15: Nominal strain rate obtained from extension-time behavior generated during constant load testing annealed 18Cr–8Ni (304) stainless steel immersed in 20 % MgCl₂ at 150 °C. Data obtained from Bleckmann and Zitter (1974).

conventional post-processing techniques (e.g. heat treatment, HIP, etc.) as the heat treatment response of such AM-processed materials may be completely different than that exhibited in conventionally processed materials (e.g. cast, rolled, forged, etc.). While EIC studies on AM processed materials are emerging (Rebak and Lou 2018; Santamaria et al. 2023; Yazdanpanah et al. 2022), which suggest the EIC propensities of AM materials will be at least equivalent to conventional alloys, a need exists to extend additional effort to identify novel surface/bulk post-processing techniques to specifically target EIC prevention for both AM and conventional metallic products.

2.7 Opportunities based on new characterization capabilities

There is an opportunity further insight into the understanding of EIC initiation based on some of the latest characterization capabilities. However, this it is still a significant challenge as the time scale of initiation could be almost instantaneous in terms of the moment an EIC crack appears from something that was a crack precursor and this may happen following a significant time which practically could be days, weeks or years and in laboratory experiments could still be many hours. This could be a major issue restricting the use of highly time-resolved probes to investigate initiation involving huge data streams and 'wasted' equipment time to move past incubation and capturing initiation events. Similarly, the location of initiation events can be widely distributed across a sample surface, and it is not possible to know exactly where the initiation event will occur. It is a challenge to maintain high spatial resolution analysis over a large area. Reducing the area observed or creating pre-cursor features such as pre-cracks, will localize initiation but this may not represent the real situation depending on the application where initiation occurs on preferred sites and not pre-cracks.

The direct detection of hydrogen using mass spectrometry techniques of NanoSIMs (Li et al. 2020) and atom probe tomography (APT) (Gault et al. 2012), Hydrogen trapping and embrittlement in high-strength Al alloys (Zhao et al. 2022) can be used to support predictions of hydrogen trapping at specific microstructural locations. NanoSIMS is capable of mapping a surface with a resolution between 50 and 200 nm to detect hydrogen and APT is capable of near atomic resolution. However, the sample preparation and ultra-high vacuum characterization environment make it very difficult to preserve the distribution of hydrogen in the microstructure and this may be limited to identification only of deep traps where the hydrogen atoms are relatively stable. Cryopreparation, transfer and measurement are helping to address this issue (McCarroll et al. 2000). Another opportunity is based on the use of deuterium or other isotopic labels to identify exactly which source of environment is responsible for the observed features e.g. fracture path and can separate this hydrogen source from any background or any hydrogen pre-existing in the metal. An investigation of the oxidation behavior of zirconium alloys using isotopic tracers and high-resolution SIMS (Yardley et al. 2013) and NanoSIMS analysis of hydrogen and deuterium in metallic alloys: Artefacts and best practice (Aboura and Moore 2021).

Neutron imaging and diffraction is another technique which can directly detect the presence of hydrogen (Griesche et al. 2014). Three-dimensional hydrogen distribution and quantitative determination of titanium alloys via neutron to-mography (Yang et al. 2020). However, acquisition times are long and resolution is relatively low in the 10's of microns range. But it is non-destructive and non-contact which means *in situ* studies which preserve the test environment can be conducted. The resolution is a limiting factor as it does not match the scale of the microstructural features where hydrogen is trapped.

Scanning Kelvin probe microscopy, following a specific methodology of sample preparation can also be used to detect and spatially map hydrogen (Ma et al. 2021) This time at a scale of 10 s of nanometres and typically across a 100 μ m or less field of view. It is well suited to studies of initiation especially from corrosion sites based on it's very high spatial resolution, and capability to work in liquids and to conduct

time-lapse studies (Blanc and Oltra 2023). It is however limited to surface analysis.

Whilst X-ray computed tomography cannot directly detect hydrogen it is a high-speed, high resolution technique which with synchrotron sources is capable of observing fast fracture in 3D over time (Maire and Withers 2014). This technique can provide the requisite microstructural scale and as a non-destructive, non-contact technique tests can be conducted in any environment and directly observed. This means that it is now possible to see the influence of different environments or strain conditions on the failure/fracture process (Gudla et al. 2020; Koko et al. 2023; Singh et al. 2014). Combination of X-ray diffraction and X-ray scattering and spectroscopy techniques are also gaining attention to add additional structural and chemical information (Kim et al. 2023) although it can be challenging to optimize the conditions for materials testing, imaging and diffraction simultaneously especially for time-resolved experiments (King et al. 2008; Örnek et al. 2023). The technique is extremely powerful for understanding different behaviour as cracking evolves and relating it directly to post-mortem studies which might typically involve electron microscopy fractography but can also include other techniques such as nanoSIMS and APT. The nondestructive, non-contact nature of neutron and X-ray tomography also means that many different probes can be used during testing to observe, mechanical, electrical, chemical and other changes taking place during experiments.

Relatively simple experimental setups using optical microscopy (Euesden et al. 2023) or highly sensitive detection using electrical probes for mechanical (Crane and Gangloff 2016; Harris et al. 2016) or electrochemical detection (Yang et al. 2016) can also be extremely effective and have the advantage of being simple and allowing many repeat tests to be carried out.

In all of the above techniques it is often difficult to properly capture the critical microstructural scales which covers at the upper end, many grains and the second phase particles as well as the nanoscale particles and atomic scale interfaces which are of critical in determining EIC susceptibility. Especially as to appreciate the creep or time-dependent strain behaviour of a metal requires detailed examination across multiple grains and the capture of evolving microstructural information. X-ray diffraction can achieve this in a nonspatially resolved way but latest in situ scanning electron microscopy techniques (Taylor et al. 2024; Yavuzyegit et al. 2023) are enabling microstructurally resolved studies covering a wide range of scale whilst extracting quantitative structural details (Gutierrez-Urrutia et al. 2013; Wang et al. 2023). However, challenges still remain to apply to capture the influence of the environment.

Although these techniques are extremely powerful, they are not able, individually to give all the perspectives needed to understand EIC and the incubation and initiation of cracks (Koyama et al. 2017). The temporal and spatial scales that have to be traversed as well as the environmental, mechanical and microstructural context means that our best chance of studying EIC initiation is through a multimodal, multiscale and correlative approach (Burnett and Withers 2019).

3 Conclusions

Experimental evidence for EIC for a wide range of metallic alloy systems, including: aluminum, magnesium, titanium, high and low strength and stainless steels and nickel alloys has shown that:

EIC Initiation and propagation involve two time-resolved phenomena.

Initial microcrack growth may arrest prior to and without the establishment of crack propagation conditions.

Initial surface conditions and associated immediate subsurface alloy microstructure layers generated during creation (i.e. disturbed layers) can dictate whether or not EIC initiation occurs under mechanical loading conditions sufficient to enable initiation and growth.

Allowance of sufficient primary creep exhaustion ahead of introduction of an aggressive environment can prevent EIC initiation, despite the mechanical driving force being well above conventional threshold (σ_{IEC} or K_{IEIC}) requirements.

Time-dependent local strain accommodation processes are important during EIC initiation at temperatures below $0.4 T_m$.

Significant advances in the understanding the initiation of EIC in structural metals are now possible with the development of a wide range of new characterisation techniques that are starting to make an impact on this complex.

Research ethics: Not applicable.

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