

Chapter Eleven

Corrosion fatigue

S.A. Shipilov

*Department of Mechanical and Manufacturing Engineering,
University of Calgary, Canada*

Abstract

Corrosion fatigue is generally recognized as an important phenomenon that can lead to unexpected cracking behaviour and failure of structures under certain conditions. Such conditions depend on the specific combination of material, cyclic loading and environment of concern that in turn represent the metallurgical, mechanical and physicochemical (electrochemical in aqueous solutions) components of the corrosion-fatigue problem, respectively. Since the earliest research made during the First World War, significant progress has been made, especially in the last four decades, in understanding the corrosion-fatigue phenomenon. However, despite the progress made, researchers are still far from solving many problems related to corrosion fatigue. At this time, no effective method for preventing corrosion-fatigue failures has been identified, and it is not possible to predict which combinations of material and environment will result in intensive corrosion fatigue under in-service conditions. The theory of corrosion fatigue is far from comprehensive. Little is known about the basic mechanisms of corrosion-fatigue crack propagation, and even less is known about the mechanisms by which the environment can accelerate such crack growth. The purpose of this paper is to outline the present state of knowledge and current controversies concerning the phenomenon of corrosion-fatigue crack growth and its mechanisms.

1 Introduction

The subject of corrosion fatigue of metallic engineering materials has attracted considerable attention from researchers throughout the world beginning in the mid-1910s when the first research on record was carried out [1]. This means that



the history of corrosion fatigue research is a part of the history of engineering of the 20th and 21st centuries. The problem may have had humble beginning in observations made of breakages in the Royal Navy's paravane towing cables during the First World War [1] but today corrosion fatigue is acknowledged as one of the most important areas of engineering research. Since the early 1960s, corrosion fatigue, along with stress-corrosion cracking (SCC), has been responsible for many, if not most, service failures in a wide variety of industries [2]. The economic and humanitarian aspects of corrosion-fatigue failures have led to considerable scientific and engineering efforts directed at the understanding and prevention of such failures. Since the earliest research [1,3–8], significant progress has been made, especially in the last four decades, in understanding corrosion-fatigue phenomena. Nevertheless, despite the efforts that have been exerted and the progress that has been made, researchers are still far from solving many problems related to this mode of materials failure. At this time, no effective method for preventing corrosion-fatigue failures has been identified, and it is not possible to predict which combinations of material and environment will result in intensive corrosion fatigue under in-service conditions. The theory of corrosion fatigue is far from comprehensive. Up to now, no firm consensus exists on the crack-growth mechanism in any one material–environment combination, a concern that is central to answering questions related to the possibility, mode and rate of corrosion-fatigue cracking. Even less is known about the mechanisms by which the environment can accelerate such crack growth.

In this paper, some areas of corrosion fatigue—including corrosion-fatigue crack growth (FCG)—in which the author has had both a direct interest and conducted research, are discussed. The author is fully conscious of many deficiencies of this discussion. First, because of the complexity of the phenomenon, a full and reliable interpretation might not be possible in a single chapter. Secondly, only a limited number of references could be quoted, and as such some important aspects of the problem could not be discussed deeply enough. Thirdly, because of the large number of variables influencing corrosion FCG, the generalizations presented here may not have universal validity. The first part of the chapter entitled “Principles of corrosion-fatigue testing and research” is devoted to considering: the terminology used in corrosion-fatigue-related research and publications; the early history of corrosion-fatigue research from 1917 when the first research [1] was carried out up to 1947 when Evans and his colleagues [9,10] summarized the work on the electrochemistry of corrosion fatigue carried out up to that time; and the fracture-mechanics technology in corrosion-fatigue research. The purpose of the second part of the chapter entitled “Mechanisms for corrosion-fatigue crack propagation” is to briefly review and evaluate experimental results and mechanistic models for corrosion FCG. This review outlines the present state of knowledge and current controversies concerning corrosion FCG mechanisms. Since this chapter is primarily concerned with the acceleration of corrosion-fatigue cracks in aqueous solutions, milder environments such as dry gases and air will not be discussed in detail. Information on SCC needed to clarify our understanding of corrosion



FCG behaviour in metals is given in some sections but should not be considered as complete and/or exhaustive.

2 Principles of corrosion-fatigue testing and research

2.1 Corrosion-fatigue-related terminology

“Corrosion fatigue” is a term used to describe the phenomenon of the gradual accumulation of damage (cracking and eventual fracture) in material under the combined interactions of external chemical environment and fluctuating (or cyclic) stress with its microstructure, where the environment does not have to be corrosive [2,11]. In this definition, the word “combined” should be emphasized since neither cyclic stress in inert environments nor aggressive environmental attack applied separately produces the same damaging results as their conjoint action. That is, a pre-corroded specimen does not necessarily show appreciable reduction in fatigue life (for example, when it is tested in mild environments such as dry gases and air), nor does pre-fatiguing in an inert/mild environment visibly increase the corrosion rate of metals. Also, it should be emphasized that most textbooks and handbooks, including those that were recently published [12,13] (in contrast to the above definition), require that the external environment that causes this type of failure be corrosive (deleterious) or aggressive. That is, according to the early published definitions [12,13], the term “corrosion fatigue” conjures up the notion of the severe disintegration of the material through chemical attack, accompanied by fatigue-crack initiation and growth. In reality, however, a relatively innocuous environment such as, for example, ambient air and atmospheric moisture can greatly accelerate the cracking process without producing visible corrosion in the commonly accepted sense. This fact is too well known [11] to require detailed discussion, but in order to avoid any misunderstanding related to the terms “corrosion fatigue,” “SCC” and “fatigue” that are used in this chapter, a little necessary information should be given.

According to Ref. [2], SCC as a phenomenon is a cracking process caused by the conjoint action of a corrosive environment and nominally static or slowly increasing tensile stress. The tensile stress may be either applied service stress or residual stress resulting from casting, welding or other fabrication processes. [Note: Usually technical journals use SCC as a general term to classify all modes of materials fracture due to environmental (usually aqueous solutions of various compositions) factors.] Also, SCC can be defined as a special case of corrosion FCG in a metal exposed to a specific corrosive environment at the stress ratio (R = minimum/maximum load) equal to 1 [14,15]. Although pure SCC can be obtained in a laboratory when a specimen is tested under sustained or monotonically increasing stress, it cannot be realized under realistic operating conditions because most real engineering structures are exposed to service stresses of varying amplitudes that usually are a mixture of stochastic and deterministic components [16]. Despite this obvious fact, much effort and



material expenditures have been directed at studying SCC and much less is known about corrosion-fatigue crack initiation and propagation.

In 1984, Speidel [17] summarized environments causing SCC in engineering alloys. Table 1, prepared by him, shows a variety of these environments. Most of them are aqueous solutions of various compositions that represent a wide spectrum of modelling and, sometimes, technological environments. Our concern here is an “inert” environment such as pure (distilled) water. According to the table, pure water causes SCC in certain alloys of iron (carbon steels and austenitic stainless steels), aluminium, copper, nickel, magnesium, titanium or uranium and possibly others. That is, pure water is known as a SCC agent, particularly when the strength of an alloy is high [17]. These data could lead to the erroneous conclusion that just about all materials are susceptible to SCC in pure water. This would make it impossible to operate any plant with steam and water cycles or even in a rainy outdoor environment. Fortunately, and it is thus necessary to emphasize, SCC occurs only in certain limited ranges of temperature, potential, stress, stress intensity factor, strain rate, time, and alloy composition and strength [17,18].

The number of environments that cause corrosion-fatigue failures are practically unlimited. If SCC occurs in alloys only in specific environments (Table 1), almost any external chemical environment differing from absolute (high) vacuum must be considered as “aggressive,” i.e. accelerating both fatigue-crack(s) initiation and propagation, if fluctuating loading is present. Alloys subject to corrosion are subject to corrosion fatigue in any corrosive environment. Gough and Sopwith [19], as early as 1932, showed that the fatigue strengths of several metals were higher in vacuum than they were in normal indoor atmosphere. For most metals, air contributes quite strongly to increasing fatigue-crack propagation and this fact has been well known since the 1960s [20–23]. Most fatigue data obtained to date in inert gases were treated as reference data for more aggressive environments [24,25]. However, Shimojo and his colleagues [26] in 2000 studied the FCG behaviour in titanium at room temperature in an environment described as either vacuum (4×10^{-5} Pa) or high-purity inert gas such as helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) of 1×10^5 Pa and found that inert gases were not completely inactive. These gases increased FCG rates and changed the fracture-surface appearance as compared to those in vacuum. That is, summarizing the data in the literature, it is fairly certain that both fatigue-crack initiation and fatigue-crack propagation are affected by normal air environment and even by pure inert gases. This means that the majority of fatigue failures that were studied in the literature over the last 150 years (beginning in the 1850s [27]) were, in fact, corrosion-fatigue failures, since only fatigue occurring in high vacuum could be termed as “pure fatigue”.

Thus, the terms “corrosion fatigue” and “SCC” are not semantically exact as many environments that are not corrodents in the ordinary sense can induce intensive cracking of metals [11,17–23,26]. Contrastingly, other environments



Table 1: Environments causing SCC [17].

Carbon steels ^a		Austenitic stainless steels	Al alloys	Cu alloys	Ni alloys
H ₂ O + NO ₃ ⁻	I	H ₂ O + Cl ⁻	H ₂ O + Cl ⁻	H ₂ O + NH ₃	H ₂ O + HF
H ₂ O + OH ⁻	I	H ₂ O + OH ⁻			H ₂ [SiF ₆]
H ₂ O + CN ⁻	T				
H ₂ O + PO ₄ ³⁻	T	H ₂ O + F ⁻	H ₂ O + Br ⁻	H ₂ O + OH ⁻	H ₂ O + Cl ⁻
H ₂ O + SO ₄ ²⁻	T	H ₂ O + Br ⁻	H ₂ O + I ⁻	H ₂ O +	H ₂ O + OH ⁻
H ₂ O + CO ₃ ²⁻	I	H ₂ O + SO ₄ ²⁻	N ₂ O ₄	- amines	Polythionic acid
H ₂ O + CO-CO ₂	T	Polythionic acid	HNO ₃	- citrates	Chromic acid
H ₂ O + H ₂ S	T	H ₂ O + H ₂ S	Organic liquids	- tartrates	Acetic acid
H ₂ O + FeCl ₃	T	H ₂ O + H ₂ SO ₃	Liquid Hg, Ga	H ₂ O + NO ₃ ⁻	Molten caustics
Organic liquids	T	Liquid I, Te, Al	Moist air	H ₂ O + NO ₂ ⁻	Steam
Liquid ammonia	T	H ₂ gas	Moist H ₂ , O ₂ , N ₂	H ₂ O + SO ₄ ²⁻	Organic liquids
Liquid Zn, Li, Bi-Pd				H ₂ O + SO ₃ ²⁻	Liquid Li, Hg, Sn, Zn, Bi, Pb
				H ₂ O + S ⁻	Air
				H ₂ O + F ⁻	
				Liquid Hg, Bi, Pb atmosphere	
				Steam	
H ₂ O	T	H ₂ O	H ₂ O	H ₂ O	H ₂ O

^a The mode of crack propagation: transgranular (T) or intergranular (I).

Mg alloys	Ti alloys	Zr alloys	U alloys	Co alloys
Humid air	H ₂ , F ₂ , Cl ₂ , Br ₂	H ₂ , Cl ₂ , Br ₂ , I ₂	Dry O ₂ , H ₂ , air	H ₂
Outdoors	Humid air	H ₂ O + FeCl ₃	Humid air	H ₂ O + NO ₃ ⁻
H ₂ O + Cl ⁻	H ₂ O + Cl ⁻	H ₂ O + CuCl ₂	Humid N ₂ , O ₂ , H ₂	H ₂ O + Cl ⁻
H ₂ O + Br ⁻	H ₂ O + Br ⁻	H ₂ O + HI	H ₂ O + Cl ⁻	H ₂ O + HCl
H ₂ O + I ⁻	H ₂ O + I ⁻	H ₂ O + Br ₂		H ₂ O + H ₂ SO ₄
H ₂ O + SO ₄ ²⁻	CH ₃ OH, CCl ₄	H ₂ O + I ₂		H ₂ O + H ₂ S + Cl ⁻
	CH ₂ I ₂ , CHCl ₃	CH ₃ OH, CCl ₄		H ₂ O + HNO ₃
	CH ₃ CCl ₃	CHCl ₃		H ₂ O + NaOH
	Freon, ClF ₅	Organic liquids + I ₂		Hydrocarbons + HF + BF ₃ + H ₂ O
	Alkanes	Fused salts		
	Fused salts	Hg, Cs, Mg, Cd		
	N ₂ O ₄			
	HNO ₃ (RFNA)			
	H ₂ O + NaOH			
	Hg, Ag, Cd			
H ₂ O	H ₂ O		H ₂ O	

that are strong corrodents may be more beneficial to engineering structures than ambiguous atmosphere [14,28]. To avoid this misconception, the term “environmentally assisted fatigue cracking” is now preferred [11,15], and the use of the term “corrosion fatigue” in the chapter is to be understood within this context.

2.2 Early history of corrosion-fatigue research: 1917–1947

The discovery of corrosion fatigue during the First World War was made by Haigh of the Royal Naval College, Greenwich when he sought an explanation for the frequent failure of paravane towing ropes, which were kept in a state of



vibration whilst exposed to seawater. Those failures were among the first failures to be specifically labelled “corrosion fatigue.” The first published account of laboratory experiments on corrosion fatigue of brasses was given by Haigh in 1917 [1]. He found that “the effects of corrosion and fatigue are mutually associated, and that fatigue is accelerated, and occurs under lower stresses, when the conditions tend to promote corrosion” [1]. Haigh stated at the end of his paper that he had noticed that fatigue was accelerated in mild steel and other metals exposed to corrosion by acids, sal-ammoniac and salt water. In addition, in 1919, Langdon [3] in the discussion on the penetration of iron by hydrogen, stated that the fatigue limit of a 9.5-mm diameter steel rod was reduced by 30–50% after the rod was immersed for five minutes in a 10% solution of sulfuric acid at 50°C.

No further attention was paid to the subject until about 1925, when investigations were started both in the USA and in England. The most important work was that by McAdam and his colleagues, first at the U.S. Naval Engineering Experiment Station and then at the National Bureau of Standards [4], and that by Gough and his colleagues at the National Physical Laboratory [8,20]. These researchers laid the foundations of our knowledge of the subject and exerted a profound influence on other workers in the field. McAdam carried out a most comprehensive series of investigations covering many variables, and it was he who introduced the term “corrosion fatigue.” In his first paper on the corrosion fatigue of metals [4], McAdam pointed out that “very slight corrosion when simultaneous with fatigue causes low resistance to fatigue. The damaging effect is greater the harder the steel. ... Corrosion fatigue is undoubtedly of more importance in machinery parts subjected to repeated bend or torsion than in parts subjected to repeated axial stress”. In 1926, Lehmann [5] showed that strongly corrosive liquids exhibited a surprisingly small effect on the fatigue resistance when they contained little dissolved air. The importance of oxygen on corrosion-fatigue properties was further demonstrated in work carried out by Binnie [7]. Speller, in 1926, pointed out in discussing one of McAdam’s papers that hydrogen penetration along grain boundaries may play a part in the corrosion fatigue of steel [6].

The 1926 papers [4,5] aroused great interest, and corrosion fatigue has since been the subject of vigorous research. Between 1926 and 1930 (and at later intervals) McAdam carried out a magnificent series of studies on this subject, which was conventionally reviewed by Gough in 1932 [8] and Dorey in 1933 [29]. He published upwards of 20 papers on the subject in the period 1926–1941 and studied relationships between the stress range, time, number of cycles, and endurance limit for a wide variety of materials, including ingot iron, steel, low-alloy steels, stainless irons and steels, nickel, Monel, copper, Cu-Ni alloys, brasses, aluminium bronze, aluminium, duralumin and Al-1¼ Mg alloy. In 1930, Harvey wrote, “At present, the discovery of the “corrosion fatigue” phenomenon is universally recognized as one of the eminent metallurgical achievements of the twentieth century. Within four years of its initial study, corrosion-fatigue has

been recognized as a vital problem to every engineer whose products are subject to repeated stress” [31].

Thereafter, it became evident that corrosion fatigue is responsible for many kinds of failure in marine propeller shaft and rudders, steering arms and axles of motor vehicles, boilers and super-heater tubes, pump shafts, rods and bodies and other equipment [30]. Due to this fact, the volume of literature on corrosion fatigue that appeared between 1925 and the beginning of the Second World War was considerable. Subsequently, however, interest in the subject has declined somewhat. The number of papers published during the 16-year period 1940–1955 is of the order of one-half of the number published during the 15-year period 1925–1939 [32].

In 1935, DeForest [33] noted that the majority of fatigue failures in service were found to initiate at pre-existing defects (including various notches resulting from design, such as fillets, screw threads, oil holes or resulting from defects of surfaces such as grinding marks, grooves coming from machining operations, decarburized surfaces, or the accidental bruising received in hardening, or the surface produced by corrosion) and the useful life of the component was primarily dependent upon the rate of FCG. He was the first to present experimental data on the rate of crack growth and on the size of cracks.

The most important researches on corrosion fatigue since 1939 were those of Evans and his co-workers at the University of Cambridge on electrochemical aspects of corrosion fatigue [9,10,34]. For example, Gould and Evans, by measuring an electrode potential during corrosion fatigue tests on steel wire in chloride and chromate mixture, found that a sudden drop in potential occurred at a certain stage, indicating breakdown of a protective surface film [34]. Early in the study of corrosion fatigue, it was shown that cracking could be delayed or prevented by cathodic protection by contact with a less noble metal [8]. Evans and Simnad showed that the same result could be produced by applied cathodic potential [9]. In 1947, Evans summarized the work on the electrochemistry of corrosion fatigue carried out at Cambridge up to that time [10].

2.3 Stress–life ($S-N$) corrosion-fatigue behaviour

Traditionally, beginning with the first research [1], investigations of susceptibility to corrosion fatigue have involved the stressing of smooth cylindrical specimens—by some convenient means, involving bending, axial or torsional stress, usually with cycles of reversed stress—until they failed or survived some pre-determined target number of stress cycles. The tests are carried out on the same types of machine as are used for ordinary fatigue tests, suitably modified to enable the desired corrosive environment to be maintained round the specimen or part of the specimen. Test data from this type of experiment are typically presented in the form of an $S-N$ (stress–life) diagram (Fig. 1), which shows the number of cycles to failure, N , as a function of the cyclic-stress range, S . [Note: For a long time, such curves were labelled as a “Wöhler curve” [27] instead of the now more frequently used the term “ $S-N$



curve”.] The same technique and method of results presentation [1,27] are still used today, particularly in the context of engineering qualification tests on components and welded connections. High test frequencies, often much higher than 10 Hz (e.g., 160 Hz [35]), are necessary if the complete $S-N$ curve, including low-stress ranges and high-cyclic lives greater than 10^6 cycles, is to be defined in an acceptably short period of time.

The horizontal portion of an $S-N$ curve represents the maximum stress that the metal can withstand for an infinitely large number of cycles. This maximum stress is known as the fatigue (or endurance) limit. For steels, but not necessarily for other metals, a true fatigue limit exists that is approximately half the tensile strength. Most non-ferrous metals do not exhibit a fatigue limit. Instead, their $S-N$ curves continue to drop at a slow rate at high numbers of cycles. For these types of metals, fatigue strength, rather than fatigue limit, is reported for a specific number of cycles.

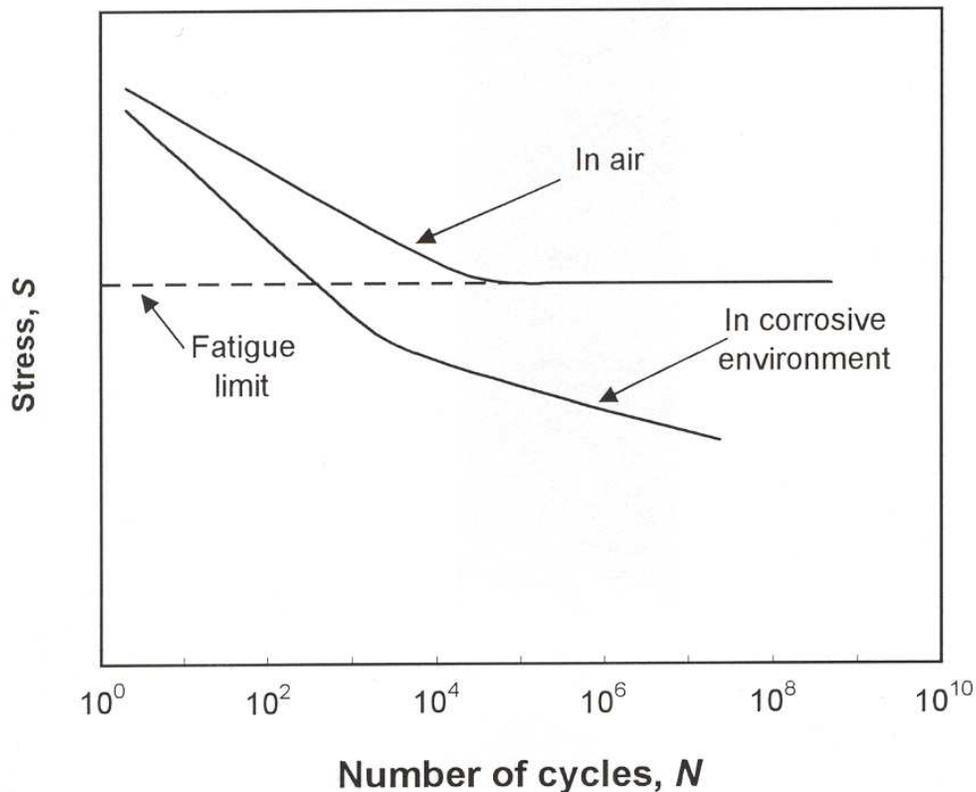


Figure 1: $S-N$ curves for fatigue tests in air and in a corrosive environment.

In corrosive environments, the $S-N$ curve never becomes truly horizontal, and there is thus no true corrosion-fatigue limit (Fig. 1); metals can eventually fail under any alternating stress if the number of cycles is sufficiently large. In such cases, corrosion-fatigue strength is determined as a fatigue limit at a specific (prescribed) number of cycles. Figure 1 also shows that the number of stress

cycles that any metal can resist before failure is always less for corrosion fatigue than for fatigue. Corrosion-fatigue strengths were found to be insensitive to the metallurgical condition, showing no correlation with tensile strength in contrast to that observed in air. If the fatigue limits of steels for bending loading in air are about one-half their tensile strengths, their corrosion-fatigue strengths may possibly be no more than 10% of their fatigue limits. For example, Fig. 2 shows that the fatigue limit in air was much higher for high-strength steel (465 MPa) than for low-strength steel (160 MPa). But in water both steels showed the same, extremely low corrosion-fatigue strength that continued to fall further as the number of load cycles increased from 10^7 (65 MPa) to 10^9 (10 MPa) [35]. It is noteworthy that the large effect of water was observed despite the use of high

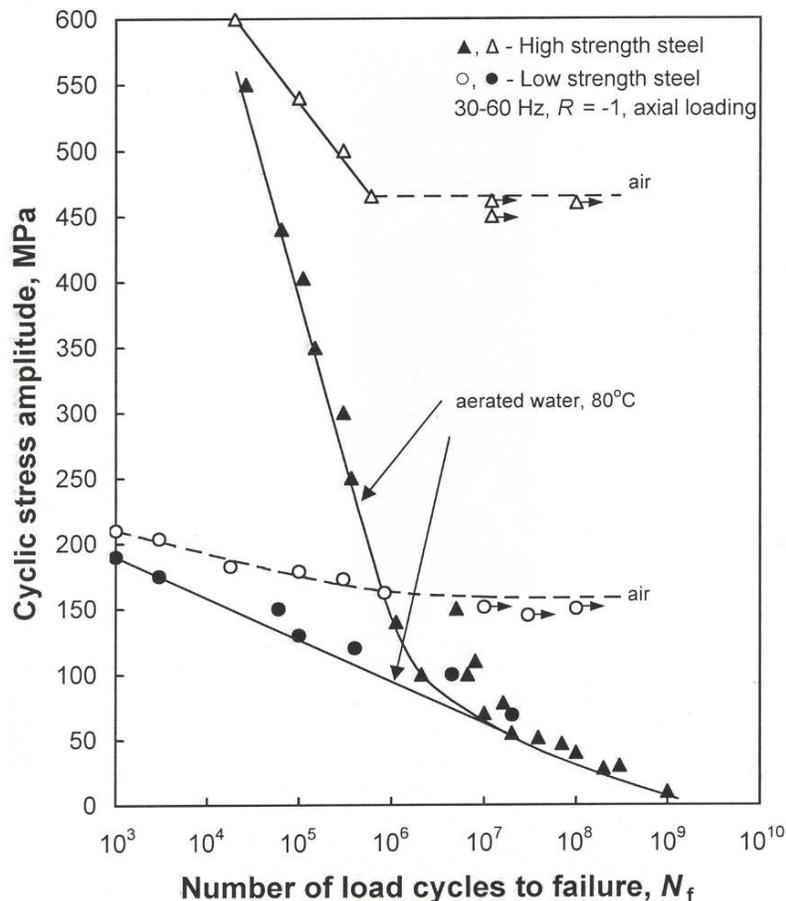


Figure 2: $S-N$ curves of low-strength steel G 10050 (0.02%C; UTS = 294 MPa) and high-strength steel K 08500 (0.8%C; UTS = 1100 MPa) tested in air and in water (after Speidel [35]).

cyclic frequency (30 to 60 Hz) when, as will be shown in Sect. 2.4.3, environmental effects on corrosion FCG rates would be negligible. Corrosion resistance, often specifically pitting resistance, was much more important in determining the corrosion-fatigue strength. If pitting corrosion is allowed, all carbon steels, no matter how high their carbon contents or their tensile strength,

will all have the same extremely low corrosion-fatigue strength. Most comprehensive compilations of fatigue strength as a function of alloy strength are reproduced in Fig. 3 [35]. From this figure, it can be concluded that the fatigue strength of carbon steels in air increased from 100 MPa to about 600 MPa with increasing tensile strength from 200 MPa to 1200 MPa, but the corrosion-fatigue strength was equally low for all steels in aerated water (110 MPa) and seawater (40 MPa), i.e. in environments that cause pitting corrosion. Similar observations were made with a large number of alloys, a ranking of which is illustrated in Fig. 4. All materials from the same alloy group exhibit the same low corrosion-fatigue strength, almost independent of composition and strength level. Figure 4 shows that cobalt alloys and titanium alloys permit some of the best corrosion-fatigue strength levels to be obtained. This is one reason why materials from these groups are used not only in modern high technology but also where their corrosion-fatigue resistance is most immediately felt—for example, as implants in the human body [35].

The type of loading (reversed bending of a specimen with $R = -1$) and its frequency (much higher than 10 Hz) in the tests described above are both not typical for realistic operating conditions. For example, daily pressure fluctuations in a liquid pipeline correspond to cyclic loading with the stress ratio of about 0.6 to 0.8 at a cyclic frequency from about 2 to 5 cycles per day; under other circumstances, the stress ratio can vary from zero to 0.9 and a cyclic frequency can be in the range between 0.7 and 1.3 cycles per day [15]. Moreover, tests of this type do not allow for separating the crack-growth stage, which is of special practical interest—the higher the rate of subcritical crack growth, the shorter the lifetime of a structure that experiences a crack-type defect(s)—from the total corrosion-fatigue lifetime that includes the five stages of material failure: nucleation of crack/defect(s); initiation of crack(s) from the nucleus/defects; growth of small mutual cracks; growth of subcritical crack(s); and the final (brittle) fracture of material [15]. The total duration required for such corrosion-fatigue tests can exceed six months [36]. If several materials are to be tested under various conditions, the time problem starts to be critical. A dramatic decrease in the total time required for evaluating the corrosion-fatigue resistance as well as obtaining more applicable experimental data in comparison with those described above can be reached by using fracture-mechanics technology [11,17,35–37].

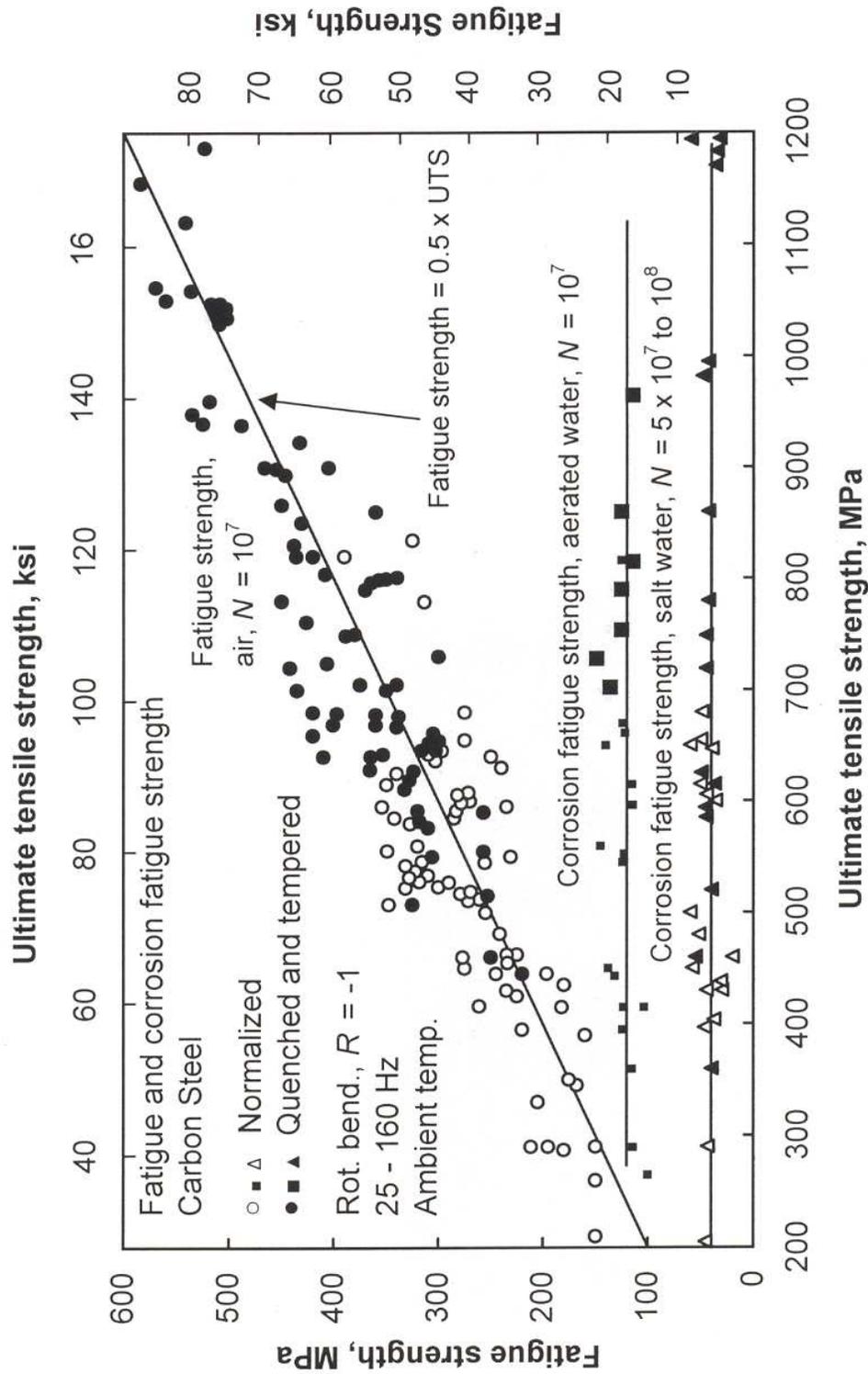


Figure 3: The fatigue strength of carbon steels of varying tensile strengths in air, aerated water and seawater (after Speidel [35]).

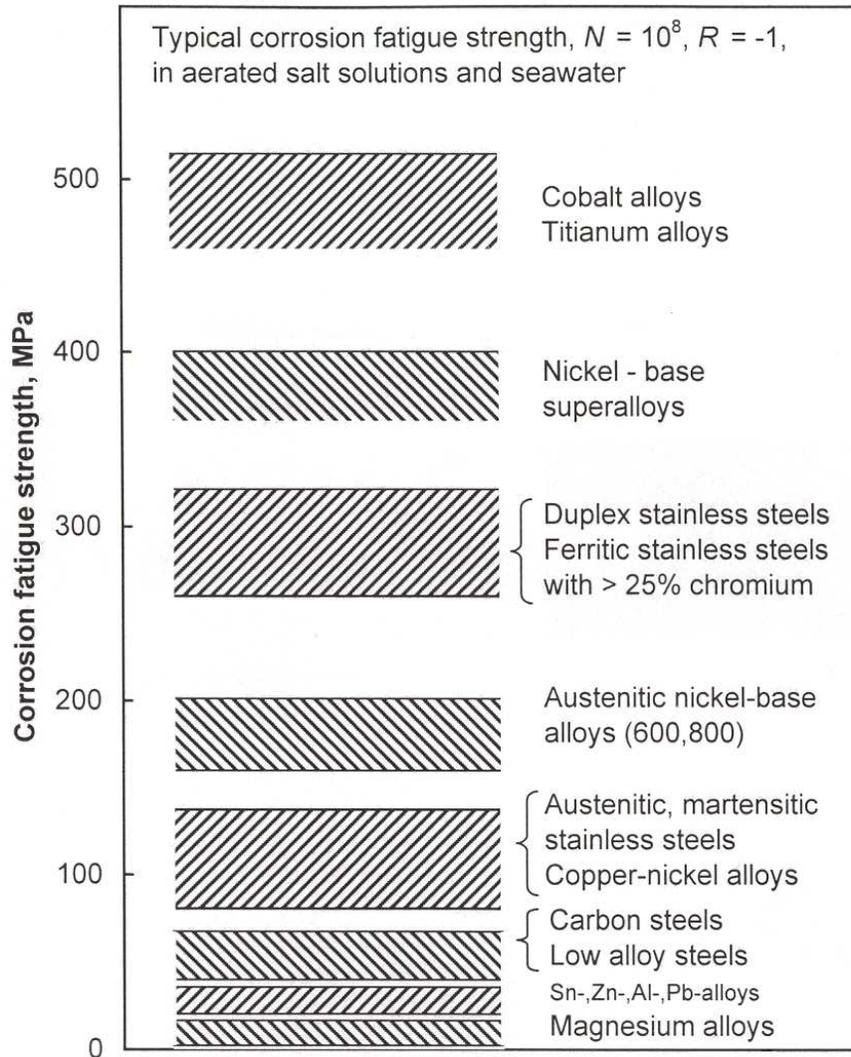


Figure 4: Corrosion-fatigue strength levels for various alloy systems in aerated salt solutions or seawater (after Speidel [35]).

2.4 Corrosion-fatigue crack growth ($da/dN-\Delta K$) behaviour

The process of corrosion fatigue is usually discussed in terms of crack initiation (incubation and nucleation) and crack propagation. It begins with the initiation of a crack(s), and with continued cyclic loading the crack propagates, finally leading to the fracture of a component/specimen or structure. That is, for many materials and under a wide variety of experimental and in-service conditions, unstable fracture may be preceded by a period of stable (subcritical) crack propagation. In this period, crack propagation will cease if the cyclic loading or an external chemical environment is removed; conversely, with continued loading and/or environmental action, crack growth will continue until the

process is no longer self-limited, i.e. further crack propagation is very rapid and loading is unnecessary. With the development of linear elastic fracture mechanics (LEFM) in the early 1960s and the recognition that FCG rates per cycle, da/dN , could be expressed as a simple function of the stress-intensity factor range, ΔK [38,39], increasing attention has been focused on measuring the rates of corrosion-fatigue crack propagation. The introduction of LEFM technology in corrosion-fatigue research was one of the significant developments in the understanding of corrosion-fatigue phenomena and the utilization of crack-growth data in the design and evaluation of engineering structures.

2.4.1 Fracture mechanics in SCC research

The results of Brown [40] and Brown and Beachem [41] were those that pioneered, in the mid-1960s, an extension of LEFM methods to SCC testing and stimulated a great body of subsequent research in SCC and corrosion FCG. Brown and Beachem [40,41] introduced into SCC and fracture-mechanics practice the threshold stress-intensity factor, K_{ISCC} , below which SCC does not occur. Since that time, K_{ISCC} has been a key parameter characterising susceptibility of a material to SCC.

The K_{ISCC} parameter is commonly referred to as the SCC threshold, meaning that it is the stress-intensity factor in the opening mode (Mode I) below which SCC will not initiate. K_{ISCC} is considered to be a material property for a particular material–environment system. The use of the K_{ISCC} parameter based on the relationship between the stress-intensity factor, K , nominal applied stress, σ , and the crack length, a , has practical significance. Once the appropriate value of K_{ISCC} has been determined, it can be used for structural design to establish the critical combination of applied stress and defect size below which SCC will not occur for a given material–environment system. When K_{ISCC} is known, it can be used to calculate either the allowable crack size in the structure (at the given level of applied stress) or the allowable stress below which SCC will not be expected.

Another manifestation of the SCC phenomenon is illustrated schematically in Fig. 5, where the average stress-corrosion crack growth rate, da/dt , is plotted as a function of the applied stress-intensity factor, K . Crack growth rates in susceptible material–environment systems often follow three distinct regions as first indicated by Wiederhorn in 1967 [42]. In Region I, or the linear region at low K with a strongly stress-dependent crack growth rate, the crack growth rate increases with increase in stress-intensity factor. In cases where K_{ISCC} is time dependent, its value is determined from Wiederhorn's diagram as the value corresponding to the crack growth rate of 3×10^{-11} m/s (or roughly one mm/y). In Region II, or the steady-state crack-growth region at intermediate K , the crack growth rate is relatively independent of stress-intensity factor (plateau region). Crack growth rates in plateau region ("plateau crack growth rates") can vary widely and data from 10^{-12} to 10^{-1} m/s were reported [17]. In Region III, or the

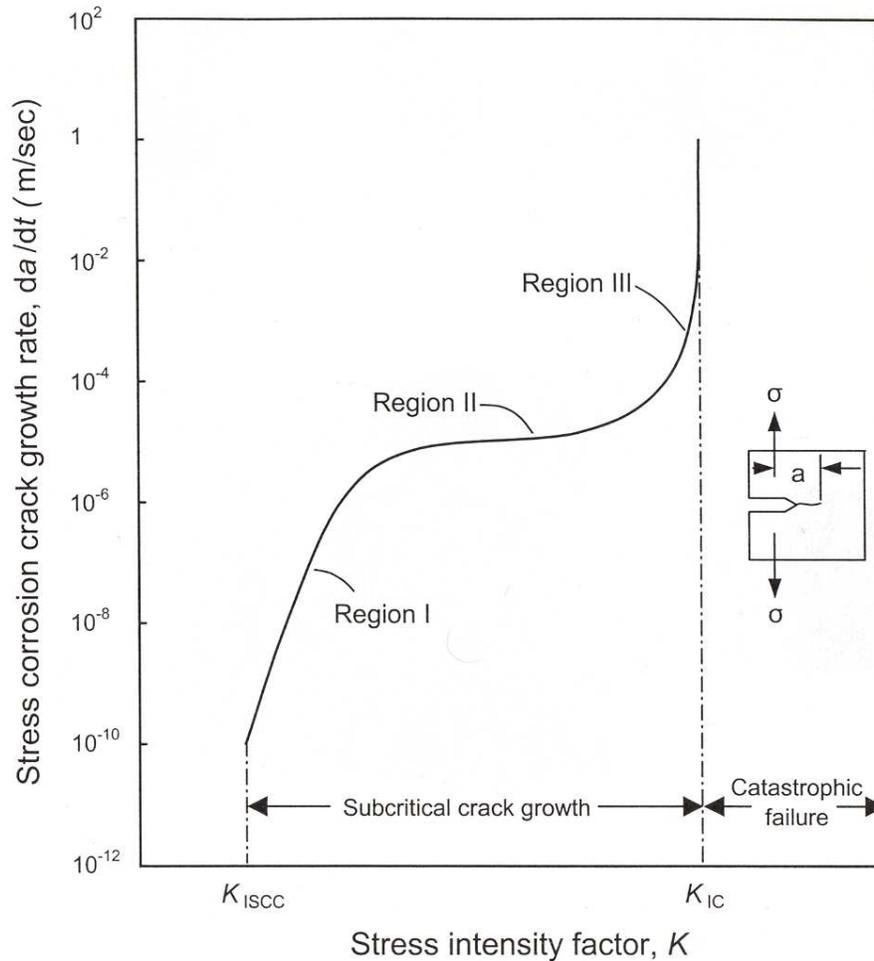


Figure 5: A schematic representation of stress-corrosion crack growth rate, da/dt , as a function of stress-intensity factor, K .

fast-fracture region, the crack-growth rate again accelerates with increase in stress-intensity factor. The use of the crack-growth data such as those shown in Fig. 5 allows for an estimation of how long it would take to break a specimen/component containing a crack(s) of known length under an applied load. If the environment is inert or if the material is fully resistant to SCC, no crack growth will occur until the critical stress intensity (i.e., fracture toughness, K_{IC}) is reached. If the environment is “aggressive” and the material is susceptible to SCC in this environment, subcritical crack growth will occur at stress-intensity factors below or even far below K_{IC} . It is presumed that once SCC starts, it will propagate at increasing rates following first the Region I curve and then the Region II curve until the stress-intensity factor is sufficiently large that K_{IC} is reached and catastrophic failure is reached.

There is a strong effect of yield strength on K_{ISCC} and crack growth rates. For example, as Fig. 6 shows, a doubling of the yield strength of AISI 4340 steel

(from 800 to about 1600 MPa) is accompanied by a ten-fold (from 70 to 7 MPa m^{1/2}) decrease of K_{ISCC} [41]. Figure 7 shows, the “plateau crack growth rate” in low-alloy steel of 1700 MPa yield strength in deaerated water at 100°C was equal to 10⁻⁴ m/s and exceeded that (~10⁻¹¹ m/s) in a similar steel of 760 MPa yield strength by seven orders of magnitude [17]. The data show that steels with higher yield strength (near 1500 MPa) will result in fast stress-corrosion crack growth whereas steels with yield strength below 1000 MPa may still not be entirely immune to SCC, but the crack growth rates in such steels are many orders of magnitude lower.

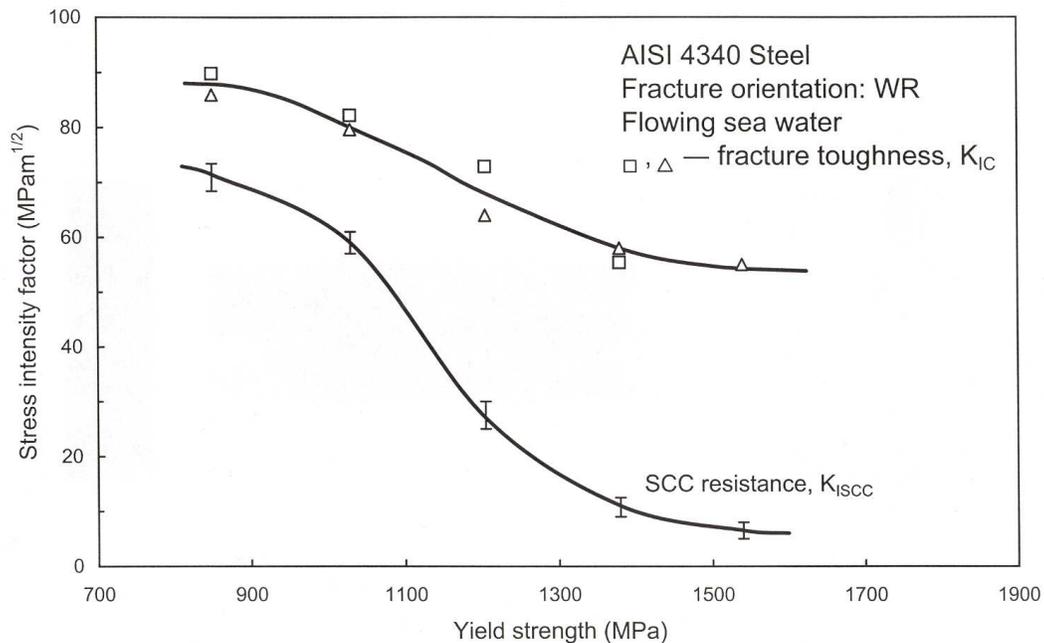


Figure 6: Effect of yield strength on the fracture toughness, K_{IC} , and on the threshold stress-intensity factor, K_{ISCC} , for AISI 4340 steel (after Brown and Beachem [41]).

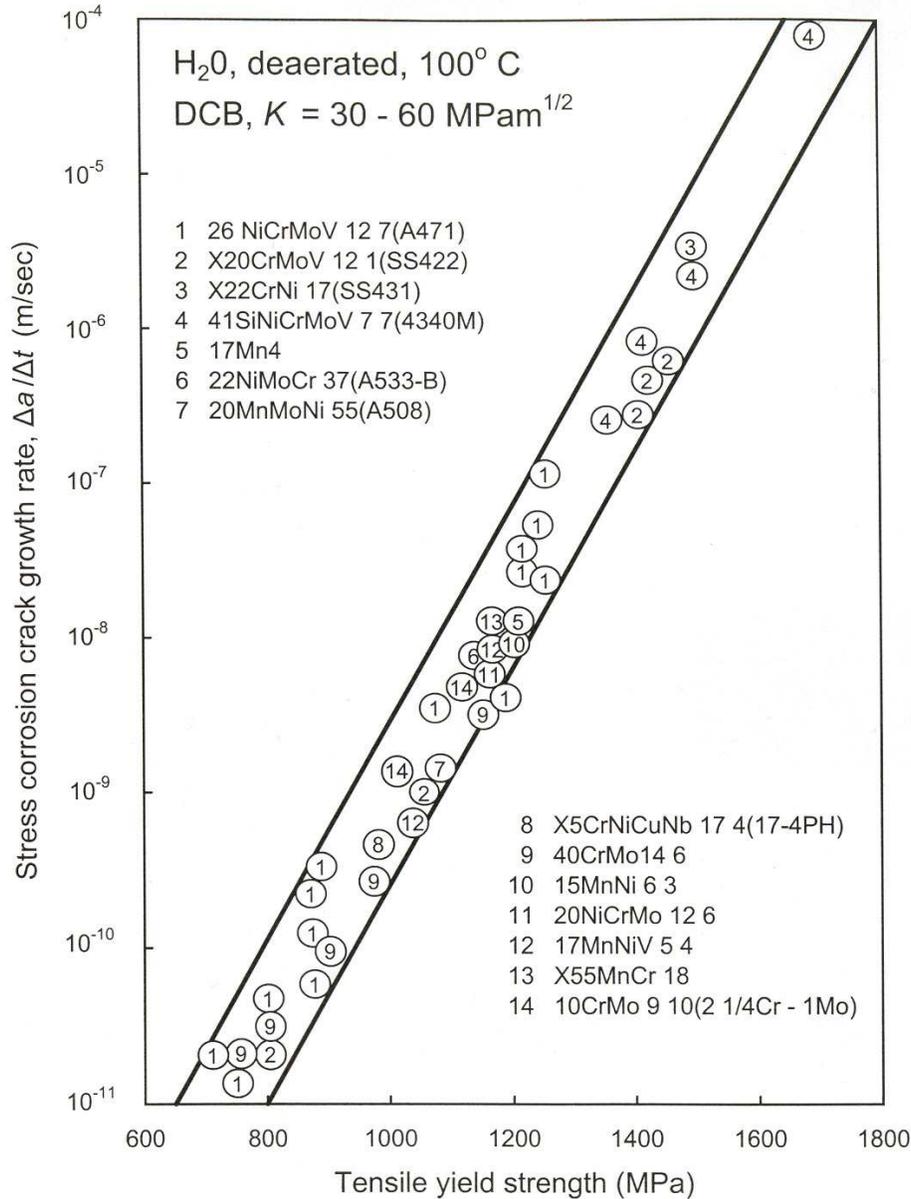


Figure 7: Effect of yield strength on stress-corrosion crack growth rates in steels (after Speidel [17]).

2.4.2 Fracture mechanics in corrosion FCG research

During the past 40 years, systematic studies of the kinetics of corrosion-fatigue crack propagation in metals have led to an improved understanding of the effects of those mechanical, metallurgical and environmental variables that control the possibility, mode and rate of corrosion-fatigue damage [14,37]. Such an understanding has been developed quantitatively through the use of LEFM [11,17,35–37]. Most corrosion FCG tests are conducted by subjecting a pre-cracked specimen to constant-amplitude cyclic-load fluctuations. An incremental increase of crack length is measured, and the corresponding number of elapsed

load cycles is recorded. The FCG data are most commonly presented on a log-log plot of da/dN versus ΔK , as shown schematically in Fig. 8 [43]. Also shown in this figure is the general form of the time-dependent (not cycle-dependent) SCC rate, da/dt , as a function of the applied stress-intensity factor and how this can be superimposed on corrosion FCG if the stress-intensity factor in the stress cycle exceeds K_{ISCC} .

The da/dN - ΔK curve is usually divided into three regions (Fig. 8). In an inert environment, the FCG behaviour in Region I exhibits a threshold value, ΔK_{th} , below which there is no observable crack growth. This threshold occurs at crack growth rates in the order of 10^{-10} m/cycle or less, as defined in ASTM Standard E647 [44]. Below ΔK_{th} , cracks are characterized as nonpropagating fatigue cracks. Microstructure, mean stress, frequency and environment mainly control the Region I crack growth. Region II (Paris region) shows essentially a linear relationship between $\log da/dN$ and $\log \Delta K$, which corresponds to the equation

$$da/dN = C(\Delta K)^n, \quad (1)$$

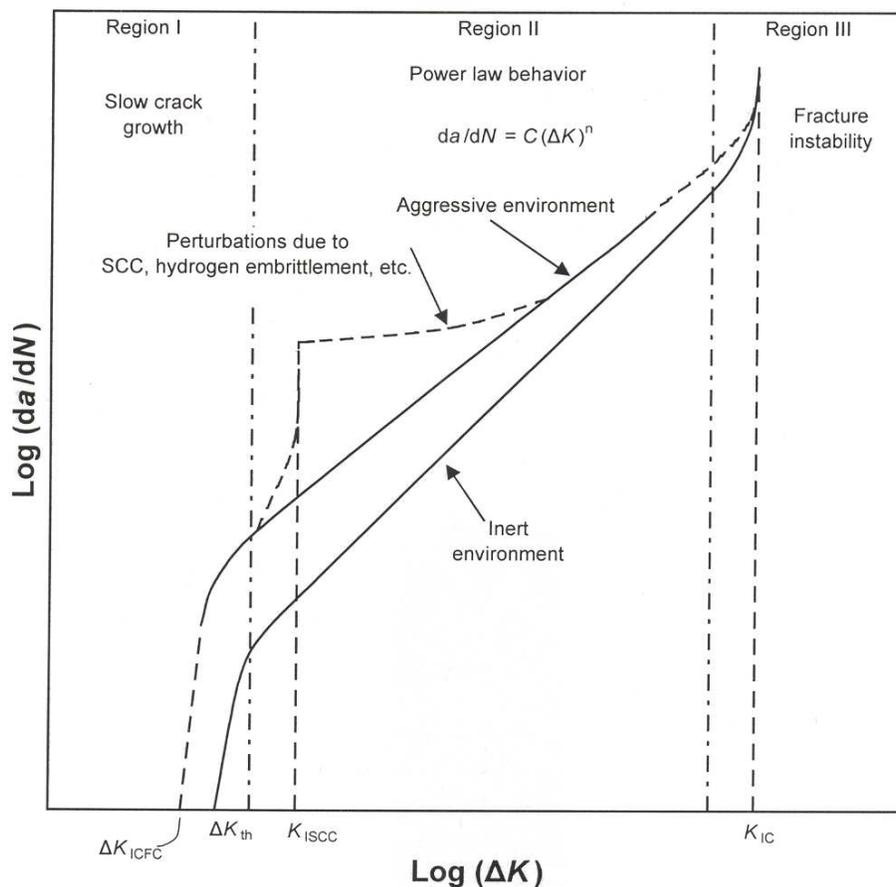


Figure 8: A schematic representation of corrosion FCG rate, da/dN , as a function of stress-intensity factor range, ΔK (after Sprowls [43]).

first suggested in 1963 by Paris and Erdogan [39]. Here n and C are constants for a given material and stress ratio. Region II corresponds to stable macroscopic crack growth that is typically controlled by the environment, whereas microstructure and mean stress have less influence on FCG behaviour in Region II than in Region I. Typically, FCG rates in this region are larger than 10^{-8} m/cycle and smaller than 10^{-3} m/cycle; that is, the region covers the crack growth rates and stress-intensity factor ranges in which most published FCG studies in controlled environments were carried out. In Region III, the FCG rates are higher than those predicted for Region II as they approach instability, and little useful life in the structure remains before disintegration. This region is controlled primarily by fracture toughness, K_C or K_{IC} , which in turn depends on the microstructure, mean stress and environment.

In an aggressive environment, the $da/dN-\Delta K$ curve can be quite different from the pure fatigue curve, depending on the sensitivity of the material to the given environment and the occurrence of static SCC above K_{ISCC} . In addition, certain loading factors such as cyclic frequency, stress ratio and loading waveform can have marked effects on the crack-growth curves in the same environment. An applied electrode potential also can have a marked effect on the crack-growth curves. The application of potential can, with all other conditions (specimen, solution, pH, cyclic frequency, stress ratio, loading waveform, temperature, etc.) being equal, accelerate or retard the propagation of the crack by a factor that may range up to many times [14,28,45]. Therefore, a variety of curves can be expected from the broad range of material–environment–loading systems that will produce various corrosion FCG behaviours.

2.4.3 Basic types of corrosion FCG behaviour

The schematics in Fig. 9 show three general patterns of corrosion FCG behaviour in aggressive environments compared with crack-growth behaviour in an inert environment. [Note: The first representation of the patterns by McEvily and Wei [46] was based on the maximum stress-intensity factor, K_{max} , and later Austen and Walker [47] re-represented these patterns based on ΔK .] The first type of corrosion FCG behaviour represents those material–environment systems in which the environmental effect results from the synergistic interaction between the cyclic plastic deformation (fatigue) and the environment (corrosion). The environmental effect is evidenced by a reduction in the apparent threshold stress-intensity factor range (from ΔK_{th} to ΔK_{ICFC} as in Fig. 8) and an increase in the crack growth rate at the given level of ΔK . This behaviour pattern is referred to as “true corrosion fatigue” [48] and is typical for low- to moderate-strength alloys that are either immune to SCC or exhibit high K_{ISCC} and low da/dt . Figure 10 shows an example of this type of corrosion FCG behaviour for an aluminium alloy with high resistance to SCC [49]. The crack growth rates are ranged up to one order of magnitude higher in 0.6 M NaCl solution than those in dry air (Fig. 10).

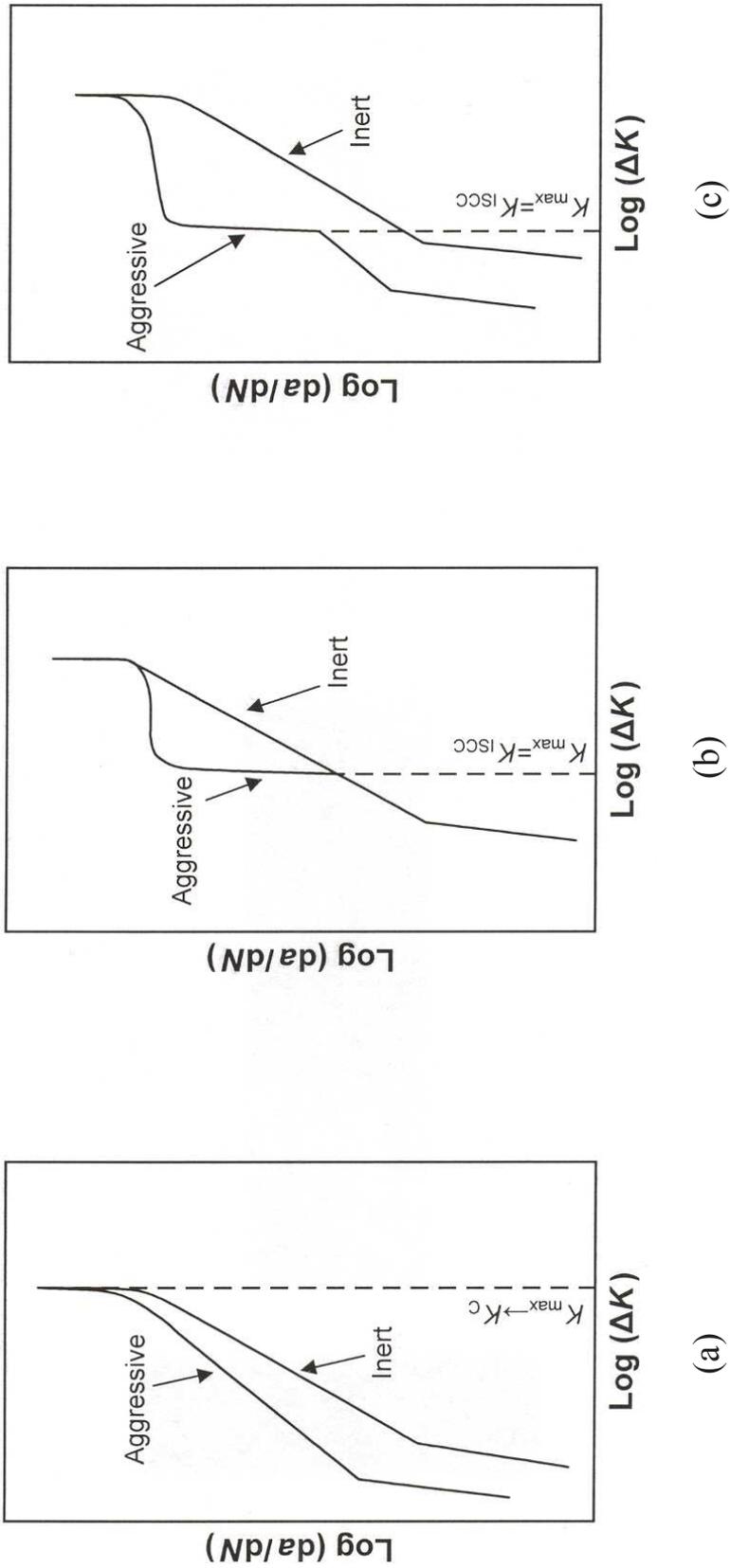


Figure 9: Schematic representations of basic types of corrosion FCG behaviour (after Austen and Walker [47]).

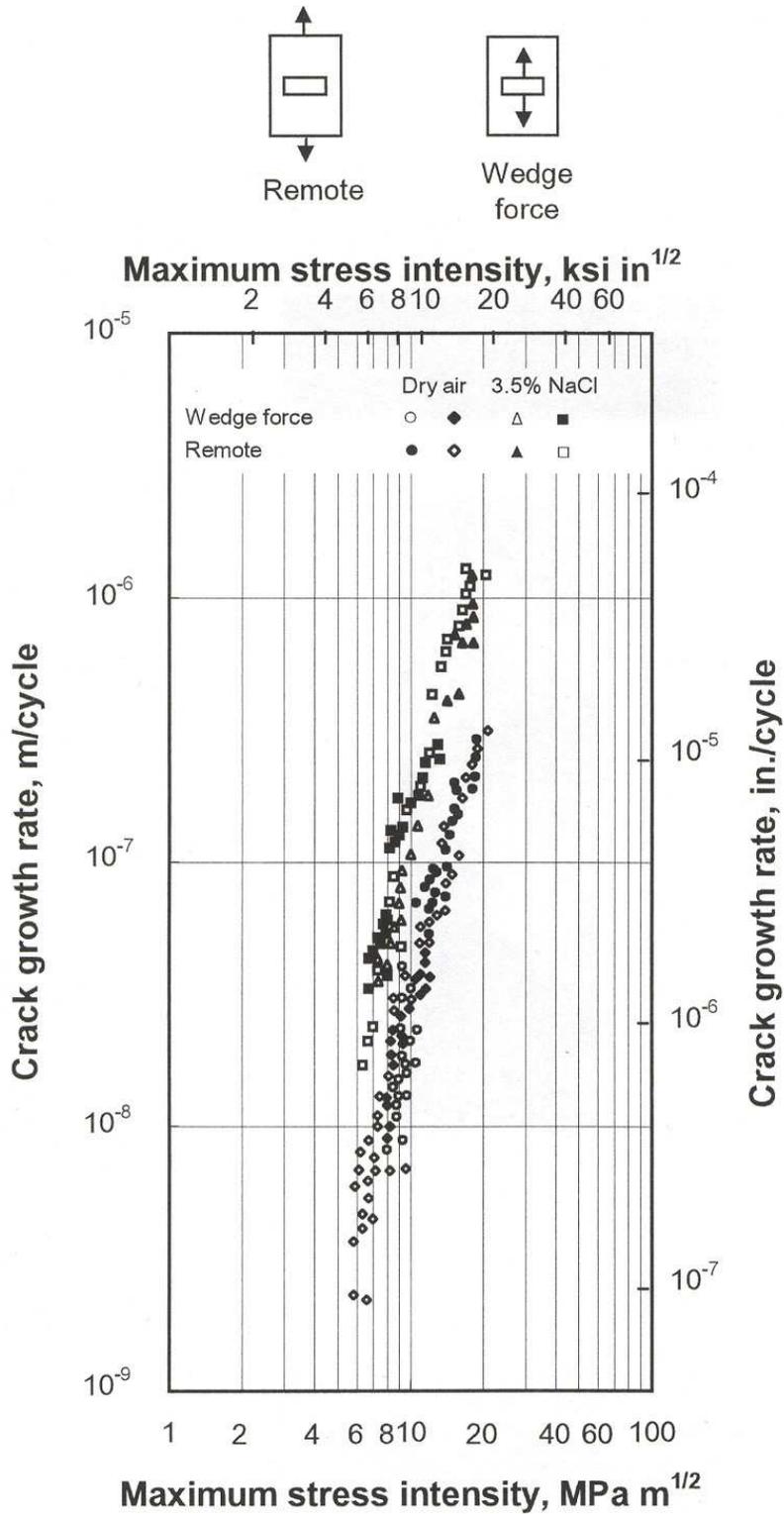


Figure 10: Corrosion FCG rates for 7075-T6 aluminium alloy in 0.6 M NaCl. The data also illustrate the similar behaviour when tested with either a K -increasing (remote load) or K -decreasing (wedge force) loading method (Feeney et al. [49]).

The second type of behaviour in Fig. 9 represents those material–environment systems in which there is a substantial environment-enhanced sustained load crack-growth component. The environmental effect is quite strong above K_{ISCC} and is negligible below K_{ISCC} . This behaviour pattern is referred to as “stress-corrosion fatigue” [48] and is typical for high-strength steels in water vapour and argon. Figure 11 shows an example of this type of corrosion FCG behaviour for high-strength steel 4340 M tested in distilled water at room temperature [35]. In this example, at a frequency of 10^{-3} Hz, distilled water increased crack growth rates by five orders of magnitude in comparison with those in vacuum.

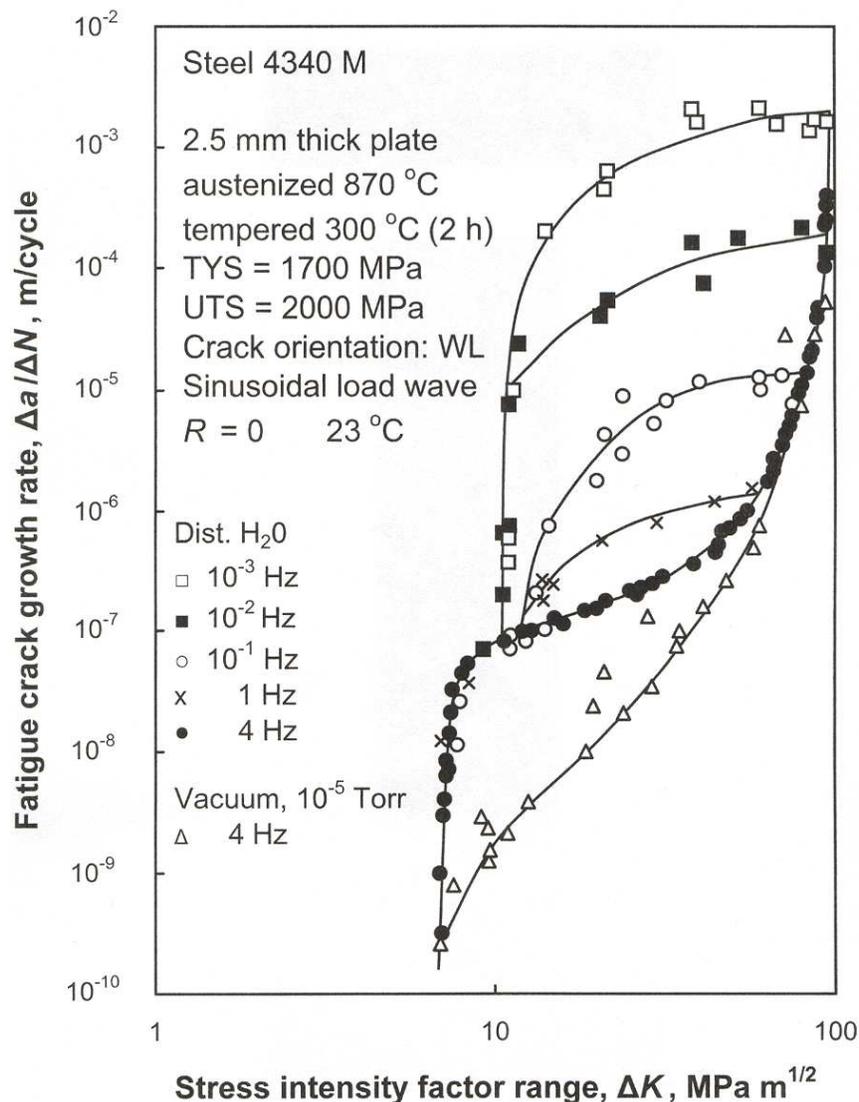


Figure 11: Effect of cyclic frequency on the corrosion FCG rate in high-strength steel 4340 M tested in distilled water (after Speidel [35]).

The third type in Fig. 9 represents the corrosion FCG behaviour of a broad range of material–environment systems that exhibit “stress-corrosion fatigue” above K_{ISCC} and also “true corrosion fatigue” at all levels of ΔK . The transformation from one type of behaviour to the other can be made by the change in cyclic frequency, stress ratio and electrode potential. For example, Figure 12 shows how increasing frequency shifts the “stress-corrosion fatigue” plateau crack

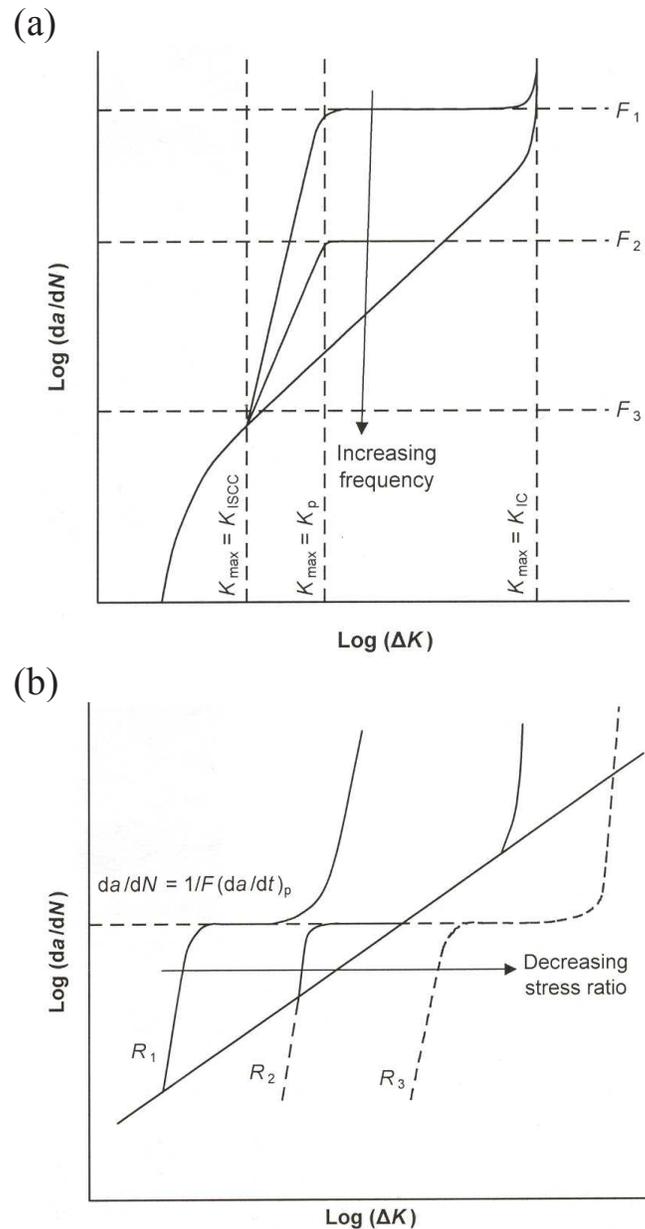


Figure 12: The effects of: (a) increasing frequency ($F_1 < F_2 < F_3$) at constant R , and (b) decreasing stress ratio ($R_3 < R_2 < R_1$) at constant frequency on corrosion FCG behaviour (after Austen and Walker [47]).

growth rate vertically downwards and decreasing the stress ratio shifts the “plateau crack growth rate” horizontally to the right [47]. Thus, increasing frequency and/or decreasing the stress ratio suppresses the appearance of “stress-corrosion fatigue” such that only “true corrosion fatigue” remains and the corrosion FCG behaviour changes from type two (or three) to type one as in Fig. 9. This occurs because FCG is a cycle-dependent process such that Region II governed by (1) is invariant despite a change in frequency and stress ratio. On the other hand, SCC is a time-dependent process such that increasing frequency decreases the “plateau crack growth rate” in terms of da/dN [Figs. 11 and 12(a)]. In addition, the values of ΔK_{SCC} under cyclic loading that correspond to K_{ISCC} under static loading and the values of K_p that correspond to the onset of the plateau on the $da/dN-\Delta K$ curve vary with stress ratio in a $(1 - R)$ relationship [47]. If, for a constant ΔK , the stress ratio is increased, the environmental acceleration of FCG is expected to increase also [Fig. 12(b)]. On the other hand, if, for a constant K_{max} , the stress ratio is increased, the environmental acceleration of FCG decreases. This is why in the literature there are two mutually exclusive statements: “the corrosion FCG rate increases with increasing stress ratio” and “the corrosion FCG rate decreases with increasing stress ratio.” In order to determine which one of the statements is correct, it is necessary to show which of the two stress-state parameters, ΔK or K_{max} , was taken into consideration.

It is necessary to note that a complete $da/dN-\Delta K$ curve (Fig. 9) beginning from 10^{-10} m/cycle is difficult to obtain due to the long time needed to measure low crack growth rates. Cyclic frequencies of 10 to 100 Hz that are usually used in standard fatigue and FCG tests are too high for studying corrosion FCG behaviour, and frequencies of 0.01 and 0.1 Hz are required to obtain realistic corrosion FCG data. This implies that weeks and even months of test time are needed. Using sensitive methods of crack-growth monitoring such as, for example, direct-current potential drop method that allows for detecting as little as 0.001 mm crack extension [14,28], does not make it easier to take the measurement of low crack growth rates because in this case it is difficult to keep the high resolution of the method for longer than say two hours. Thus, most corrosion da/dN data available in the literature are for more than 10^{-8} m/cycle that comprises Regions II and III in Fig. 9.

3 Mechanisms for corrosion-fatigue crack propagation

By now, the influence of mechanical, metallurgical, and environmental variables on the corrosion FCG behaviour of a broad range of material–environment systems has been studied in some detail [11,14,17,20–24,26,28,35–37,46–49]. However, the search for prevention methods, including the selection of materials resistant to the failure mode, is complicated by the fact that quite a number of fundamental questions regarding the possibility of corrosion fatigue remain unanswered. Foremost among these questions is the problem of the corrosion FCG mechanism(s) [14,37]. The basic mechanisms, which have generally been



proposed to explain corrosion FCG, are similar to those invoked in explaining SCC and began with research in SCC [50]. Two processes—hydrogen-induced cracking (HIC, or “hydrogen embrittlement”) and stress-assisted dissolution (SAD) of metal at the crack tip—are given main consideration as possible mechanisms of corrosion FCG. Choosing correctly from among the various measures—alloying elements, heat treatment, parameters of cathodic/anodic protection, and inhibitors—for the prevention of corrosion-fatigue failures is impossible if there is no way to make a reliable identification and quantitative estimation of the role of each of these two principally different mechanisms such as HIC and SAD in corrosion-fatigue crack propagation.

In the case of high-strength low-alloy steels and titanium alloys, for example, no firm consensus exists on the corrosion FCG mechanism in any one material–environment combination. For these materials, some authors propose that HIC plays a dominant role in corrosion-fatigue crack propagation [51–61]. As evidence of HIC they point to the deleterious effect of increasingly negative cathodic potential on corrosion FCG rates [51–59] and the similarity between features of the fracture surfaces produced by crack growth in aqueous solutions and in hydrogen gas [51,58,60,61]. Others provide evidence that SAD is the dominant mechanism for corrosion FCG in high-strength steels [62–64] and titanium alloys [48,65]. In contrast to the emphasis placed on high-strength steels and titanium alloys, there is very little information on the corrosion FCG behaviour of materials such as magnesium alloys that have high strength-to-density ratios [66], although much more effort has been devoted to studying SCC in magnesium alloys [67–76]. The mechanism of SCC of magnesium alloys has been ascribed to either continuous crack propagation as a result of SAD [67,68,72], or discontinuous crack propagation as a result of a series of hydrogen-induced fractures at the crack tip [71,73–76]. Also, SCC of magnesium alloys can involve the repeated cycles of a slow stage of SAD, followed by a fast stage of mechanical fracture [69,70]. One of the main arguments in favour of the SAD mechanism is that SCC of magnesium alloys can be stopped by cathodic polarization and restarted after polarization is removed [67,72].

At least two techniques are preferred among those commonly used for identifying corrosion FCG mechanism(s). The first is the technique based on studying the effect of controlled (applied) potential on the corrosion FCG rates [51–60,62,77]. Fractographic analysis of fracture surfaces is the second most popular technique and is usually employed in conjunction with the first technique [51,58,60,62].

3.1 Controlled-potential technique

In aqueous environments, anodic dissolution of metal at the crack tip and the ingress of hydrogen derived from the environment [78] into the crack-tip plastic zone occur simultaneously during corrosion-fatigue crack propagation. As a result, both SAD and HIC are involved in the acceleration of crack growth in



comparison to crack growth in vacuum. [Note: Crack growth due to internal hydrogen occurring in materials such as, for example, titanium alloys when testing in vacuum was not included in this analysis.] Depending on mechanical (stress level, mode of loading, cyclic frequency, stress ratio, waveform), metallurgical (chemical composition and microstructure of material, grain-boundary composition, surface condition, specimen orientation) and environmental (composition and concentration of solution, pH, potential, dissolved oxygen, temperature, flow rate) variables, one of the two mechanisms plays a dominant role in crack propagation. The intensity of anodic and/or cathodic reactions in the vicinity of the crack tip, the hydrogen-dependent properties of material and the hydrogen content in the crack-tip zone also determine the controlling corrosion FCG mechanism [14]. Generally, anodic polarization increases metal dissolution and decreases hydrogen generation, whereas cathodic polarization decreases metal dissolution and increases hydrogen generation. This statement identifies the controlled-potential technique [79–81] as a technique for distinguishing between HIC and SAD as possible mechanisms of corrosion FCG by studying the effect of applied potential on the crack growth rate [51–60,62,77].

The basic idea of the controlled-potential technique was proposed by Uhlig in 1950 [79] and then developed by Phelps and Loginow in 1960 [80] to distinguish between HIC and SAD as possible mechanisms of SCC in tests using smooth specimens. They suggested that, for example, if the application of small cathodic current decreases the time to failure, whereas small anodic current increases this time, the SCC mechanism operating in the absence of applied currents would be HIC. Similarly, the open-circuit mechanism is considered SAD if the time to failure increases with the application of small cathodic current and decreases with the application of small anodic current. Although at first glance this appears to be a simplistic approach, it has proved useful on occasions. In 1967, Leckie [81] adopted this approach to studying SCC in pre-cracked specimens loaded statically. In 1971, Barsom [51] and Gallagher [52] pioneered the application of the controlled-potential technique to distinguish between HIC and SAD during corrosion-fatigue crack propagation. In addition, Barsom [51], Meyn [53], and, more recently, Rungta and Begley [62] first examined in greater detail the features of the fracture surfaces produced by corrosion FCG under applied potentials by scanning electron microscopy (SEM) and transmission electron microscopy of plastic/carbon replicas. These examinations were conducted to provide further information concerning the corrosion FCG mechanisms. However, none of the above-mentioned attempts [51,52,60,62], nor numerous attempts of other authors [53–59,77] who employed the controlled-potential technique and fractographic evidence, allowed for the possibility of quantifying the role of any one mechanism in corrosion-fatigue crack propagation.