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## CHAPTER 1

# Mechanisms of Stress-Corrosion Cracking\*

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STRESS-CORROSION CRACKING (SCC) is a term used to describe service failures in engineering materials that occur by slow, environmentally induced crack propagation. The observed crack propagation is the result of the combined and synergistic interaction of mechanical stress and corrosion reactions.

Before SCC can be discussed in detail, several things must be clearly defined: the type of loading involved, the types of materials involved, the types of environments that cause SCC, and the nature of the interactions that result in this phenomenon. The term *stress-corrosion cracking* is frequently used to describe any type of environmentally induced or assisted crack propagation. However, this discussion focuses on the normal usage of the term as defined subsequently.

One common misconception is that SCC is the result of stress concentration at corrosion-generated surface flaws (as quantified by the stress-intensity factor,  $K$ ); when a critical value of stress concentration,  $K_{crit}$ , is reached, mechanical fracture results. Although stress concentration does occur at such flaws, it does not exceed the critical value required to cause mechanical fracture of the material in an inert environment ( $K_{scc} < K_{crit}$ ). Precorrosion followed by loading in an inert environment will not result in any significant crack propagation, while simultaneous environmental exposure and application of stress will cause time-dependent subcritical crack propagation. The term *synergy* is used to describe this process because the combined si-

multaneous interaction of mechanical and chemical forces results in crack propagation, whereas neither factor acting independently or alternately would result in the same effect. The exact nature of this interaction is the subject of numerous scientific investigations and is covered in the section “Crack Propagation Mechanisms” in this chapter.

The stresses required to cause SCC are small, usually below the macroscopic yield stress, and are tensile in nature. The stresses can be externally applied, but residual stresses often cause SCC failures. However, compressive residual stresses can be used to prevent this phenomenon. Static loading is usually considered to be responsible for SCC, while environmentally induced crack propagation due to cyclic loading is defined as corrosion fatigue. The boundary between these two classes of phenomena is vague, and corrosion fatigue is often considered to be a subset of SCC. However, because the environments that cause corrosion fatigue and SCC are not always the same, these two should be considered separate phenomena.

The term *stress-corrosion cracking* is usually used to describe failures in metallic alloys. However, other classes of materials also exhibit delayed failure by environmentally induced crack propagation. Ceramics exhibit environmentally induced crack propagation (Ref 1.1), and polymeric materials frequently exhibit craze cracking as a result of the interaction of applied stress and environmental reactions (Ref 1.2–1.5). The mechanical properties of composites will degrade if exposure to the environment attacks the matrix, the reinforcing phase, or the matrix-to-reinforcement interface; if crack propagation results during static loading, this degradation is SCC. Until recently, it was thought that

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pure metals were immune to SCC, but it is now known that this is not true (Ref 1.6, 1.7). Because considerably more research has been conducted on the SCC behavior of metallic alloys, the discussion in this chapter focuses on SCC of metals and their alloys.

Environments that cause SCC are usually aqueous and can be either condensed layers of moisture or bulk solutions. Stress-corrosion cracking is alloy/environment specific; that is, it is frequently the result of a specific chemical species in the environment. For example, the SCC of copper alloys, traditionally referred to as season cracking, is usually due to the presence of ammonia in the environment, and chloride ions cause or exacerbate cracking in stainless steels and aluminum alloys. Also, an environment that causes SCC in one alloy may not cause it in another. Changing the temperature, the degree of aeration, and/or the concentration of ionic species may change an innocuous environment into one that causes SCC failure. Also, different heat treatments may make the same alloy

either immune or susceptible. As a result, the list of possible alloy/environment combinations that cause SCC is continually expanding, and the possibilities are virtually infinite. Some of the more commonly observed alloy/environment combinations that result in SCC are listed in Table 1.1.

In general, SCC is observed in alloy/environment combinations that result in the formation of a film on the metal surface. These films may be passivating layers, tarnish films, or dealloyed layers. In many cases, these films reduce the rate of general or uniform corrosion, making the alloy desirable for resistance to uniform corrosion in the environment. As a result, SCC is of greatest concern in corrosion-resistant alloys exposed to aggressive aqueous environments. The exact role of films in the SCC process is the subject of current research and is covered in the section “Crack Propagation Mechanisms” in this chapter. Table 1.2 lists several alloy/environment combinations and the films that may form at the crack tip.

**Table 1.1 Alloy/environment systems exhibiting stress-corrosion cracking**

Alloy	Environment
Carbon steel	Hot nitrate, hydroxide, and carbonate/bicarbonate solutions
High-strength steels	Aqueous electrolytes, particularly when containing H <sub>2</sub> S
Austenitic stainless steels	Hot, concentrated chloride solutions; chloride-contaminated steam
High-nickel alloys	High-purity steam
α brass	Ammoniacal solutions
Aluminum alloys	Aqueous Cl <sup>-</sup> , Br <sup>-</sup> , and I <sup>-</sup> solutions
Titanium alloys	Aqueous Cl <sup>-</sup> , Br <sup>-</sup> , and I <sup>-</sup> solutions; organic liquids; N <sub>2</sub> O <sub>4</sub>
Magnesium alloys	Aqueous Cl <sup>-</sup> solutions
Zirconium alloys	Aqueous Cl <sup>-</sup> solutions; organic liquids; I <sub>2</sub> at 350 °C (660 °F)

### 1.1 The Phenomenon of Stress-Corrosion Cracking

Stress-corrosion cracking is a delayed failure process. That is, cracks initiate and propagate at a slow rate (e.g., 10<sup>-9</sup> to 10<sup>-6</sup> m/s) until the stresses in the remaining ligament of metal exceed the fracture strength. The sequence of events involved in the SCC process is usually divided into three stages:

- Crack initiation and stage 1 propagation
- Stage 2 or steady-state crack propagation
- Stage 3 crack propagation or final failure

**Table 1.2 Alloy/environment combinations and the resulting films that form at the crack tip**

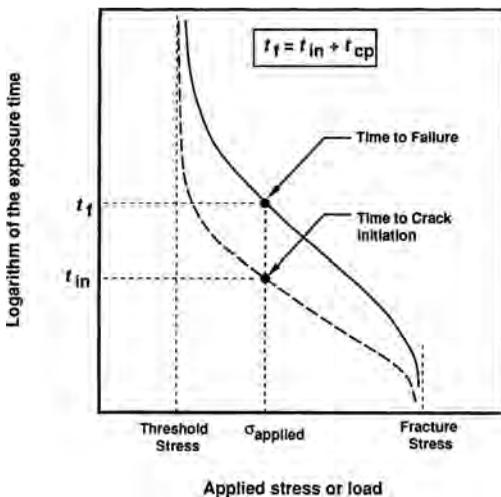
Metal or alloy	Environment	Initiation layer
α brass, copper-aluminum	Ammonia	Dealloyed layer (Cu)
Gold-copper	FeCl <sub>3</sub>	Dealloyed layer (Au)
Iron-chromium nickel	Acid sulfate	Dealloyed layer (Au)
	Chloride	Dealloyed layer (Au)
	Hydroxide	Dealloyed layer or oxide
	High-temperature water	Dealloyed layer or oxide
α brass	Nitrite	Oxide
Copper	Nitrite	Oxide
	Ammonia (cupric)	Porous dissolution zone
Ferritic steel	High-temperature water	Oxide
	Phosphate	Oxide (?)
	Anhydrated ammonia	Nitride
	CO/CO <sub>2</sub> /H <sub>2</sub> O	Carbide
	CS <sub>2</sub> /H <sub>2</sub> O	Carbide
Titanium alloys	Chloride	Hydride
Aluminum alloys, steels	Various media	Near-surface hydrogen

The characteristics of each of these stages are subsequently discussed in greater detail. First, however, the techniques used to measure SCC are reviewed briefly. Stress-corrosion cracking experiments can be categorized as:

- Tests on statically loaded smooth samples
- Tests on statically loaded precracked samples
- Tests using slowly straining samples

More detailed information on these tests can be found in Chapter 17, "Evaluation of Stress-Corrosion Cracking," in this book, and in Ref 1.8.

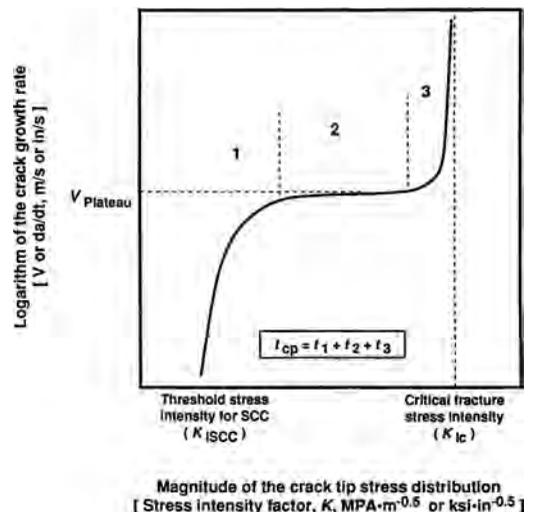
**Tests on statically loaded smooth samples** are usually conducted at various fixed stress levels, and the time to failure of the sample in the environment is measured. Figure 1.1 illustrates the typical results obtained from this type of test. In Fig. 1.1, the logarithm of the measured time to failure,  $t_f$ , is plotted against the applied stress,  $\sigma_{\text{applied}}$ , and the time to failure can be seen to increase rapidly with decreasing stress; a threshold stress,  $\sigma_{\text{th}}$ , is determined where the time to failure approaches infinity. The total time to failure at a given stress consists of the time required for the formation of a crack (the incubation or initiation time,  $t_{\text{in}}$ ), and the time of crack propagation, ( $t_{\text{cp}}$ ). These experiments can be used to determine the maximum stress that can be applied in service without SCC crack propagation, or to evaluate the influence of metallurgical and environmental changes on SCC. However, the time required for crack initiation is strongly de-



**Fig. 1.1** Schematic of a typical time to failure as a function of initially applied stress for smooth-sample stress-corrosion cracking (SCC) tests

pendent on a wide variety of parameters, such as surface finish. The presence of flaws that concentrate stress or crevices that alter the environment may dramatically change the threshold stress or the crack initiation time (Ref 1.9, 1.10). The entire crack initiation process is presently not well understood.

**Tests on statically loaded precracked samples** are usually conducted with either a constant applied load or with a fixed crack opening displacement, and the actual rate or velocity of crack propagation,  $da/dt$ , is measured (Ref 1.11). The magnitude of the stress distribution at the crack tip (the mechanical driving force for crack propagation) is quantified by the stress-intensity factor,  $K$ , for the specific crack and loading geometry. As a result, the crack propagation rate,  $da/dt$ , is plotted versus  $K$ , as illustrated in Fig. 1.2. These tests can be configured such that  $K$  increases with crack length (constant applied load), decreases with increasing crack length (constant crack mouth opening displacement), or is approximately constant as the crack length changes (special tapered samples). Each type of test has its advantages and disadvantages. However, in service, most SCC failures occur under constant load conditions, so that the stress intensity increases as the crack propagates. As a result, it is usually assumed in SCC discussions that the stress intensity is increasing with increasing crack length.



**Fig. 1.2** Schematic diagram of typical crack propagation rate as a function of crack-tip stress-intensity behavior illustrating the regions of stage 1, 2, and 3 crack propagation as well as identifying the plateau velocity and the threshold stress intensity

Typically, three regions of crack propagation rate versus stress-intensity level are found during crack propagation experiments. These are identified according to increasing stress-intensity factor as stage 1, 2, or 3 crack propagation (Fig. 1.2). No crack propagation is observed below some threshold stress-intensity level,  $K_{ISCC}$ . This threshold stress level is determined not only by the alloy but also by the environment and metallurgical condition of the alloy, and, presumably, this level corresponds to the minimum required stress level for synergistic interaction with the environment. At low stress-intensity levels (stage 1), the crack propagation rate increases rapidly with the stress-intensity factor. At intermediate stress-intensity levels (stage 2), the crack propagation rate approaches some constant velocity that is virtually independent of the mechanical driving force. This plateau velocity is characteristic of the alloy/environment combination and is the result of rate-limiting environmental processes such as mass transport of environmental species up the crack to the crack tip. In stage 3, the rate of crack propagation exceeds the plateau velocity as the stress-intensity level approaches the critical stress-intensity level for mechanical fracture in an inert environment,  $K_{Ic}$  (Ref 1.12).

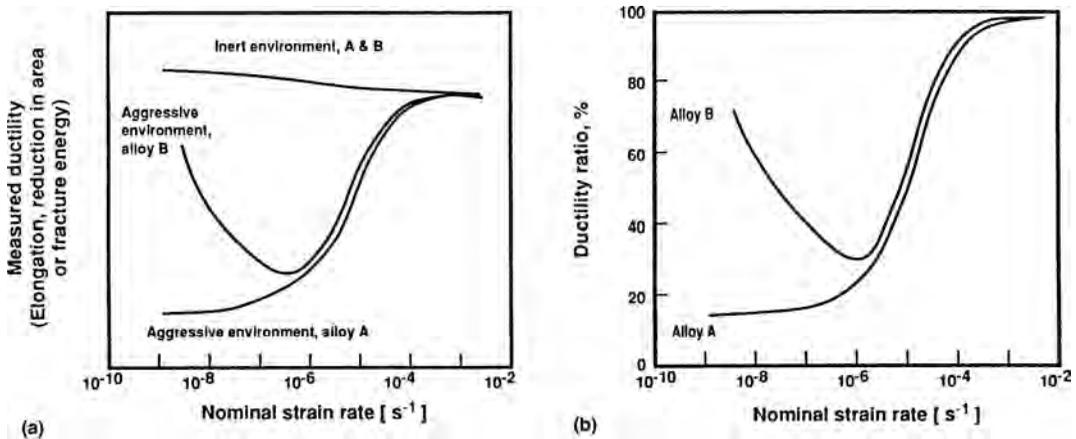
**Slow-Strain-Rate Testing.** Stress-corrosion tests can also be conducted by slowly increasing the load or strain on either precracked or smooth samples. These tests are called constant-extension-rate tests, slow-strain-rate tests, or straining electrode tests. Usually, a tensile machine pulls a smooth sample that is exposed to

the corrosive environment at a low crosshead speed ( $10^{-5}$  to  $10^{-9}$ m/s). The strain-to-failure in the corrosive environment and the strain-to-failure in an inert environment can then be plotted against the strain rate, as shown in Fig. 1.3(a), or the ratio of these measurements can be plotted as shown in Fig. 1.3(b). The ratio of other tensile property measurements, such as reduction in area and ultimate tensile strength, may be plotted.

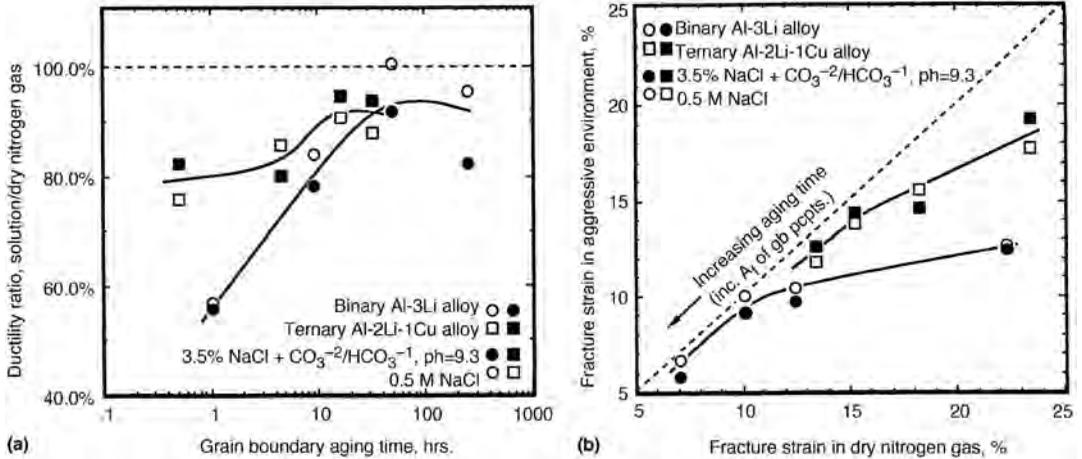
Frequently, this type of test is used to evaluate the influence of metallurgical variables, such as heat treatment, on SCC resistance. This type of experiment yields rapid comparisons. However, because the mechanical properties of the samples also vary with the metallurgical condition, such evaluations can become difficult. As a result, it was proposed (Ref 1.13) that the environment-dependent property be plotted versus the inert-environment or environment-independent value of this property, as shown in Fig. 1.4. In this manner, the strength of the material in the environment, or the “situation-dependent strength” (Ref 1.10), and the extent of any environmental effect can be visualized simultaneously. However, the application of these data to the prediction of actual in-service lifetimes is difficult and unreliable.

### 1.2 Overview of Stress-Corrosion Cracking Mechanisms

Many different mechanisms have been proposed to explain the synergistic stress-corrosion



**Fig. 1.3** Strain-to-failure plots resulting from slow-strain-rate testing. (a) Schematic of typical ductility vs. strain-rate behavior of two different types of alloys tested by the slow-strain-rate technique. (b) Schematic of the ductility ratio vs. strain-rate behavior of two different types of alloys. The ductility ratio is the ratio of a ductility measurement such as elongation, reduction in area, or fracture energy measured in the aggressive environment to that obtained in the inert reference environment.



**Fig. 1.4** Comparison of (a) slow-strain-rate data plotted as a ductility ratio to (b) the same data plotted as an environment-dependent property vs. the environment-independent value of the same property. Source: Ref 1.13

interactions that occur at the crack tip, and there may be more than one process that causes SCC. The proposed mechanisms can be classed into two basic categories: anodic mechanisms and cathodic mechanisms. That is, during corrosion, both anodic and cathodic reactions must occur, and the phenomena that result in crack propagation may be associated with either type. The most obvious anodic mechanism is that of simple active dissolution and removal of material from the crack tip. The most obvious cathodic mechanism is hydrogen evolution, absorption, diffusion, and embrittlement. However, a specific mechanism must be able to explain the actual crack propagation rates, the fractographic evidence, and the mechanism of formation or nucleation of cracks. Some of the more prominent of the proposed mechanisms are covered in greater detail in the section “Crack Propagation Mechanisms” in this chapter, but they usually assume that breaking of the interatomic bonds of the crack tip occurs either by chemical solvation and dissolution or by mechanical fracture (ductile or brittle). Mechanical fracture includes normal fracture processes that are assumed to be stimulated or induced by one of the following interactions between the material and the environment:

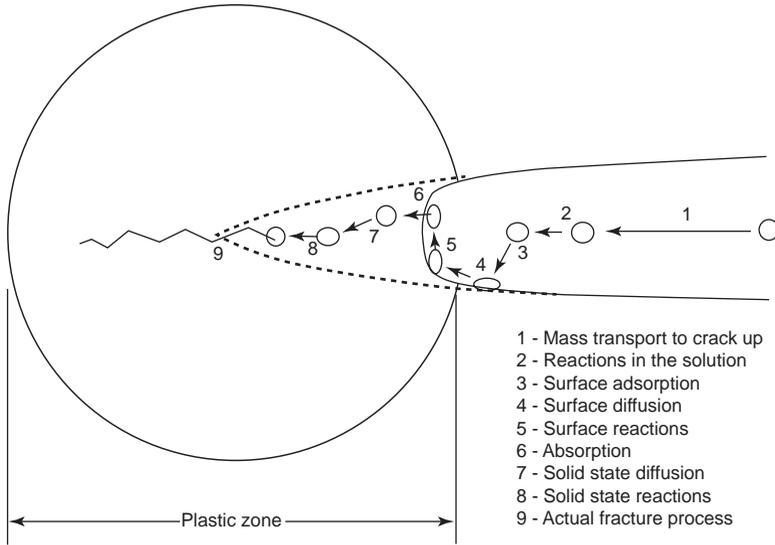
- Adsorption of environmental species
- Surface reactions
- Reactions in the metal ahead of the crack tip
- Surface films

All of the proposed mechanical fracture mechanisms contain one or more of these processes as an essential step in the SCC process. Specific mechanisms differ in the processes assumed to be responsible for crack propagation and the way that environmental reactions combine to result in the actual fracture process.

### 1.3 Controlling Parameters

The mechanisms that have been proposed for SCC require that certain processes or events occur in sequence for sustained crack propagation to be possible. These requirements explain the plateau region in which the rate of crack propagation is independent of the applied mechanical stress. That is, a sequence of chemical reactions and processes is required, and the rate-limiting step in this sequence of events determines the limiting rate or plateau velocity of crack propagation (until mechanical overload fracture starts contributing to the fracture process in stage 3). Figure 1.5 illustrates a crack tip in which crack propagation results from reactions in metal ahead of the propagating crack. This example was chosen because it maximizes the number of possible rate-limiting steps. Close examination of Fig. 1.5 reveals that potential rate-determining steps include:

- Mass transport along the crack to or away from the crack tip



**Fig. 1.5** Schematic of crack-tip processes that may be the rate-determining step in environmentally assisted crack propagation. For this illustration, an internal hydrogen embrittlement mechanism is assumed in order to maximize the number of possible rate-determining steps.

- Reactions in the solution near the crack
- Surface adsorption at or near the crack tip
- Surface diffusion
- Surface reactions
- Absorption into the bulk
- Bulk diffusion to the plastic zone ahead of the advancing crack
- Chemical reactions in the bulk
- The rate of interatomic bond rupture

- Temperature
- Pressure
- Solute species
- Solute concentration and activity
- pH
- Electrochemical potential
- Solution viscosity
- Stirring or mixing

Changes in the environment that modify the rate-determining step will have a dramatic influence on the rate of crack propagation, while alterations to factors not involved in the rate-determining step or steps will have little influence, if any. However, significantly retarding the rate of any one of the required steps in the sequence could make that step the rate-determining one. In aqueous solutions, the rate of adsorption and surface reactions is usually very fast compared to the rate of mass transport along the crack to the crack tip. As a result, bulk transport into this region or reactions in this region are frequently believed to be responsible for determining the steady-state crack propagation rate or plateau velocity. In gaseous environments, surface reactions, surface diffusion, and adsorption may be rate limiting, as well as the rate of bulk transport to the crack tip (Ref 1.14, 1.15).

Altering any of these parameters may affect the rate of the rate-controlling steps, either accelerating or reducing the rate of crack propagation. Also, it may be possible to arrest or stimulate crack propagation by altering the rate of an environmental reaction. It is well known and generally accepted that the environment at occluded sites, such as crack tips, can differ significantly from the bulk solution. If an alteration to the bulk environment allows the formation of a critical SCC environment at crack nuclei, then crack propagation will result. If the bulk environment cannot maintain this local crack-tip environment, then crack propagation will stop. As a result, slight changes to the environment may have a dramatic influence on crack propagation, while dramatic changes may have only a slight influence.

Several different environmental parameters are known to influence the rate of crack growth in aqueous solutions. These include, but are not limited to:

- The magnitude of the applied stress or the stress-intensity factor

- The stress state, which includes (a) plane stress and (b) plane strain
- The loading mode at the crack tip (e.g., tension or torsion)
- Alloy composition, which includes (a) nominal composition, (b) exact composition (all constituents), and (c) impurity or tramp element composition
- Metallurgical condition, which includes (a) strength level, (b) second phases present in the matrix and at the grain boundaries, (c) composition of phases, (d) grain size, (e) grain-boundary segregation, and (f) residual stresses
- Crack geometry, which includes (a) length, width, and aspect ratio, and (b) crack opening and crack-tip closure

#### 1.4 Important Fracture Features

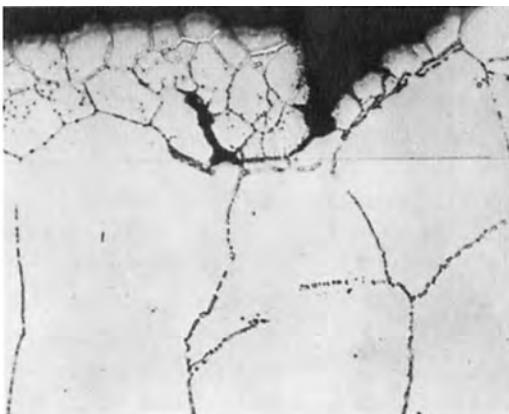
Stress-corrosion cracks can initiate and propagate with little outside evidence of corrosion and with no warning as catastrophic failure approaches. The cracks frequently initiate at surface flaws that either preexist or are formed during service by corrosion, wear, or other processes. The cracks then grow with little macroscopic evidence of mechanical deformation in metals and alloys that are normally quite ductile. Crack propagation can be either intergranular or transgranular; sometimes both types are observed on the same fracture surface. Crack openings and the deformation associated with crack propagation may be so small that the cracks are

virtually invisible except in special nondestructive examinations. As the stress intensity increases, the plastic deformation associated with crack propagation increases and the crack opening increases. When the final fracture region is approached, plastic deformation can be appreciable because corrosion-resistant alloys are frequently quite ductile.

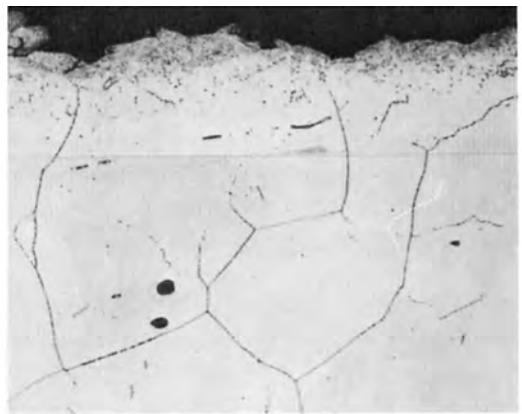
#### 1.5 Phenomenology of Crack Initiation Processes

**Crack Initiation at Surface Discontinuities.** Stress-corrosion cracking frequently initiates at preexisting or corrosion-induced surface features. These features may include grooves, laps, or burrs caused by fabrication processes. Examples of such features are shown in Fig. 1.6; these were produced during grinding in the preparation of a joint for welding. The feature shown in Fig. 1.6(a) is a lap, which is subsequently recrystallized during welding and could then act as a crevice at which deleterious anions or cations concentrate. The highly sensitized recrystallized material could also more readily become the site of crack initiation by intergranular corrosion. A cold worked layer and surface burrs, shown in Fig. 1.6(b), can also assist crack initiation.

**Crack Initiation at Corrosion Pits.** Stress-corrosion cracks can also initiate at pits that form during exposure to the service environment (Fig. 1.7) or during cleaning operations, such as pickling of type 304 stainless steel before fabrication. Pits can form at inclusions that

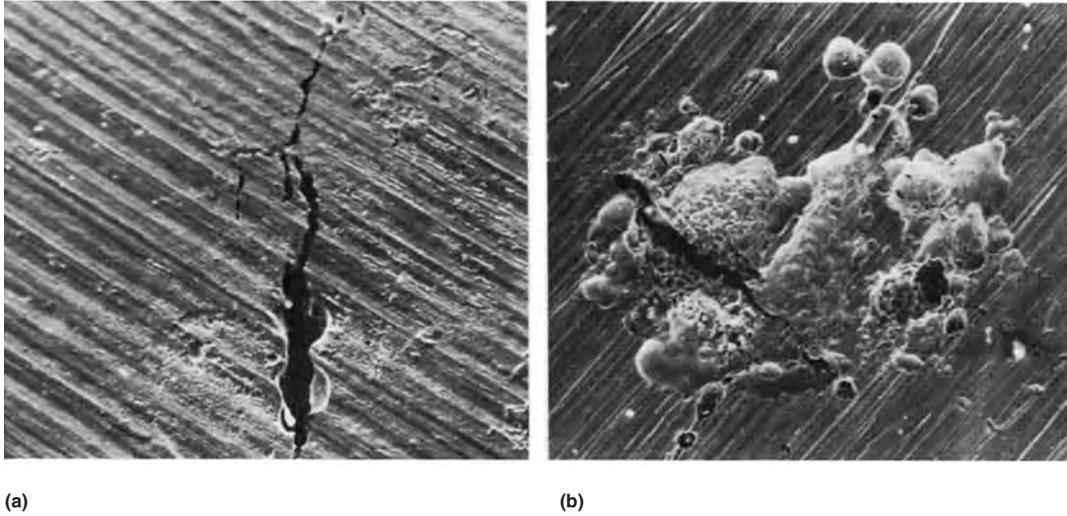


(a)



(b)

**Fig. 1.6** Optical micrographs showing defects on the inner surface of type 304 stainless steel pipe (a) near weld root and (b) near through-crack. Original magnification of both: 1000 $\times$



**Fig. 1.7** Stress-corrosion crack initiating from a corrosion pit in a quenched-and-tempered high-strength turbine disk steel (3.39Ni-1.56Cr-0.63Mo-0.11V) test coupon exposed to oxygenated, demineralized water for 800 h under a bending stress of 90% of the yield stress. (a) Original magnification: 275 $\times$ . (b) Original magnification: 370 $\times$ . Courtesy of S.J. Lennon, ESCOM, and F.P.A. Robinson, University of Witwatersrand

intersect the free surface or by a breakdown in the protective film. In electrochemical terms, pits form when the potential exceeds the pitting potential. It has been shown that the SCC potential and pitting potential were identical for steel in nitrite solutions (Ref 1.16, 1.17).

The transition between pitting and cracking depends on the same parameters that control SCC, that is, the electrochemistry at the base of the pit, pit geometry, chemistry of the material, and stress or strain rate at the base of the pit. A detailed description of the relationship between these parameters and crack initiation has not been developed because of the difficulty in measuring crack initiation. Methods for measuring short surface cracks are under development but are limited to detecting cracks that are beyond the initiation stage. The geometry of a pit is important in determining the stress and strain rate at its base. Generally, the aspect ratio between the penetration and the lateral corrosion of a pit must be greater than approximately 10 before a pit acts as a crack initiation site. A penetration to lateral corrosion ratio of 1 corresponds to uniform corrosion, and a ratio of approximately 1000 is generally observed for a growing stress-corrosion crack. As in the case of a growing crack, the pit walls must exhibit some passive-film-forming capability in order for the corrosion ratio to exceed 1.

A change in the corrosive environment and potential within a pit may also be necessary for

the pit to act as a crack initiator. Pits can act as occluded cells similar to cracks and crevices, although in general their volume is not as restricted. There are a number of examples in which stress-corrosion cracks initiated at the base of a pit by intergranular corrosion. In these circumstances, the grain-boundary chemistry and the pit chemistry were such that intergranular corrosion was favored. Crack propagation was also by intergranular SCC in these cases.

Although the local stresses and strain rates at the base of the pit play a role in SCC initiation, there are examples of preexisting pits that did not initiate stress-corrosion cracks. This observation has led to the conclusion that the electrochemistry of the pit is more important than the local stress or strain rate (Ref 1.16). A preexisting pit may not develop the same local electrochemistry as one grown during service, because the development of a concentration cell depends on the presence of an actively corroding tip that establishes the anion and cation current flows. Similarly, an inability to reinitiate crack growth in samples in which active growth was occurring before the samples were removed from solution, rinsed, dried, and reinserted into solution also suggests that the local chemistry is very important.

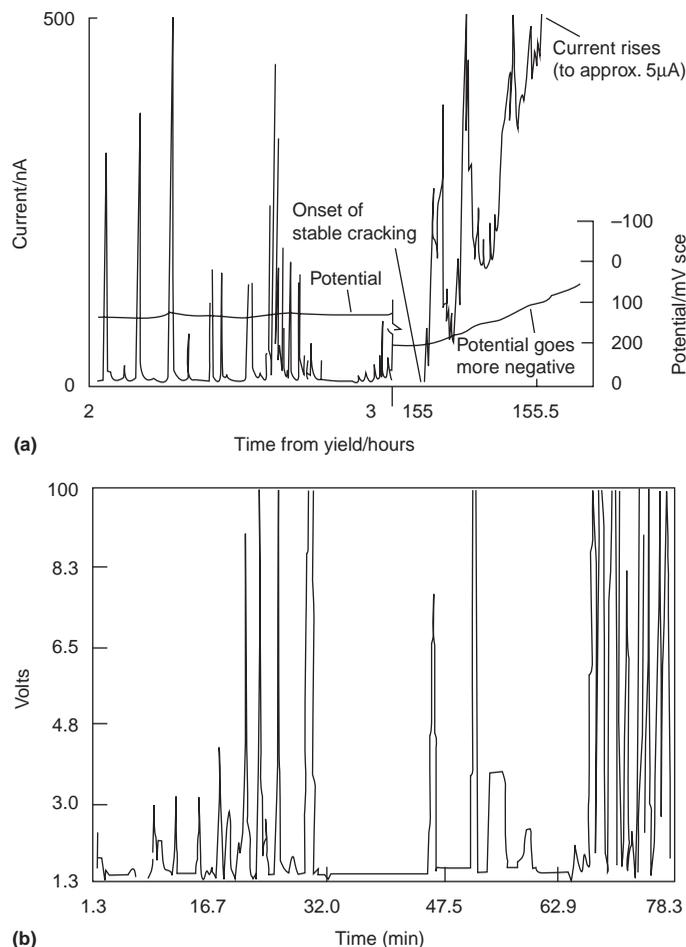
**Crack Initiation by Intergranular Corrosion or Slip Dissolution.** Stress-corrosion crack initiation can also occur in the absence of pitting by intergranular or slip-dissolution processes. In-

tergranular corrosion-initiated SCC requires that the local grain-boundary chemistry differ from the bulk chemistry. This condition occurs in sensitized austenitic stainless steels or with the segregation of impurities such as phosphorus, sulfur, or silicon in a variety of materials. Slip-dissolution-initiated SCC results from local corrosion at emerging slip planes and occurs primarily in low stacking-fault materials. The processes of crack initiation and propagation by the slip-dissolution process are in fact very similar.

Crack initiation can be thought of as occurring in several stages, including the first few atomic layers that fail due to the transition from short-crack to long-crack behavior. Evidence obtained by electrochemical (Ref 1.18) and acoustic emission monitoring (Ref 1.19) of crack initiation in austenitic stainless steel suggests that the

process occurs by the initiation of multiple short cracks prior to the propagation of a single dominant crack. Examples of the electrochemical and acoustic emission transients thought to be associated with the growth and retardation of multiple short cracks are given in Fig. 1.8. Retardation of the initiated cracks occurs because of variations in grain-boundary sensitization, crack angle, electrochemistry, and so on, with cracks being arrested after they grow approximately one grain diameter. Details of the conditions required for a single dominant crack to propagate have not been fully evaluated, but most likely it is a statistical process where there is a finite probability for a crack to find a path that does not retard its growth.

Another concept suggested by Parkins (Ref 1.21) for gas pipeline SCC initiation involves crack coalescence. It has been suggested that



**Fig. 1.8** Comparison between (a) current transients vs. time observed by Stewart and (b) AE events vs. time observed during IGSCC of sensitized type 304 SS. Ref. 1.20

crack initiation in gas pipeline steels occurs by these steps:

1. Penetration of ground water to the pipeline surface and generation of a critical SCC environment
2. Initially rapid formation of multiple cracks, the velocity decreasing with time to a constant value
3. A period of constant crack growth velocity
4. Conventional stages 1, 2, and 3 as described by single-crack behavior, during which time crack coalescence leads to final fracture

## 1.6 Crack Initiation Mechanisms

Although the features causing SCC initiation, such as pits, fabrication defects, and intergranular corrosion, are easily observed and identified, there are few well-developed models of SCC initiation, for several reasons. For example, the initiation of a crack is difficult to measure experimentally, even though it is not difficult to detect the location from which a growing crack has emanated. Furthermore, crack initiation has not been precisely defined, and it is difficult to determine at what point a pit is actually a crack and when intergranular corrosion becomes intergranular SCC. Also, the fracture mechanics concept of design assumes preexisting flaws in materials, although these may not be surface flaws that can become stress-corrosion cracks. It has been demonstrated that the corrosion fatigue threshold of 12% Cr and 2.0% NiCrMoV steels could be related to the minimum depth of surface pits, as shown in Fig. 1.9. Using a linear-elastic fracture mechanics approach and relating a pit to a half-elliptical surface crack, one researcher has shown that the critical pit dimension could be expressed by the relationship (Ref 1.22):

$$\alpha_0 = \frac{1}{\pi} \left( \frac{\Delta K_{th}}{F \Delta \sigma_0} \right)^2 \quad (\text{Eq 1.1})$$

where  $\Delta K_{th}$  is the corrosion fatigue threshold,  $F$  is a constant, and  $\Delta \sigma_0$  is the alternating surface stress. A pit could be represented by a half-elliptical surface crack because it had intergranular corrosion at the base that caused the pit to have cracklike characteristics.

A model for stress-corrosion crack growth from pits in brass tested in a nontarnishing ammoniacal solution was developed (Ref 1.23). The

researchers evaluated the corrosion and stress aspects of a pit to develop a model for crack initiation. They assumed that the corrosion conditions in the base of the pit were essentially the same as those on a flat surface and that initiation required that a critical crack-tip opening displacement be exceeded. Using linear-elastic fracture mechanics, the researchers developed the relationship for the time to initiate a crack:

$$t_{inc} = \frac{(K_{ISCC})^2}{\pi B(\sigma^2 - \sigma_0^2)} \exp\left(\frac{-V_m}{V_0}\right) \quad (\text{Eq 1.2})$$

where  $K_{ISCC}$  is the stress-corrosion threshold for crack growth for brass in ammoniacal solution,  $\sigma$  is the applied stress,  $\sigma_0$  is the stress needed to close the crack,  $B$  is a constant,  $-V_m$  is the electrochemical potential of the sample, and  $V_0$  is the reversible potential. However, the assumption that the pit corrosion conditions are equal to the flat surface conditions limits the applicability of this model, because it is generally accepted that the electrochemistry in a pit is considerably different from that of a flat surface. Also, this model does not explicitly describe the transition from a pit to a crack but treats a pit as a small crack in which the crack-tip opening and crack depth are affected by corrosion.

The transition between intergranular corrosion and intergranular SCC was evaluated for nickel with segregated phosphorus and sulfur (Ref 1.24, 1.25). Because phosphorus and sulfur inhibit the formation of a passive film on nickel, it was expected that intergranular SCC would be similar in these two materials. It was observed, however, that only shallow intergranular corrosion to a depth of approximately 0.1 mm (0.004 in.) resulted in nickel in which sulfur was segregated to the grain boundary when tested at a strain rate of  $10^{-6}$  in 1 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ). On the other hand, in a test under similar conditions, rapid intergranular SCC resulted in nickel in which phosphorus was segregated to the grain boundaries. Using crack-tip chemistry modeling, it was shown that intergranular corrosion did not convert to a stress-corrosion crack in Ni + S because the sulfur remained on the crack walls, causing the electrolyte in the solution to become saturated and the crack-tip corrosion rate to drop to zero. Starting from a flat surface, the corrosion current at the tip of the intergranular corrosion penetration was approximately 30 mA/cm<sup>2</sup> (195 mA/in.<sup>2</sup>) and decreased to 0 at a depth of approximately 0.08 mm (0.003 in.), as shown in Fig. 1.10. A similar corrosion depth