

## STRESS CORROSION CRACKING IN IRON-BASE ALLOYS

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Recent developments in theories of stress corrosion cracking in high strength steels and stainless steels have been discussed in this paper. The use of fracture mechanics concepts to stress corrosion testing has been outlined and the application of modern instruments such as the high voltage electron microscope and scanning electron microscope in the study of stress corrosion cracking has been described.

**Keywords :** Stress Corrosion Crack; Iron-base Alloy; High Strength and Stainless Steels; Fracture Mechanics; Brittle & Passive Film Rupture; Tunnel; Stress-Sorption Hydrogen & Decohesion Models

### INTRODUCTION

STRESS corrosion cracking is the failure of metals under the conjoint action of a tensile stress and a specific environment. What makes stress corrosion cracking especially insidious is its catastrophic nature that leads to structural failures without warning. Stress corrosion has been a recognized source of metal failure for over 25 years. Despite the expenditure of large sums of money on research during that period of time, however, it is still a relatively little understood phenomenon about which there exist considerable ambiguity and argument. To compound the problem, the number of alloys known to be susceptible to stress corrosion and the number of environments that cause cracking have risen sharply during this period. Actually, fully one fifth of all the corrosion failures in metals have been attributed to stress corrosion (see for example Table I) (Stahle, 1971). Speidel (1971) has summarized the occurrence of stress corrosion failures in service in the aircraft industry for a ten year period. His figures have shown that the trend of failures is on the rise, though some control has been achieved perhaps due to a better understanding of the phenomenon in recent years.

### MANIFESTATION OF STRESS CORROSION IN VARIOUS ENVIRONMENTS

The environments which promote stress corrosion cracking in steels are numerous. Carbon steels are known to undergo stress corrosion cracking in hot aqueous nitrate and hydroxide solutions (Henthorne & Parkins, 1967; and Parkins, 1971). The crack path in these cases is intergranular, but addition of inhibitors to hydroxide solutions is known to promote transgranular cracking. Transcrystalline stress corrosion cracking of ferritic steels has been reported in  $\text{CO-CO}_2\text{-H}_2\text{O}$

TABLE I

*Metal failure frequency corrosion failures—1968, 1969*  
(313 cases; corrosion 56.9 per cent mechanical 43.1 per cent)

Form	Per cent
General	31.5
Cracking-Stress Corrosion—	21.6
Corrosion Fatigue	1.8
Pitting	15.7
Intergranular	10.2
Erosion Corrosion	7.4
Cavitation	1.1
Fretting	0.5
Crevice	1.8
De(metal) ification	1.1
Two-metal	0.0

environment (Kowaka & Nagata, 1968). The austenitic stainless steels undergo transgranular stress corrosion cracking in hot  $MgCl_2$  solutions and in waters containing  $Cl^-$  ions. Even 1. Oppm chloride in single phase aqueous solution is sufficient to cause stainless steel to crack at 200 °C (Stahle, 1977). It is this transgranular cracking of austenitic stainless steels that has received much fundamental attention, although environments in which they fail intergranularly are also well known. Table II lists some of the environments promoting SCC.

TABLE II

*Stress corrosion environments*

	Transgranular	Intergranular	Mixed
Mild Steels	Hot Aqueous $NaOH + Na_2H_2PO_4$ inhibitor Dilute HCN	1. Hot aqueous nitrates and hydroxides 2. $(NH_4)_2CO_3$ with HCN and $H_2S$ 3. Anhydrous $NH_3$ in the presence of $CO_2$ in air	
Austenitic Stainless Steels	1. Hot $MgCl_2$ solution 2. $Cl^-$ containing 3. Lead contaminated oxygenated high temperature water 4. Hot $H_2SO_4$ 5. $CaCl_2$ solution at 100 °C 6. $H_2SO_4 + NaCl$ solutions	1. High Purity water in nuclear environments at 300 °C 2. Oxygenated high temperature water	1. Aqueous NaOH solution; poten- tial dependent cracking mode

## PROPOSED MECHANISMS OF SCC

While a review of all the theories to explain the detailed processes by which stress corrosion cracking occurs would be too extensive here, central aspects of several models are outlined briefly.

Table III lists the major models that have been proposed (Forty & Humble, 1963; McEvily & Bond, 1965; Pugh, 1971; Hoar & Hines, 1954, 1956; Hoar & West, 1962; Latanision & Stahle, 1969; Stahle, 1971; Vermilyea, 1973; Nielsen, 1964; Pickering & Swann, 1963; Swann & Embury, 1965; Uhlig, 1959; Uhlig & Johnson, 1963; Vaughn *et al.*, 1963; Edeleanu, 1953; Birley & Tromans, 1971; Cotterill, 1961; Zappfe & Sims, 1941; Williams & Nelson, 1970; Frohmberg *et al.*, 1955; Troiano, 1960; and Oriani, 1970) and Table IV lists specific failures *vis-a-vis* the proposed modes.

TABLE III

*Models of stress corrosion cracking in iron base alloys*

Model	Authors
1. Brittle Film Rupture	Forty McEvily and Bond, Pugh
2. Film Rupture	
(a) Hoar Model	Hoar
(b) Slip Dissolution	Stahle and coworkers
(c) Film Rupture by Creep	Vermilyea
3. Tunnel Model	Nielsen Swann and coworkers
4. Stress-sorption Model	Uhlig
5. Hydrogen Models	
(a) Hydride Model	Vaughn <i>et al.</i> Gilman
(b) Hydrogen Induced Martensite	Edeleanu, Birley and Tromans
(c) Hydrogen-Dislocation	Cotterill
(d) Molecular Hydrogen	Zappfe and Simms
(e) Hydrogen Adsorption-Decohesion	Williams and Nelson, Troiano and coworkers, Oriani

*Brittle Film Rupture*

The essential features of this model are shown in Fig. 1. Although this model was originally proposed for stress corrosion cracking in alpha brass, it is thought to be relevant to other systems, notably to intergranular cracking of low strength ferritic and austenitic steels.

TABLE IV

*Specific failures and proposed mechanisms*

Failures	Major Models
(i) Transgranular Cracking of Austenitic Stainless Steels	1. Film Rupture (proposed for failures i, ii, iii, v, vi)
(ii) Intergranular Cracking of Low-Strength Ferritic Steels	2. Brittle Film Rupture (failures ii and iii)
(iii) Intergranular Cracking of Austenitic Stainless Steels	3. Tunnel (failure i)
(iv) Cracking of High-Strength Steels	4. Adsorption (generalized model)
(v) Transgranular Cracking of Low-Strength Ferritic Steels	5. Hydrogen Embrittlement (failures i, iv, v, vi)

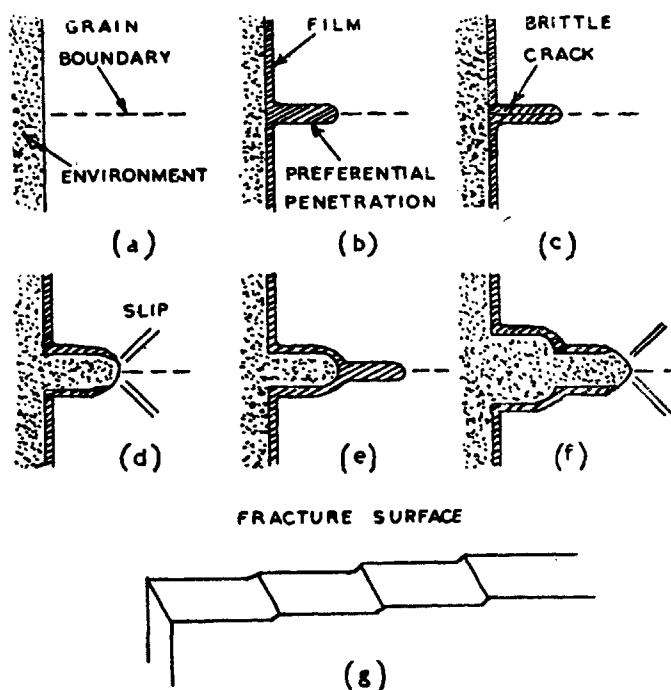


FIG. 1. Schematic representation of model based on brittle film rupture (after Forty & Humble, 1963; McEvily, Jr. & Bond, 1965; and Pugh, 1971).

In its support Pugh (Pugh, 1971) has presented fractographic striations on the intergranular fracture as indicative of brittle fracture over relatively large distance ( $>1000\text{\AA}$ ). However, the major question facing the brittle film rupture model has been the mechanism by which film undergoes fracture at some critical thickness. The recent suggestion by Vermilea (1973) that creep of metal ahead of the

advancing intergranular crack might play an important role in film rupture has been put forward as an explanation, but clearly more work needs to be done to verify this possibility.

### *Passive Film Rupture*

The model of passive film rupture due to emergence of slip steps as originally proposed by Hoar and coworkers (1954, 1956, 1962) is shown schematically in Fig. 2. This model has been refined in detail by Stahle and his colleagues (Latanision & Stahle, 1969; and Stahle, 1971), who have termed it the "slip dissolution" model. The essential features of the slip dissolution model are shown in Figs. 3(i) and 3(ii).

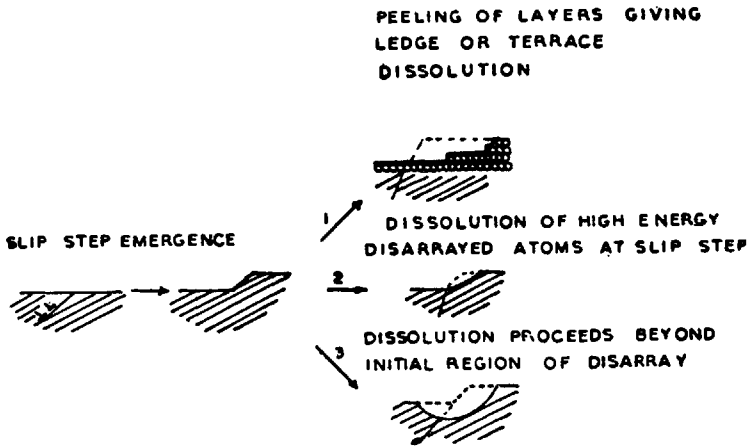


FIG. 2. Schematic figure illustrating the Hoar Process for metal dissolution after slip step emergence (after Hoar & Hines, 1954 & 1956; and Hoar & West, 1962).

According to slip dissolution model, film rupture is considered to result from the emergence of slip steps through the thin passive film and repassivation is thought to proceed to completion after a stage of transient dissolution. An essential aspect of the slip dissolution model concerns the kinetics of the repassivation process. Three dissolution models are envisioned, ([Fig. 3 (i)] namely, I) repassivation is extremely rapid so that the amount of dissolution at the slip step is very small, II) an intermediate stage favouring cracking and III) repassivation is slow, giving rise to extensive lateral dissolution. These concepts have led to widespread interest in experimentally determining repassivation rates and correlating them with stress corrosion data.

A basic objection to the slip dissolution model as applied to transgranular SCC in austenitic steels is that it cannot be reconciled with fractographic observations. The transgranular fracture surfaces in austenitic stainless steels unquestionably have characteristics of cleavage. They are relatively flat and exhibit surface markings which are similar to "river patterns" of cleavage fracture, and are

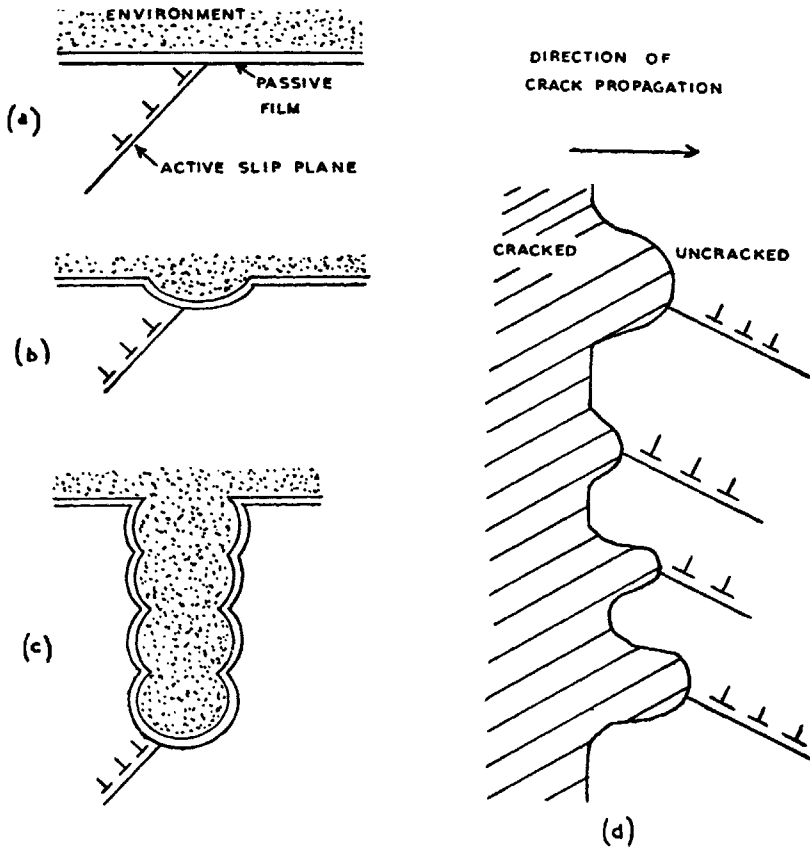


FIG. 3(i) Schematics illustrating the film rupture model (a)–(c) are sections, (d) is a plan view of the fracture surface showing the crack tip intersected by several active slip planes (after Latanision & Stahle, 1969; and Stahle, 1971).

approximately parallel to the direction of crack propagation. On the other hand, the slip dissolution model requires that the transient dissolution and repassivation sequences lead to closely spaced striations on the fracture surface perpendicular to the direction of crack propagation. However, Stahle (1971) had defended the model with the rejoinder that replica electron fractography lacks the necessary resolution to distinguish the minute terrace ledge aspects of the transient dissolution processes.

#### *Tunnel Model*

Essentially, this model involves the formation of corrosion tunnels at slip steps (Fig. 4) which weaken the metal and eventually lead to ductile rupture. The process is then repeated, leading to a discontinuous crack propagation.

The occurrence of corrosion tunnels in austenitic stainless steels exposed to cracking media is well established. Moreover, Hartson and Scully (1969) have pre-

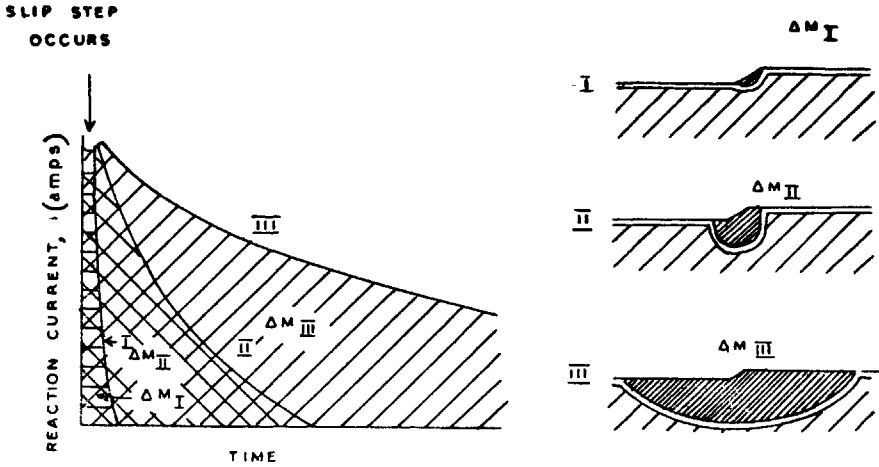


FIG. 3(ii) Schematic figure illustrating relationship between current versus time transient, and amount of material dissolved for given slip event (after Latanision & Stahle, 1969; and Stahle, 1971).  
 Case — I Rapid repassivation.  
 Case — II Intermediate repassivation—favors stress corrosion cracking.  
 Case —III Extensive or non restricted lateral dissolution.

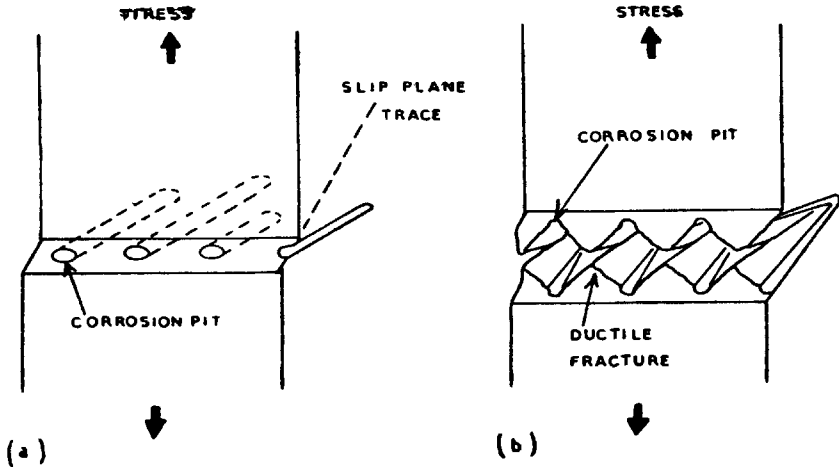


FIG. 4. Schematic representation of tunnel model (after Pickering & Swann, 1963; and Swann & Embury, 1965).

sented persuasive evidence that tunnel formation can lead to cracking in a steel containing 18Cr-10Ni exposed to a sulphuric acid-sodium chloride solution. Nevertheless, it is the general consensus now that the tunnel model represents a special and rather rare case, and Stahle's contention (1971) that environmental conditions which cause cracking also lead to tunnel corrosion but the latter does not, in general, cause cracking has been generally upheld.

*Adsorption Induced Cleavage or Stress-Sorption Model (Uhlig, 1959; and Uhlig & Johnson, 1963)*

The model proposes that adsorption of specific species reduces the surface energy term in the Griffith equation, thus leading to a reduction in stress required to produce brittle fracture. Stated more atomistically, it suggests that the specific species adsorb and interact with strained bonds at the crack-tip, causing a reduction in bond strength (Fig. 5).

The major objection to this mechanism is that crack propagation would be controlled by the rate of transport of the damaging species to the crack tip. It is difficult to imagine that an atomistically sharp crack can remain stable in a ductile alloy at such low crack velocities as required by the diffusional transport.

*Hydrogen Models*

It is generally accepted that hydrogen plays a key role in stress corrosion cracking of high strength steels. The source hydrogen is external, usually aqueous but sometimes gaseous. Several workers have suggested that transgranular stress corrosion cracking in austenitic steels might be a hydrogen induced phenomenon. The various proposed hydrogen mechanisms have been summarized below.

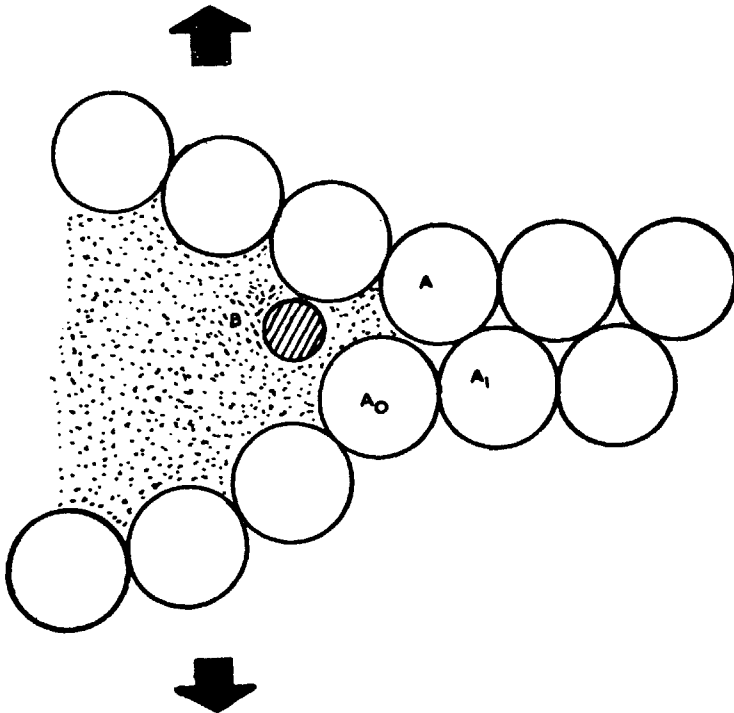


FIG. 5. Schematic illustration of the adsorption model (after Uhlig, 1959; and Uhlig & Johnson, 1963). The model requires that a specific ion from the environment, "B" interacts and reduces the cohesive strength of strained bond A-A at the tip of brittle crack.



(a) *Hydride Models* — Hydrides are thought to play key roles in the stress corrosion cracking of austenitic steels by acting as barriers to dislocation motion and hence promoting brittle fracture of the matrix, or by providing paths for brittle fracture, i.e., through the hydride phase. The absence of a stable hydride has caused these models to be generally overlooked in iron-base alloys. Recently, Gilman (1973) has suggested that stable “surface hydrides” might form in ferrous alloys which could promote brittle transgranular failure. Vaughn and coworkers (1963) suggest that stress induced hydrides are formed near the crack tip to provide preferential paths for the crack propagation. Their ideas are schematically shown in Fig. 6.

(b) *Strain Induced Martensite* — In 1953, Edeleanu suggested that strain-induced martensite may be responsible for the observed transgranular cracking in austenitic stainless steels. Although existence of martensite on the fracture surface of type 304L steel has been reported, there is no general acceptance of this model because the cracking occurs in stable alloys such as type 310 in which there is no evidence of a strain induced martensite.

(c) *Interaction of Hydrogen with Dislocations* (Cotterill, 1961) — It has been proposed that the role of hydrogen in embrittlement is to pin dislocations and thereby favour brittle fracture. However, the interaction between dislocations and hydrogen is relatively weak and therefore dislocation pinning is unlikely to be the main cause of hydrogen induced cracking.

(d) *The Molecular Hydrogen Model* (Zappfe & Sims, 1941) — According to this model, high internal pressures are produced by the formation of molecular hydrogen in internal voids and cavities. Although such internal hydrogen pressures

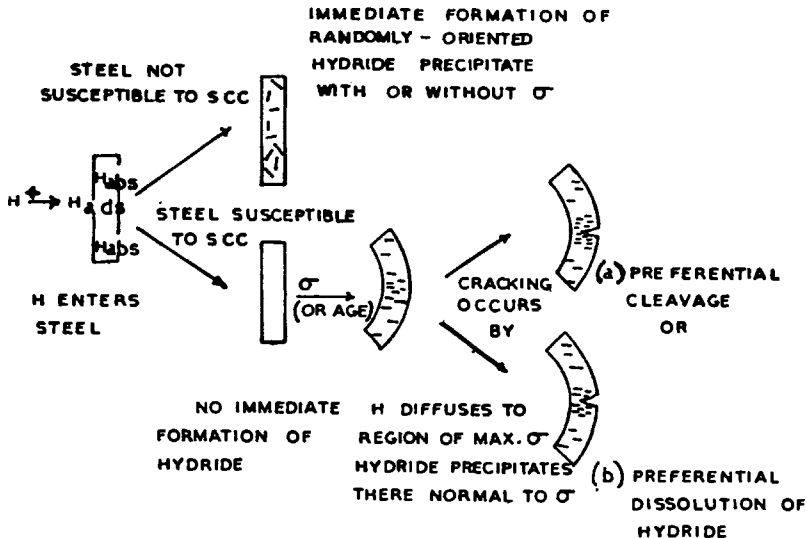


FIG. 6. Schematic figure illustrating the essential arguments advanced by Vaughn and collaborators (1963) for rationalizing the behaviour of hydrogen in stainless steels of varying stress corrosion susceptibilities.

might assist the applied stress in the propagation of cracks, the model fails to explain why a normally ductile steel should fail in a brittle manner under stress corrosion conditions.

(e) *The Adsorption and Decohesion Models* — The adsorption model is similar to the stress-sorption mechanism of Uhlig in that hydrogen reduces the bond energy in iron. However, the sites of embrittlement according to this are supposed to be in the bulk rather than on the surface as in the stress-sorption mechanism. The hydrogen adsorption model has been found to work well in explaining stress corrosion cracking in high strength steel (Williams & Nelson, 1970), but its applicability to low strength austenitic stainless steel remains to be confirmed. The decohesion model was first proposed by Troiano (1960) and his colleagues for high strength steels. These workers proposed that hydrogen diffuses to regions of large triaxial stress ahead of the crack, thus producing large hydrogen concentrations. Reduction of cohesive strength in these regions was considered to result in crack nucleation when the local hydrogen concentration attains a critical value. The main features of this mechanism are shown schematically in Fig. 7.

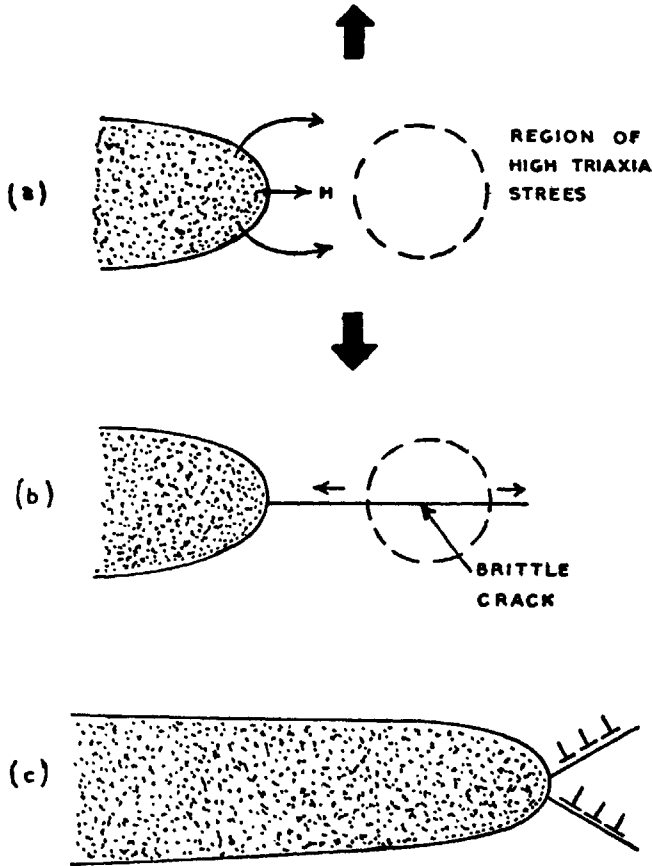


FIG. 7. Schematic figure illustrating the decohesion model for hydrogen embrittlement proposed by Troiano and others (1960) (after Frohmberg *et al.*, 1955; and Troiano, 1960).

## TECHNIQUES FOR STUDYING STRESS CORROSION CRACKING

The past decade has witnessed a spurt of corrosion research activities around the various laboratories in the world. These activities have been directed towards elucidating the basic mechanism of SCC in alloy systems using increasingly sophisticated experimental techniques. Some of the more sophisticated techniques and the field of their application in stress corrosion are listed in Table V.

TABLE V

*Modern instrumental techniques for the study of stress corrosion cracking*

Technique	Application
Ellipsometry	Film Thickness measurements
Straining Electrode Techniques	Current transients due to film rupture
Scanning Auger Microprobe	Grain boundary and surface Compositions; elemental distributions in passive films.
Transmission Electron Microscope	Metallurgical structures, deformation mode, dislocation substructure
High Voltage Electron Microscope	Examination of SC tunnels and cracking
Replica Technique	Fractography
Scanning Electron Microscope	Fractography

#### *Transmission Electron Microscope*

Early transmission electron microscope observations showed that presence of planar dislocation arrays in lightly deformed austenitic stainless steels might be related to the emergence of coarse slip steps on the specimen surface, and the consequent film rupture. Since the formation of coplanar arrays is related to the stacking fault energy of the alloy, the variation of the stress corrosion susceptibilities of the alloys with their stacking fault energies, determined by TEM techniques, was soon established (Swann, 1963). Over the years, transmission electron microscope has remained an active research tool for cracking in susceptible alloy systems.

#### *Scanning Electron Microscope*

The advent of scanning electron microscope has provided a new instrument for fractographic studies and has thereby given fresh impetus for such work. This instrument is uniquely suited for stress corrosion studies. First, it has a very large depth of focus that permits examination of even very rough fracture surfaces. Second, the very wide range of magnifications that can be obtained with the instrument allows a general survey at low magnifications (< 200X) to be made before examining a particular feature at high magnifications. Ready measurements of such large scale features as the dimple/intergranular or dimple/cleavage ratios can therefore be readily made. On a small scale, quantitative aspects of depth of dimples, the height of tear ridges, the shape of tunnels and any other facts can be derived from the use of stereoscopic parts of fractographs. A further advantage of the instrument is that the broken specimens can be examined immediately without any prior preparation.

### *High Voltage Electron Microscopy*

Use of high voltage (800–1000kV) electron microscope permits examination of thicker specimens with better resolution than normally possible in a conventional electron microscope. With suitable modifications of the specimen stage of the instrument, stress corrosion cracking in relatively thick foils can be studied *in situ*. Swann (1971) has used high voltage electron microscope to study the morphology of colonies of corrosion tunnels in Ni–Au alloys and to examine how brittle stress corrosion cracks formed with these colonies.

### *Auger Electron Spectroscopy*

The technique of Auger Electron Spectroscopy (AES) which is being increasingly used now for basic studies in stress corrosion cracking, is a highly sensitive technique for surface chemical analysis. It involves energy analysis of secondary electrons which include characteristic Auger electrons. The depth of analysis corresponds to the escape depths of Auger electrons and is usually in the 5–20Å range. The AES data is usually presented in the form of a first derivative of the energy distribution,  $\frac{dN(E)}{dE}$ , as a function of kinetic energy,  $E$ . An example of an Auger spectrum is shown in Fig. 8. The elements are identified from the peak positions in the spectrum and approximate quantitative information is easily obtained from the peak height data. Results of Auger analysis for the fracture surface of a high strength Al–Zn–Mg alloy susceptible to SCC, taken from the work of Joshi *et al.*\* is shown in Fig. 9. These figures indicate that much information can be obtained by use of this technique on the composition of grain boundaries and the thin reaction films formed on corroding surfaces.

## FRACTURE MECHANICS APPROACH TO STRESS CORROSION TESTING

Most of the mechanistic studies of stress corrosion fracture discussed above are based on the data obtained from conventional tests using smooth laboratory test specimens. Typically in these tests, the time to failure under stress corrosion conditions is determined as a function of the nominal applied stress. However, such data normally do not distinguish between the crack initiation and crack growth phases of stress corrosion fracture. Consequently, smooth specimen tests do not provide information regarding the effect of pre-existing flaws on the component life. In the presence of a pre-existing defect, the total stress corrosion time to failure is primarily dependent on the rate of crack growth, and therefore the smooth specimen time-to-failure data cannot be used to quantitatively establish the useful life of structural components in service.

Recent advances in linear elastic fracture mechanics have done much to eliminate the confusion associated with stress corrosion crack growth behaviour. In addition, this relatively new technology provides a unique quantitative approach to the prevention or prediction of structural failures caused by stress corrosion. The

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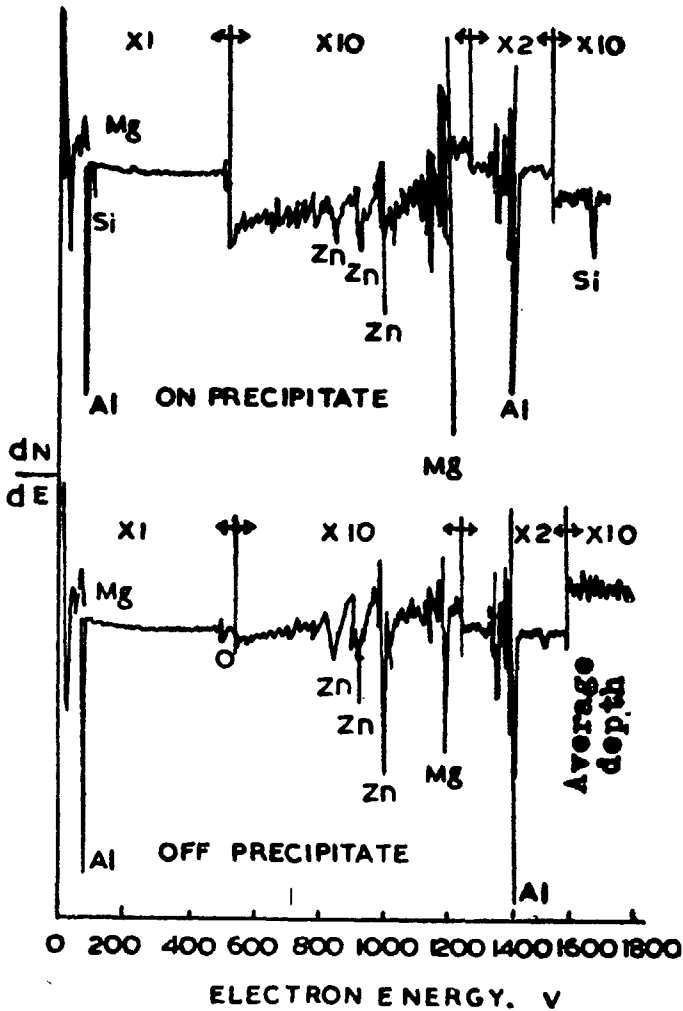


FIG. 8. Typical Auger analysis data obtained on the intergranular fracture surface of a high strength Al-Zn-Mg alloy (after Joshi *et al.* see p. 387).

basic premise of this approach is that since crack growth and stress corrosion attack would be expected to occur in the highly stressed region at the crack tip, the stress distribution in this region is of primary importance. It has been shown that the crack tip stress and displacement fields for an isotropic elastic body can be characterized in terms of a single parameter  $K$ , the crack-tip stress intensity factor, which governs the intensity or magnitude of the local stresses at the crack tip.  $K$  depends on the type of loading and on the configuration of the body, including the size and shape of the crack.  $K$  factors for many different loading conditions and body configurations, and numerical solutions for  $K$  factors of practical test specimens have been well documented in the literature. For stress corrosion cracking studies,

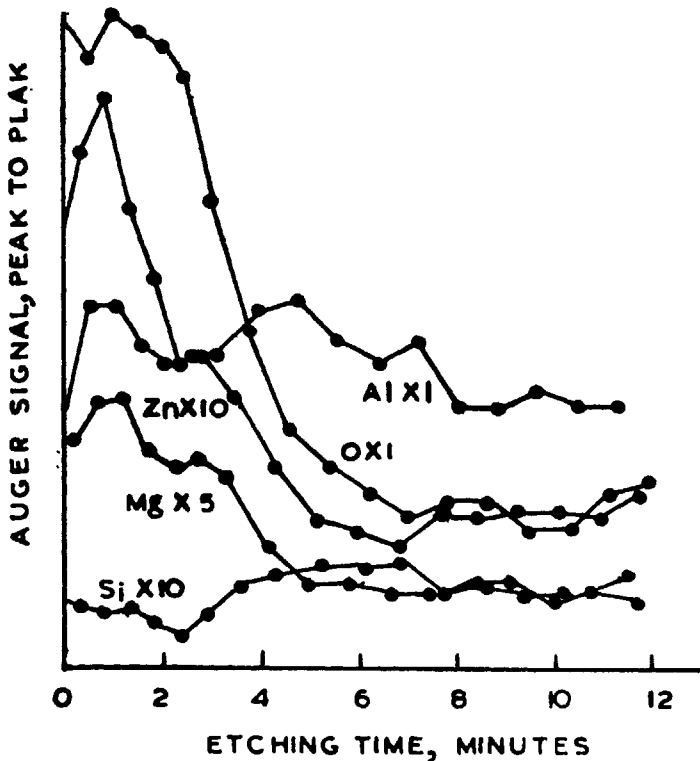


FIG. 9. Composition profile across the grain boundary obtained from AES in a high strength Al-Zn-Mg alloy (after Joshi *et al.* see p. 387).

the opening mode (mode I) of crack growth is generally used since the opening mode predominates in stress corrosion cracking.

When stress corrosion crack velocities are plotted against the crack-tip stress intensity factor  $K_I$ , typically a kneeshaped curve results. Three regions are generally observed. In region I crack velocity is strongly dependent upon  $K_I$ , but at low values of  $K_I$ , it becomes exceedingly small so as to approach zero at a limiting value of stress intensity designated as  $K_{I_{sc}}$ . In region II, termed as the "plateau" region, the crack velocity is independent of stress intensity. Stage III represents the initial fast growth of stress corrosion crack at high stress intensities. Knowledge of  $K_{I_{sc}}$  is useful for comparison of stress corrosion resistance of alloys under different environmental conditions as well as in calculating the maximum length of pre-existing flaw or crack that will remain in the structure without propagating under stress corrosion conditions.

#### CONCLUDING REMARKS

It is obvious from the preceding discussion that our understanding of mechanisms of stress corrosion cracking in iron base alloys is still extremely limited. A major disagreement has developed in the case of transgranular cracking of austenitic

steels, where a large group favours slip dissolution model but is opposed by a number of other workers who contend that this failure is a form of hydrogen embrittlement. The hydrogen hypothesis is consistent with the fractographic evidence in this system, but faces serious questions. Moreover, the specific role of hydrogen in the embrittlement process is far from understood.

The phenomenology of intergranular failures of both low strength ferritic and austenitic stainless steels is closely similar. A number of workers attribute these failures to slip dissolution at the boundaries, while others suggest that the evidence is more consistent with a brittle-film rupture model. Again there is a lack of a general agreement.

Clearly, there is an acute need for information on basic metal environment characteristics before a complete understanding of the phenomenon of stress corrosion cracking could be achieved. Some of the areas where further work needs to be done are summarized here under :

1. Surface energies for aqueous, liquid metal and gaseous environments as influenced by alloy substance need to be determined.
2. The relative coplanarity of slip as influenced by alloy structure, applied stress, strain rate and surface properties should be established. One also needs to know the conditions of acuity and blunting of crack tips, breaking of film at the crack tip and the reactions there with the environmental species.
3. Criteria and rates of segregation of major and minor alloying elements to grain boundaries and dislocations have to be determined. One has to establish the criteria for drag of solutes such as H, C, O, N, S, P by dislocations.
4. Influence of hydrogen, liquid metals and oxygen on the metal-metal bond energies needs to be investigated.
5. Effect of environmental alterations and applied potential on the chemical conditions at the crack-tip are not well understood. Also the conditions for the formation of protective films in concentrated solutions existing near the crack tips are not well known. Further, conditions of adherence such as epitaxy, local stresses etc. for protective film need to be studied.

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