

## Stress corrosion cracking: Characteristics, Mechanisms and Experimental study

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### Abstract

Stress corrosion cracking (SCC) is a phenomenon in which the cracking of a metal alloy usually results from the combined action of a corrodent and tensile stress. Stresses that cause cracking can be residual or may be applied during service. A degree of mechanistic understanding of SCC will enable most metallic engineering materials to operate safely though stress corrosion cracking failures still continue to occur unexpectedly in industry. In this paper, the characteristics, mechanisms and methods of SCC prevention are reviewed. The results of experimental studies on alpha brass are also reported of which the failure mode conformed with the film-rupture and anodic dissolution mechanism.

**Keywords:** Stress corrosion cracking, film –rupture, dissolution, intergranular, transgranular failure

## 1. Introduction

Among the different forms of electrochemical corrosion is the stress corrosion cracking. Cracking will always reveal itself in a matter of days or weeks. However, it is quite common that a period of several years may pass before cracking becomes evident. A striking difference of SCC from the general corrosion is that while the latter can be seen, monitored, and allowed for or corrected, SCC will often not show itself until the metallic engineering material suddenly fails. In the process industries, the consequences of SCC are largely economic. These include among others, loss of product, lost production time due to failure, high initial material costs when selecting resistant alloys, maintenance, replacement and inspection costs. Stress corrosion cracking (SCC) was defined by Dix [1] as 'spontaneous failure by cracking of a metal under the combined action of high stress and corrosion'. There has been agreement by most workers in the field of stress corrosion that stress corrosion cracking results from tensile stresses at the metal surfaces acting for prolonged period of time. In his expanded definition, Champion [2] commented that susceptibility of a metal to stress corrosion implies a greater deterioration in the mechanical properties of the material through the simultaneous action of a static and exposure to a corrosive environment than would occur by the separate but additive action of those agencies. Though most authors [3] now define stress corrosion cracking as the failure of a metal resulting from the conjoint action of stress and chemical attack, a particularly striking definition was given by Thompson [4] who defined stress corrosion cracking (SCC) as slow brittle failure, frequently of a ductile material, that is the result of the concomitant action of stress and corrosion. Harwood [7] was, however, of the opinion that the term stress corrosion cracking, should be limited to cases in which no significant corrosion damage occurs in the absence of stress. In the absence of a corrosive environment, a material exhibits normal mechanical behavior under the influence of stress; and prior to the development of stress corrosion crack, there is little deterioration of strength and ductility. Thus, it is believed that in the stress corrosion cracking process, there is a greater deterioration in the mechanical properties through the simultaneous action of static stress and exposure to corrosive environment than would occur as the result of the separate but additive action of these agencies.

## 2. Characteristics of Stress Corrosion Cracking (SCC)

Sheinker and Wood [3, 4] believed that there are two different types of mechanisms by which stress corrosion cracking occurs. These are the active path corrosion and hydrogen embrittlement. They agreed that in the active path corrosion type, cracking is caused by localized corrosion of the crack tip, and proceeds along a path which is electrochemically active with respect to the surrounding metal. In the hydrogen embrittlement mechanism, cracking results from the entry of hydrogen into the metal, which reduces its ability to deform plastically. Fontana and Greene [5] were however, of the opinion that since hydrogen embrittlement is not a corrosion process in the classical sense, cracking occurring by this mechanism is sometimes excluded from the term 'stress corrosion cracking'. The above mentioned mechanism will be further reviewed later. Romanov [6] showed that stress corrosion results in the appearance of corrosion cracks on the surface of the metal. These cracks, he said, are propagated in a direction perpendicular to the acting stress and are of intergranular or transgranular character, and sometimes of both. Fontana and Greene [5], in observing stress corrosion cracks showed that intergranular cracking advances without apparent preference for boundaries. They also showed that both types of cracking often occur in the same alloy, depending on the environmental or the metal structure. On investigating the characteristics of stress corrosion cracking with particular reference to 18Cr-8Ni steels, Scully [8] concluded that an alloy is likely to be susceptible to transgranular stress corrosion cracking when:

- An active/passive transition is possible or when reactions in the alloy surface produce a noble surface, which may be an oxide or a metal..

- The alloy exhibits co-planar arrays of dislocations, or for other reasons,, the alloy matrix has a high work-hardening rate, and
  - There is some specific electrochemical reactions (which is frequently the penetration of passive films by chloride
- All the above three conditions, he said, must be fulfilled. He also believed that the change in the cracking mode of the intergranular cracking is the result of alterations to the environment or of metallurgical operations that produce a high density of dislocations in grain-boundary regions. It is now known [3-7, 9] that for stress corrosion cracking to occur, the following characteristic conditions are necessary:
- A specific environment.
  - A susceptible metal/alloy – (metallurgical aspects).
  - A tensile stress, and
  - Time.

### **2.1. Environmental Factor**

The specific nature of the environment is the most marked corrosion aspect of stress corrosion cracking [8]. Many alloys fail in chloride solutions, others in concentrated alkali and ammoniacal solutions. Environments in which cracking occurs have been found to be those in which corrosion is highly localised, usually without appreciable general surface corrosion [7]. Parkins [9] considered the concept that stress corrosion cracking only occurs in environments highly specific to a particular alloy to persist, but in a much diluted form from the days, not long ago, when it was thought for example, that mild steels only suffered this form of failure in hot hydroxide or nitrate solutions, or brasses in ammoniacal environments. The concept, he said persists, in the sense that not all possible corrosive environments will promote such failure, although the list of potent environments for a given material grows with the passage of time. And, moreover, for nominally constant stress conditions in the very high strength steels, the idea that solution of specific chemical composition are necessary to promote stress corrosion cracking can, for most practical purposes, be forgotten, since such materials will fail in any aqueous solution, organic medium or gaseous environment from which hydrogen can be released to enter the metal. He further added that to initiate and propagate a crack under environmental influence in the presence of a nominally static stress requires, for retention of crack geometry, the rate of advancement of the crack tip shall be markedly greater than any lateral spreading from the crack sides, since otherwise a pit or more general form of corrosion will result if the conditions are conducive to metal dissolution. But what constitutes the crack sides at any time were at an earlier stage of the growth part of the tip, so that having been active when part of the tip, these surfaces must become relatively inactive, or passive, at a later time. This transition from active-passive behavior will only occur for a given metal in certain environments over particular ranges of potential, hence the specificity of solutions for stress corrosion crack growth by a dissolution related mechanism. It is believed [6] that the initiation of stress corrosion cracks is possibly only in such cases when an electrochemical corrosion process takes place on the surface. It has been shown that the composition of the corrosive environment has a basic and diverse influence on the stress corrosion cracking of the metal. By varying the composition of the corrosive environment, it is possible to change the character of stress corrosion cracks, i.e. transgranular cracking partly or completely becomes intergranular or vice versa, essentially changing the shape of stress corrosion cracking curves, and in so doing, greatly increasing or decreasing the rate of stress corrosion cracking. At present, there appears to be no general pattern to the environments which cause stress corrosion cracking of various alloys [5, 10]. Fontana and Greene [5] agreed that stress corrosion cracking is well known in various aqueous media, but it also occurs in certain liquid metals, fused salts and non-aqueous inorganic liquids. The presence of oxidisers often has a pronounced influence on cracking tendencies. In fact, the presence of dissolved oxygen or other oxidizing

species is critical to the cracking of austenitic stainless steels in chloride solutions, and if the oxygen is removed, cracking will not occur. Le and Foley [11] used the solutions of 1M NaClO<sub>4</sub>, 1M NaCl, 1M Na<sub>2</sub>SO<sub>4</sub> and 1M NaNO<sub>3</sub> for the stress corrosion cracking of high strength aluminium alloy AA 7075-T651. From the results obtained, to study metallurgical effects in the SCC of this alloy, the authors thought it advisable to use perchlorate instead of chloride solutions to avoid specific anion effects, e.g. the formation of transitory species that enhance metal dissolution; perchlorate is a non-complexing anion. It is known [5, 12] just as is the case with most chemical reactions, that stress corrosion is accelerated by increasing temperature. In some systems, such as magnesium alloys, cracking occurs readily at room temperature. In other systems, boiling temperatures are required. Tempered martensitic Type 403 stainless steel has been found [13] to suffer pitting corrosion and intergranular stress corrosion cracking in 0.1M NaSO<sub>4</sub> at temperatures of 75 and 100°C, but not at the lower temperature of 25 and 50°C. The physical state of the environment is also important [5,6]. Alloys exposed to single-phase aqueous environments are sometimes less severely attacked than metals at the same temperature and stress when exposed to alternative wetting and drying conditions.

## 2.2. Metallurgical Aspects

The composition and structure of alloys have been known to influence their environment sensitive cracking responses for any or all of a number of reasons, related to their effects upon electrochemical and mechanical factors [6, 9]. Thus according to Parkins [5], the critical balance between activities and passivity required for stress corrosion cracking may be expected to be influenced by alloying, which in other cases may affect local cell action by changes in the chemical heterogeneity that restricts dissolution to retain crack geometry. The susceptibility to stress corrosion cracking is affected by the average chemical composition, preferential orientation of grains, composition and distribution of precipitates, dislocation interactions, and progress of the phase transformation (or degree of metastability) [5]. These factors further interact with environmental composition and stress to effect time to cracking, but these are secondary considerations. Scully [14] has expressed that many metallurgical variables have an effect upon stress corrosion susceptibility. Susceptibility is usually reduced as the grain size is diminished. Heat treatment affects susceptibility which is often greatest at the peak strength of an alloy and diminishes as that is lowered. Mechanical strength is of major importance. Cold work usually increases susceptibility. The effect of some metallurgical factors on the corrosion behaviour of C-Mn steels in acidic solutions has been expressed [15]. It has been shown that the corrosion process is influenced by the extent of the ferrite-pearlite interface, and that a banded structure is unfavourable. The addition of aluminium to a magnesium alloy has been proved to increase the rate of stress corrosion cracking [7]. The rate of corrosion of magnesium is also known to increase with the increase in its aluminium content [16]. According to Timonova [17], the addition of manganese or zinc to a magnesium alloy with an 8% Al content, increases its resistance to stress corrosion cracking. This effect is most pronounced when these elements are added to the alloy separately; it may decrease considerably when they are added together. He also showed that the acceleration of stress corrosion cracking, due to the addition of aluminium increases with the increase of the iron content in the alloy. It has been a common generalization in the past that pure metals do not crack [2]. This has been challenged by observations of cracking in 99.999% pure copper exposed in ammoniacal solutions containing Cu(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> complex ions [18]. Electron microscope observations [10] have suggested that the metals and alloys most susceptible to transgranular stress corrosion cracking have low stacking fault energies. Whether this means that the stacking fault themselves are the targets for the localized attack or whether piled-up groups of dislocations are attached is not clear. It implies, however, that resistance to this type of stress corrosion cracking may be increased by adjusting the alloy composition to increase the stacking fault energy. It has been shown [9] that stress corrosion cracks

are observed to initiate where slip steps expose bare metal by disruption of surface films. The crystallographic implications of dislocation distribution and motion suggest [9], in broad terms, that transgranular fracture paths also may be expected to display a marked crystallographic dependence, although not necessarily coincident with the slip planes, as Lui et al [20] showed clearly in their recent detailed work in this area.

### 2.3 Stress Effects

It is well known that for stress corrosion cracking to occur, surface or sub-surface tensile stress must be present [7]. But according to Edeleanu [21], the theory favoured does not depend on stress having a substantial influence as the rate of cracking at the tip of crack. It is believed [21] that though there may be some acceleration of corrosion by stress, it does not however, alone lead to cracking because:

- If high stress were sufficient reason for rapid corrosion, this type of failure would even more common and would be met in a wider range of alloy systems.
- At really high rates if our understanding of electrochemistry is to be trusted, corrosion reactions are highly dependent on happenings in the solution (e.g. diffusion,) and is very hard to understand how that can be influenced by stress.

It is well known [5-7, 9] that increasing the stress decreases the time before cracking occurs. There is, however, some conjecture concerning the minimum stress required to prevent cracking. This minimum stress depends on the temperature, alloy composition, and environment composition [5]. Various authors [6, 7, 9, 21], agreed that for each alloy environment combination there should be an effective minimum or 'threshold' stress; the 'limiting' stress below which stress corrosion cracking does not occur in some finite period of time. The assertion that the process of stress corrosion cracking may commence only after this threshold is reached cannot, however, be applied to all cases of stress corrosion cracking [6]. It is difficult for instance, to find a threshold for austenitic stainless steel as shown by Heines [22] and Hoar [23]. The threshold of minimum stresses depends essentially on the nature of the alloy and the composition of the corrosive environment [6]. It has been pointed out [9] that below the threshold stress in dissolution controlled crack growth systems, the surface film repair remains protective because its rate of repair does not fall below the rate at which it is disrupted. Above the threshold stress, the film repair rate falls behind the disruption rate and the limiting conditions relates to the rate at which the bared metal can dissolve to promote crack growth. He further observed that at even higher stresses, ductile or other essentially mechanical modes of fracture becomes kinetically more favourable than dissolution controlled crack growth and there is a transition to the former. The net effect therefore, he noted, is the well-known crack velocity-stress intensity factor relationship, shown schematically in **Figure 1**, which is applicable to initially plain specimens as it is to those containing pre-cracks. Parkins concluded that the essential feature of the role of stress in this simplified model is its ability to promote a deformation rate that, above the threshold, exceeds the rate at which the bare metal is re-filmed at emergent slip steps, that is, it is the effective strain rate that is mechanically important rather than stress itself, although clearly, the strain rate derives from the stress.

### 2.4 Time Factor

The fourth factor involved in stress corrosion cracking [4], the one which is a measure of resistance is time. SCC may occur in as little time as a few minutes in an accelerated laboratory test or it may take years. It is agreed [7] that the parameter of time in the stress corrosion cracking phenomena is important since the major physical damage during stress corrosion cracking occurs during the later stages. SCC tests should be conducted until failure occurs.

STABLE FILM	DEFORMATION	RATE
	EXCEED FILM GROW TH	
	RATE	
	SCC GROWTH	RATE
	EXCEEDS	DUCTILE DUCTILE FRACTURE
	FRACTURE RATE	
	SCC	MAXIMUM
		DISSOLUTION
		RATE

**Figure 1:** Schematic illustration of the various rate controlling processes that result in the observed effects of stress (or stress intensity factor) upon crack velocity in stress corrosion cracking by a dissolution process [19]

### 3. Mechanisms of Stress Corrosion Cracking

The mechanisms of SCC are not completely understood. There has been disagreement as to the mechanism of cracking in any given system and there is confusion as to whether the mechanism varies from one system to another.

Using the characteristics of SCC just reviewed above, as a basis, a number of mechanisms have been developed. It is now widely held [24] that SCC can be due to a number of different mechanisms, and that and that there are alloy-environment systems where one or more of the mechanisms may apply. According to Krugger [24], of the many proposed mechanisms, three are currently the ones most actively used, and the others proposed can be considered as variations or sub-sets of the three major ones. He believed that all the mechanisms involve the complex interactions of the three disciplines that control SCC: chemistry (electrochemistry), metallurgy and mechanics. He described the three mechanisms as:

- Stress-sorption mechanism
- Film-rupture – metal dissolution mechanism
- Hydrogen - embrittlement mechanism.

Other authors [6, 25] considered the mechanism of stress corrosion cracking to be basically electrochemical-mechanical. Logan [25] pointed out that since stress corrosion cracking can be accelerated by the application of an anodic current and stopped by the application of a cathodic current (cathodic protection), then it should be assumed that SCC is, in parts, at least electrochemical in nature. He approached the mechanisms of SCC mainly from:

- The electrochemical aspects, and
- The mechanical aspects.

#### 3.1 The Stress-sorption Mechanism

The stress-sorption mechanism, most actively advocated by Uhlig [26, 27], proposes that a specific species adsorbs and interacts with strained bonds at the crack tip causing a reduction in bond strength, or thermodynamically stated, a reduction in the surface energy,  $\gamma$ , which leads to a lowering in the stress required to produce brittle fracture [2]. The relationship between the theoretical stress to produce brittle fracture,  $\sigma_f$ , and  $\gamma$  is given by the well known expression:

$$\sigma_f = \left( \frac{E\gamma}{d} \right)^{1/2} \quad (11)$$



Where  $E$  is the Elastic modulus and  $d$  is the atomic spacing. In terms of fracture mechanics, for a perfectly brittle material,

$$G_c = 2 \gamma \quad (11a)$$

Where  $G_c$  = critical strains energy release rate Where  $K$  = stress intensity factor,  $K_c$  = critical stress intensity factor (fracture toughness) and  $K_{ISCC}$  = value of  $K$  below which failure does not occur.

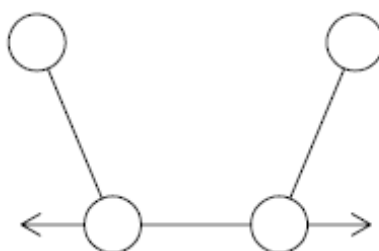
$$K = K_c = E G_c \quad (11b)$$

$$\text{Hence } K_{ISCC} = 2E \gamma_{SCC} \quad (11c)$$

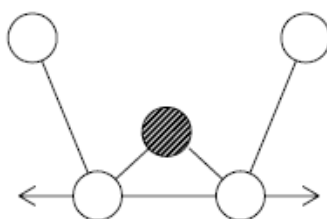
The adsorption of a damaging species at a crack tip is known to lower  $\gamma$  and therefore the threshold stress for SCC is the minimum value to which  $\gamma$  is lowered by adsorption. Uhlig further proposes that an important factor arguing for this mechanism is the existence of a critical potential below which the SCC does not occur. He explains that the effect of potential can be attributed to the strong dependence of adsorption on potential. This was based on various studies by electrochemists who have found that the adsorption of an anion takes place at potentials above the point of zero charge for a given surface in a given environment. Uhlig also believed that environment plays a role in the stress-sorption mechanism because of the specificity of adsorption of a particular species on a surface, and because environment brings the potential to a value where adsorption can or cannot take place. And moreover, if an extraneous species that displaces the damaging bond-weakening adsorbed species into the environment, cracking becomes more difficult. Thus, he pointed out that the stress-sorption mechanism is more widely accepted in the case of liquid metal embrittlement or stress cracking of plastics.

Among the problems [28, 29] with the stress-sorption mechanism for SCC in aqueous environments, are:

- The large amount of metal dissolution observed in many straining electrode experiments poses the question of what happens when the metal dissolves out from under the adsorbed film.
- In the cracking of ductile alloys, the ductility present is sufficient to produce extensive plastic deformation at a crack tip. The blunting that this produces estimates the infinite sharpness required for this mechanism to work.
- Crack growth rates are considerably slower than one would expect from this model.
- The mechanism of stress-sorption can be outlined as shown in **Figure 2**.



**(a) Sub-critical stress**



**(a) Adsorption reduces strength**

**Figure 2:** Stress-sorption mechanism for SCC, (a) Chemisorption of ion at tip of crack and (b) Weakening of interatomic bond at the tip of the tracks so that applied stress leads to the breaking of this bond.

### 3.2 *Mechanical Mechanism*

This theory first proposed by Keating [30] assumes that the function of stresses during SCC is to disrupt mechanically the metal layer under the bottom of cracks, and thus cause them to develop further, i.e., when the initial stress raisers which were developed by local corrosion processes reach a critical point, the concentration of the stress forces them open till the metal fails completely. In agreeing with the above, Logan [25] pointed out that the electrochemically propagated stress corrosion crack penetrates into the material, stress concentrations will build up at the crack tip until there is sufficient energy available to initiate mechanical cracking. This energy, he added, is required to form new surfaces and to deform material at the tip of the crack. As purely mechanical cracking is unlikely, Keating [30] tries to connect the mechanical process of cracking with the electrochemical process of cracking with the electrochemical process of corrosion. According to Keating and other authors [5, 25] the purely mechanical development of cracks proceeds until encounters obstacle, and so the concentration of stresses is limited to values which are insufficient for the failure of the metal. Such obstacles may be non-metallic inclusions, discontinuities of the lattice, or specific position of the crystal faces. Keating further pointed out that when the development of the cracks is stopped, the corrosive medium which penetrates to its bottom may induce a notch detected from the initial crack. In such a case the concentration of stress will develop this notch in a different direction from the initial crack; this may be the explanation for the irregular shape of stress corrosion cracks. When the active corrosive agent reaches the bottom of the crack, it causes new centres of stress raisers from which new cracks are afterwards developed. Logan [25] believed that when the mechanically propagated crack stops, the electrochemical process takes over building up stress concentrations at the tip of the crack and the process is repeated. However, the fact that the process of stress corrosion cracking may be stopped by cathodic polarization at the moment when a visible development of cracks takes place indicates very convincingly that in principle a purely mechanical development of cracks is quite impossible.

### 3.3 *Electrochemical Mechanism*

Dix et al [35] proposed the first electrochemical theory of stress corrosion cracking. They postulated that:

- There must exist in the alloy, a susceptibility to selective corrosion along more or less continuous paths, as for instance, the grain boundaries. This susceptibility is present when the internal structure of the alloy is microscopically heterogeneous and the phase forming the continuous path is anodic in the specific corrosive medium to the areas composing the major part of the structure.
- There must be a condition of high stress acting in a direction tending to pull the metal apart along these continuous paths.

If the two conditions above exist simultaneously and the metal is subjected to a corrosive environment producing the specified potential relations, corrosion will start along the anodic paths. This will produce a concentration of stress at the bottom of the notches so formed. And as the stress increases, fissures will begin to develop, destroying any protective film and thus exposing fresh anodic material to the corrosive medium. Corrosion will proceed more rapidly and at the same time, the stress will increase at an accelerated rate, especially if the material is subjected to a high external load. These mutually accelerated actions will continue at an increasing rate until the metal fails. This theory also explains why cracking is observed only in specific corrosive media. It has since long been known [35] however, that the Dix's theory can neither explain the cracking of relatively homogeneous alloys such as brass and stainless steel, nor transgranular cracking.

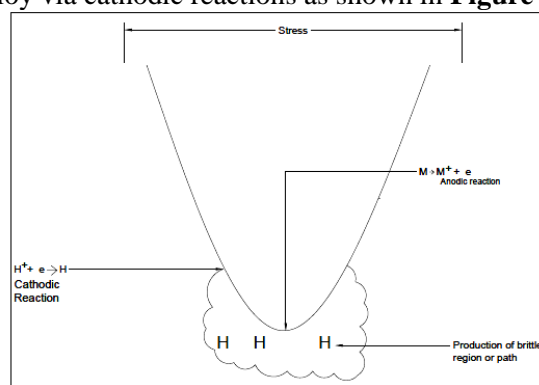


### 3.4 Film Rupture – Metal Dissolution Mechanism

Essentially, this mechanism can be regarded as an extension of electrochemical mechanism, but most literature works refer to it as above. The mechanism was originally suggested by Logan [37] and Champion [38]. It has also been extended and refined by some other researchers [29, 39-44]. The mechanism proposes that the protective film normally present on a metal surface is ruptured by continued plastic deformation at a crack tip where the exposed metal becomes a very small and restricted anodic region where metal dissolution takes place [24]. The rest of the metal surface, especially the walls of the crack, acts as a cathode. Susceptibility depends on the rate at which the metal exposed by film rupture is repassivated vis-à-vis the rate of metal dissolution. The specific review for the case alpha brass or brass alloys will be mentioned later in this review report.

### 3.5. Hydrogen Embrittlement Mechanism

This has been considered [3, 5] to be a different phenomenon from SCC. But Krugger [24] believed that since cathodic reactions (which produce hydrogen under proper conditions) are as much a part of corrosion as anodic ones (producing films and / or metal dissolution), it is difficult to exclude it in a discussion of SCC. It is generally agreed that in this mechanism, fracture results from the production of a brittle region at the crack tip because of the introduction of hydrogen into the alloy via cathodic reactions as shown in **Figure . 3**.



**Figure 3:** Hydrogen embrittlement mechanism for SCC. Cathodic reduction of  $H^+$  at the tip of a crack produces hydrogen which enters the vicinity of the tip and embrittles the metal immediately ahead of an advancing crack.

The embrittlement of metals by hydrogen has been attributed to a number of causes among which decohesion [45], new phase formation [46, 48] and pinning of dislocations [49] can be mentioned. It was further pointed out by Krugger [24] that environment affects the process by influencing the rate of production of hydrogen and by enhancing or inhibiting the entry of hydrogen into the metal by interposition of adsorbed or reaction layer films. He added that in the aqueous systems the potential at the crack tip determines whether the production of hydrogen of the surface is thermodynamically feasible. The composition by the environment, he said, influences what potential is necessary to produce hydrogen, its rate of production, and by means of the presence of inhibiting or enhancing species, whether it can readily enter the metal lattices. In gaseous systems, he believed that the hydrogen pressure plays the same role as potential in aqueous environments. In agreeing with the above, Fontana and Greene [5] also indicated that a large fraction of all the environmentally activated cracking of ferritic and martensitic iron-base alloys and the titanium base alloys is due in some way to the interaction of the advancing crack with hydrogen. Working on the cracking of the type 4340 steel (0.40 C, 0.070 Mn, 0.04 P, 0.04 S, 0.030 Si, 1. Ni, 0.8 Cr, and 0.25 Mo), Davis, Dreyer and

Gallagher [50], showed that higher stresses cause cracking to occur more rapidly. It is thus believed that these trends are in fact general for most alloys subject to hydrogen embrittlement, i.e. the alloys are most susceptible cracking in their highest strength level. It is known [51] that the tendency for embrittlement is also increased with hydrogen concentration. In fact, it has been suggested by some workers, for example Troiano et al [52] that almost all aqueous SCC is hydrogen embrittlement. They found that austenitic stainless steels, which have been assumed to be non-susceptible to hydrogen embrittlement could be made less ductile by hydrogen charging, and that one could observe the permeation of hydrogen at positive currents (where one should only expect metal dissolution). Some other workers [46 - 48, 53, 54], have also found the formation of a phase or phases capable of undergoing hydrogen embrittlement. Though all these findings do point to greater universality of application for the hydrogen embrittlement mechanism, some of the recent work ran counter arguments against such universality. For example, Bernstein and Pickering [55] found that anodic dissolution can occur in the cracks of cathodically polarized ferrous alloys. In addition, Wilde and Kim [56] showed that for an austenitic stainless steel, while rate of hydrogen permeation was higher at negative potentials, time- to- failure was also higher at these hydrogen producing potentials. This finding is also known to agree with results that show that cathodic protection (which should promote the production of hydrogen) does retard SCC for a number of alloys [57]. A mixture of anodic dissolution and cathodic hydrogen embrittlement processes for the SCC of some high strength steels in HCL and NaCl solutions has been shown [58, 59].

#### 4. Method of Prevention of SCC

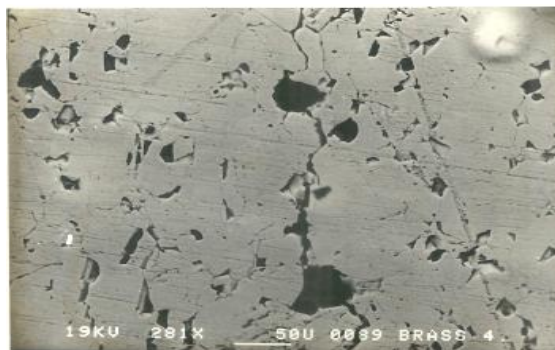
As mentioned earlier, the mechanism of stress corrosion cracking is imperfectly understood. Methods of preventing this type of attack are, as a consequence, either general or empirical in nature. Stress corrosion cracking may be reduced or prevented by application of one or more of the following methods [60]:

- Lowering the stress below the threshold value if one exists. Annealing and stress relieving prior to service are both used to minimize cracking by reducing the stresses of a fabricated item.
- Eliminating the critical environmental species by, for example, degasification, demineralization, or distillation.
- Materials selection. If neither the environment nor stress can be changed, changing the alloy can be an alternative way.
- Applying cathodic protection to the structure with an external power supply or consumable anodes. However, since hydrogen embrittlement effects are accelerated by impressed cathodic currents, cathodic protection should only be used to protect installations where it is positively known that stress corrosion cracking is the cause of the fracture.
- Addition of inhibitors to the system where possible.

#### 5. Application of Electrochemical Noise Method in SCC:

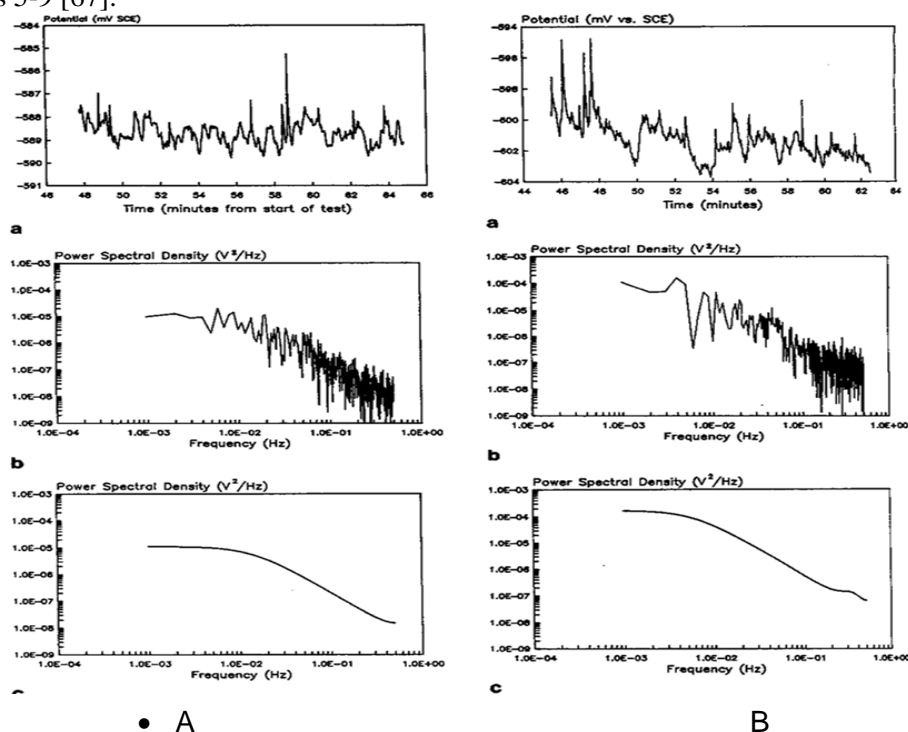
The application of electrochemical noise measurement in corrosion is not limited to its use in monitoring pitting, general and crevice corrosion and some other surface inhomogeneity alone. A comprehensive review has been made on this [61]. In some investigative research work, Loto and Cottis [62-65] had also applied the technique to stress corrosion cracking. Different work on electrochemical noise generation during stress corrosion cracking of alpha brass, high strength carbon steel, high strength aluminium alloy 7075-T6 and austenitic stainless steel, - Type 316, had been carried out in different test media [62 -66]. The maximum entropy method, and with the Fast Fourier transform for the high strength carbon steel, Figs 5 and 6 were used. The growth of the stress corrosion crack was shown to result in an increase in the electrochemical noise as measured from the standard deviation of the power spectrum. The cracking of the specimen gave the highest noise amplitudes in most cases; the cracking failure was also indicated by the highest standard deviation peaks. All the noise amplitudes generally increase with decreasing frequency and the

power spectral density were inversely proportional to some power of the frequency, thus indicating LF (1/f) or “flicker” noise. Characterization of the corrosion processes/behaviour could be made using the roll-off slopes of the spectral curves. The source of the electrochemical noise was assumed to be repassivation transients resulting from the exposure of fresh metal surface by anodic dissolution probably as a result of hydrogen embrittlement cracking of the aluminium alloy, austenitic stainless steel and high strength carbon steel. **Figure 4** shows the crack failure of SCC on the surface of the C-ring sample in Mattsson’s solution.



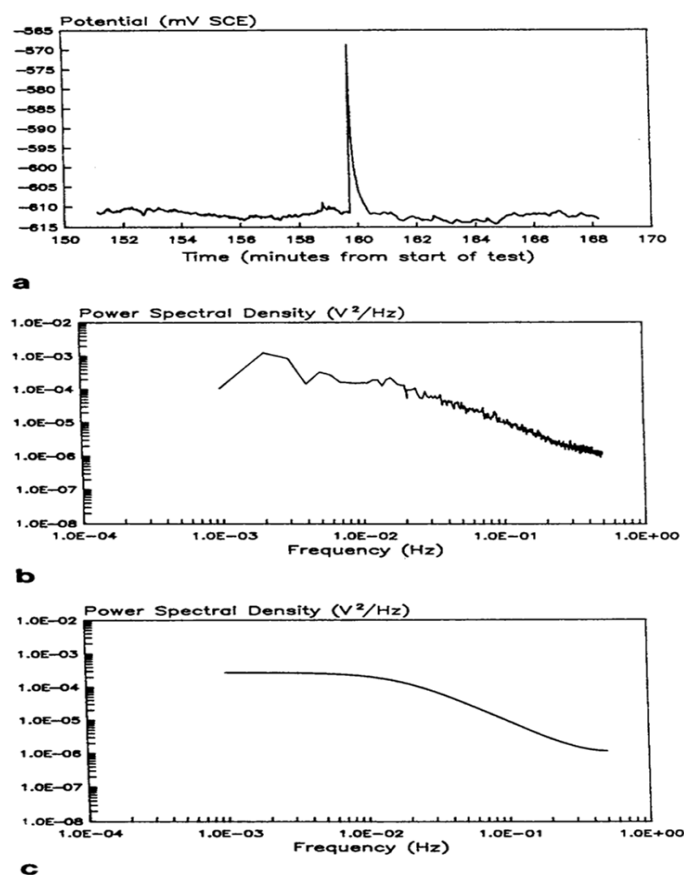
**Figure 4:** Pits and crack failure during SCC of  $\alpha$ - brass C-ring specimen in Mattsson’s solution [62, 66]

Further statistical analysis of results of the data obtained on the above work for alpha brass and aluminium alloy are presented in **Figure s 5-9** [67].

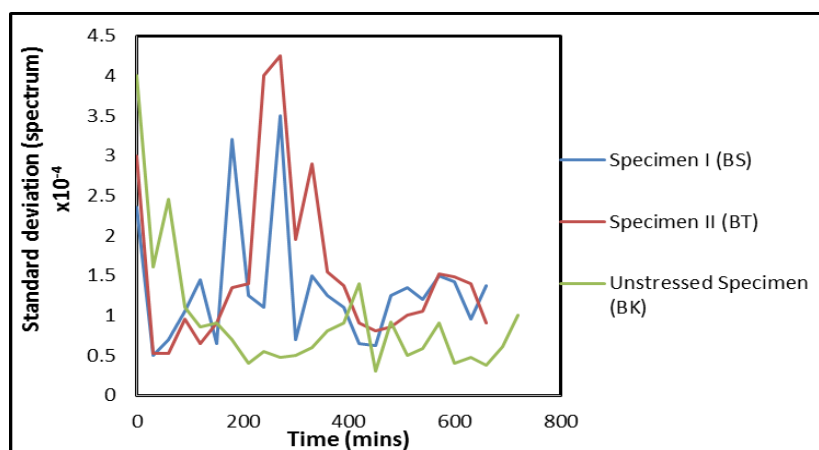


**Figure 5:** Power spectral density for an unstressed specimen for the period from 40 to 57 minutes after immersion: (a) time record, (b) FFT spectrum, (c) MEM spectrum.

B. Power spectral density for a stressed specimen for the period from 40 to 57 minutes after immersion: (a) time record, (b) FFT spectrum, (c) MEM spectrum [61, 64].



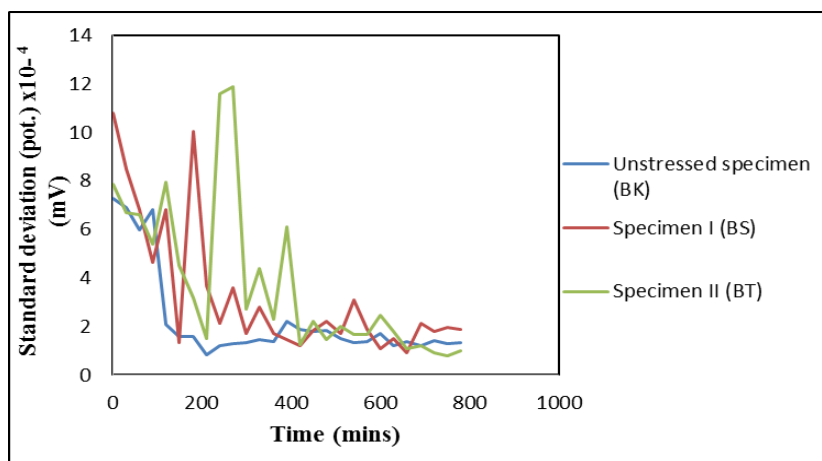
**Figure 6:** Power spectral density for the stressed specimen for the period from 140 to 157 minutes after immersion: (a) Time record, (b) FFT spectrum, and (c) MEM spectrum. This specimen fractured during the measurement of the time record [61, 64]



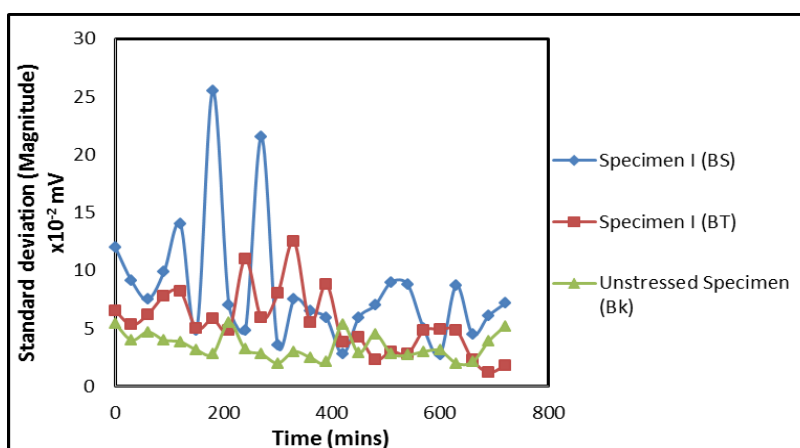
**Figure 7:** Standard deviation (spectrum) versus Time of exposure curves for the stressed (BS, BT- (specimens I & II respectively)) and unstressed (BK) specimens [67].

Various mechanisms for the stress corrosion cracking of alpha-brass in ammoniacal cupric sulphate solution (Mattson's solution) have been proposed and the main theories fall into three groups [62]: 1. Those involving a continuous electrochemical dissolution which proceeds rapidly along susceptible paths [68]. 2. Those in which the electrochemical stage alternates with a mechanical propagation of the crack through metal that is locally embrittled by chemical means or of dislocation pile-up [69]. 3. Those involving a film rupture mechanism [37; 66, 70]. There are

other various authors [71-88] who have worked on the stress corrosion cracking mechanism of alpha brass in Mattsson's solution whose work were related to either one of the above propositions.



**Figure 8:** Standard deviation (potential) versus Time of exposure curves for the stressed (BS, BT- (specimens I & II respectively)) and unstressed (BK) specimens [67].



**Figure 9:** Standard deviation (magnitude) vs. Time curves for the stressed and unstressed specimens [67].

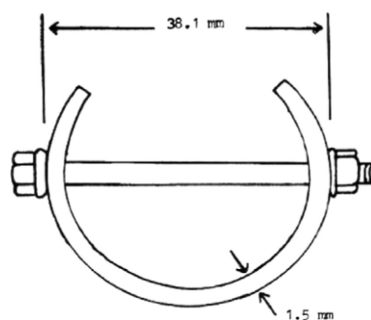
## 6. Materials and methods

### 6.1. Stress corrosion cracking inhibition – experimental study

The stress corrosion cracking inhibition of alpha brass samples were investigated using 4-Bromoaniline, and Pentylamine, as the inhibitors. The testing samples were obtained as tubes and cut into several C-ring samples. Various stress levels were used in a time-to-failure experiment to determine threshold/test the best stress levels to use. The following equation was used to calculate the stress that has been applied to a C-ring specimen, **Figure 10**, for the constant strain experiment:

$$OD_f = OD - \Delta, \quad \Delta = f\pi D^2 / 4Etz$$

Where  $OD$  is the outside diameter of C-ring before stressing, in. (or mm), and  $OD_f$  is the outside diameter of stressed C-ring in. (or mm),  $f$  is the desired stress, MPa (within the proportional limit),  $\Delta$  is the change of OD giving desired stress, mm,  $D$  is the mean diameter ( $OD - t$ ), mm,  $t$  is the wall thickness, mm (or in.),  $E$  is the modulus of elasticity, MPa;  $z$  is the correction factor for curved beams. The test media used was Ammonium hydroxide – 0.5M  $NH_4OH$  respectively



**Figure 10:** The C – ring test specimen [62, 66]

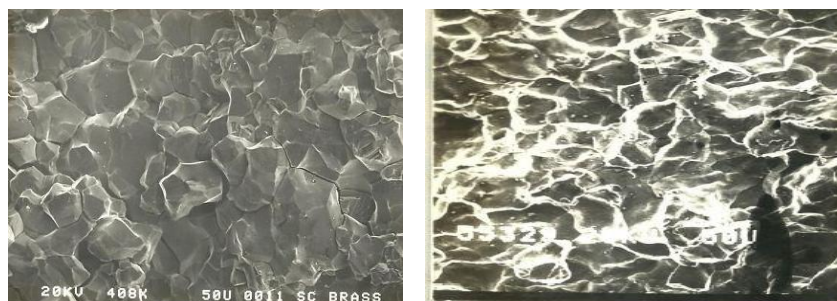
## 6.2 Experimental procedure

The metals were prepared and treated according to the ASTM G38 standard. The most susceptible percentage of stress was determined by carrying out a control experiment with various stress levels. Concentration of 0.5M of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was prepared using the distilled water, beakers and pipette in large quantities and stored in plastic containers. The brass alloy samples were immersed in the 0.5M solution of the ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) to serve as control experiments in the experiments. Care was taken to ensure that only the stressed part was in contact with the solution. 0.5M of the ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution was prepared with 18.75% of 4 – Bromoaniline using the method described earlier and the brass samples were immersed in the solution. This served as the test for the first inhibitor. Further 0.5M of the ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution was prepared with 15% of the Pentylamine solution and the alloy samples were immersed as shown on the table to serve as our second inhibitor test. Synergistic test experiments of the two inhibitors were also performed by preparing 0.5M of the ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution with 18.75% of 4 – Bromoaniline and 15% of the Pentylamine solution. All experiments which were performed at the laboratory ambient temperature of  $28^\circ\text{C}$  ran concurrently with the first samples serving as the control experiment. The alloy samples were left immersed for a period of 21 days and they were checked on regular intervals to determine SCC initiation, growth and failure for the different environments.

## 7. Results and Discussions

The results obtained are contained in the series of Tables below. Further discussion and explanations are provided for each of the Tables (Tables 1 – 4). It should be noted in this control experiment (Table 1) that the thickness of the alloys used played a role in inhibiting failure as research showed that brass was most susceptible in this form of medium and in order to get clear distinct observations an alloy of considerable thickness was used. The cracks initiated on the 7<sup>th</sup> day and grew steadily until when the metal failed on the 17<sup>th</sup> day of exposure. However it could be clearly observed that the corrosion effect was more felt on the alloy and if not for the thickness in question failure would have occurred within the first few days. The effect of the first inhibitor was not really pronounced as presented in Table 2, though the same effects as seen earlier were found in this alloy too, it only delayed the crack initiation but could do nothing about the growth as failure took almost the same time as it did in the control experiment. The cracks initiated on the 10<sup>th</sup> day and failure didn't occur up until the 20<sup>th</sup> day of the experiment. In Table 3, the effect of the pentylamine inhibitor was less than that of 4- bromoaniline as cracks were initiated on the 9<sup>th</sup> day. The stress corrosion cracking velocity growth rate was also the same as failure occurred on the 18<sup>th</sup> day. In Table 4, the synergistic effect was clearly seen in this experiment as corrosion occurred very slowly and thus indicating apparent resistance to corrosion reactions. The first cracks were noticed on the 15<sup>th</sup> day and no further crack was observed till the end of that experiment.





**Figure 11:** SEM photomicrograph of intergranular corrosion morphology of SCC of alpha brass.

The cracking failure mechanism had been determined by various authors to be film rupture and anodic dissolution mechanism [62, 66, 71-79]. The failure mode was that of intergranular corrosion as contained in **Figure 11**.

**Table 1:** Brass + 0.5M of  $\text{NH}_4\text{OH}$  – (Control experiment)

Hours	Observation	Remarks
0-72	No visible signs of reactions taking place.	-----
72-144	Change of coloration of the environment suggesting beginning of corrosion	-----
144-216	Brown coloration over the bent radius	SCC crack initiation
216-288	Moderate pitting at a few places over the stressed radius,	SCC growth,
288-360	Small pits and cracks are seen at outer radius.	Hair line cracking distributed all along the bent radius
360-432	Pitting at a few places over the stressed region.	SCC Failure
432-504	-----	-----

**Table 2:** Brass + 0.5M of  $\text{NH}_4\text{OH}$  + 18.75% of 4 – Bromoaniline

Hours	Observation	Remarks
0-72	No visible signs of reactions taking place.	-----
72-144	Change of coloration of the environment suggesting beginning of corrosion	-----
144-216	Faint brown coloration over the bent radius	-----
216-288	Moderate pitting at a few places over the stressed radius	SCC crack initiation
288-360	Increased reaction with the environment and further coloration	SCC growth
360-432	Pitting at a few places over the stressed radius	Hair line cracking distributed all along the bent radius
432-504	Further pitting at a few places over the stressed radius	SCC failure

**Table 3:** Brass + 0.5M of NH<sub>4</sub>OH + 15% of Pentylamine

Hours	Observation	Remarks
0-72	No visible signs of reactions taking place.	-----
72-144	Change of coloration of the environment suggesting beginning of corrosion	-----
144-216	Brown coloration over the bent radius	SCC crack initiation
216-288	Moderate pitting at a few places over the stressed radius,	SCC growth
288-360	Small pits and cracks are seen at outer radius.	Hair line cracking distributed all along the bent radius
360-432	Pitting at a few places over the stressed region	SCC Failure

**Table 4:** Brass + 0.5M of NH<sub>4</sub>OH + 18.75% of 4 - Bromoaniline + 15% of Pentylamine;

Hours	Observation	Remarks
0-72	No visible signs of reactions observed	-----
72-144	Change of coloration of the environment suggesting beginning of corrosion	-----
144-216	Faint brown coloration over the bent radius	-----
216-288	Brown coloration over the bent radius	-----
288-360	Small pits and cracks are observed.	SCC crack initiation
360-432	Increased reaction with the environment and further coloration	SCC growth. Hair line cracking observed.
432-504	Pitting at a few places over the stressed region	No Failure after 500+ hours

## 8. Conclusion

- Stress corrosion cracks result in a non-ductile type of failure. Depending on the alloy and corrosive medium, the fracture path may be either intergranular or transgranular, although the latter is the most common.
- Electrochemical dissolution plays a major role in the SCC mechanism. Crack initiation may be at a surface pit or notch and the crack tip acts as a local anode.
- Since SCC is a conjoint phenomenon of a stress being applied while a component is in a corrosive environment; removal of either the stress or the environment will prevent crack initiation or cause the arrest of cracks that are already propagating.
- The most susceptible stress level, from the experiment was at 90% of the ultimate tensile strength (UTS) of the brass specimens.

- The 4- bromoaniline inhibitor had better inhibition effect on the SCC of brass in 0.5M NH<sub>4</sub>OH solution. It inhibits corrosion better in brass in ammonium environments than the pentylamine.
- The synergistic experiments had clear SCC effect on brass in ammonium hydroxide environment.
- The two inhibitors, 4-bromoaniline and pentylamine, gave better SCC inhibition performance at their lower concentrations of use.

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