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FA-TR-76066

THE ROLE OF SOLVATED ELECTRONS IN STRESS CORROSION CRACKING PHENOMENA
Part I. Conceptual Considerations

by

Sheldon J. Cytron

October 1976

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U.S. ARMY ARMAMENT COMMAND
FRANKFORD ARSENAL
PHILADELPHIA, PENNSYLVANIA 19137

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REPORT DOCUMENTATION PAGE

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BEFORE COMPLETING FORM

1. REPORT NUMBER
FA-TR-76066

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
THE ROLE OF SOLVATED ELECTRONS IN STRESS
CORROSION CRACKING PHENOMENA
Part I. Conceptual Considerations

5. TYPE OF REPORT & PERIOD COVERED
Technical rsch report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
SHELDON J. CYTRON

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
FRANKFORD ARSENAL
Attn: SARFA-PDM
Philadelphia, PA 19137

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
AMCMS CODE: 61101.11.84400
DA PROJ: 1T1611101A91A

11. CONTROLLING OFFICE NAME AND ADDRESS
FRANKFORD ARSENAL

12. REPORT DATE
October 1976

13. NUMBER OF PAGES
25

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The author wishes to thank K. Lukens and J. Gordon for their helpful discussions and J. Rinnovatore, S. Nash, F. Pearlstein and A. Gallaccio for their comments on the manuscript.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Stress Corrosion Cracking Theory
Solvated Electrons
Hydrated Electrons
Electron Ejection

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A model is presented in this report that postulates an important role for solvated electrons in stress corrosion cracking phenomena. The cogent feature of this model is the claim that the strain energy released at the crack tip is sufficient to cause the ejection of electrons from the metal. Such electron transfer across the metal/solution interface results in the generation of solvated electrons

20. ABSTRACT - Cont'd

in the crack tip region. The immediate consequences of this stress induced electron transfer are uninhibited metal dissolution at the crack tip and possible hydrogen atom formation and incorporation into the metal lattice. The validity of this model is yet to be tested. Nevertheless from a conceptual standpoint it offers an intriguing microscopic outlook on what may be occurring during stress corrosion cracking. Several experiments are proposed to test the hypothesis.

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INTRODUCTION

The purpose of this report is to present some new arguments and speculations concerning the role of solvated electrons in stress corrosion cracking (SCC) phenomena. The belief that solvated electrons, as transient chemical species, may play some important, but as yet undefined role in SCC phenomena was first reported at the 1971 NATO Conference on SCC.[1*] Since then, this writer has found no significant exploration of this idea in the literature and therefore has undertaken to examine its merits and consequences in some detail.

Stress corrosion cracking (SCC) is a type of material failure that occurs when a susceptible metal is subjected to the combined effects of stress and a specific environment. For a more thorough account of SCC phenomena, the reader is referred to the abundant literature on this subject.[2-6] The current mechanisms seeking to explain the phenomena generally fall into three basic categories: (1) electrochemical dissolution[7,8], (2) stress-sorption[9-11] or (3) hydrogen-assisted cracking.[12-15] As is often the case, each of these mechanisms draws its support from a large body of experimental observations. This has made it difficult to accept any one of them as being uniquely responsible for all observed cases of SCC. In general, however, most mechanisms that have been put forward to explain SCC have either been based on electrochemical or mechanical concepts of failure. Each of these particular concepts envisions a unique set of controlling processes occurring at the propagating crack tip. Besides those processes believed to be controlling the failure, many others are occurring in the vicinity of the propagating crack tip during SCC. A schematic representation, credited to Staehle[16], of these many processes is shown in Figure 1.

Notwithstanding the present complexity of this montage, there exists the conviction that further research may uncover some crucial principle that may lead to a more finite resolution of SCC phenomena. This conviction has its basis in the desire to integrate into a more unifying scheme the various electrochemical and mechanical concepts underlying current SCC mechanisms. It is within this context that the speculation about the possible role of solvated electrons in SCC phenomena is believed to have arisen. The intent of this report is to go beyond this speculation. We shall argue here that there is a strong probability that solvated electrons do exist during the cracking process and that they have an important role to play in SCC phenomena.

Before presenting this hypothesis a review of the nature of solvated electrons will be presented next. In view of the extensive chemical literature already devoted to solvated electrons, only a brief account of their nature will be given in this report. Following this, we will examine the claim for the existence of solvated electrons during SCC. We will present

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*Refer to REFERENCES

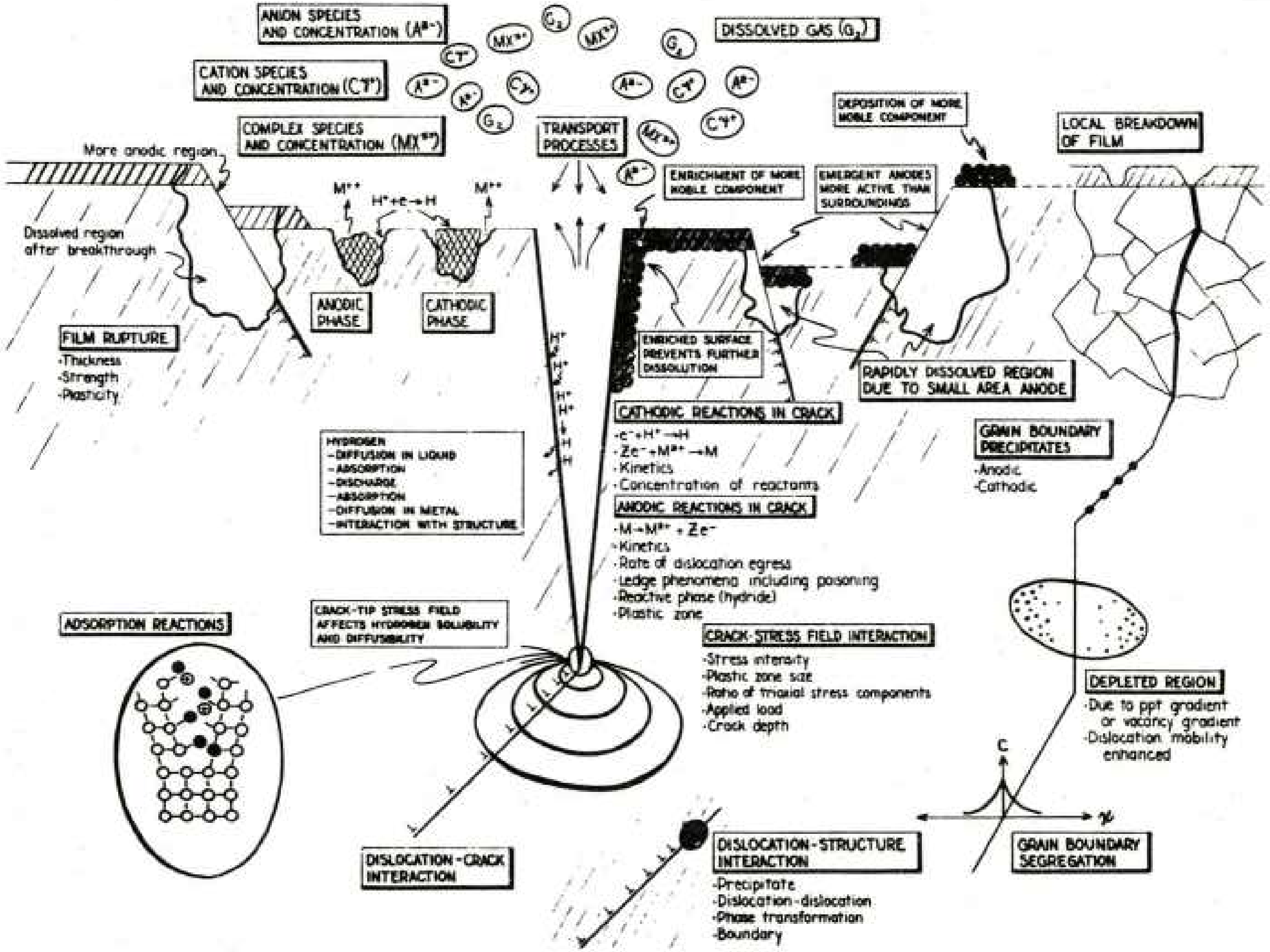

Figure 1. Montage Showing Processes Operating in Environment and Within Metal Which Are Significant in the Mechanistic Interpretation of Stress Corrosion Cracking (Ref. Staehle[16])

here an hypothesis calling for their playing an important role in SCC phenomena. Following this, we will propose several experiments that are intended to substantiate this hypothesis. The report will conclude with a discussion of the merits of this hypothesis from the standpoint of unifying the various failure concepts attributed to SCC.

NATURE OF THE SOLVATED ELECTRON

Historical Perspective

Kraus[17] in 1908 was the first to postulate the formation of solvated electrons (e_s^-) as ammoniated electrons during the dissolution of alkali metals in liquid ammonia. Earlier suspicions of the existence of such chemical species can be found in the studies of Weyl[18] and Palmear[19]. The first substantiated evidence for the existence of hydrated electrons, e_{aq}^-, came about in the early 1960's with studies into the radiolysis of water[20,21]. At present, sufficient experimental data exist in various media to establish the feasibility of generating solvated electrons by the following processes:[22]

1. Alkali metal dissolution
2. Radiolysis
3. Photolysis
4. Photoinduced ejection from a metal electrode
5. Direct cathodic ejection

Only the second and fourth of these processes have so far been shown to be acceptable means for generating hydrated electrons in aqueous solutions.

Chemical and Physical Properties

The conceptual picture of a solvated electron can best be described as an excess electron associated with a region of polarized and oriented solvent molecules.[22] As such, the solvated electron displays many chemical and physical characteristics comparable to the more usual solvated charged species. The solvated electron exhibits distinct optical[23] and ESR[24] absorption bands, electrical conductances comparable to other ions in the same environment[25] and diffusion and chemical reaction rate values characteristic of other similar chemical species[26]. Since we will be principally concerned with aqueous environments, we shall confine our subsequent discussion mainly to the hydrated form of solvated electrons. Thus, in aqueous media researchers have found that the hydrated electron and the hydrogen atom are, from a chemical standpoint, barely distinguishable from each other. Both are extremely reactive and are very powerful reducing agents. Comprehensive reviews describing in detail the properties of these hydrated electrons are available in the literature[27,28] so that an in-depth discussion here is unnecessary. However, some of the more pertinent properties and chemical reactions of hydrated electrons that will be briefly discussed here are given in Table I. Reaction #3 in Table I reveals that the hydrated electron has a comparatively slow decomposition rate in pure water. The hydrated electron thus has a distinct identity with lifetimes of the order of microseconds and should be capable of playing an intermediary role in various chemical reactions. As the pH of the aqueous environment decreases the hydrated electron principally becomes a precursor to the hydrogen atom (Reaction #1 in Table I). At high concentrations of hydrated electrons, Reaction #4 dominates to directly yield hydrogen molecules without passing through the expected intermediate stage of hydrogen atom formation[30]. Chemically, hydrated electrons have been found to react at diffusion controlled rates not only with each other, H_3O^+ and H_2O but also with a large assortment of reagents[31]. Because of the extreme reactivity of these hydrated electrons, their discovery provided the impetus for extensive re-examinations of many reduction processes occurring in aqueous media. This led to speculations on the possible involvement of hydrated electrons as chemical intermediates in such electrochemical processes as hydrogen gas evolution, and metal dissolution.[32] The evidence upon which these speculations are based are briefly discussed in the next section.

Role of Hydrated Electrons in Electrochemical Processes

Walker[33] and Pyle and Roberts[34] have proposed the direct formation of hydrated electrons as being the primary discharge step in a number of electrochemical hydrogen evolution reactions occurring in aqueous media. In electrochemical operations involving inert electrodes, the hydrated electron is believed to be formed from an electron ejected from a cathode. The primary discharge step is conceived as

$$e^-(\text{cathode}) \longrightarrow e^-_{aq}$$

followed by Reactions #1, 3 or 4 in Table I, depending upon solution pH and hydrated electron concentration. Hydrogen gas is then evolved through the reaction: $2H \longrightarrow H_2$.

With regard to metal dissolution in aqueous acidic media, the accepted theory calls for the metal to evolve hydrogen gas by the following scheme:

$$M \longrightarrow M^+ + e^-_M \text{ (in metal)}$$

$$e^-_M + H^+ \longrightarrow H_{\text{absorbed}}$$

$$2\,H_{\text{absorbed}} \longrightarrow H_2$$

TABLE I.

Properties and Chemical Reactions of the Hydrated Electron, e_{aq}[29]

Charge	-1
Mean radius of charged distribution (calc.)	2.5-3.0 Å
Hydration energy (calc.)	40 kcal/mole (1.74 ev)
Diffusion constant	4.5×10^{-5} cm^2/sec
Mobility	1.8×10^{-3} cm^2 sec^{-1} V^{-1}
Mean half life in pure water (pH7)	230 μ sec

Chemical Reactions

	Reaction	pH	Rate constant M^{-1} sec^{-1}
1.	$e^-_{aq} + H_3O^+ \longrightarrow H + H_2O$	2-4	2×10^{10}
2.	$H + OH^- \longrightarrow e^-_{aq}$	11	2×10^{7}
3.	$e^-_{aq} + H_2O \longrightarrow H + OH^-$	8	16
4.	$e^-_{aq} + e^-_{aq} \longrightarrow H_2 + 2OH^-$	10-13	10^{10}
5.	$H + H \longrightarrow H_2$	2	2×10^{10}

However, those advocating an hydrated electron mechanism believe that what is occurring in aqueous media is similar to what is occurring during alkali metal dissolution in liquid ammonia[35], namely that:

$$M \longrightarrow M^{+n} + e^-_{aq}$$

to be followed again by either Reactions #1, #3 or #4 from Table I depending upon solution pH and e_{aq} concentration. Likewise, gas evolution comes about by the reaction: $2\,H \longrightarrow H_2$.

Evidence consistent with these postulated roles for hydrated electrons comes only from two types of experiments. One type of experiment involves evaluating the competitive kinetics of various hydrated electron scavenger reagents[33]. The other type of experiment is a spectrophotometric identification of the transient chemical species at the cathode during the electrolysis of an aqueous solution[36]. Advocates of an hydrated electron mechanism contend by these two types of studies that no possible chemical species other than the hydrated electron could account for the results obtained. However, various counterarguments have been presented[37,38,39] to seriously question the possibility that these hydrated electron reactions are occurring. The details of the controversy are not of major concern here and the reader may find the necessary information in the cited references. It is sufficient to note here only that the existence of solvated electrons as transients in these electrochemical processes remains unresolved and that further investigation is required to substantiate the claims of Walker[33], Pyle and Roberts[34].

Our purpose in relating the controversial roles attributed here to hydrated electrons is to raise the question whether, under suitable conditions, metals can dissolve in aqueous solutions with the direct release of solvated electrons. Since such a process duplicates the accepted electrochemical dissolution process believed to be occurring during SCC of metals, an assessment of its feasibility would be desirable. Fortunately, one outgrowth of this controversy was the general concensus that it is feasible for electrons to be ejected from a metal at a metal/solution interface, undergo thermalization and subsequently become solvated, provided the necessary energy conditions prevail for such a process. These energy conditions are discussed next as a prelude to proposing a mechanism whereby hydrated electrons can be generated during SCC.

Energetics of Direct Ejection of Electrons

A metal can dissolve nonelectrochemically provided it dissolves dissociatively into metal ions and solvated electrons. This can occur if the energy to remove the electron from the metal and put it into the solvated state is less than the energy gained in solvating that electron.

In 1931, Gurney[40] was the first to consider this problem in energetic terms. He proposed that electron transfer from a metal to an aqueous solution must obey the condition that:

$$\Psi_e - eV \leq S_e$$

where:

Ψ_e = electronic work function of the metal for a metal/vacuum interface

V = electrical potential at metal surface

S_e = solvation energy of electron

e = electronic charge

Conway and MacKinnon[41] have used this criterion to estimate that hydrated electrons will tend to form only when a metal is at a very large negative potential (e.g., -2 to -3 volts with respect to the reversible hydrogen scale). Frumkin[42] approached this same problem by evaluating the relevant electronic work function. This work function would represent the energy required to transfer an electron across the metal/solution interface as compared to the more classical metal/vacuum interface. He found that:

$$\Psi = \Psi_e + V_{M,S} - G$$

where:

Ψ = electronic work function for a metal/solution interface

$V_{M,S}$ = Volta potential difference at a metal/solution interface

G = free energy of solvation for electron

Estimated values of Ψ were found by Frumkin to be less than Ψ_e, indicating a somewhat greater tendency for electron injections to occur into suitable solutions than into vacuum.

Conway[37] subsequently defined an energetic criterion for the preferred dissociation of a metal into ions and hydrated electrons (i.e., $M \rightarrow M^{+n} + ne^-_{aq}$) as opposed to a dissolution that involved the transfer across the interface of only metal ions (i.e., $M \rightarrow M^{+n} + ne^-_M$). Using a Born-Haber cycle the additional energy required for the hydrated electron process was found to be ($n\,\Psi_e - n\,S_e$). Since the solvation energy of the hydrated electron, S_e, has been estimated to be 40 kcal/g. mole (1.74 eV),[43] the electronic work function of the metal must be less than 1.74 eV for metal dissociation to be favored. Under normal circumstances, this eliminates the possibility of electron ejection from most metals with the possible exception of the alkali metals. In this regard the treatment for alkali metal dissolution in aqueous media has already been considered by Pyle and Roberts[34] and Bass[44] in terms of the controversial hypothesis that solvated electrons are precursors to the observed hydrogen evolution.

All the energy criteria for electron ejection considered above apply to transitions that involve no additional energy inputs. When, however, some form of energy is supplied to induce electron ejection these criteria are no longer applicable. For example, in photo-assisted emission, the electron ejection process is assisted by quanta absorption so that the criterion proposed by Gurney should be modified to:

$$\Psi_e - eV - h\,u \leq S_e$$

where:

h = Planck's constant

u = frequency of incident radiation

Photoemission experiments at a metal/solution interface have been shown to basically follow the above equation.[45] Furthermore, it has been shown that the application of a large negative potential to metals immersed in liquid ammonia predisposes the metal electrodes to electron ejection.[35] The only evidence of a similar electron ejection mode for metals immersed in aqueous media is Walker's electrolysis experiment.[33] More substantial evidence for this mode of direct electron ejection is not available presumably because of the overiding tendency for the hydrogen evolution step to preempt the electron transfer process.

To summarize, direct ejection of electrons from a metal immersed in a solution is a feasible process provided the proper energy condition is satisfied and any interposing reactions (e.g., hydrogen gas evolution) are appropriately suppressed. The fact that hydrated electrons can arise from various metal electrodes by a photoinduced ejection mechanism attests to the feasibility of this process.[45,46] In the next section a new process for generating hydrated electrons at a metal/solution interface will be proposed which is based on a stress induced mechanism. Subsequent discussions will then center on the plausibility of using this new process to enhance metal dissolution rates.

SOLVATED ELECTRONS IN STRESS CORROSION CRACKING

Stress Induced Generation of Hydrated Electrons During Metal Dissolution

In the general electrochemical model for metal dissolution in acidic aqueous media, the mode of metal removal is conventionally taken as an anodic reaction: $M \rightarrow M^{+n} + n\,e^-_M$, where only the metal ions are transported across the metal/solution interface while the electrons remain in the metal phase. To preserve electroneutrality and insure continued metal dissolution the anodic reaction must be balanced by a complementary cathodic reaction taking place somewhere on the same metal surface. The anodic and cathodic processes are thus coupled and both must then proceed at some equivalent intermediate rate.[47] This corrosion or metal dissolution rate then becomes basically charge transfer limited in the sense that either one of the reactions (i.e., anodic or cathodic) or the ion flow process in the solution will usually exercise overall rate control of the metal dissolution process. There are situations, however, where very high metal dissolution rates can occur that need not necessarily require the existence of a compensating cathodic reaction in order to conserve local electroneutrality. Such a situation exists during the spontaneous dissolution of alkali metals in liquid ammonia where a transfer of electrons out of the metal is occurring.[48] A similar condition can conceiveably exist where metal dissolution is occurring from a highly localized stressed region that is undergoing intermittent stress relaxation (e.g., a propagating crack tip). Under these unique circumstances sufficient energy released by the reduction of lattice strain energy that accompanies crack growth could be made available to the metal electrons at the dissolving surface to induce their ejection into the solution. Once in the solution the electrons thermalize and subsequently solvate. The overall metal dissolution process can now be looked upon as:

$$M \longrightarrow M^{+n} + n\ e^{-}_{aq}$$

where both the metal ions and electrons cross the metal/solution interface. The noteworthy aspect of this hypothesis compared to several other stress assisted concepts[49-54] that attempt to account for stress enhanced metal dissolution rates is the assertion here that electron emission from the metal surface is occurring simultaneously with metal dissolution. The major advantage of this hypothesis is that metal dissolution can now proceed at a much faster rate since it no longer is limited entirely by the need to be coupled with a cathodic reaction. To the extent that both metal ions and electrons are removed from the metal surface, no charge separation has occurred at the metal/solution interface and by implication the dissolution process can be considered electroneutral in nature (i.e., dissociative). In summary, we have postulated here that hydrated electrons can be formed in an aqueous enviroment at a stressed metal/solution interface provided the stressed metal is uniquely suited, by an appropriate relaxation of lattice strain energy, to eject electrons. Our next consideration will be to establish what role this hypothesis can have in SCC phenomena.

Generalized Dissolution Model for SCC

It is generally recognized that an understanding of SCC phenomena must come from further clarifications of the processes occurring at the propagating crack tip. It is this region that is the focal point for the interplay of three major variables that markedly influence SCC; the chemistry of the environment, the metallurgy of the metal, and the mechanics of the stressed system. Apparently, various crucial factors relevant to each of these variables interact in a dynamic manner at the crack tip to bring about continued crack propagation and eventual failure. An acceptable explanation as to what is occurring at the crack tip in terms of these crucial factors has so far eluded us principally because the conditions at the crack tip are very different from those that can be measured externally. There is therefore a reluctance to postulate any mechanism for the crack tip region that is solely based on external measurements. For example, we know that the application of an electrical potential has a major influence on SCC phenomena. Yet we are not sure what form this influence takes at the crack tip. Likewise, the role of stress at the crack tip is unknown, even though empirical correlations of a stress intensity factor vs. nominal crack velocities are well established. In the final analysis, any unified concept of SCC must eventually address itself to this crack tip region in order to explain (1) the necessary and sufficient conditions for the occurrence of SCC, (2) the decisive influence various factors have on SCC and (3) the kinetics of the process. We hope to show in the discussion that follows that a more unified dissolution mechanism for SCC which incorporates the proposed solvated electron postulate does indeed address itself to this crucial crack tip region. We shall attempt to show that this more unified SCC mechanism leads to a self-perpetuating process whereby SCC can be propagated through the material provided the necessary preconditions of stress and environment are fulfilled. Furthermore in future reports we hope to demonstrate that this generalized mechanism will also be capable of embracing the various other SCC mechanisms currently in vogue as well as provide a logical basis into which the influences of various factors from each of the pertinent variables can be incorporated.

Postulated Mechanism

The available experimental evidence on SCC strongly suggests an electrochemical mechanism for SCC, in that metal dissolution occurring as an anodic reaction at the crack tip is believed to be the dominant mode of crack propagation. The current density of this anodic reaction ($M \rightarrow M^{+n} + n\, e_M^-$) is often equated to a nominal propagation velocity for the stress corrosion crack. However, observations in several SCC systems reveal crack velocities that cannot be entirely accounted for by measurable anodic current densities. Thus in order for this electrochemical model of SCC to reasonably account for observed crack propagation rates, only a highly restricted region at the crack tip should be undergoing rapid dissolution. Furthermore, to maintain electroneutrality, surfaces away from the tip must provide sites for cathodic reactions to take place. Since materials susceptible to SCC are in general corrosion resistant in that they rapidly form very protective films on exposure, the question of material susceptibility to SCC appears to hinge upon a balance being established between the dissolution and passivation processes at the crack tip.[55] Thus for materials to be susceptible to SCC, there must exist a unique set of circumstances that will favor: (1) crack tip dissolution occurring instead of passivation, (2) concentrated frontal dissolution occurring in preference to laterial dissolution at the crack tip and (3) an unencumbered cathodic reaction taking place so that it does not become the rate limiting step in the overall dissolution process.

Various models[56-61] have been proposed that postulate these same favorable set of conditions. These models mainly deal with the role surface films play in predisposing the metal to these conditions. They rely upon the rapid formation of a passive film on the crack sidewalls to localize anodic dissolution at slip bands emerging at the tip of the growing crack. Surfaces covered by the newly formed passive film are presumably relegated to act as sites for the cathodic reaction. Since, however, cathodic activity will now require electron transport through this newly formed surface film, one cannot overlook the possibility that these same surface films may inhibit electron transport and thereby limit the cathodic reaction. Depending upon conditions, passive oxide films have been shown to produce effective barriers to electron transport.[62] Thus, the extent of anodic dissolution at the crack tip may be rate limited by the cathodic response occurring at the film/solution interface. In essence then, the surface film models can account for SCC only so far as to propose that anodic dissolution is occurring preferentially at sites where emerging slip bands penetrate the passive film layer, while the crack walls by virtue of this same passive film remain inactive to dissolution. Where the compensating partial cathodic current should be coming from is not entirely made clear by these models. Three sites are possible: (1) the original undisturbed external surface of the material, (2) the stress relieved crack wall surface and (3) the stressed bare metal surface exposed at the crack tip. Sites (1) and (2) are film-covered surfaces and the properties of the film will dictate the availability of electrons at the film/solution interface. At location (3) the partial cathodic reaction must compete with the proposed dissolution occurring there. Since to affect the cathodic reaction in acidic media requires an activated adsorption state for H_3O^+, [47] the ability to sustain such a condition and maintain unrestricted cathodic rates at a dissolving surface may prove difficult.

A way out of this dilemma would involve divorcing the metal dissolution reaction at the stressed crack tip from any need to couple with a cathodic reaction. This can be accomplished by proposing that a stress induced electron ejection mechanism operates concurrently during metal dissolution at the crack tip. Considering that frontal dissolution at the crack tip is occurring under non-equilibrium conditions, there is no obvious constraint preventing one from viewing this dissolution as proceeding under conditions that could encourage the ejection of electrons into the solution during the metal "bond-breaking/dissolution" state. With a transfer of electrons out of the metal at the crack tip, dissolution there need not require a balanced cathodic response. Thus at the crack tip metal dissolution would be occurring as:

$$M \longrightarrow M^{+n} + y\, e^-_{aq} + x\, e^-_M \qquad \begin{bmatrix} x + y = n \\ 0 \leq x \leq n \end{bmatrix}$$

where the dissolution would be proceeding at a rate dependent upon the degree of electron ejection occurring. Once metal at the crack tip surface is stress relieved it becomes a part of the crack wall. Then as a stress relieved bare metal surface the newly formed crack sidewall becomes subject to the usual classical anodic and cathodic reactions.

Self-perpetuating Process at Crack Tip

In the previous section a novel metal dissolution mode was postulated as occurring at the stressed crack tip during SCC. This type of dissolution is unique in that it entails the transfer of both metal ions and electrons across the metal/solution interface. This form of dissolution abruptly ceases once the newly exposed metal surface becomes a part of the crack sidewalls. There, the normal anodic electrochemical reactions operate to either passivate the surface or continue metal dissolution. The electrochemical kinetics of these competing anodic reactions dictate to a large degree whether crack growth will continue. If conditions are such that the dissolution rate far exceeds the passivation rate, extensive lateral dissolution will occur and effectively enlarge the crack opening. This will blunt the crack by reducing the stress level below the critical level required for continued crack propagation (i.e., inhibit further crack growth). If, however, conditions in the crack lead to a passivation rate far greater than the dissolution rate, the crack will remain sharp; a high stress level will be sustained at the crack tip and crack growth is expected to continue. However, with each crack advance a re-adjustment of stress levels ahead of the crack tip can also be expected. How the material accommodates itself to this incremental crack advance will determine the newly re-adjusted stress level at the crack tip. Cracking will persist provided the new stress level is still above a critical level that is capable of continuing the advance of the crack. This sequence of events just described becomes self-perpetuating under the proper SCC conditions. It also suggests the presence of a cyclic type process occurring at the crack tip to insure continuing crack growth.

Such a cyclic process can be thought of as occurring in the following manner:

1. A stress relieving crack extension occurs at the crack tip. The newly exposed metal surface undergoes metal dissolution with concurrent electron ejection across the metal/solution interface.

2. The ejected electrons solvate and in the acidic aqueous medium[26] at the crack tip quickly convert to hydrogen atoms (i.e., $e^-_{aq} + H_3O^+ \rightarrow \cdot H + H_2O$); their conversion taking place in a matter of microseconds at the metal surface. This conversion occurs before the new surface of the metal, now the crack sidewalls, enters into the passivating electrochemical reaction essential to maintain a sharp crack.

3. The absorbed hydrogen atoms diffuse into the metal and migrate to the stressed region ahead of the crack tip. There they interact with the metal lattice in any one of a number of possible ways[63,64] that basically lower the cohesive strength of the metal. If the re-adjusted stress concentration at the crack tip is sufficient to overcome this decreased cohesive strength, further extension of a stress relieving crack occurs at the crack tip.

4. With this next crack extension, the cycle of events is repeated.

Several interesting aspects emerge from a consideration of this hypothetical process. For example, one's point of view as to what is the predominant failure mode in SCC will dictate what follows the electron ejection event. If one supports a brittle-type failure mechanism for SCC, then the main purpose of the ejected electrons is to quickly solvate and give rise to hydrogen atoms. The rapid incorporation of these hydrogen atoms into the metal lattice will then lead to a hydrogen embrittlement type failure. If, however, one views SCC as a dissolution-type failure, then the purpose of the electron ejection event is to provide for very rapid metal dissolution (one may even say dissociation) at the crack tip. The above considerations also suggest that both hydrogen-assisted cracking and metal dissolution can occur simultaneously. Regardless of which scenario prevails, the important point is the considered need for the ejection phenomenon to occur at the crack tip.

The physical reality of this proposed electron ejection phenomenon has yet to be experimentally demonstrated. Such a demonstration is not without genuine problems since this microscopic event at the crack tip is not readily accessible to experimental observation. Nevertheless from a conceptual standpoint, this model may provide new insights into the events at the crack tip. Such considerations should, therefore, encourage a closer look at ways to test the validity of this model. With this in mind, a number of experiments are suggested in the next section which hopefully may cast some light on the plausibility of this model.

PROPOSED EXPERIMENTS

The experiments proposed in this section are mainly intended to demonstrate that it is indeed plausible for electron ejection to occur at a crack tip during SCC. As a first consideration an order of magnitude estimate of the energy released by the stressed metal lattice during crack growth should tell us whether it is sufficient to provide for electron ejection from the metal surface. This information can be gotten from the Griffith brittle crack criterion which tells us that the elastic energy released during crack growth is sufficient, at least, to account for the surface energy of the newly formed crack surfaces. Typical values for these surface energies (1600 ergs/cm^2 $\approx$ 1 eV/atom)[65] are comparable within an order of magnitude to the classical electronic work function values of metals (i.e., 2-5 eV/atom). The electronic work function represents the energy required to eject an electron from the metal into vacuum. A lower work function value can be expected, however, because the ejections are occurring into an aqueous solution rather than into vacuum. Evidence to support this expected reduction comes from photoemission experiments where lower photoelectric thresholds were observed for emissions from a metal/solution interface than from a metal/vacuum interface.[45] Thus, the magnitude of the released energy made available during crack growth is comparable to the energy needed to eject electrons. In pursuing this line of thought, more concrete evidence to substantiate the existence of this interfacial electron transport phenomenon is needed. The several experiments that are briefly described next hopefully will provide this evidence.

Detection of Electron Ejection During Fracture in Ultra High Vacuum (UHV)

Several emission phenomena exist that allude to the possibility of electron ejection occurring during extensive plastic deformation and fracture of metals. The observed degassing in UHV of metals experiencing mechanical stresses shows that such stress can impart sufficient energy to cause the ejection of various adsorbed gases that have desorption energies in the range of 1 eV/atom.[66] Emitted electrons know as exoelectrons have also been detected from plastically deformed metal surfaces having depressed work functions caused by adsorbed gases.[67] In order to detect ejected electrons during the fracturing process, various metals can be fractured in a UHV and the specimens instrumented to detect electron emission. To enhance the probability of detecting these emissions, the tests should be performed on those metals where the energy release rate at fracture can be kept high while the plastic dissipation rate is kept to a minimum. Another condition is for the test material to possess a low electronic work function. Cold brittle fracture tests on metals possessing a low electronic work function are thus well suited to assess whether electron ejection can arise from metal fracture.

Stress Induced Electron Ejection at Metal/Solution Interface

Metals that have a high hydrogen overvoltage in liquid ammonia can act as electron electrodes and under appropriate potentials can eject electrons into the solution. The ejected electrons subsequently solvate and their presence can be detected either spectrophotometrically or by conductivity measurements. A repetition of these experiments with stressed metal electrodes should reveal whether stress enhanced electron ejection is detectable. These tests resemble somewhat the strained electrode experiments conducted in aqueous solution, where an increase in the anodic current is attributed to stress enhanced metal dissolution. In these tests proposed here the increased currents would be attributable to a stressed enhanced electron ejection phenomenon. Besides liquid ammonia, various organic solutions possessing high solvated electron mobilities could be employed as test solutions for various stressed metal electrodes. Photostimulation would then be used to eject electrons from the metal/solution interface. In these cases the stressed electrodes can be expected to influence the photoemission. As a first attempt at detecting electron emission in aqueous solutions, various solvated electron scavenger reagents could be used to detect any preferential electron ejection from stressed metal electrodes.

Detection of Solvated Electrons During SCC

The detection of solvated electrons generated during SCC is a difficult undertaking and the writer at present is unable to suggest appropriate techniques to accomplish this task. In dealing with the detection of hydrated electrons one major difficulty that needs to be overcome is that as one attempts to increase the concentration of hydrated electrons in order to aid their detection, their mean lifetime is correspondingly shortened. Consequently efforts at detection will necessitate the use of sensitive and rapid detection techniques similar to those used in the spectrophotometric investigations of Walker.[36] At best, tests that simulate the crack tip environment and SCC conditions can be devised. Occluded cell geometries like those employed by Pourbaix[68] can be used to simulate crack tip solution chemistries. Likewise stress conditions can be simulated by pulsed laser stressing of thin metal foils susceptible to SCC, while photoinduced electron ejection yields can be studied as stress is applied to these foils.

In summary, the experiments proposed here are basically exploratory in nature. The main intent of these experiments is to establish: (1) the existence of an electron ejection phenomenon during metal fracture, (2) that there is a greater probability of electron ejection occurring at a metal/solution interface than at a metal/vacuum interface and (3) that such a process can be stress induced as under conditions of SCC. At the present stage in the development of this model, we are far from devising experiments capable of determining whether electron ejection is a necessary and sufficient condition for SCC to occur.

DISCUSSION AND SUMMARY

We have briefly discussed in this report the nature of solvated electrons and their characteristics in aqueous media. In many fields of chemistry where electron transfer phenomena play a part (e.g., photochemistry, radiation chemistry) this type of bound electron state in water has been gaining importance. Whether the solvated electron plays a prominent role in electrochemical reactions that call for similar electron transfer phenomena (e.g., hydrogen evolution) is still a matter of controversy. Nevertheless, an important outgrowth of this controversy is the consensus that electron ejection from a metal/solution interface is feasible provided certain energetic requirements can be satisfied. These requirements are believed to prevail at the crack tip in a metal undergoing SCC, where a stress assisted mechanism is evoked to induce electron ejection from the metal/solution interface. The immediate consequences of this ejection phenomenon are twofold. One is that rapid metal dissolution at the crack tip is feasible without having recourse to a coupled cathodic reaction. The other consequence is that the rapid solvation of the ejected electron leads to hydrogen atom formation in aqueous acidic media. Whether subsequent hydrogen atom incorporation into the metal lattice is principally responsible for SCC or whether rapid metal dissolution at the crack tip is the primary failure mechanism remains unresolved at this time. Both modes of failure, however, are the direct result of the electron ejection mechanism at the crack tip and in this respect the ejection phenomenon can be considered a forerunner of SCC.

If we are willing to accept that the emission of electrons at the crack tip is crucial to SCC, then our perception of the SCC failure mechanism no longer conforms to the established electrochemical corrosion model. This is because one of the basic tenents of the electrochemical model holds that no transfer of electron charge occurs across the metal/solution interface. The postulated occurrence of interfacial electron transfer at the crack tip basically nullifies this tenet and its restricting aspects. The metal dissolution at the crack tip, formally considered a faradaic anodic process, need not now be balanced by a corresponding cathodic process in order to remove the electrons produced during the metal dissolution process. The kinetics of metal dissolution are thus not severely restricted by the necessity of coupling anodic and cathodic reactions. In place of the usual electrochemical SCC model, we are proposing a conceptual model of SCC that is compatible with the role solvated electrons appear to play in the failure mechanism. The metal dissolution occurring at the crack tip is now looked upon as more of a chemical dissociation. Thus, the practice of partitioning the overall reaction into partial electrochemical reactions is not tenable here because no charge separation is occurring at the metal/solution interface.

The usefulness of this proposed SCC model will depend in part upon its ability to identify the role that pertinent variables have in influencing the failure process. As a means of further developing this model, the contributions that stress, metallurgy and chemistry make to bring about SCC will be discussed next within the context of this postulated SCC model.

Experimentally, we know that the level of stress is an important factor in determining whether SCC is feasible. Threshold stress levels exist for most metal/environment systems as well as empirical correlations that relate a stress intensity factor to crack velocities. These observations lead one to believe that the major function of a stressed state in the material is basically to insure that sufficient energy, in some readily convertible form, is available to drive the failure process. The familar Griffith criterion tells us that the strain energy released as the crack propagates must be at least equal to the work required to propagate the crack. For ideally elastic material this work is equated to the surface energy of the crack surfaces. For elastic-plastic materials additional energy must be supplied to accommodate the plastic relaxation occurring at the crack tip. In the postulated solvated electron model of SCC, the energy needed for the electron ejection process must also be supplied by a portion of the strain energy released at the crack tip. Thus the mechanics of the stress system serve the function of insuring that sufficient stored energy in the material is effectively released at the crack tip. The magnitude of this stored strain energy or the level of the threshold stress necessary to affect the failure will be dictated by how the material partitions the released strain energy among the various dissipation modes available to it either within its bulk or locally at the crack tip.

The efficiency of this energy release as well as the mode in which this energy dissipation occurs falls within the scope of the second major variable associated with SCC, namely, the metallurgy of the metal. The broad metallurgical aspects of a metal, ranging from microscopic considerations of dislocation dynamics to macroscopic features such as grain orientations, are all relevant in the sense that they provide clues to a large mosaic representing the various energy dissipation mechanisms available to the metal. Another important function to be attributed to the metallurgy of a metal is that of providing structural features that are more prone to eject electrons (e.g., grain boundaries) when brought into contact with appropriate solutions.

The last major variable that is involved in SCC is the chemistry of the solution or environment, in particular the microscopic chemical environment in the crack tip region. The solution at the crack tip is multifunctional. For one, it must be predisposed to accept the solvation of the ejected electron with the least loss of energy. It also controls the fate of the solvated electron and determines whether hydrogen atom formation and incorporation into the metal lattice will play a role in the failure process. Furthermore, the rapidity with which the solution can passivate the emerging crack faces will determine the sharpness of the propagating crack and thereby the adjusted stress level that can be maintained at the crack tip. The solution is also expected to play a major role in the crack nucleation process. This aspect of SCC has not been given any consideration in this report.

In conclusion, this report represents the first in a series of reports in which the postulated role played by solvated electrons in SCC phenomena will be explored and discussed. This first report purposes and discusses in a preliminary manner a model and a unified mechanism for SCC which conceives of a stress induced interfacial electron transfer phenomenon occurring at the stress corrosion crack tip. Such electron transfer gives rise to solvated electrons in the crack tip region, the consequences of which are uninhibited crack tip metal dissociation and possible hydrogen atom incorporation into the metal lattice. The immature state of this novel SCC model is such that it is presently unable to account quantitatively, for many of the existing SCC observations. Nevertheless, from a conceptual standpoint the model offers an intriguing new outlook on what may be occurring during SCC. In future reports attempts will be made to bring this model into mature form.

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Date Printed: 3 Feb 1977