Electrochemical Considerations of Crack Growth in Ferrous Alloys

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ABSTRACT

Environmentally assisted crack growth in ferrous alloys in aqueous environments is a multi-faceted problem of technological importance. Recent studies of electrochemical reactions with bare metal surfaces and of crack growth response have provided a clear demonstration of electrochemical reaction control of crack growth in steels. These studies also showed the importance of localized transient reactions with bare metal surfaces at the crack tip and the need for a new approach to the measurement of electrochemical reaction kinetics. In this paper, a framework is outlined for the identification and modeling of crack growth response in aqueous environments in terms of the underlying chemical processes. This framework serves as a basis for fundamental understanding, and for the rational interpretation and utilization of crack growth data. Modeling of electrochemical reaction control of crack growth for steels in aqueous environments and a new method for measuring the kinetics of reactions with bare metal surfaces are briefly summarized. The influences of electrochemical variables on crack growth are reexamined, and are illustrated by data on steels. The engineering implications of these findings and areas for further research are discussed.

KEYWORDS

Environmental effects; fracture mechanics; crack growth; corrosion fatigue; stress corrosion cracking; electrochemistry; corrosion; modeling; steels.

INTRODUCTION

Environmentally assisted crack growth (both corrosion fatigue and stress corrosion cracking) in high strength alloys is well recognized as an important factor in determining the reliability and durability of engineered components and structures. As a major class of structural materials, ferrous alloys are used in many applications where exposures to aqueous environments and cracking are of concern. The components and structures include pressure vessels and piping in the chemical and power industries, bridges, ships and off-shore structures. Cracking involves complex interactions between loading (mechanical), environmental and metallurgical variables. These interactions are manifested through the influences of temperature, stress-intensity factor and cyclic-load frequency on the crack growth rates and the cracking response, and may depend on a host of electrochemical variables (such as, electrode potential, ionic strength, and solution pH).

To understand environmentally assisted crack growth and to make the test data useful for quantitative design and for alloy development, it is essential to identify the processes that control crack growth and to model the cracking response in terms of these processes and their interactions. The importance and the multi-disciplinary nature of environmentally assisted crack growth have been recognized. Considerable attention has been given to the study of crack growth in gaseous environments during the last twenty years. A reasonable conceptual understanding has evolved in terms of the underlying chemical processes (namely, gas transport, surface reaction and hydrogen diffusion) and of the microstructure for fatigue (see, for example, Wei and Simmons, 1986; Wei, 1987) and for hydrogen embrittlement (Wei and Gao, 1985; Wei et al., 1984a). Because of greater complexity of the problem, comparable levels of understanding of crack growth in aqueous environments have not been achieved (Wei et al., 1984b). Recent studies (Alavi et al., 1986; Chu, 1987; Thomas et al., 1986; Wei, 1985; Wei and Alavi, 1988) showed that crack growth in steels is controlled by localized transient reactions with bare metal surfaces at the crack tip (vis-à-vis, the steady-state reactions associated with the conventional polarization measurements). As such, a new approach and new techniques had to be developed to measure the kinetics of electrochemical reactions (Alavi et al., 1987; Shim and Wei, 1986; Wei, 1985; Wei and Alavi, 1988). A re-examination of the influences of electrochemical variables on crack growth is also needed.

In this paper, a framework is outlined for the identification and modeling of crack growth response in aqueous environments in terms of the underlying chemical processes. This framework serves as a basis for fundamental understanding, and for the rational interpretation and utilization of crack growth data. Modeling of electrochemical reaction control of crack growth for steels in aqueous environments and a new method for measuring the kinetics of reactions with bare metal surfaces are briefly summarized. The influences of electrochemical variables on crack growth are re-examined, and are illustrated by data on steels. The engineering implications of these findings and areas for further research are discussed. Although emphasis is being placed on crack growth, many of the considerations are also germane to crack initiation and early growth.

CRACK GROWTH PROCESSES

The processes that are involved in the enhancement of crack growth in high-strength alloys by aqueous environments (electrolytes) are considered first. Similar to the case of gaseous environments, these processes are as follows (after Wei, 1979; Wei et al., 1984b):

1. Transport of the deleterious species to the crack tip.
2. Reactions of the electrolyte with newly produced crack surfaces to produce hydrogen or to effect dissolution.
3. Hydrogen entry (or absorption).

4. Diffusion of hydrogen to the fracture (or embrittlement) site.
5. Partitioning of hydrogen among the various microstructural sites.
6. Hydrogen-metal interactions leading to embrittlement (that is, the embrittlement reaction).

These processes operate consecutively or in sequence. The overall crack growth response is governed by one or more of these processes in conjunction with the mechanical driving force for crack growth, which may be characterized by either the applied or local stress or by the crack tip stress intensity factor K (Johnson and Paris, 1968; Wei, 1970).

The first step in the sequence involves transport of the various species (such as chloride ions) in the electrolyte. The transport processes include fluid flow, electro-migration and diffusion (Turnbull, 1984; Wei et al., 1984b). The second step involves the reactions of newly created crack surfaces with the electrolyte to produce hydrogen. The remaining processes (3 through 6) are identical to those for the gaseous environments, and involve the entry and transport of hydrogen through the material by diffusion, and the distribution of hydrogen within the material. Embrittlement, or the final step in the sequence, however, is a function of microstructure (Gao and Wei, 1985). The extent of embrittlement or the rate of cracking along each microstructural path is a function of the local hydrogen concentration, which in turn is expected to depend on the external environmental conditions (hydrogen fugacity and temperature). Cracking along the various microstructural elements (or paths) is expected to take place concurrently (i.e., in parallel). The overall crack growth rate is the weighted average of the individual rates along the different crack paths or of the operative micromechanisms.

For a dissolution mechanism (see Devereux et al., 1972), on the other hand, the anodic (dissolution) reactions in the second step would be directly responsible for crack growth enhancement, and the subsequent processes (3 through 6) do not need to be considered. Electrochemical reaction and crack growth data, however, suggest that the dissolution mechanism underestimates crack growth rates by almost 3 orders of magnitude (Allison, 1988; Wei and Alavi, 1988). As such, it cannot be the principal mechanism for crack growth, although the reactions themselves are an integral part of the overall process. For the remaining discussions, therefore, this mechanism for crack growth will not be considered.

Clearly, advances in the understanding of corrosion fatigue and stress corrosion cracking in aqueous environments require a framework through which the environmental contributions can be isolated and related to the process that control crack growth. Such a framework is essentially in place, and is based on one that has been used successfully for understanding environmentally assisted crack growth in gaseous environments (Wei et al., 1984a; Wei et al., 1984b). The basic elements of this framework consist of a superposition model (for fatigue), chemical modeling of crack growth response, definition of crack tip chemistry, and consideration of electrochemical reactions with bare metal surfaces. A more detailed discussion of each relevant element is given in the following sections in connection with considerations of the influences of electrochemical variables on corrosion fatigue and stress corrosion crack growth in steels.

ELECTROCHEMICAL REACTIONS AND CRACK GROWTH

Important understanding of crack growth response in aqueous environments is beginning to emerge through modeling and experimental verification of the role of electrochemical reactions at the crack tip (Wei, 1985; Alavi et al., 1987; Shim and Wei, 1986; Thomas et al., 1986; Wei and Alavi, 1988). Crack growth is considered to occur as a result of embrittlement by hydrogen that is produced by local reactions at the crack tip. The rate of reaction is governed by the electrochemical conditions (such as, solution chemistry, electrode potential and pH) and the surface conditions (bare versus oxidized) at the crack tip. The electrochemical conditions near the crack tip can be different from those of the external (bulk) environment, and are expected to depend on the kinetics of the transport processes and of the reactions with the crack surfaces. As in the case of gaseous environments, correct representation and modeling of crack growth response depend on the proper recognition of which one of the processes is in control, coupled with quantitative characterization and description of that process. Suitable models, therefore, must address the following two topics: (i) the formation of the crack-tip electrochemical environment, and (ii) the kinetics of reactions with the crack-tip environment, as discussed by Turnbull (1984), and by Wei et al. (1984b).

Electrochemical Reaction Controlled Crack Growth

For crack growth in high strength steels in aqueous environments, it is reasonable to assume that embrittlement is by hydrogen, while the crack growth rate, or the growth response, is governed by the rate of electrochemical reactions. This assumption was based on the study of reactions of water vapor with iron and steels (Dwyer et al., 1977; Wei and Simmons, 1979), and is gaining increasing support from electrochemical and crack growth data (Alavi et al., 1987; Allison, 1988; Chu, 1987; Shim and Wei, 1986; Thomas et al., 1986; Wei, 1985; Wei and Alavi, 1988; Wei and Shim, 1983).

A model for reaction-controlled corrosion fatigue crack growth has been formulated as an analogue to the gaseous case (Wei, 1985). Here the extent of surface reaction per cycle is identified with the fractional amount of electrical charge transferred during each fatigue cycle from the reactions of the newly formed crack surfaces with the electrolyte at the crack tip. The amount of charge transferred (q) is assumed to be directly proportional to the amount of hydrogen that is produced each cycle, and is determined by the integral of current flow (i) over the loading cycle; i.e., $q = \int i dt$. The corrosion fatigue crack growth rate is as follows (Thomas et al., 1986; Wei, 1985):

$$(da/dN)_{cf} = [(da/dN)_c - (da/dN)_r][q/q_s] \qquad (1)$$

where, $(da/dN)_{cf}$ is the cycle dependent component of the measured crack growth rate; $(da/dN)_c$ is the "pure" corrosion fatigue crack growth rate; $(da/dN)_r$ is the mechanical fatigue crack growth rate (i.e., rate in an inert environment); q is the amount of charge transferred per cycle; and q_s is the "saturation" amount or that required to complete the reactions. The amount of charge transfer is proportional to the reaction rate-constant (which is a function of temperature) and the time for reaction. It is recognized that the reactions may be composed of several steps.

The overall dependence of q and $(da/dN)_{cf}$ on temperature and time (or frequency) would reflect the temperature dependence of the individual reaction steps. The appropriateness and efficacy of models depend on proper modeling in terms of the controlling processes and of the possible transfer of control with changes in environmental conditions. The relationship between corrosion fatigue crack growth and electrochemical reactions can be probed through two of the important variables in corrosion fatigue: temperature and frequency. Temperature is reflected through its effect on the kinetics of reactions, while frequency establishes the available reaction time during a given loading cycle.

For stress corrosion crack growth, on the other hand, the crack growth rate in the K-independent Stage II is expected to reflect the "average" rate of reactions (Wei, 1981), and may be represented by eq. (2):

$$(da/dt)_{II} = C_s \exp(-E_s/RT) \qquad (2)$$

where C_s is an empirical rate constant; E_s is the apparent activation energy for the electrochemical reactions; R is the universal gas constant; and T is the absolute temperature. The apparent activation energy is to be determined from the "average" reaction rate. Because the reactions can involve several steps, which are still not well understood, this rate is determined operationally from the inverse of the time required to attain a certain fraction (say 90 to 95 percent) of the saturation charge, q_s (Wei, 1981; Chu, 1987).

Crack Tip Chemistry

The kinetics of the bare surface reactions are expected to depend upon the electrochemical conditions at the crack tip (i.e., the crack tip chemistry). These reactions are localized in a region that is estimated to be on the order 1 mm from the crack tip, and having an opening of tens of microns (Wei et al., 1984b). The problems associated with the characterization of crack tip chemistry are considered here, and those with the measurement of bare surface reaction kinetics are discussed in the following subsection.

Prediction of the crack-tip electrochemical conditions as a function of crack geometry, bulk solution chemistry and surface electrode potential requires solving the set of transport equations, eqs. (3) to (6), which are coupled with those for the surface reactions (Turnbull, 1984; Wei et al., 1984b). The transport of a species in an electrolyte occurs by migration, diffusion or convection, or by any combination of the three processes. Migration refers to the transport of ionic species under an electrical potential gradient; diffusion, due to a concentration gradient; and convection, by fluid/electrolyte flow. The flux ($\mathbf{J}_i$) of the ith species in the electrolyte is given by eq. (3).

$$\mathbf{J}_i = - z_i u_i F C_i \nabla\Phi - D_i \nabla C_i + C_i \mathbf{v} \qquad (3)$$

In eq. (3), z_i is the charge; u_i is the the mobility of ions; F is the Faraday constant; C_i is the concentration of the ith species; Φ is the electrode potential; D_i is the diffusion coefficient; and $\mathbf{v}$ is the fluid velocity.

The conservation of mass of the ith species is given by eq. (4).

$$\partial C_i/\partial t = - \nabla \cdot \mathbf{J}_i + R_i \qquad (4)$$

$\partial C_i/\partial t$ is the rate of change of concentration with time, and R_i is the rate of production (or consumption) of the i^{th} species. In addition, the solution is electrically neutral to a good approximation. Charge neutrality is expressed by eq. (5).

$$\sum_i z_i C_i = 0 \tag{5}$$

The current density in the electrolyte is given by the motion of charged particles (anions and cations) as follows:

$$\mathbf{i} = F \sum_i z_i \mathbf{J}_i \tag{6}$$

Equations (3) to (6) provide a consistent description of the transport processes in an electrolyte (Turnbull, 1984).

Solution of the coupled transport and reaction equations is very difficult, and has been considered in terms of specific models. The various models have been summarized by Wei et al., (1984b). Most of these models were formulated on the basis of one-dimensional transport and utilized a rectangular crack (i.e., one with a constant opening), and considered only one or, at most, two of three possible transport mechanisms. The assumed reactions at the crack tip and on the crack "walls" included single anodic and cathodic reactions, and simultaneous multi-electrode reactions of anode and cathode, but were based by and large on steady-state kinetics (presumably for already "filmed" surfaces). The use of steady-state kinetics can be seriously questioned. Because the environment of interest is localized to a constricted region within about 1 mm from the crack tip, direct experimental measurements are extremely difficult and may not be possible.

Bare Surface Reactions

To identify the relationship between electrochemical reactions and environmentally assisted crack growth in high strength steels, a 3-electrode in situ fracture method was developed for measuring the kinetics of transient electrochemical reactions for a bare metal surface which is coupled to a filmed (or oxidized) surface of the same material under open circuit conditions (Alavi et al., 1987). While the technique has been used successfully to demonstrate correlations between electrochemical reaction kinetics and crack growth response of high-strength steels under both sustained and fatigue loads for free corrosion, it was recognized that the 3-electrode corrosion cell is not a correct analogue for the crack tip when an external potential is imposed (Thomas et al., 1986; Wei and Alavi, 1988).

In essence, the crack tip must be viewed as a composite electrode, which consists of the bare surfaces at the very tip and filmed (or oxidized) surfaces along the crack flanks (Wei and Alavi, 1988). These portions of the crack surfaces are linked electrically through the specimen. In potentiostatically controlled tests, this composite electrode is polarized with respect to an appropriate reference electrode by means of a separate counter electrode; both located outside of the crack. Thus, the appropriate analogue would be a 4-electrode cell, consisting of a bare surface, a filmed or "oxidized" surface, and external counter and reference electrodes. A schematic illustration of an electrochemical analogue of the crack-tip corrosion cell is shown in Fig. 1, and a schematic diagram of the 4-electrode arrangement is given in Fig. 2 (Wei and Alavi, 1988). The salt bridge is used to

simulate the conductive path along the crack. An auxiliary reference electrode has been included so that the cell potential can be monitored independently.

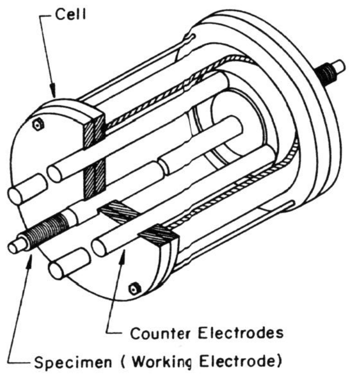

Fig. 1. Schematic illustration of an electrochemical analogue of the crack-tip corrosion cell.

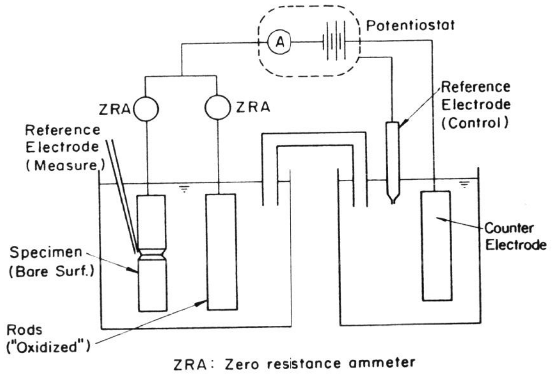

Fig. 2. Schematic diagram of the 4-electrode corrosion cell.

Measurements are carried out by first polarizing the composite electrode (consisting of the fully isolated specimen and the oxidized rods) to the desired potential, and then breaking the specimen in tension to expose fresh fracture surfaces to the electrolyte. The current and potential transients following fracture are recorded, and the amount of charge transferred is determined from the current transient by numerical integration. Detailed experimental procedures are given by Wei and Alavi (1988).

EXPERIMENTAL OBSERVATIONS

Measurements of the rate of reactions with bare steel surfaces have been made and have been correlated with crack growth data in deaerated sodium chloride, sodium sulfate and sodium carbonate-bicarbonate solutions for high strength steels and for a 304 stainless steel (Allison, 1988; Alavi et al., 1987; Alavi and Wei, 1987; Chu, 1987; Thomas et al., 1986; Wei and Alavi, 1988). Independent measurements of the influences of salt bridge resistance, solution pH and ionic concentration on electrode potential have also been made (Xu and Wei, 1988). Although incomplete, these data now provide credible information for understanding the influences of a number of key parameters on crack growth. These results are summarized in the following subsection, and the influences of specific parameters are considered in a subsequent section.

Electrochemical Reactions

Measurements of the rate of reactions with bare steel surfaces have been made. Typical potential and current transients following specimen fracture are shown in Figs. 3 and 4, respectively, for an AISI 4340 steel in deaerated 0.15N Na_2SO_4 solution (pH = 6.8) at room temperature (Wei and Alavi, 1988). Charge transfer, derived from such current transients, are shown in Fig. 5 as a function of the cell ("crack-tip") electrode potential. Independent measurements showed that the bare surface potential (immediately following fracture) had reached -975 mV SCE, which is well below (more cathodic than) the free corrosion potential of -780 mV SCE. Because of potential drop along the salt bridge (or along the crack), the reactions within the cell cannot proceed under potentiostatic control. The mixed potential within the corrosion cell decreased abruptly upon specimen fracture and recovered rapidly to its initial value. The measured decrease in mixed potential, however, was only on the order of 30 mV (Fig. 3).

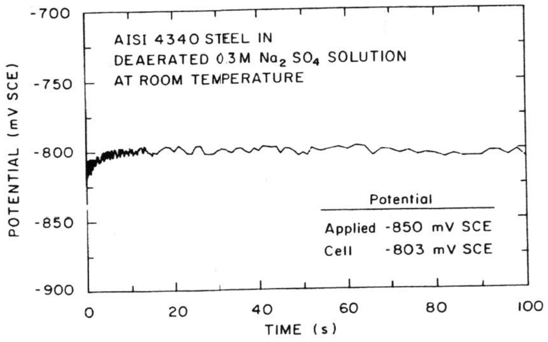

Fig. 3. Typical cell-potential transient following specimen fracture under an externally applied cathodic potential (Wei and Alavi, 1988).

The results showed that the reactions are localized, and are those that bring the bare surface (crack tip) to the same oxidation state as that of the "filmed" surface (crack flank). These equilibration reactions are driven by the potential difference between the two surfaces, which tended to enhance anodic reactions at the bare surface and cathodic reactions at the filmed surface. The amount of charge transferred during the equilibration reactions reflects the influence of the local potential (i.e., of the oxidation state of the "filmed" surface). Because of potential (IR) drop along the salt bridge, the mixed potential within the corrosion cell (or at the crack tip) tended to differ from the applied potential and to remain close to the free corrosion potential (see Fig. 3, and Doig and Flewitt, 1978). At higher temperatures and for low conductivity electrolytes, the IR drop is expected to keep the cell potential essentially at the free corrosion potential (Doig and Flewitt, 1978; Wei and Alavi, 1988).

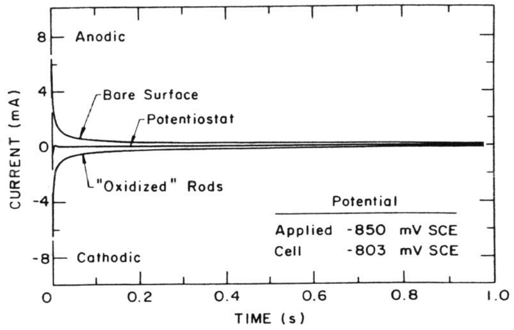

Fig. 4. Typical current transient following specimen fracture in a deaerated 0.15N Na_2SO_4 solution under an externally applied potential at 295 K (Wei and Alavi, 1988).

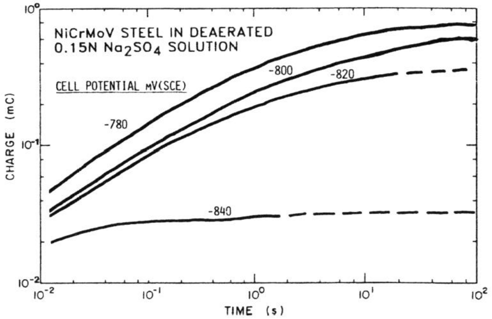

Fig. 5. Amount of charge transferred by the reactions of bare AISI 4340 steel surface with deaerated 0.15N Na_2SO_4 solution as a function of electrode potential at 295 K (Wei and Alavi, 1988).

Comparable results have been obtained on high strength steels in deaerated sodium chloride, sodium sulfate and sodium carbonate-bicarbonate solutions and on a 304 stainless steel in the chloride and sulfate solutions (Allison, 1988; Alavi and Wei, 1987; Chu, 1987).

Corrosion Fatigue Crack Growth

Preliminary examinations of the connection between the kinetics of electrochemical reactions and corrosion fatigue crack growth have been made by directly comparing the cycle-dependent component of corrosion fatigue crack growth rate with the amount of charge transferred in the electrochemical reaction experiments through eq. (1). Good correlation between the electrochemical and fatigue crack growth data has been shown by Thomas et al. (1986) for X-70, HY-80 and HY-130 steels in sodium chloride solutions, and by Nakai et al. (1986) for a NiCrMoV steel in a sodium sulfate solution.

Additional experiments have been carried out, and the data are shown in Figs. 6 and 7. Figure 6 shows a comparison of the charge transfer data, obtained from the transient reaction currents on AISI 4340 steel, with the corrosion fatigue crack growth data for a NiCrMoV steel in deaerated 0.15N Na_2SO_4 solution as a function of temperature and applied potential. A direct comparison of charge transfer data in deaerated 0.6N NaCl and 1N Na_2CO_3+1N $NaHCO_3$ solutions, at room temperature, with the companion corrosion fatigue crack growth data in X-70 steel, is given in Fig. 7. These results again show the good correlation between charge transfer and corrosion fatigue crack growth data. The fatigue data in Fig. 6 suggest that the crack-tip potential remained close to the free corrosion potential, even at an applied potential of -1000 mV(SCE). This observation is consistent with the electrochemical measurements (see Fig. 5). These comparisons provide support of electrochemical reaction control of corrosion fatigue crack growth in steels in aqueous environments, and demonstrate the usefulness of the 4-electrode corrosion cell as an analogue of the crack tip.

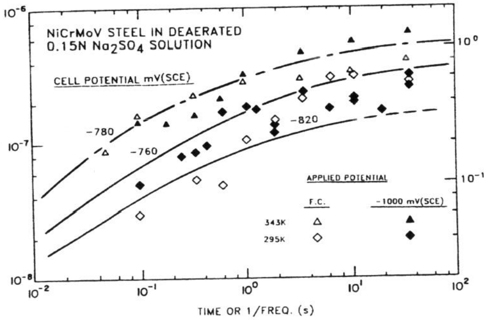

Fig. 6. Correlation of corrosion fatigue crack growth rate data of a NiCrMoV steel with charge transfer data (solid lines) in 0.15N Na_2SO_4 solution. (After Nakai et al., 1986).

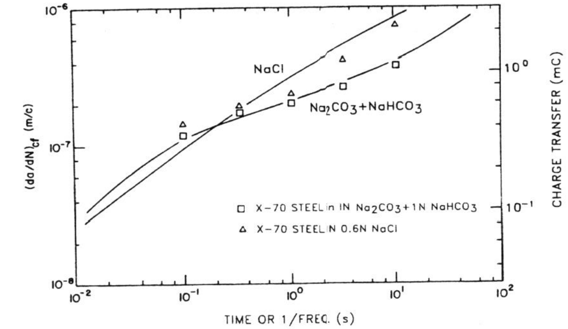

Fig. 7. Comparison of charge transfer and corrosion fatigue crack growth rate data in deaerated 0.6N NaCl and 1N Na_2CO_3+1N $NaHCO_3$ solutions at room temperature.

Sustained-Load Crack Growth

Crack growth experiments on AISI 4130 and AISI 4340 steels, in deaerated distilled water, 0.6N NaCl solution and 1N Na_2CO_3 + 1N $NaHCO_3$ solution, were carried out to examine the role of different anions (namely, chloride and carbonate-bicarbonate ions) in affecting crack growth rates (Chu, 1987). Distilled water was used as a reference. The results showed that the K-independent Stage II crack growth rates in AISI 4340 steel were generally about 3 to 10 times higher than those in AISI 4130 steel in each of the electrolytes (compare Figs. 8 and 9). The rates in distilled water were faster than those in the sodium chloride solution, which in turn were faster than those in the carbonate-bicarbonate solution, with the exception of AISI 4340 steel. For this steel, the crack growth rates in the carbonate-bicarbonate solution exhibited two plateaus (Fig. 9). The plateau rates at the lower K levels were consistent with the effect of carbonate-bicarbonate ions on crack growth in the AISI 4130 steel. But, the growth rates at the higher K levels were comparable to those for distilled water. This two-level response depended on ion concentration (Fig. 10), and suggested transport control which limits the access of carbonate-bicarbonate ions to the crack tip. The temperature dependence for crack growth was found to be essentially the same in all of the environments, with an apparent activation energy of about 35 kJ/mol (Table 1). The temperature dependence and the relative growth rates for each steel correlated well with the temperature dependence and the kinetics for the electrochemical reactions, and are identical to those for corrosion fatigue crack growth.

These experiments provided support for electrochemical reaction control of sustained-load crack growth (Chu, 1987). Crack growth is believed to be controlled by the rate of anodic reactions of the electrolyte with the bare steel surfaces, which are moderated by the added anions in solution. The apparent transport control in the carbonate-bicarbonate solution at the faster growth rates (i.e., at greater than 10^{-7} m/s) has been tentatively attributed to the net repulsion of anions away from the crack tip by the very negative potential of the bare crack tip surfaces. This transport control may extend to the chloride solution and to other electrolytes. The differences in crack growth rates between the two steels in the various environments appear to be related principally to carbon level, and are consistent with the estimated differences in trap density at the prior-austenite grain boundaries.

Table 1. APPARENT ACTIVATION ENERGY (kJ/mol)

Environment	Crack Growth 4130 Steel	 4340 Steel	Chemical/ Electrochemical Reactions
H_2O	27±11*	37±5	36±28(vapor)
NaCl	34±7	35±9	47±6
$Na_2CO_3+NaHCO_3$	40±13	44±3	28±7
Pooled	34±4	38±3	34±4

(After Chu, 1987;Simmons et al., 1978)
*Estimated 95% confidence intervals.

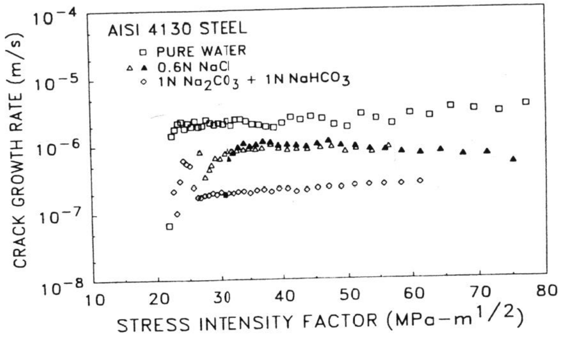

Fig. 8. A comparison of the kinetics of sustained-load crack growth for AISI 4130 steel in aqueous environments at 294 K (Chu, 1987).

Influence of Electrochemical Variables on Crack-Tip Potential

It is now clear that the reactions that control crack growth are those associated with the equilibration of the bare crack tip surfaces against the "oxidized" crack flank (Wei and Alavi, 1988). The crack growth response is, therefore, strongly influenced by the state of the crack flank, which may be characterized by its electrode potential near the crack tip. The crack tip potential is influenced by the external polarization, solution resistance

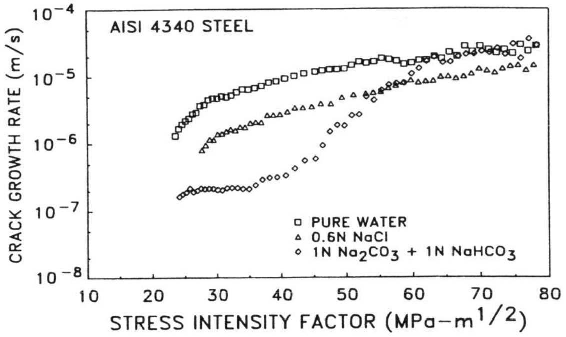

Fig. 9. A comparison of the kinetics of sustained-load crack growth for AISI 4340 steel in aqueous environments at 294 K (Chu, 1987).

along the crack, and a range of electrochemical variables. To assess the influences of some of the key variables, a simulation cell was used (Xu and Wei, 1988). It is made of two separate cells, with the working electrode (representing the crack flank) in one cell and the counter and reference electrodes in another. The two cells are connected with a salt bridge to simulate the conduction path along the crack, and its resistance can be easily adjusted through the use of a stopcock.

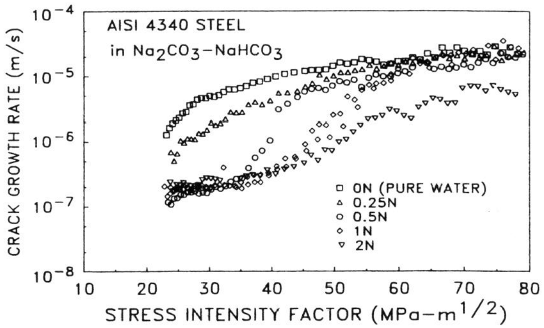

Fig. 10. A comparison of the kinetics of sustained-load crack growth for AISI 4340 steel in the influence of concentration of carbonate-bicarbonate solution (0N, 0.25N+0.25N, 0.5N+0.5N, 1N+1N and 2N+2N) at 294 K (Chu, 1987).

Experiments were carried out in deaerated 0.6N NaCl solution at room temperature, using an AISI 4340 steel as the working electrode. The effect of salt bridge resistance on the electrode potential, at pH = 6.3, was examined as a function of the externally applied potential (from -5,000 to +5,000 mV

SCE), and is shown in Fig. 11. The change in electrode potential (E_{int}) with externally applied potential (E_{ext}) reflected the polarization response of the working electrode, and is consistent with the results reported by Turnbull and Ferris (1987).

The influence of pH on the free corrosion potential and on the electrode potential (for a given external potential and salt bridge resistance) is illustrated in Fig. 12. The effect of pH on solution conductivity is shown in Fig. 13. From these figures, it is clear that both the free corrosion potential and the electrode potential under a given externally applied potential varied with pH, and were relatively constant from pH values of about 3 to 10. The ability to drive E_{int} away from the free corrosion potential was poor at the very acidic and very basic pH values. Over the intermediate range of pH values (3 to 10), it was easier to impose a cathodic polarization at low values of pH, and an anodic polarization at high pH values. It is to be recognized that the salt bridge resistance was maintained constant for these measurements. In reality, the results would be modified by the change in solution conductivity with pH. With increasing temperature and the concomitant increase in reaction rates, the ability to drive E_{int} away from the free corrosion potential is expected to be further impaired.

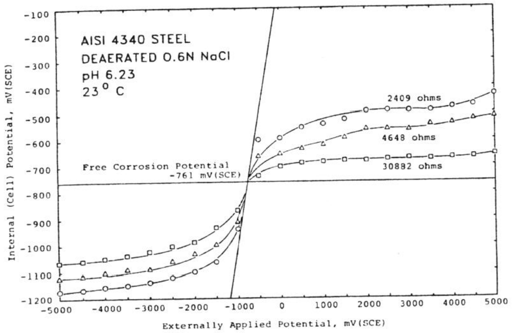

Fig. 11. The effect of salt bridge resistance on the electrode potential (E_{int}) as a function of the externally applied potential (E_{ext}) in deaerated 0.6N NaCl solution (pH = 6.3) at room temperature (Xu and Wei, 1988).

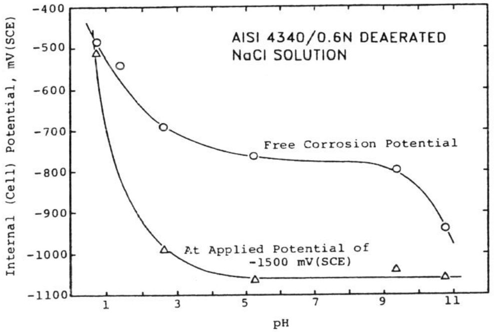

Fig. 12. The influence of pH on the free corrosion potential and on the electrode potential (for an externally applied potential of -1,500 mV(SCE) and salt bridge resistance of 2,500 ohms) of AISI 4340 steel in deaerated 0.6N NaCl solution at room temperature (Xu and Wei, 1988).

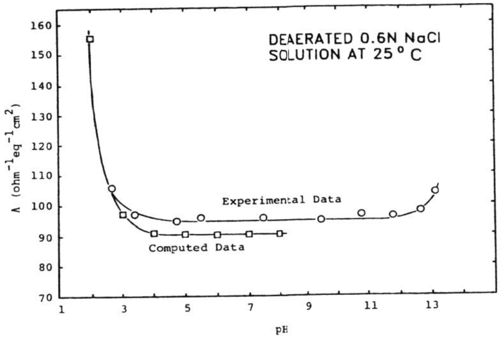

Fig. 13. The effect of pH on the conductivity of deaerated 0.6N NaCl solution at room temperature.

The influence of ferrous ion concentration was also examined by adding $FeCl_2$ to the 0.6N NaCl solution. Data obtained at pH = 3.4 to 3.6 suggested that higher currents were needed to achieve a prescribed electrode potential as $FeCl_2$ concentration increased from 0 to 0.05M.

These results suggest that the crack-tip electrode potential could be very different from the externally imposed potential during stress corrosion cracking and corrosion fatigue (cf, Doig and Flewitt, 1978; Turnbull and Ferris, 1987). The actual value will depend on a range of variables, and may remain close to the free corrosion potential. Care must be exercised, therefore, in the interpretation and extrapolation of test results. The influences of pH and ion concentration on the rates of reaction with bare steel surfaces are not understood, and must be examined thoroughly.

FACTORS THAT INFLUENCE CRACK GROWTH

Based on the foregoing discussions and the limited experimental data, some observations can be made on the influences of several key variables on crack growth in ferrous alloys that are exposed to aqueous environments. These variables include temperature, cyclic-load frequency, electrode potential, solution pH, ionic species, and crack geometry. It is recognized that some of the observations cannot be very specific, and may change with time. Furthermore, many other variables may be of importance. Their considerations, however, will have to be left to future investigators. It must be emphasized that the following observations deal principally with crack growth, and should not be extend to crack initiation without careful consideration.

Temperature

Temperature is the most important variable in affecting environmentally assisted crack growth. Through its influence on the kinetics of chemical/ electrochemical reactions, it increases the rate of crack growth under sustained loading (Chu, 1987; Wei and Gao, 1984; Wei and Simmons, 1979). The influence of temperature on corrosion fatigue crack growth is manifested through a coupling with frequency. The increase in reaction kinetics with increasing temperature is reflected principally through a shift in the crack growth response into a higher frequency domain (see, for example, Fig. 6).

The effect of temperature on crack growth may be exerted indirectly through changes in the electrochemical conditions at the crack tip. For example, the increased reaction rates at higher temperatures make it increasingly difficult to polarize the crack tip away from the free corrosion potential. Changes in electrolyte composition and solution pH can also occur as a result of changes in the rates of reactions and transport processes, and in reaction mechanisms. These changes, or lack of changes, are then reflected in the crack growth rates and cracking responses. Detailed investigations are needed to develop improved understanding of these more "subtle" influences on the cracking response.

Frequency

Frequency plays a significant role in influencing corrosion fatigue crack growth since it defines the available time for reactions during each loading cycle and, through its influence on convection, the crack-tip chemistry. In conjunction with the kinetics of reactions, it determines the extent of reaction and the amount of hydrogen production during each cycle of loading, and thereby establishes the extent of crack enhancement each cycle. At very low frequencies, where the time is more than sufficient to complete the equilibration reactions at the crack tip, no further increase in crack growth rates is expected. With increasing frequency, the convective contribution to ionic transport increases and can significantly change the crack tip chemistry. At sufficiently high frequencies, cavitation may also occur and thereby drastically alter the nature of the problem.

As indicated in the foregoing subsection, the effect of frequency is coupled with that of temperature through the changes in reaction kinetics, and with that of transport to determine crack tip chemistry. Because of these coupling, frequency and temperature serve as important probes for developing an understanding of environmentally assisted crack growth.

Electrode Potential

Electrode potential is known to be an important factor in influencing corrosion, and is expected to significantly affect crack initiation. Its impact on crack growth, however, is limited by the ability to alter the potential at the crack tip. Figures 5 and 6 suggest that the kinetics and extent of reactions are influenced by the local electrode potential. Through this influence, crack growth rates and cracking response can be altered. Because electrode potential at the crack tip can depend on variables (such as, solution composition and pH, solution conductivity or potential drop along the crack, and temperature), its influence on crack growth would depend on the material and electrolyte and cannot be inferred simply from the externally imposed potential (Allison, 1988; Shim, 1984; Shim et al., 1988; Wei and Alavi, 1988).

Solution pH

Solution pH, like electrode potential, is known to influence corrosion and is expected, therefore, to affect crack initiation. Data on 304 stainless steel in deaerated sodium chloride and sodium sulfate solutions, however, indicate that the kinetics of equilibration reactions on bare surfaces are not significantly changed over a broad range of pH, from 3 to 10 (Alavi and Wei, 1987). Data for the sodium chloride solutions are shown in Fig. 14. These results suggest that there may be very little influence of pH on crack growth rates in certain systems. These data, however, are quite limited. Additional investigations are required before definitive conclusions can be made for a broader range of materials and environments.

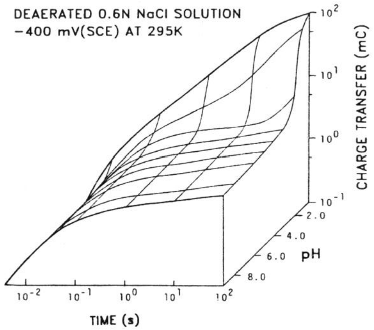

Fig. 14. The influence of solution pH on charge transfer for 304 stainless steel in deaerated 0.6N NaCl solution at -400 mV (SCE) and 295 K (Alavi and Wei, 1987).

Ionic Species

Corrosion fatigue and sustained-load crack growth data have clearly shown that different anions (for example, chloride and carbonate-bicarbonate) in solution alter the reaction kinetics and, hence, the rate of crack growth and cracking response (see Figs. 7 to 9). Influence of ionic transport on crack growth is also seen (see Fig. 10); this influence appears to be dependent on the nature of the ionic species. The results suggest that both the bare surface reaction kinetics and crack growth rates are retarded by the addition of anions. These findings are internally consistent, but run counter to those for corrosion and crack initiation. Further clarification of this important difference is needed.

Crack Geometry/Crack Closure

Crack geometry and crack closure phenomenon can alter both the chemical conditions within the crack and the effective mechanical driving force. Under certain electrochemical conditions, insoluble corrosion products or hydrogen bubbles can form within the crack. These products of reactions can impede the various transport processes and affect current flow (increasing potential drop) along the crack, and thus alter the electrochemical conditions at the crack tip. The insoluble corrosion products can act as a wedge and reduce the effective driving force for corrosion fatigue crack growth. This effect is especially pronounced near the so-called threshold region, and can lead to apparent arrest in crack growth. On the other hand, in the case of stress corrosion cracking, volume expansion associated with corrosion product formation (or "swelling") can itself provide the crack driving force and sustain crack growth in the absence of external loading.

ENGINEERING IMPLICATIONS AND FUTURE RESEARCH

It is clear that environmentally assisted crack growth of ferrous alloys (of any alloy, for that matter) in aqueous environments is quite complex. Understanding of chemical control crack growth now provides a useful basis for extrapolating data for design applications. Crack growth data may be extrapolated "reliably" to other temperatures and frequencies through the measurement of chemical/electrochemical reaction kinetics, vis-à-vis, extensive mechanical testing. On the other hand, designers must recognize that cracking response for different materials in a variety of environments can be different. Apparently "immunity" under one set of conditions does not ensure adequate performance under another set of conditions, because changes in underlying reaction kinetics can result in a shift in the region of cracking susceptibility. Corrosion products can significantly alter environmentally assisted crack growth response. Their presence may be beneficial under certain circumstances (e.g., for near-threshold fatigue crack growth), and can be detrimental in others (e.g., for stress corrosion cracking). The designers should be wary and not be taken by surprise.

The work summarized here represents only the beginning. Environmentally assisted crack growth reflects a material's response to stress and the concomitant interactions with the environment. Much more work is needed to address (i) the mechanisms and kinetics of reactions of the material with the chemical environment, (ii) quantitative characterizations of the crack tip environment, and (iii) the interactions of stress and environment with the microstructure which lead to cracking. A framework and a workable approach have been established as a scientific basis for understanding. Basic understanding that emerges from the ensuing studies must be transformed into tools that can be used in design.

SUMMARY

Based on available experimental results and models, it is clear that a formalized basis for understanding environmentally assisted crack growth for ferrous alloys in aqueous environments has been established. Crack growth results from embrittlement by hydrogen that is produced by the reactions of the environment with newly created surfaces at the crack tip. Crack growth rate under sustained loading is proportional to the effective rate of reactions, and that for corrosion fatigue is proportional to the extent of reaction (or the charge transferred) per cycle. The reactions are localized to the crack tip region and reflect equilibration between the bare surfaces created by crack advance and the filmed (oxidized) crack flank.

Understanding of crack growth response in terms of the controlling chemical and electrochemical processes is beginning to emerge through the coupling of chemical and crack growth measurements with quantitative modeling. The use of fracture mechanics methodology and the development of electrochemical analogues have contributed significantly to this evolution in understanding. A more complete understanding of crack growth in aqueous environments, however, requires detailed knowledge of the mechanisms and kinetics of reactions, particularly with bare surfaces. It is necessary also to quantify the transport processes and their interplay with chemical and electrochemical reactions to define the crack tip environment. More sophisticated chemical and analytical techniques will need to be brought to bear.

A number of key variables have been identified. These variables include temperature, cyclic-load frequency, electrode potential, solution pH, and ionic species. Some of the effects have been examined. Because of the complexity of the interactions, however, generalizations cannot be made at this time. On the other hand, the results do suggest that some long held ideas in corrosion may not be directly applicable to crack growth; for example, the need for specific ions and critical potential ranges to cause cracking. Care and judgement must be exercised in using this information in design. Concepts based on crack initiation do not necessarily hold true for crack growth, or vice versa.

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