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STRESS CORROSION CRACK PROPAGATION

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ABSTRACT

Stress corrosion crack propagation in a susceptible alloy occurs as a result of a series of complex interactions between a deforming alloy surface that is mostly covered with a film and the environment in the region of the crack tip. The deformation at the crack tip enables reaction to occur between bare surface alloy and the environment, a process that will result frequently both in metal dissolution and hydrogen absorption. One or both of these events is responsible for crack propagation. Two kinetic processes control the crack propagation rate: (i) the deformation rate at the crack tip which will be determined by mechanical and metallurgical factors, including the testing arrangement, and (ii) the repassivation and dissolution characteristics of the metal surface and electrolyte. The corrosion current flowing results directly from the interaction of the two processes and increases logarithmically with increase in deformation rate. The interdependence of mechanical end electrochemical reactions is emphasized by the observation that the maximum stress corrosion velocity may depend either on diffusion within the testing environment, or on the creep characteristics of the alloy. Such general concepts are applicable both to high strength alloys, e.g., Al and Ti alloys, and to the lower strength alloys, e.g., 18Cr - 10Ni steels and 70Cu - 30Zn brasses. Examples of repassivation kinetics, crack velocity measurements and fractograhpic investigations which illustrate these concepts are drawn from these and other alloy systems.

INTRODUCTION

Stress corrosion crack propagation can occur in a wide variety of alloys exposed to numerous environments, both aqueous and non-aqueous. The whole subject of stress corrosion cracking has been the subject of many investigations and many conferences [1 - 5]. It occupies a prominent place in the corrosion literature. Cases of stress corrosion failure are observed in all the major alloy systems. While in most practical examples failures occur in water or steam contaminated with chloride ions, failures can occur in high purity water, e.g., Inconel [6], and in many other environments, e.g., organic liquids [7], gases [8], molten salts [9], liquid metals [10], and solid metals [11]. It is not always clear whether failures in alloys in so many different environments arise from as many different causes but it is clear that there is no one common mechanism of environmentally-assisted cracking. In recent years ostensibly similar environmental cracking phenomena have been observed in many non-metallic materials, e.g., glasses [12], ceramics [13] and organic polymers [14]. For the sake of both brevity and clarity, in this paper it is intended to confine mechanistic considerations to failures that can occur in alloys

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in either aqueous or methanolic environments. It is intended also that this paper succeed the previous Plenary Lecture of the 3rd Conference [15] which reviewed much of the previous literature.

Stress corrosion cracking in alloys can be considered as the most localized form of corrosion. Why the corrosion is so localized is not fully understood. The earliest suggestion [16], that there is a pre-existing path for preferential corrosion, is the simplest and does appear to be applicable to certain cases of intergranular cracking. For 70Cu - 30Zn brass in 15N NH_3 solutions [17], mild steels in NO_3^- solutions [18] and α Ti alloys in CH_3OH/HCl solutions [19], for example, preferential intergranular corrosion occurs, to some extent at least, in unstressed specimens under open circuit conditions and in each case it is stimulated by anodic polarization. Why such preferential corrosion takes place has not been established but it is generally assumed to result from the segregation of unspecified impurities to the grain boundaries. Where the corrosion of the grain boundaries in unstressed specimens is only slight it appears that one function of the stress is to break repeatedly the corrosion films that form and reduce corrosion by a blocking action. The degree of protection afforded by such films appears to vary even for a single corrosion product and is dependent upon the composition of the environment in which it forms. Cu_2O formed in neutral ammoniacal solutions, for example, appears to be more protective than Cu_2O formed in highly alkaline solutions [20]. In this case the difference may arise from differences in film porosity between the Cu_2O formed at the two pH values, although possible additional morphological and compositional factors must not be ignored. Even in such simple examples of cracking a pre-existing path is not the only important part of the cracking mechanism.

For other examples of cracking, e.g., intergranular cracking of high strength steels [21] and the transgranular cracking of austenitic stainless steels [22], α brasses [23] and α Ti alloys [24], no such pre-existing path exists. No preferential corrosion occurs in unstressed specimens. Explanations of susceptibility have therefore centered around the concept that the dislocations created by the action of the stress provide a reactive path [25, 26], possibly for reasons centering around the highly localized, solute enrichment at dislocations. Cracking on {111} planes in austenitic stainless steels [27] and α brasses [28] has been observed, which is consistent with a simple picture of preferential attack on pile-ups of dislocations but cracking on {210} [29] and {100} [30] planes in austenitic steels has not been explained. Details of fracture mechanisms on an atomistic level are not available for such systems.

The cracking mechanism may not be due to either a pre-existing path or a path continually created by dislocation movement but from the local absorption of cathodically discharged hydrogen. It appears to be responsible for cracking in high strength steels [21] and transgranular cleavage cracking in α Ti alloys [24], and recent work has indicated a critical role for hydrogen in Mg alloys [31] and Al alloys [32]. Where H is responsible for inducing crack growth by cleavage, the localized aspect of the corrosion process may not be so necessary. The corrosion may be quite widespread, as in maraging steels [33], with the local stress causing the hydrogen-charged lattice to break.

In the elucidation of stress corrosion mechanisms the fine detail of a particular sequence of events remains to be determined, as these brief introductory remarks have indicated. On a somewhat higher scale, however, a general picture has emerged which appears to be near to physical reality.

In the Sections below this general picture is described, then the two important aspects are considered separately. Finally, some detailed specific points about individual systems are discussed and an attempt is made to focus attention upon important questions that need to be answered.

THE GENERAL PICTURE

The complexity of cracking mechanisms has long been recognized. Both electrochemical and metallurgical variables are important but in complicated interdependent ways. In recent years, in order to attempt a conceptual explanation, much attention has been focused upon the sequence of events occurring at the tip of a propagating crack. A simple, rather general, schematic model has been put forward [34] which represents an extremely simple picture of what is a very complicated series of events, yet which leads to experiments which provide some insight into cracking mechanisms.

The simple description of the events at the tip of a propagating crack, drawn schematically in Figure 1, has been described previously [34]. In a quite general way it is envisaged that at the tip of a crack, plastic deformation occurs. The plastic deformation results in the creation of a plastic zone which will increase or decrease in size or remain of a constant size, depending upon the experimental arrangement. The necessity for yielding to take place before crack propagation can occur has been shown very clearly by experiments on single crystals [35, 36]. During crack propagation the volume of plastically deforming metal ahead of the crack tip results in a continually changing configuration of the tip surface. This is caused by creep processes appropriate to the temperature of the test and can be described by a tensile strain-rate at the crack tip. It serves to cause the continual creation of fresh metal surface. On many alloys, e.g., stainless steels, Al and Ti alloys, the metal surface is covered by a passive film. In other alloys, e.g., Fe and Cu alloys, the film cannot be so described but the film forming on these surfaces perform much the same function as the passive films: they serve to reduce the rate of reaction from what it would be between the environment and the bare surface created by the local deformation. Such events of film fracture and repair are depicted schematically in Figure 1 by an emergent slip step fracturing a thin film, although it must be emphasized that deformation may be more complicated than is represented by a single emergent step. In a general sense, any process that creates fresh metal area can be included. The failure by shear of non-stress corroded metal ligaments remaining in the cracking plane [22] or the rapid cleavage of a section [19] would be examples of such processes. The morphological aspects of fracture may be of considerable importance. It might be supposed, for example, that the larger the cleavage length that is created during fracture, the more difficult it would be for that part of the surface to repassivate since the whole dynamic process of crack propagation consists conceptually of fresh metal area being created more rapidly than it can be repassivated. The fresh metal surface generated will exhibit at least one of two possible reactions: (i) metal dissolution, and (ii) hydrogen absorption. Both of these reactions are important in stress corrosion crack propagation in different alloy systems. The occurrence of either of these reactions, and the rates of each, will be determined by the value of the electrochemical potential of the bare metal surface. The rate of either reaction, and possibly the ratio of the two, will change as film growth occurs on the metal surface.

The repassivation process is of primary importance since the amount of damage caused by corrosion, measurable as the current flowing over a period of time, constituting a coulombic flow [37], will be dependent upon the time taken for the film to repair. If the time is short then the number of coulombs passing may be insufficient to cause a further increment of crack growth. Crack arrest will then occur. If the time is too long then the corrosion attack will occur on too broad a front, corresponding to a number of coulombs in excess of that necessary for crack growth. The crack will become broad, blunted and then a fissure, an elongated pit, and no longer will be a crack. If the repassivation time is infinitely long then pitting will ensue [38]. For stress corrosion cracking to occur as a result of dissolution it can be argued that the repassivation time must be of a critical length, neither too short nor too long. If the main cause of crack propagation is hydrogen absorption then the length of the repassivation time need only be above a certain minimum value, corresponding to the time required for the metal to absorb sufficient hydrogen to become embrittled. The situation will depend to some extent upon both the hydrogen permeability of the forming film and its conduction properties since the latter will control the discharge of hydrogen atoms on the film surface. Allowing for these different points, which must all be considered, it can be expected that too rapid a repassivation will still cause crack arrest because insufficient hydrogen has been absorbed.

This simple description of the events at the tip of a propagating crack provides an analysis that the rate of creation of fresh metal surface area and the rate of repassivation are coupled together in a stress corrosion crack propagation process. The creation of fresh metal surface is related to the tensile strain-rate at the surface which will be both a mechanical and metallurgical variable. The repassivation rate is an electrochemical variable [39] but it may be affected by metallurgical variations such as surface composition, cleavage step length (as already indicated) etc. It can equally be argued that electrochemical events will affect the creation of fresh metal surface. The removal of atoms by dissolution, for example, may lead to a higher localized deformation rate as a result of easier dislocation movement. Thus it must be borne in mind that the separation of the mechanical and metallurgical factors from the electrochemical factors is convenient for examining individual variables of the cracking process but it may not always give an unequivocal answer upon which to make mechanistic analyses. In some examples of stress corrosion cracking, at least, the phenomenon is a conjoint one. The creep behaviour of an undissolving metal and the repassivation behaviour of a non-creeping alloy may each be different from that exhibited under crack propagation conditions. While the extent of such differences, or even their existence, cannot be gauged, it is useful to consider the two behaviours separately and that is what is done below.

REPASSIVATION AND STRAIN-RATE EFFECTS

A clear example [40] of the role of repassivation kinetics is shown in Figure 2 and is very similar to previously reported work [15]. Tensile specimens of a Ti-O alloy were strained to failure at different crosshead speeds on an Instron Tensile Testing Machine. In the aqueous solution in which titanium is passive cracking occurs over a narrow range of crosshead speeds because at low values repassivation is possible, (Curve A). In the methanolic solution, in which titanium corrodes, cracking occurs over a much wider range of crosshead speeds because no passivation is possible, (Curve B). The exact variation of such results will be

affected by both metallurgical and electrochemical factors.

The rate at which fresh metal area is created will be determined by the effective surface creep rate of the alloy which, in the simplest analysis, must be assumed to either equal to or directly proportional to the bulk creep rate. The observed changes in crack velocity with change in the stress intensity factor, K, can be explained by the effect of K upon the effective strain-rate at the crack tip. There is much direct evidence that the strain-rate at the tip of a crack is the main mechanical variable controlling crack velocity. A number of examples can be cited. In austenitic stainless steels in $MgCl_2$ solutions at 154-60°C it has been shown [41] that constant stress conditions result in a constant crack velocity. Constant K specimens of Al alloys give constant crack velocities [42]. It has been shown [43] for Cu-Be alloys that both the crack velocity and the associated fractography are dependent not upon the absolute value of K but upon the rate at which K is changing, $\dot{K}$. Results on steel in HCO_3^-/CO_3^{2-} solutions [44] and Mg-Al alloys in Cl^-/CrO_4^{2-} solutions [45] give the same result: cracking is strain-rate dependent. This is the main mechanical factor that controls crack velocity.

The relationship between K and log V has been reported for glasses, metals and polymethacrylate, as previously summarized [15]. Similar results on Al_2O_3 in H_2O have been reported [46]. A schematic diagram is shown in Figure 3. Explanations of why K should affect the chemical reaction responsible for crack propagation have centered upon the crack sharpening criterion of Charles and Hillig [47], the induced diffusion of species as described by Liu [48] and the creation of reactive sites, stemming perhaps from the work of Hoar [49]. It is simpler and probably truer to consider there is a general explanation: namely that K is responsible for its effect upon velocity by its effect upon the crack tip strain-rate. Such an effect has been demonstrated for a Ti alloy [50], α brass [28, 51] and an austenitic stainless steel [52] as well as for the examples already described [41 - 45].

In a Ti-O alloy, the crack velocity in a CH_3OH/HCl solution depends upon the applied crosshead speed as shown in Figure 4 [40]. The velocity for each point was measured over 4 or 5 successive 2 and 3 mm intervals and was constant. A typical series of results is shown in Table 1. Lowering the crosshead speed immediately after the initiation of cracking resulted in a fall in crack velocity corresponding to the value that would have been obtained in a single lower crosshead speed test [50]. In an aqueous NaCl solution the results in Figure 5 show that below a certain crosshead speed cracking was not observed, a result already described in Figure 2. The use of double crosshead speed tests showed that the absence of cracking at low crosshead speeds was due not merely to difficulties in nucleation but to difficulties in maintaining propagation. If the crosshead speed was lowered below the minimum value for which cracking was observed in single crosshead speed tests crack arrest occurred immediately. This result emphasized that the effective strain-rate at the tip of a propagating crack must be above a certain value in order to prevent repassivation, a value that has been designated $\dot{\varepsilon}_r$ [37]. With reference to Figure 3, it may be claimed that K_{ISCC}, when it is observed, would appear to be that value of K which produces a value of $\dot{\varepsilon}$ equal to $\dot{\varepsilon}_r$. For a given material and temperature the strain-rate at the crack tip will be dependent upon K. Variation in K_{ISCC} for an alloy, therefore, will depend only upon the type of environment in which testing is done, a point that emphasizes that K_{ISCC} is an environmental constant, and not a material constant. It is necessary to point out a further qualifying aspect however. What controls the behaviour at the crack tip is not the repassivation characteristics of the bulk solution but those of the volume of liquid immediately adjacent to the crack tip. The composition of the volume of liquid may differ from that of the bulk solution as a result of hydrolysis, etc. [53]. The relative rates of hydrolysis appears to be a very important factor. The attainment of a critical degree of hydrolysis is an absolute necessity for crack initiation. Its maintenance is equally important for maintaining the cracking process. It is not known what type of dependency is found between velocity and crack tip solution composition. All that has been reported are variations in velocity and bulk composition changes, e.g. in Al [42] and Ti [54] alloys.

The similarity between Figure 3 and both 4 and 5 is clear but one difference must be commented upon. In the crosshead speed tests a 'plateau' velocity was not observed. In the plane strain specimens the plateau arises from a diffusion limited chemical reaction [15]. In the sheet specimens employed in the crosshead speeds mixing of the bulk solution with the solution at the crack tip would occur to a greater extent than for the thicker plane strain specimens. The establishment of an occluded cell would be more difficult for the thinner specimens. Consistent with this consideration is the type of dependence of plateau velocity upon solution viscosity observed in the two different types of specimens. In plane strain specimens $V_{II} \alpha \eta^{-1/2}$ for Ti alloys [55] whereas for thin specimens $V_{II} \propto \eta^{-0 \cdot 16}$ [40], where V_{II} is the plateau velocity or the highest velocity that was measured.

The influence of strain-rate upon crack velocity in austenitic stainless steels has been examined in a simple test from which the average velocity is calculated [52]. Results are shown in Figure 6. This can be compared with the measured crack velocities in the same type of material tested in a cantilever beam arrangement [41]. These are plotted as a function of applied stress in Figure 7 in which two plateau regions can be seen on each of which crack branching occurred so that there were four propagating fronts when the test was stopped. The upper plateau velocity (16 μm/min) is similar to the plateau velocity shown in Figure 6. It is probably caused by a limited diffusion control reaction for the corrosion process. The cause of the lower plateau is not known but may be caused by the work hardening of the specimen creating a situation in which a constant strain-rate is maintained at the crack tip. Identical results have been observed on α brass in ammonical solutions [28]. A low velocity plateau is observed in cantilever beam specimens but not in SEN specimens subjected to a series of tensile strain-rates. The conclusion to be drawn from results on FCC highly ductile alloys with high work hardening rates, therefore, is that a plateau velocity may arise either from a diffusion-limited chemical reaction or from a constant crack tip strain-rate condition.

REPASSIVATION CHARACTERISTICS

Much of the strain-rate work discussed in the preceding section was done under open circuit control. While the results do fit a model of repeated film fracture with inadequate repassivation, it must be emphasized that electrochemical control of a test is of extreme importance, either where an analytical approach to a cracking mechamism is being attempted or where it is wished to compare several alloys or several heat treatment conditions. It is just as important to specify the electrochemical potential of a specimen as it is to establish the correct criteria for plane strain conditions. Principally, the value of the potential will control at least 3 important reactions, which have already been described: (a) the dissolution rate, (b) the hydrogen ion discharge rate, and (c) the repassivation rate. Since the significance of the repassivation rate, has been discussed in the preceding section, the characteristics of the process are now considered briefly.

Repassivation has been examined by a number of workers who have used potentiostatically controlled specimens subjected to tensile strain-rates or to surface scratching techniques, [56 - 59]. In relation to stress corrosion cracking, interest lies both in the effect of a constant strain-rate and in a diminishing strain-rate. The latter situation might correspond to the period of time immediately following an increment of discontinuous crack growth when the volume of metal in front of the tip is undergoing plastic relaxation. In the general case, the rate of passive film growth on a metal surface, monitored electrochemically, decays logarithmically: log i α - log t, [60]. On a surface that is deforming plastically the fresh surface generated during that period will consist of a large number of increments of new surface which have been generated over the period of time between the beginning of yielding and the stopping of the straining of scratching. The sum total of currents generated will appear to decay more rapidly than the general case since at any period of measurement most of the surface will already be filmed to some extent. The summation of a series of log i increments can be expected to show that log i α - t, [61]. This relationship has been found for 18Cr-10Ni steel in HCl [61], and Al in NaCl [62]. A typical result is shown in Figure 8, [61]. The repassivation constant, β, measured as the logarithmic decay in the current as a function of time, is affected by alterations in the electrochemical conditions, Cl^- concentration, temperature, etc. The variation of β with potential is shown in Figure 9, [61]. The slowing down of the repassivation rate at the active and passive ends of the passive range of the potential corresponds to the potential approaching the region of the passive-to-active transition and the pitting potential respectively. It is in both such regions that cracking might be anticipated since, from the description of the propagation process outlined in Figure 1, it is in those regions that repassivation kinetics are rapidly changing. It can be expected that in such regions the critical delay time in the repassivation process might be observed, probably within some very narrow potential range. That cracking in 18Cr-10Ni steels in $MgCl_2$ solutions occurs within a potential region just below the pitting potential has been reported, [63].

From the observed log i/t relationship, the relationship between strain-rate and steady-state current can be predicted as $\dot{\varepsilon}$/log i, [37] and this has been widely observed in Al, [64]; Fe, [65]; 60Cu-40Zn brasses, [66]; 18Cr-10Ni steels at room temperature, [58]; and at 154°, [67]. This relationship is an important observation since it provides an immediate connection between the mechanical and electrochemical events occurring at the tip of a propagating crack: the rate of decay of the tensile strain-rate (plastic relaxation) determines the rate of change of the rate of the chemical reaction at the crack tip. From this relationship a simple analysis can be made, [37] on the assumption that an increment of crack growth occurs when a certain amount of charge, Q, flows (Q = i.t).

At room temperature many metals, [68], exhibit a creep strain, ε, related to time, t, as:

$$\varepsilon = k \log t \qquad (1)$$

where k is a constant.

From (1):

$$\frac{d\varepsilon}{dt} = \frac{k}{t} \qquad (2)$$

but since $\frac{d\varepsilon}{dt} \alpha \log i$ where i is the current flowing,

$$\frac{k}{t} \alpha \log i \qquad (3)$$

On the assumption that increments of crack growth occur over very long periods of time in comparison to the decline of the creep rate, the latter will be almost constant for the major part of the time in which the increment is occurring. This almost constant creep rate is likely because the stress on the remaining cross section of a cracking specimen will increase very little for each small increment of crack growth. As the stress rises, the constant k will increase and from equation (3) log i will increase. The time for incremental growth will decrease accordingly as log t since (log i + log t) is constant. In this rather simple way the velocity is shown to increase logarithmically, corresponding to Region I cracking, on the assumption that dissolution is causing cracking. Where cracking arises directly from causes not associated with dissolution such a relationship between log i and strain rate will not apply. Instead, a constant strain hypothesis might be applied in which ε_i might be defined as the additional strain required to cause an increment of crack growth. Provided that k increases in proportion to the increasing stress, since ε/log t = k, with increasing k cracking for a fixed value of strain, ε_i, will occur at time intervals that decrease logarithmically. This is a very simple analysis which may apply to the various forms of embrittlement encountered in non-metallic examples of environmental cracking as well as to hydrogen embrittlement of metallic materials where a Region I cracking is observed.

CRITICAL POINTS

The Role of Hydrogen

The role of absorbed hydrogen has been emphasized during the last few years, as indicated in a recent review [69]. In Ti, Al and Mg alloys embrittlement experiments have all shown identical results. Pre-exposed unstressed specimens when fractured in air showed fractures similar to those obrained in stress corrosion tests. Deliberate delays between exposure and fracture, sometimes above ambient temperatures, have shown a restoration of mechanical properties. All these effects can be attributed to the absorption and desorption of dissolved hydrogen. Typical results are shown in Figures 10 - 12, which show the change in mechanical properties for a Ti-O alloy exposed to CH_3OH/HCl solution and the associated changes in fractography [40]. Upon aging the amount of transgranular cleavage caused by hydrogen is gradually reduced and eventually does not occur. In Al alloys hydrogen has been detected as being desorbed during the intergranular fracture of embrittled specimens [70]. Recovery from the embrittled condition has been examined at different temperatures. Such evidence for the possible role of hydrogen in the crack propagation process is in apparent contradiction to simple considerations of the various kinetic processes, which have been analyzed with reference to the important ratio D/V where D is the hydrogen diffusivity and V is the maximum observed crack velocity. For Ti and Al alloys the value of D appears to be too low to enable hydrogen atoms to embrittle the zone in front of the crack tip. It has been suggested [70] that since the matrix solubility for hydrogen is low it may become saturated and thereby permit rapid diffusion of hydrogen down grain boundaries at rates 10^5 greater than in the matrix of Al alloys.

There are two possible ways of reconciling such differences. First, in the zone undergoing plastic deformation the diffusivity of hydrogen may be increased. A model involving dislocation sweeping of hydrogen atoms has been proposed [71] which would enhance diffusivity. In support of such a model, radioactive tracer studies of tritium in an austenitic stainless steel have shown [72] that plastic deformation can cause an increase in the hydrogen transport rate. Secondly, the analysis employing D/V is for a crack propagating through only metal embrittled by hydrogen and this may not always represent the correct situation. It has been argued [73] that for Ti alloys, for example, cracking is initiated by the interaction of absorbed hydrogen with the deforming lattice but the resulting cleavage crack, once initiated, propagates into the non-embrittled lattice until arrested by a barrier, e.g., a grain boundary, across which it cannot translate. This has been called a "long range" effect [73]. If such an effect exists it would remove one of the difficulties of the kinetic problems posed by a D/V analysis.

Many of the difficulties of analyzing the role of hydrogen arise from the problems of analyzing absorbed hydrogen. More radiotracer studies [74] and measurements of local concentrations [75] are required in order to provide quantitative data about the various proposed mechanisms. For high strength steels, Ti and Mg alloys, and possibly, for Al alloys, hydrogen may play a critical role in the cracking mechanism, as has been described above. Further progress in elucidating the atomistic mechanisms of such embrittlement processes and the precise causes is urgently required.

The Role of Microstructure

The reasons for the transgranular cracking of FCC alloys received much attention from electron microscopists 10 - 15 years ago, [25, 26]. The necessity for co-planar arrays of dislocations in susceptible alloys is recognized. Since that time little further progress has been made. The full explanation for the type of fractograph obtained in austenitic stainless steels on either a coarse [76] or fine [77] scale is still awaited. The adverse role of P and N upon susceptibility [26] is of industrial importance but has not been elucidated. The fractography of 70Cu-30Zn brass has been little examined [28]. The transitions from transgranular to intergranular and why either occurs are both difficult to explain and require methodical examination, including perhaps the possible role of minor constituents. Preferential corrosion has been attributed to the occurrence of zinc-rich regions, and while this may be correct, the role of minor constituents in austenitic stainless steels at least indicates the need to consider them for brass also. Structural considerations have been questioned in recent work on ferritic stainless steels [78]. These are immune in $MgCl_2$ solutions at 154° C but become susceptible when 1%Ni is added. Transgranular cracking is then observed which resembles fractographically cracking in austenitic grades. Any proper understanding of cracking mechanisms might be expected to be able either to predict or at least explain such points. Neither is possible at the moment. Despite all the work and money expended on the subject of stress corrosion cracking, very little is done on single crystals. This seems a peculiar omission since such work would allow a much simpler analysis of crystallographic, fractographic and velocity analyses.

The Role of Surface Films

The description of the cracking process in Figure 1 places considerable emphasis upon the surface film for reasons that have been discussed at length in this paper. Experimentally, little is known about the state of the film. Since repassivation begins within a period of 20-30 msec [57], the metal surface will be uncovered for only a very small proportion of the time. Instead what might be considered is the average condition and how it affects both the dissolution process and the hydrogen absorption process. Additions of inhibitors, for example, produce reductions in crack velocity for a given value of stress (and therefore strain-rate) [40]. Additions of species that delay repassivation, e.g., Cl^- for Al alloys [42], produce increases in crack velocity for a given value of stress. In both cases it is the average condition of the filmed surface that determines the crack velocity.

The methods for analyzing such films are difficult. Repassivation behaviour as a function of alloy composition is an obvious investigation that needs to be made. Analytical techniques outside of the environments are more questionable since changes in the film brought about by drying can create doubts about the effect of such changes. Auger spectroscopy can indicate the composition of such films however [79].

The nature of the film at the tip of a propagating crack requires a systematic investigation. Film composition, repassivation kinetics and plasticity are the three major subjects that should be examined.

Mechanical Considerations

The crack tip strain-rate has been referred to above as the major mechanical factor controlling crack velocity. How this would depend upon microstructure can only be surmised. Transitions from transgranular to intergranular cracking, for example, arising from alloying, could be attributed to the changes in strain-rate produced in the different parts of the microstructure. Information of this kind might be obtained by a broad study of dislocation distribution as a function of strain. Equally important is how the strain-rate is affected by the work hardening exponent. Under constant loading conditions, for example, the change in strain-rate will depend upon the work hardening characteristics of the alloy. This is illustrated in the value of the second velocity observed in the double crosshead speed tests. This is dependent upon the level of the stress when the crosshead speed is lowered, as illustrated in Table 2. As this stress is raised the work hardening rate of the alloy is lowered and resistance to crack propagation is gradually reduced. The stress on the specimen is imposing a strain-rate in addition to that imposed by the machine and lowering the crosshead speed reduces the effective strain-rate by a proportion that diminishes as the changing stress increases. The inter-relationship between work hardening characteristics and crack velocity has been very little examined for stress corrosion cracking. Because of the importance of the crack tip strain-rate and the rate at which it changes, this is an important subject that requires investigation. Whether cracking occurs by a dissolution mechanism or by a hydrogen absorption mechanism the work hardening characteristics are important since they will determine the value of log i and also the ability of a lattice to arrest a propagating cleavage crack.

CONCLUSION

The previous lecture [15] reviewed the atomistic mechanisms that may be operative during stress corrosion crack propagation. In this paper great emphasis has been placed upon a more general picture arising from the creep processes at the crack tip. In particular, such an analysis provides a direct connection between the electrochemical and metallurgical events occurring at the crack tip, either of which may exert control over the propagation kinetics. The importance of examining this connection has been closely argued since cracking arises from the interaction of two competing rate processes: repassivation and creep. Additional phenomenological aspects concerning the creation of reactive sites and the absorption of hydrogen are of importance also but if the balance between the two rate processes is such as to produce rapid repassivation then cracking will not occur.

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Table 1 Variation in Crack Velocity Across Specimen Width in 3 wt.% NaCl Aqueous Solutions Over Successive Intervals

CHS mm/min	Distance from Notch mm	Crack Velocity mm/sec
0.5	0-2 2-5 5-8 8-11 11-13	0.103 0.105 0.107 0.108 0.15
1	0-2 2-5 5-8 8-11 11-13	0.208 0.211 0.216 0.228 0.230
2	0-2 2-5 5-8 8-11 11-13	0.362 0.380 0.395 0.402 0.460
5	0-2 2-5 5-8 8-11 11-13	0.45 0.465 0.48 0.47 0.52

Table 2 The Influence of Stress Upon Crack Velocity in Double CHS Tests. Initial CHS 5 mm/min. Final CHS 0.5 mm/min.

Stress at Changing N/mm^2	Velocity Under Initial CHS mm/sec	Velocity Under Final CHS mm/sec
661.4	0.46	0.105
734.1	0.45	0.103
907.5	0.46	0.29
595.2	0.46	0.102

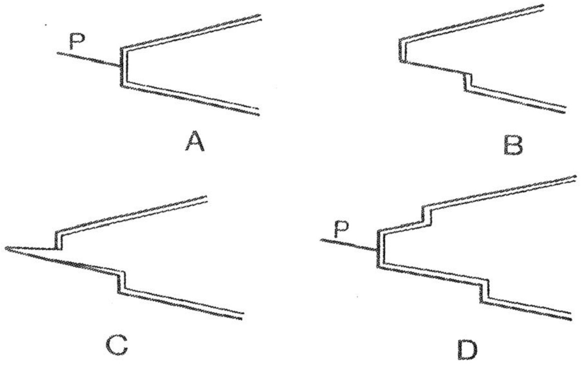

Figure 1 Schematic Diagram of the Sequence of Events Occurring at the Tip of a Propagating Stress Corrosion Crack

(A) The Tip of a Crack. The Surface is Covered by a Protective Film. P is a Slip Plane

(B) The Slip Plane Undergoes a Shear and a New, Unfilmed, Reactive Surface is Created

(C) Corrosive Attack Occurs on the Reactive Surface While Repassivation Begins on the Outer Edge. The Morphological Aspects of the Attack may vary from Alloy to Alloy and it is not Necessary that Attack Occurs Preferentially Along the Slip Plane

(D) Repassivation Occurs but not Until Sufficient Corrosion Attack and Plastic Deformation have Occurred to Ensure that an Increment of Crack Growth Occurs and Will Recur

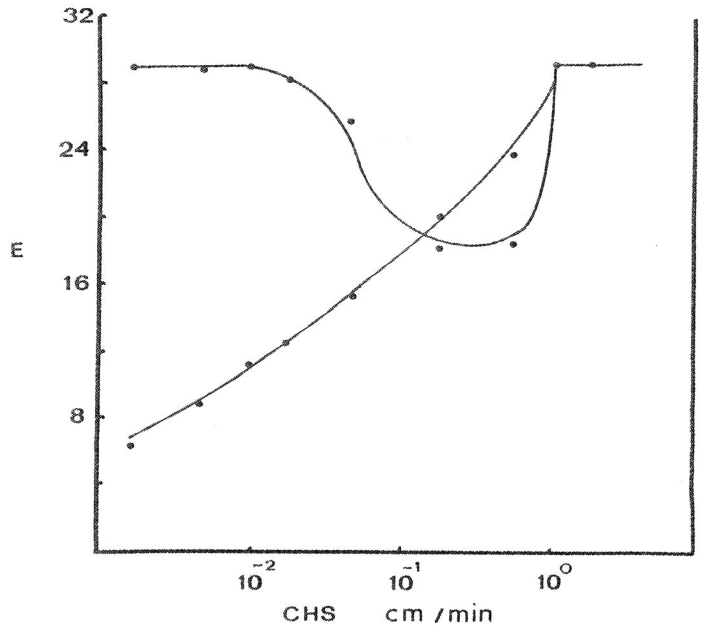

Figure 2 The Elongation to Fracture of Tensile Specimens of a Ti-O Alloy with a Gauge Length of 3 cm in 3% Aqueous NaCl and a CH_3OH-HCl Mixture as a Function of Instron Crosshead Speed

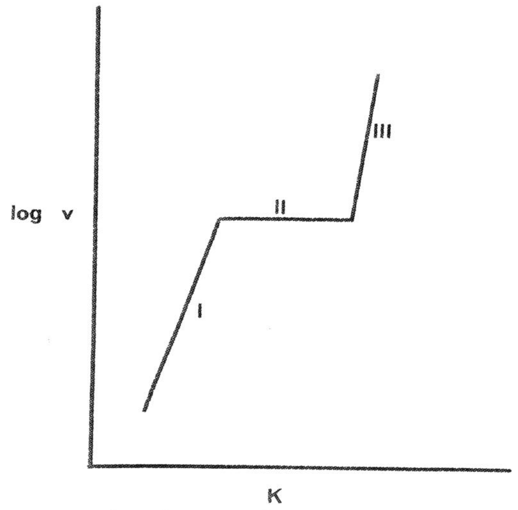

Figure 3 Schematic Diagram of Stress Corrosion Crack Velocity V Against Stress Intensity Factor K [15]

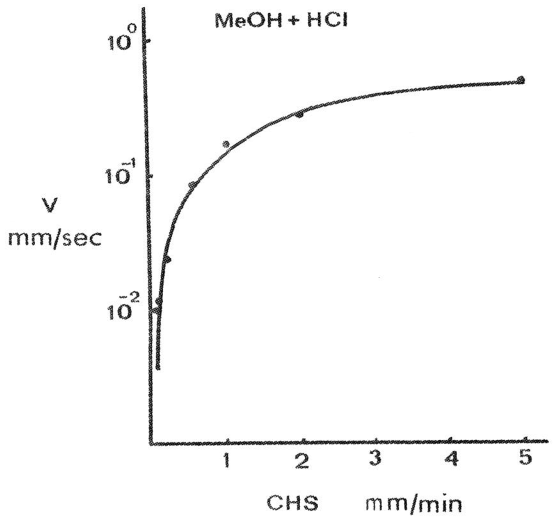

Figure 4 Stress Corrosion Crack Velocity in a Ti-O Alloy in a CH_3OH/HCl Mixture as a Function of Crosshead Speed

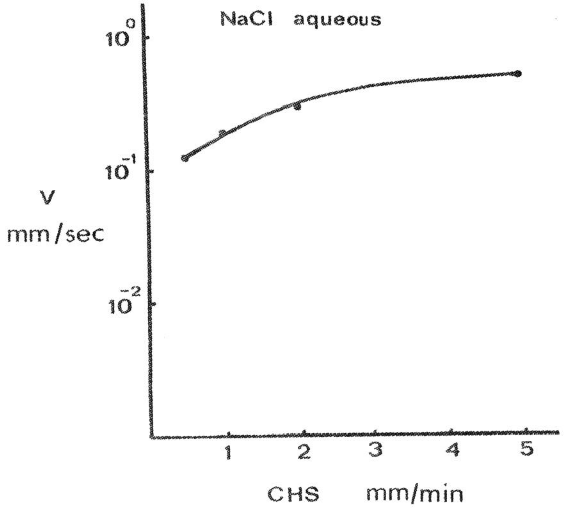

Figure 5 Stress Corrosion Crack Velocity in a Ti-O Alloy in a 3 wt.% Aqueous NaCl Solution as a Function of Crosshead Speed

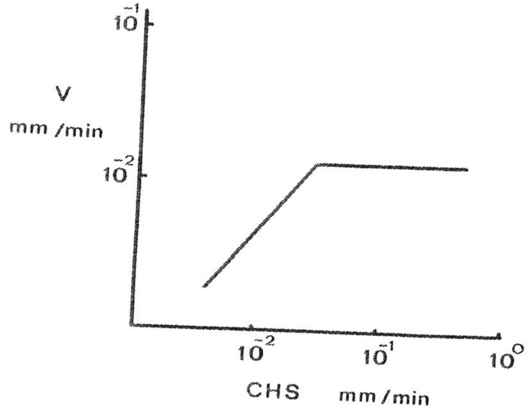

Figure 6 Average Stress Corrosion Crack Velocity in a Type 304 Steel in $MgCl_2$ Solution at 154°C as a Function of Crosshead Speed [52]

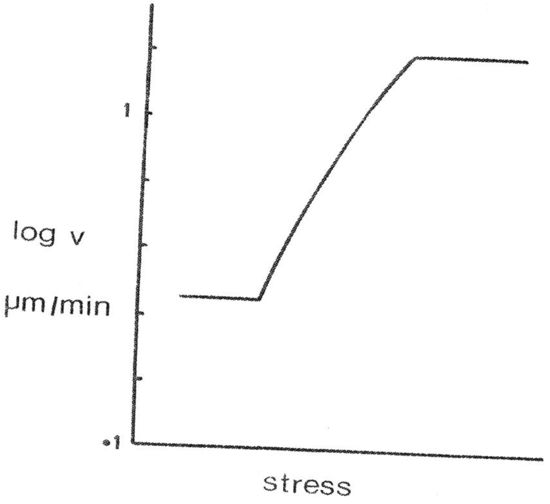

Figure 7 Stress Corrosion Crack Velocity in a Type 304 Steel in $MgCl_2$ Solution at 157.5°

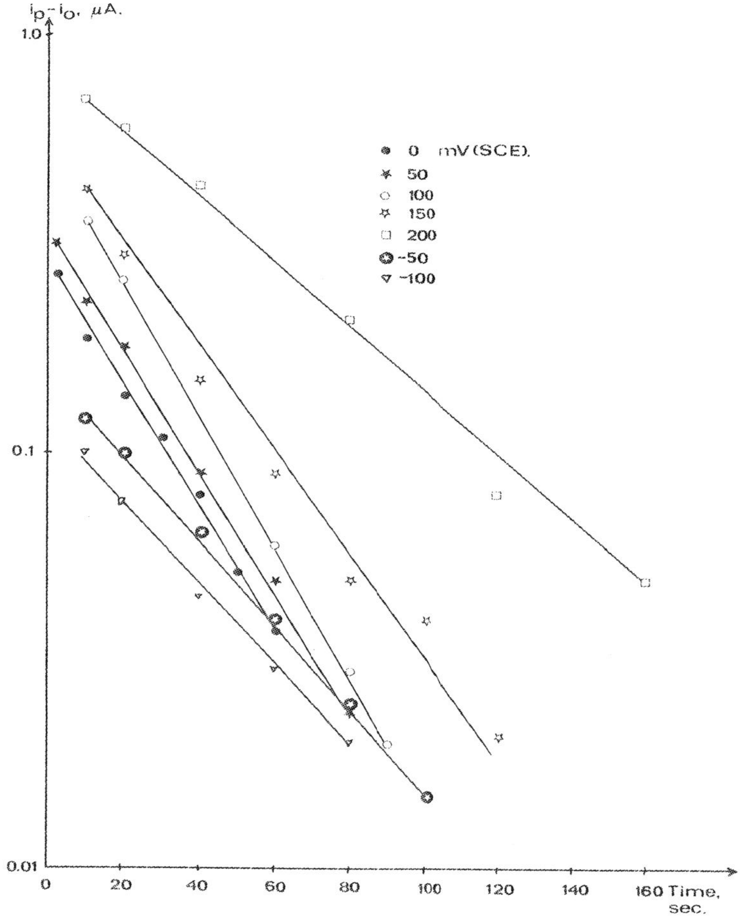

Figure 8 A Typical Current/Time Relationship Observed in 0.1M Cl^- at a Load of 300 kg at 7 Potentials in the Range - 100 to + 200 mV s.c.e. for a Specimen of Type 304 Steel After Stopping Straining

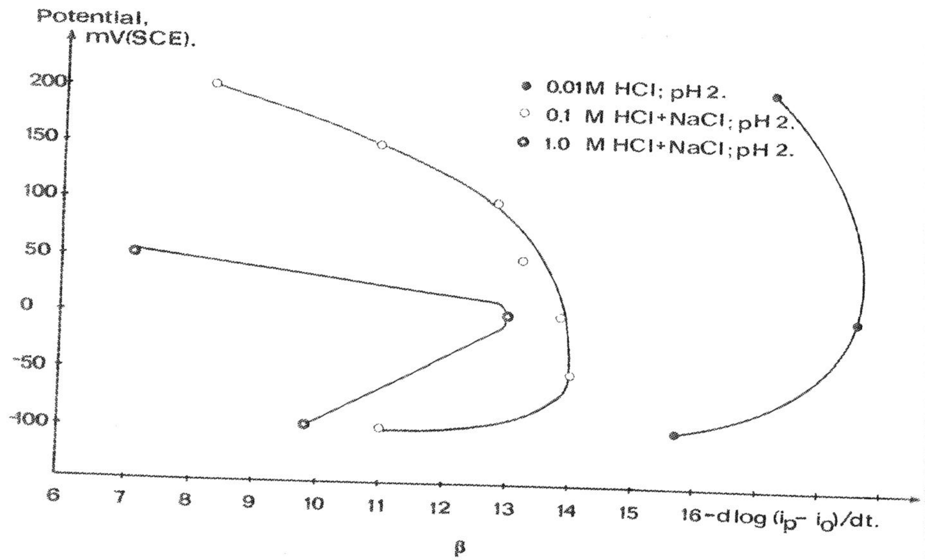

Figure 9 The Effect of Potential Upon the Repassivation Constant, β, for Three Different Chloride Solutions Under the Conditions Described in Figure 8

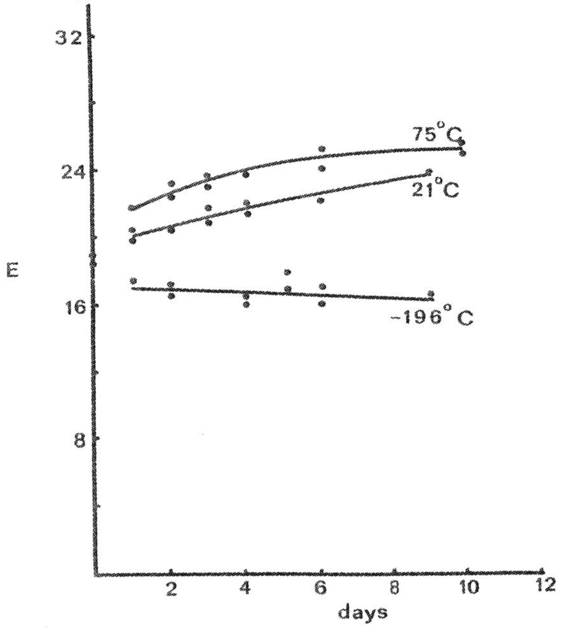

Figure 10 The Effect of Aging Time Upon the Elongation to Fracture of a Ti-O Alloy After Exposure to MeOH/HCl. At Room Temperature and 75°C the Elongation Increases Rapidly within 24 hr whereas at the Temperature of Liquid Nitrogen the Elongation is Reduced

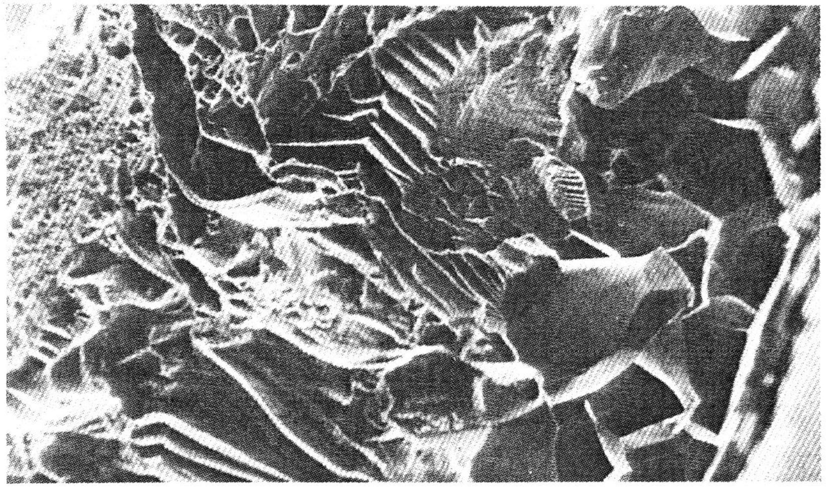

Figure 11 Fracture Surface of a Ti-O Alloy Exposed for 2 hr in MeOH/HCl and then Fractured in Air. A 3-Zone Fracture, Intergranular, Cleavage and Fluting and Dimple can be seen. SEM x 400

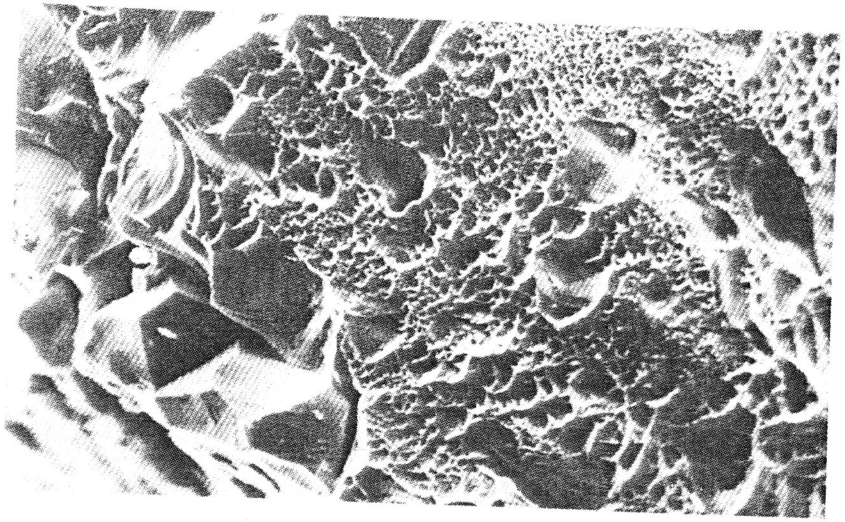

Figure 12 Fracture Surface of a Ti-O Alloy Exposed for 2 hr in MeOH/HCl and Fractured in Air after 20 Days. A 2-Zone Fracture, Intergranular and Dimple, can be seen. SEM x 400