

Environmental Factors in Crack Propagation

Dr. J. C. Scully
Department of Metallurgy, University of Leeds,
Leeds, U. K.

1. INTRODUCTION

Crack propagation occurs in materials for a number of reasons and in several different modes. In metallic materials, for example, propagation can occur as a result of fatigue, creep, cleavage or ductile instability. Much effort has been expended in developing materials in which these processes are inhibited so that they can operate under higher average working stresses and at higher temperatures. Over the last 25 years considerable progress has been achieved in the general field of material science in the development of outstanding materials strengthened by precipitation, fibre reinforcing, grain refining and various working processes. In addition to the limitations imposed by the material one recurring problem has been the effect of certain environments in causing fracture at levels of stress below those encountered in other inert environments. Such effects, variously called stress corrosion cracking, environmental stress cracking, delayed failure, have been widely encountered and they represent a major hindrance in the use of numerous groups of materials. The failure mode is very complex, it takes many forms and there have consequently been many explanations put forward.

For a complete understanding it is necessary to know both how such failures are initiated and how they propagate. In choosing to discuss the factors that affect propagation it is not intended to imply that initiation is unimportant. In recent years, however, more attention has been paid to propagation since the development of structures that did not allow propagation would clearly solve the problem. Reliance upon non-initiation in susceptible materials is potentially hazardous and has, for example, been the cause of a problem in titanium alloys exposed to marine environments when the conditions of initiation are encountered. Propagation represents

would if formed in the absence of the environment. The analyses of such processes require a knowledge of what determines surface energy and how it is affected by chemical reactions and this knowledge is not generally available. In addition to the surface interaction depicted in Figure 1 a volume interaction may also be applicable. The bonding energy of a plane of atoms in a volume of material behind the crack tip may be lowered gradually by the arrival of a species diffusing to that region from the environment/material interface, a process that will include examples where there is a change in phase after which the bonding of the interphasal interface or within the new phase is lower than that of the matrix. Species diffusing away from the region, e.g. selective dissolution of Zn from a brass, might also promote weakly bonded residual material. Such possibilities would all provide analyses of fracture occurring as a result of the rupture of weaker material. In such examples it is not the surface energy of the original material that is lowered but the surface that is changed. Furthermore if this volume of material is weak it may break at low stresses which cause little flow in the bulk of the material and therefore lower G significantly since this term incorporates both the surface and strain energy terms. In metals and polymers this latter point is important since the larger energy term associated with such flow processes about a crack tip means that the explanation for the occurrence of a crack increment must be more complicated than one requiring only a lowering in surface energy. The strain energy contributed by the volume of material undergoing flow must be reduced by some action of the environment. This might be achieved by impedance of flow by absorption of a species. Hydrogen into titanium is a possible example of such a process. It might also occur by changes in the material that make it less able to flow and the selective removal of Zn from a brass has already been indicated. Swelling of polymers from water absorption between strained chains or removal of plasticizers would appear to be analogous events in non-metallic solids. Apart from these and other processes impeding the flow of material at the crack tip and thereby reducing the strain energy component of fracture, a reduction will also be

achieved if the environment promotes fracture before the flow processes have occurred to the normal extent. This requires fracture to occur at stresses which produced little plastic flow about the crack tip or strains lower than is required for air fracture. Often the mode of fracture is changed also. While in glass the same cleavage process occurs in moist atmospheres as in dry air, in many alloys the environment contributes to the fracture process by changing the balance between potential fracture processes so that, for example, cleavage occurs in place of ductile void coalescence. From such observations on metals it might be expected that the strain energy release rate would be lowered but for metal systems such measurements have not been made. Lowered surface energies have been reported⁴ but these appeared to ignore the strain energy component although the stresses were sufficiently high to cause general yielding. What might be anticipated is that G is lowered since less rather than no plastic flow occurs than in air fracture so that the value derived would still be above that attributable only to the surface energy value. Such a result has been obtained with some polymers. Mechanical crack propagation has been measured⁵ as being accompanied by an energy release rate of $2 \times 10^5 \text{ erg/cm}^2$ in polymethylmethacrylate and of $1.7 \times 10^6 \text{ erg/cm}^2$ in polystyrene, values that are 10^3 - 10^4 times larger than the surface energy term. Similar values of energy are found in elastomers in which the tearing process is accompanied by visco-elastic rather than plastic deformation⁶. For these two materials tested in methyl alcohol, the critical stress to cause propagation, σ_c , for a given crack length, c , was found to be related to c by:

$$\sigma_c^2 c = \text{constant} \quad (2)$$

If the material is treated as Hookean, Andrews and Bevan⁵ observed that:

$$\sigma_c^2 c / 2E = W_c c = \text{constant} \quad (3)$$

where E is Young's modulus and W_c the stored energy density in the bulk of the test piece at the critical stress. Since, however,

therefore the important event in environmentally-induced failures and this subject, as it occurs in glasses, metals and polymers, is discussed below. Firstly the theoretical aspect of crack propagation is discussed briefly. The kinetic aspects of propagation in these three groups of materials are then described and compared. The phenomenological data are then presented and finally an attempt is made to amalgamate all these different aspects in order to produce a description of the current understanding of the effects of environments upon crack propagation processes.

2. CRACK PROPAGATION ENERGETICS

In all instances the criteria for crack propagation in materials can be analysed with reference to an energy balance since the energy state in the system after a crack increment must be less than that before or in the extreme case equal to it otherwise no crack growth event will take place. Such an analysis is associated with the early work of Griffith¹ on glass. Griffith derived a theory of fracture which allowed a crack to propagate only if the surface energy of the total freshly created cleaved surface in glass was not greater than the elastic stored energy lost by the bulk of the specimen as a result of the increase in crack length. Thus:

$$-\left(\frac{\partial E}{\partial A}\right)_L \geq S \quad (1)$$

where E is the total stored elastic energy, A is the interfacial area of the crack and S is the surface energy of the solid. The subscript L denotes that the loading system remains stationary, i.e. no external work is done. If plastic deformation occurs around a crack in a metal or visco-elastic flow in a polymer or any other process creating additional strain which will require an additional strain energy term then this must be included in the balance which must still be satisfied for propagation to occur. The later modification of Irwin² incorporated into the balance therefore an allowance for the additional strain energy which in metals can be very much larger than the surface energy term. Irwin chose the

term γ_p , the plastic work term, and incorporated this additional process together with S. Crack propagation occurs when G, the crack extension force, reaches the value of G_c , the critical strain-energy release rate for unstable crack extension.

These analyses have been made without reference to the presence of an environment since this is assumed to be either inert or absent. When an environment does contribute to the propagation process two questions can then arise. Firstly, the theoretical analysis must be revised so as to include the environmental contribution to the fracture. Secondly, it is of considerable importance to determine phenomenologically the specific nature of the critical event that represents the environmental effect. It is the second aspect that will provide insight into the first and considerable effort has been expended in determining mechanisms of environmentally-induced cracking. By this approach it can be anticipated that ameliorative measures can be adopted and the incidence of failures reduced. Such analyses, when achieved, should permit also the physical significance of theoretical concepts to be realised. Crack propagation in glass, for example, occurs at lower stresses in moisture than in dry air³ and an analysis of the fracture allows the effect of moisture to be attributed to a lowering of the surface energy. The question remains, therefore, as to what physical process has caused this reduction. The surface energy can be defined as the work necessary to form a unit area of surface by a process of division but this does not give any information about the atomistic or electronic processes involved. To conclude that the surface energy is lowered which process therefore allows crack extension is to attempt to explain an event by repeating the energy balance criterion. Such explanation offers no information about why it should be reduced and provides no predictive power about events in other systems.

Since the surface can form only if S is lower than it is in the absence of moisture the lower surface energy must arise at the time of fracture as each atom-atom bond is broken as indicated in Figure 1. As each pair of atoms becomes part of the fracture process they contribute less to the total energy term than they

$$-\left(\frac{\partial E}{\partial A}\right)_l = W_c \quad (4)$$

it follows that for propagation to occur

$$-\left(\frac{\partial E}{\partial A}\right)_l = \text{constant} = J \quad (5)$$

The values of energy release rate in methyl alcohol $>20^\circ\text{C}$ were calculated as a constant mean value of $4.2 \times 10^3 \text{ erg/cm}^2$. While this value is ca. 10^2 times greater than the true surface energy it is significantly smaller by ca. 10^2 times than the 'surface work' calculated for mechanical working in air. It would seem reasonable to apply such ideas to metals at low stresses and short crack lengths, particularly in those systems that exhibit a definite threshold stress intensity K_{lsc} since as in equation (2)

$$\left(K_{lsc}\right)^2 = \text{constant} \times \sigma_c^2 C$$

The assumption of Hookean behaviour would appear reasonable under conditions where K_{lsc} is very much smaller than K_{lc} .

3. KINETIC FACTORS IN CRACK PROPAGATION

The factors determining crack propagation rates can be divided into three categories. For a given specimen the crack will propagate only if the criteria determined by fracture mechanics are satisfied, corresponding to a critical value of G . Structural properties of the material are important on both a macro and micro scale since not all materials in a given group of alloys or polymers are equally susceptible or are even all susceptible. For propagation a critical chemical reaction must occur either on a very narrow front or at least be effective over a very narrow front. These mechanical, structural and chemical factors must be examined separately otherwise ambiguous and sometimes misleading results can be expected. At the same time it is important to emphasize that any proposed mechanism must include a quantitative explanation of

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the dynamic interaction of these factors since cracking occurs as the result of a unique combination of phenomenological and kinetic circumstances. In most systems this quantitative analysis is not currently available. Much work in recent years^{7,8} has recognised this lack and has attempted to achieve quantitative analyses. Several important studies have been devoted to measuring crack propagation kinetics by examining the effect of stress or stress intensity as a function of chemical and structural factors. This approach has enhanced considerably understanding of the processes involved and revealed some common effects, particularly in relation to chemical kinetics.

A reaction taking place at a surface may be divided into five steps, the slowest of which will determine the rate of the overall process. The successive stages are (i) transport of the reactant to the surface, (ii) adsorption at the surface, (iii) reaction with the surface, (iv) desorption of the products, and (v) transport of the liberated products from the surface into the bulk. In crack propagation stages (iv) and (v) are probably less important since the fracture process creates fresh reaction sites and adsorbed material will be left behind as the crack front propagates, thus having little effect upon the overall process. If stage (i) is rate-determining then the velocity will be independent of K while if stages (ii) or (iii) are rate-determining then the velocity will be dependent upon K to whatever order K affects the chemical process. This can be difficult to determine yet some common effects appear to emerge from a consideration of glass, metals and polymers.

Wiederhorn and Bolz⁹ have shown that a number of glasses exhibit an exponential relationship between K and crack velocity when exposed to water vapour, as shown in Figure 2. Studies of the effect of temperature have yielded an activation energy between 25.2-33.1 kcal/mol (105-138 kJ/mol) and the data were found to fit the equation:

$$v = v_0 \exp\left(\frac{-E^* + bK}{RT}\right) \quad (6)$$

where v is the velocity and v_0 , E^* and b are constants.

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The full relationship is shown in Figure 3 in which three different regions can be discerned with v shown as a function of stress rather than stress intensity³. As the stress increases region II is reached, the 'plateau' region, in which it can be assumed that the crack velocity is limited by the rate of water vapour transport to the crack tip. In region III a second and steeper exponential relationship is observed and it is probable that a third mechanism is operative since, unlike regions I and II, the reaction rate is independent of the water vapour concentration. Also shown in Figure 3 is the relationship observed under conditions of full immersion in water which appears similar to that in water vapour.

The theory of Hillig and Charles¹⁰ predicts the exponential relationship shown in equation (6). Crack motion occurs as the result of a heterogeneous chemical reaction between the glass and the water vapour at the tip of the crack. The essence of their analysis is that the rate of the critical chemical reaction is exponentially dependent upon the value of K . A crack front tends therefore to sharpen itself provided that the stress-dependence of the reaction rate is sufficiently high, ca. to the half-power¹¹. Why such a reaction should have this dependency is not clear and it has not been demonstrated. What is possible is to fit³ the experimental data to such an analysis which provides an equation of the form:

$$v = v_0 \exp - \left[\frac{E^*(0) - \beta P}{RT} \right] \quad (7)$$

where $E^*(0)$ is the activation energy for surface corrosion at a stress-free surface, P is the applied force which is assumed to be proportional to the crack tip stress and β is a constant. $E^*(0)$ depends upon the environment and if it is assumed that the crack velocity is proportional to the rate of chemical reaction at the crack tip then it can be deduced³ that:

$$N = ax^n \exp bP \quad (8)$$

where N is the number of water molecules per unit area per unit time reacting at the crack tip, n is the number of water molecules reacting with a single bond (the order of the reaction), a and b are

constants, and x is the mole fraction of water vapour at the crack tip. An equation of the same form can be derived from chemical reaction rate theory, as shown by Wiederhorn³. The analysis does not distinguish between bare surfaces, surfaces covered with a boundary layer, for example, of corrosion product or the effects of surface diffusion. The evidence suggests, however, that the crack tips were dry during the experiments³.

In metals more complex situations arise. Firstly, most alloys employed in aqueous solutions develop protective films which are in stable equilibrium with the environment. Reactions between the metal and the environment occur only when this film is destroyed at discrete points on the metal surface. Furthermore, propagation may be impeded by the reformation of the film, a process commonly referred to as repassivation¹². Crack arrest or changes in propagation rates may arise, for example, from alterations in the state of the unfiled surface and not only from changes in the metal/environment reaction kinetics. Repassivation and reaction kinetics are both dependent upon the value of the potential, but not in the same sense, and the effect of changing the value of the potential may be not simple. A second possible difficulty arises from the fact that metals are ductile and they develop plastic zones ahead of the crack tip which may interfere with analyses based upon linear elastic fracture mechanics unless they are very small, a condition obtained under plane strain conditions. Despite these two sources of possible complication it is remarkable that behaviour similar to that of glass is observed in higher strength alloys. For aluminium alloys, for example, a number of relationships is observed¹¹, the commonly found one being shown in Figure 4. Region I has an activation energy of 27 kcal/mol (113 kJ/mol) and corresponds to the same value observed¹³ in titanium alloys in the same region. This is also within the range found for glass as indicated above. It is not known what the principle reaction in this region is but it arises from the direct reaction between the metal and the environment. In those environments where the surface film is stable and reforms very rapidly after fracture, e.g. titanium

alloys in sea water, region I cracking is not observed. It is found, however, in strongly acidic solutions in which no surface film will be stable so that it is not associated directly with repassivation phenomena. A region II is observed with an activation energy of 3-5 kcal/mol (12-21 kJ/mol) and, as in glass in water vapour, the rate-determining factor is diffusion within the environment. If such movement is impeded, e.g. by increasing the viscosity, the velocity is lowered. Figure 5 illustrates an example¹¹ of the effect of altering viscosity in experiments upon aluminium alloys. Region II velocity is dependent also upon the value of the potential and also upon the strength level of the alloy which emphasises the importance of the microstructural properties of the alloys. It might be expected that region II velocity would be independent of strength levels since the velocity is limited by diffusion within the environment. Such a situation is observed in liquid metal embrittlement of aluminium alloys in mercury and the rate-determining factor is diffusion within the mercury¹¹. In aqueous environments it is not clear why the same situation is not observed. If it were merely that alloys aged to lower strength levels provided fewer reactive sites then the velocity might be expected to fall within region I since the saturation point would not have been reached at which the surface became dependent upon the amount of species diffusing to the surface. Instead the lowering of region II velocity must arise from the same number of reactions occurring but being less effective in causing crack extension. This could, in the simplest analysis, arise from more dissolution occurring over a wider surface giving perhaps crack blunting and thereby diminished velocity. Alternatively it could arise from an increased tolerance of hydrogen by the lattice which would therefore crack more slowly at the same reaction rate of hydrogen absorption or from an increase in the hydrogen evolved/hydrogen absorbed ratio. There are other possible speculations to explain this observation and it is not possible to distinguish between them since little work has been done on this point. That the strength affects region II serves to emphasize the interaction of environmental and structural considerations. In very susceptible high purity aluminium

alloys and in some high strength steels a region III is observed but very little investigational work has been carried out on it.

In aluminium alloys crack propagation studies in moist atmospheres provide apparently unambiguous data analogous to that obtained with glass. Typical results¹¹ are shown in Figure 6. Since the progress of the crack is dependent upon the arrival of water molecules at the tip of the crack and since at the low relative humidities there can be no pool of water present the possible reactions occurring at the tip are limited to:



The function of $Al(OH)_n$ either as a compound, e.g. $Al(OH)_3$, or as aluminium with adsorbed OH on the surface can be regarded as a process weakening the Al-Al bond at the crack tip as drawn schematically in Figure 1. Alternatively the hydrogen atoms may cause weakening through processes of absorption or adsorption. Since the kinetics of crack propagation are the same as those observed under conditions of full immersion (and in organic liquids containing traces of moisture) it is possible that the electrochemical reactions occurring under those conditions serve merely to maintain the tip surface in a state of poor film repair or 'bare' in order to allow H_2O to react with Al. Such a conclusion, however, may be too simple since the concentration of halide ion [I, Br or Cl] affects the region II velocity¹¹ according to:

$$v = v_{H_2O} + c C_{iodide} \quad (10)$$

where v_{H_2O} is the plateau velocity in distilled water, C_{iodide} is the iodide concentration of the bulk solution and c is a constant which becomes zero at 10^{-2} moles/litre of I^- . Such acceleration is very sensitive to alloy composition and strength and the observed increases can vary from $4 \cdot 10^3$ times in effect. Region I effects are less clear but at low stress intensities the effects are non-existent, a result which emphasizes the importance of the K value in considerations of kinetic data. Such results

reinforce the general point made in the Introduction of the need to define the mechanical, structural and chemical aspects of experimental results.

In titanium alloys¹³ the velocity is independent of the halide ion concentration at low values but in high molarity solutions the velocity is proportional to $C^{\frac{1}{2}} - C^{\frac{1}{4}}$ and is independent of alloy composition or type, heat treatment and fracture mode. The extent to which it occurs is dependent upon such variables however.

Liquid metals and gases that cause environmental fracture yield similar kinetic relationships to those observed in water. In aluminium alloys, for example, the maximum velocities observed in liquid mercury are $>10^5$ times greater than the most aggressive aqueous environments¹¹ but regions I and II are both obtained. In gases too similar relationships have been reported in titanium alloys and high strength steels in dry hydrogen¹⁴. In aluminium the slope of region I varies in a way dependent upon the environment, the alloy and the heat treatment¹¹. In moist gases, aqueous solutions and organic solvents containing residual moisture the slopes of region I lie in the range ca. $0.53/MN/m^{3/2}$ whereas for liquid metals the much steeper slopes can be as high as $20/MN/m^{3/2}$.

Region II in aluminium alloys has been observed as the region in which crack branching occurs, sometimes referred to as macrobranching¹⁵, in which a single front divides and becomes two propagating fronts. Such bifurcation occurs at a definite value of the stress intensity factor which can be designated K_B . At this point the strain energy release rate G is assumed to be doubled since there are then two crack fronts. From the relationship¹⁶ $K^2 = \frac{EG}{1-\nu^2}$, where ν is Poisson's Ratio, for plane strain the value of K at the beginning of region II K_p and K_B will be related from $\frac{K_B^2}{K_p^2} = 2$ and thus $\frac{K_B}{K_p} = 1.4$ and this is the observed relationship for the occurrence of branching. Such events occur only on the plateau region and require that the crack path be relatively isotropic. They are not observed in many commercial aluminium alloys which develop a strong preferred orientation and exhibit

intergranular fracture in aqueous media, but they are observed in the same alloys cracking in liquid metals where the path can be transgranular¹⁵.

Microbranching is characterized by the front splitting into several fronts separated by distances the order of a grain diameter in distance. It occurs in both region I and region II and occurs at a K value K_M such that $\frac{K_M}{K_{lsc}} = 1.4$ if a threshold

K_{lsc} exists below which crack propagation does not occur.

With the lower strength more ductile alloys analyses of the effect of stress or stress intensity have been few in number. In cold-worked α -brasses the velocity has been reported¹⁷ as proportional to K^2 up to the point of fracture and this could be interpreted as being related to the size of the plastic zones which has the same proportional relationship to K . In austenitic stainless steels two regions of constant velocity have been observed¹⁸ and on each macrobranching is obtained. On the second plateau an activation energy of 23 kcal/mol (96 kJ/mol) has been calculated.

The relationship observed in region I can be explained according to the theoretical analysis of Hillig and Charles¹⁰ as described above. Speidel¹¹ has analyzed other reactions that could give a similar exponential relationship to that described in equation (6). Following arguments derived from the theory of Hoar¹⁹, in which stress corrosion cracking occurs as a result of strain-assisted dissolution, he argues that for such a model the number of reactive sites should depend exponentially on the value of K . There is no evidence for this but it would be of interest to investigate this particular possibility. There is the model of Liu²⁰ based upon an analysis of the elastic interaction between a solute atom and the stress field in a solid ahead of the crack tip. By assuming that the crack growth rate is controlled by the reaction rate within a given volume of material an exponential relationship can be derived of a form similar to equation (6). Such a model might apply, for example, to alloys suffering from hydrogen embrittlement. It is in this area that a real under-

standing of the phenomenon of environmental-assisted crack growth lies. The explanation for region I cracking kinetics has not been discerned for any system yet it appears to be a common type of behaviour found in a wide range of materials and it would merit, therefore, careful investigation and analysis.

In polymers studies of crack velocity during environmental stress cracking have not been so extensive as with metals or glasses. Marshall et al²¹ have studied low density polyethylene in a methanol environment and have shown a decreasing rate of velocity increase with increasing K as shown in Figure 7. Such relationships hold only if the crack length/plate width ratio is not too large (<0.4) and the applied stresses not too gross. The effect of different environments is greater at high values of K as in metals, an observation that, not surprisingly, can also be made for metals and glasses.

4. PHENOMENOLOGICAL FACTORS OF CRACK PROPAGATION

It is difficult to separate kinetic aspects of crack propagation from phenomenological factors and some of these have necessarily been included in the section above. The justification for the attempt lies in the separation of the quantitative from the qualitative aspects. The quantitative discoveries referred to above have been most valuable since such measurements are essential in formulating any mechanistic analysis. Nevertheless it is the phenomenological aspect that continues to be the main source of study. This is not surprising since there are many experimental observations that can be made, employing a very wide range of techniques, and because in most cases of service failure this is all that can be considered. Despite considerable efforts to determine the precise nature of the events occurring during environmental-assisted cracking, however, in most systems where it occurs the phenomenological events have not been discerned. The problems in determining cracking mechanisms are being undertaken in two ways. The phenomenological events are investigated and their kinetics determined or the kinetics of events are determined and then an attempt is made to see what they apply to, and the latter approach provides a useful focus on the key events, as

described above, so that many possible events can be disregarded. With either approach mechanism determination is difficult. This is particularly true for metallic materials, currently and in the foreseeable future the most important series of materials. This lack of progress reflects the complexity of the average metal stress corrosion system. Chemically, for example, there are both metal/environment and film forming processes occurring at the same time, thereby giving rise to a particularly complicated set of possibilities. With other systems this is less likely to be so. Glass and polymeric materials do sometimes develop surfaces which are chemically different from the bulk and the presence of these surfaces may have a pronounced effect upon the apparent bulk behaviour of the material, e.g. the Joffe effect²². These surfaces develop over a period of time, do not always occur and are not intrinsic to the use of a material as, for example, the protective film formed on metal surfaces. In many discussions of such materials such layers are assumed not to exist.

In general, the possible ways in which an environment can cause fracture would appear to be limited to three simple divisions:

(i) Since a surface can form only when connecting bonds are fractured the action of an environment may be to weaken a bond sufficiently so that under the joint action of an external stress it is ruptured.

(ii) A surface will form if an atom is removed from a surface by dissolution, a process which will include rupturing bonds as well, provided that it is from a tip such as that drawn in Figure 1 and not from a kink or ledge site.

(iii) A surface will form if locally the mechanical properties of a material are affected either so that the flow processes are prevented by, for example, hydrogen pick up in titanium alloys, or by water absorption by polymers, or by conversion of the surface to a different state which cannot sustain the acting stress, e.g. selective dissolution in an alloy or conversion of rubber to an oily layer by ozonolysis.

With so many possible phenomenological events, the first system to be considered is the simplest: glass and water.

Glass

It has long been recognized that regions I and II arise from the interaction of the glass bonds at the tip of the crack with water molecules. The localized process may include the formation of layers of corrosion product during the reaction. The activation energy observed in region I is in agreement with that for the diffusion of Na^+ in soda-lime glass²³. Crack propagation may be controlled therefore by Na^+ ion migration in the glass²⁴. It must also be noted, however, that a similar activation energy is observed in processes involving chemisorption. In either case the propagation of the crack is associated with some form of bond weakening. From equations (6) and (7) at low values of applied stress

$$v = \frac{\text{constant } a x_o^n \exp(bP)}{n} \quad (11)$$

and at constant P v should be proportional to P^n . Data in Figure 8 do not give a straight line and this has also been interpreted as reflecting that more than one reaction is occurring. At low humidity the slope is ca. 0.5 whereas at high humidity it is unity, suggesting that reactions of this order occur at the crack tip. Since water lowers the strength of glass to about 30% of its water free strength this corresponds to a 90% reduction in fracture surface energy. Reductions from the air value of 4.0 J/m^2 to 0.4 J/m^2 have been observed²⁵.

Metals

There are many models proposed for stress corrosion cracking in alloys and it is not always possible to distinguish between them experimentally. Electrochemically, the potential at the tip of the crack is usually relatively active. It can be anticipated that material is dissolving anodically, which process is accompanied by hydrogen evolution. The metal at the crack tip may be locally embrittled by absorbed hydrogen. Protective film breakdown is generally although not always an important prerequisite for either

reaction. The process of chemisorption which will precede the specific electrochemical reaction may serve to cause bond rupture at the crack tip, i.e. fracture may occur before dissolution or at an early stage of the hydrogen absorption process. The alloy may be weakened by a process of selective dissolution of an active solute element with a flux of solute element atoms diffusing to the surface or by a general dissolution mechanism with deposition of the noble constituent. At the tip there may be direct conversion of the metal to a film of metal compound which is periodically broken. Distinction between these various general possibilities (and between mechanisms including several of them together) is not easy and in most systems more experimental information is required before further progress can be expected.

Metals generally fail in air by a tearing process that results in dimple fracture, commonly transgranular but often intergranular in high strength alloys. In stress corrosion failures such fractures are replaced, at least partly, by transgranular or intergranular fractures of a kind that is often different from an air fracture, as has already been indicated above. These occur at lower local stresses (or strains) than in air. The events that may occur at the tip are drawn schematically in Figure 1. A species will adsorb at the crack tip and the subsequent fracture will depend upon the effect of the adsorption process. It has been analyzed²⁶ that the important factor determining the type of fracture that occurs in a rupture process depends upon the ratio $\frac{\sigma_c}{\tau}$ where σ_c is the tensile stress for bond fracture (cleavage) at the tip while τ is the shear stress on the slip plane in the vicinity of the crack tip. In the absence of an environment the ratio for a ductile alloy is high and failure occurs by the dimple mode. This is replaced by a cleavage mode if an environment is present which causes either a reduction in σ_c and/or an increase in τ .

In general, it can be expected that the ease with which a metal lattice can deform plastically will be important in determining the outcome of competition between two processes of fracture. Dislocation patterns can give some indication of this. In both FCC²⁷ and hexagonal lattices²⁸ of alloys susceptible to transgranular

cracking, co-planar arrays of dislocations are exhibited in thin foils made from lightly strained material. In aluminium alloys maximum susceptibility is associated with lattices exhibiting narrow deformation bands containing high densities of dislocations²⁹. With both pile-ups and bands high stresses will be generated at the ends and high work-hardening characteristics can be expected. Additional factors have been suggested at various times, e.g. solute segregation about dislocation pile-ups creating regions locally more reactive than the matrix³⁰ or pile-ups promoting hydride formation in titanium alloys²⁹. Such additional effects cannot be ruled out and they do attempt to add a specific characterisation to a susceptible alloy which would distinguish it from a non-susceptible alloy. This is important since dislocation patterns alone do not indicate whether an alloy is susceptible. Nor is it easy to relate specifically patterns observed in foils made from alloys lightly strained to arrangements of dislocations likely to exist in small volumes of metal behind crack tips. What dislocation patterns do indicate is the prevalence of restricted slip.

An example of cleavage arising from a reduction in σ_c arises in liquid metal embrittlement and has been fully described by Latanasian and Westwood³¹. The general requirements for this phenomenon to occur appear to be (i) a tensile stress, (ii) a preexisting crack or some amount of plastic deformation so that dislocation pile-ups against an obstacle can occur resulting in a concentrated tensile stress across the potential fracture plane, and (iii) adsorption of the embrittling species at the obstacle. Limited mutual solubility is required too since too great a solubility may result in dissolution with the possibilities of crack blunting. Little tendency to form intermetallic compounds is also a requirement since this is a characteristic of high bonding strength. Velocities as high as 500 cm/sec have been reported. The proposed mechanism requires the adsorption of the metal at the strained bond at the crack tip. The redistribution of electronic bonding resulting from the process of adsorption results in bond weakening and fracture. Due to the nature of the metallic state any such electronic effect is purely a surface one since the

interior layers are screened by the mobile electrons of the atoms. Embrittlement may occur in ionic crystals, however, through a redistribution of charge arising from the adsorption of charged carriers since in such materials screening effects will be very much reduced. In agreement with such an analysis an element known to form high melting point intermetallic compounds can cause the inhibition of liquid metal embrittlement, e.g. 0.4% a/o Ba added to mercury prevents the embrittlement of aluminium³².

Liquid metal embrittlement occurs more readily in an alloy as the stacking fault energy is lowered³³. Since τ increases as the stacking fault energy is lowered this would lower the ratio σ_c/τ . In addition, it has been suggested that such alloying might be expected to lower σ_c as a result of altering the electron/atom ratio.

The most recent analysis places emphasis upon the value of σ and its temperature dependence which arises from a thermally activated adsorption process. In FCC metals the transition temperature from ductile to cleavage in liquid metal environments depends upon the environment and not upon the material. The effect of temperature upon the yield stress or the metallurgical transition is not important. This is confirmed in Figure 9 in which the strain at fracture is shown as a function of temperature for aluminium in a number of mercury/gallium solutions³⁴. Recently practical examples have been reported in which the embrittling metal was in the solid state, viz. cadmium-plated titanium fasteners³⁵ which exhibit intergranular fracture. This is not unlikely provided that the two metals are in direct physical contact.

In aqueous solutions the concept of bond breaking as indicated by Uhlig has been described as a stress-sorption process³⁶. Unlike liquid metal embrittlement it is difficult to obtain unequivocal data on the subject. Before any such process can occur, however, the protective film on the metal surface must be broken down and not allowed to repair, the only assumption being that its fracture is not an essential and continuous part of the propagation process. This subject has received much attention in recent years³⁷⁻⁴⁰. It is best considered in relation to Figure 10 in

which a filmed surface is shown to break down under the action of an emerging slip step. The amount of surface step area generated is not fully repassivated and the part that is not filmed undergoes rapid dissolution and may also be a site for preferentially high rates of hydrogen absorption since on some metals the existence of a protective film retards this process. In reality the strain at the tip may be high and cause more complicated deformation than is indicated by a simple single step but a quite general point can be made which provides a useful conceptual basis: in a given time interval more fresh metal is created than the volume of solution at the crack tip can repassivate. For stress corrosion cracking to occur there must be a relatively narrow and very critical repassivation delay. If repassivation occurs too readily then insufficient dissolution or hydrogen absorption will occur while if it occurs too slowly then the dissolution will occur on too wide a front and an elongated fissure will occur rather than a narrow crack. Such an analysis demands a careful analysis of all the factors contributing to the envisaged event. Physically, the mode of plastic deformation at the tips of cracks must be considered, determined by dislocation properties and massive flow characteristics at high local strains. Electrochemically, the repassivation rate will be dependent upon the value of the potential at the crack tip, the alloy surface composition, the local pH, the solution composition in the region of the crack tip and upon the temperature. With so many variables it is not surprising that much remains to be done in this subject. There are, however, several examples of experiments which indicate that the repassivation concept is of considerable significance. In Figure 11 are shown the results of experiments on specimens of Ti-5Al-2.5Sn alloy subjected to a range of strain-rates while exposed under open circuit conditions to a 3% NaCl aqueous solution and to an aggressive $\text{CH}_3\text{OH}/\text{HCl}$ mixture⁴¹. At high crosshead speeds there is insufficient time for crack nucleation and an air fracture occurs. As the crosshead speed employed is lowered crack nucleation and propagation occur with a consequent lowering of total elongation to fracture. At the lowest crosshead

speed employed the specimens tested in the aqueous solution exhibited air fracture only. Notwithstanding the same amount of surface deformation occurring the longer time over which it occurs allows longer time for repassivation and the absence of crack nucleation. In the $\text{CH}_3\text{OH}/\text{HCl}$ mixture no repassivation is possible since the mixture is aggressive and the longer time of the test allowed crack propagation to proceed further with a consequent decrease in total elongation. The detailed processes need further investigation. The speed of slip step emergence is not dependent upon the external strain rate and the absence of nucleation at low crosshead speeds must be explained by the non-occurrence of some critical event during the repassivation delay. Since these alloys undergo transgranular cleavage it would appear that the critical stress for this initiation is not reached at the low crosshead speed before repassivation occurs, an interpretation again emphasizing the interaction of mechanical and chemical factors.

A further demonstration of the significance of repassivation has been reported by Staehle⁴⁰. He has measured the current transients developed in a series of austenitic alloys when these are strained dynamically under potentiostatic conditions. The results are shown in Figure 12. The environment chosen did not cause cracking so that any difference in alloys normally susceptible in chloride solutions from non-susceptible alloys would not be attributable to the development of cracks. The susceptible 304 alloy developed the largest transient which would be expected therefore to be subjected to the greatest amount of attack under cracking conditions. What has not been shown is that alloys exist which exhibit very slow repassivation and therefore insufficient repassivation but it is not difficult to envisage that such materials exist.

A repassivation delay allows the critical reaction between metal and the environment to occur and would appear to be a necessary general requirement. What cannot be ascertained so readily is the nature of the initial reaction. Perhaps this might be discerned more readily under conditions where the film does not exist but experimental difficulties arise since under such conditions the

corrosion rate is usually high.

These general points can be applied to specific metal systems and it is now of interest to consider four of them briefly.

Aluminium Alloys. These alloys which have been extensively reviewed generally exhibit intergranular cracking. These have already been discussed in section 2. Metallurgically susceptibility appears to be associated with conditions near to peak hardness and fracture occurs with little or no macro deformation. At low values of K there is little evidence of deformation in the fracture surface. An example is shown in Figure 13. As the value of K increases an increasing proportion of the intergranular surface exhibits dimple fracture⁴². In high strength alloys this is intergranular and the observation can be made that a given intergranular facet is either the relatively featureless stress corrosion fracture or intergranular dimple suggesting that in alloys in a highly susceptible condition of heat treatment cracking between any pair of grains is continuous and rapid, i.e. a stress corrosion crack is only arrested when it comes to a grain boundary lying across its path of propagation. The general shape of grains and the propagation direction vis-à-vis rolling direction are of extreme importance in determining susceptibility. If the cracking mechanism is a form of stress sorption then the effect of overageing may lie in allowing preferential deformation about an incipient crack which thereby lowers the stress on the bonds between the grains. This absorption of strain energy through plastic deformation is manifested in lower levels of crack velocity for a given value of K . That commercial aluminium suffers from liquid metal embrittlement would appear to indicate that the effect of the absorbed metal on the aluminium-aluminium bond is very pronounced so that little stress is required to cause separation. Such simple thoughts are in agreement with the widespread observations of little deformation in the fracture process. In addition to affecting strength and ductility heat treatment can be expected to alter the distribution of solute elements in the grain boundary. In most examples the effect of alloying in promoting hardening of the lattice and a general lowering of ductility will probably be ^{the} predominant effect but it is at least

conceivable that alloying can strengthen the interatomic bonding and thereby make it less susceptible to environmentally-induced rupture. Suitable alloying can, for example, make metals less susceptible to liquid metal embrittlement⁴³. If stress sorption applies in aqueous stress corrosion the weakening effect is perhaps much smaller and the value of stress on the bond (X) shown in Figure 1 must be higher in order for it to break. Unless the yield point is higher than this value plastic deformation and stress relaxation will occur and there will be no possibility of environmentally-assisted fracture. Aluminium metal and low strength alloys are not susceptible, perhaps because a sufficiently high stress can never develop at a crack tip. With high strength alloys higher stresses can be achieved and it is also likely that the atom-atom bonding will be altered with the strength either increasing or decreasing. If such changes make the bonds less susceptible to weakening by adsorption they will counteract the strengthening effect of alloying which restricts ductility. In aqueous solutions such counteracting appears to be a very small effect if it exists at all while in liquid metals, as already noted, it can be quite marked⁴³. While this discussion is speculative it does offer a possible explanation for differences between alloys of similar mechanical properties for a system where in the absence of electrochemical considerations the environmental aspect is not clear.

Titanium Alloys. In aqueous conditions the α alloys exhibit a characteristic transgranular cleavage along a plane oriented $14-16^\circ$ from the basal plane⁴⁴. The β phase undergoes cleavage along the (001) plane but β phases containing Mo or V are not susceptible⁴⁴. The cleavage process is accompanied by extensive amounts of fracture which is best described as low energy tearing. An example is shown in Figure 14 in which the tearing appears as extensive fluting. The cleavage process is initiated as a result of an environmental reaction which is probably the absorption of hydrogen. This accumulates on the glide planes of the α lattice, raises τ and lowers the σ_c/τ ratio thus changing the ductile fracture to a brittle fracture⁴⁵. Once initiated

the cleavage crack will propagate mechanically over distances in excess of that included in the volume containing hydrogen to an extent that will be dependent upon the mechanical properties of the alloy. The cleavage crack is commonly arrested not by an arrest in propagation but by the continuation of the propagation by a deformation process which develops elongated voids whose walls then tear. Such a process can be seen⁴⁶ in Figure 15. The voids form at low plastic strain and the surfaces at low K values exhibit serpentine glide and at high K values more distorted surfaces. In some examples it is clear that each part of a propagating cleavage crack nucleates a void⁴⁶. Such observations are important in a number of ways. Firstly, it is clear that there is little point in attempting to interpret crack propagation by faradaic equivalence i.e. what current density of dissolution would result in the maximum crack velocities that are observed? Since these are >1 cm/min the current densities calculated are ca. 100A/cm². These calculations have no physical meaning (a) because the fracture is mainly mechanical as explained, and (b) because it is not clear that dissolution is occurring or is necessary. It is difficult to see why removing atoms from the region indicated in Figure 1 would not make slip easier rather than more difficult, which is a prerequisite for cleavage. Similar fractures occur in Zr alloys⁴⁷ and Mg alloys⁴⁸ during stress corrosion cracking and similar remarks apply to interpretations of crack propagation rates in those materials. Propagation in these systems occurs by a corrosion reaction initiating a large amount of brittle and restricted ductile fracture. Both these types of fracture are of significance since the design of resistant alloys can be approached by attempting to provide a matrix that does not cleave easily but also one that does not tear so easily. The two processes have much in common, both arising from impeded or restricted localized ductility, but it is likely that various metallurgical treatments might affect one more than the other.

In practice the principle alloys used, Ti-6Al-4V and Ti-8Al-1Mo-1V, contain non-susceptible β and resistance to cracking is improved by providing a Widmanstätten structure of α needles in

a β matrix providing discontinuous α and a multiplicity of crack arresting α/β interfaces. Orientation of the needles with respect to the propagation direction and texture are very important since if a crack front encounters a suitably oriented needle extending across a larger β grain crack propagation will be rapid.

The evidence of hydrogen causing such fractures is not conclusive but such evidence has been accumulating in recent years. Hot salt cracking, a phenomenon occurring >250°C in the presence of solid NaCl and oxygen, has been shown to be associated with hydrogen pickup by the titanium surface⁴⁹. Atmospheres containing as little as 0.25 ppm of water cause hydrogen contents >12,000 ppm in fracture surfaces of specimens containing residual levels of 70 ppm. At room temperature the most striking indirect evidence arises from the exposure of unstressed specimens of α alloys to CH₃OH/HCl mixtures which cause corrosion and hydrogen absorption. Subsequent fracture in air of such specimens gives rise to fracture surfaces that are similar to stress corrosion. Ageing of specimens at room temperature between the exposure and fracture for long periods of time (6000h) results in a fracture in which the stress corrosion type is absent⁵⁰. It is difficult to see how such phenomena can be interpreted other than by the absorption of an embrittling species followed by its diffusing away from the surface during the ageing time. Anodic polarization experiments have shown that if the metal is dissolved at a rate comparable to that of hydrogen diffusion then subsequent fracture in air does not give a typical stress corrosion fracture⁵¹. This has been interpreted as showing that under such conditions hydrogen accumulation ahead of the dissolving front cannot occur and this would account for the absence of the typical fracture.

The potential at which cracking occurs can be noble with respect to the hydrogen evolution potential. This is not necessarily evidence that hydrogen discharge cannot occur under such conditions since there appears to be a considerable IR drop down a crack⁵². The measured potential is noble by the value of the drop to that at the surface at the crack tip. The effect of potential upon the K/log v curve⁵² is shown in Figure 16. Even at

+1000mV hydrogen is discharged at the crack tip and it cannot, therefore, be discounted as the embrittling species.

High Strength Steels. All the recent work in these materials has indicated that hydrogen is responsible for intergranular stress corrosion. The effects of heat treatment upon times to failure can be explained from changes that such treatments produce in the tolerance of the lattice for atomic hydrogen. The effects of polarization arise from the increased hydrogen ion discharge rates that occur under both anodic and cathodic conditions⁵³. What is important is the manner of its absorption and the proportion of discharged hydrogen ions that enter the material. These processes and the actual way in which hydrogen causes embrittlement have not been elucidated and require much further work. It is common to refer to hydrogen embrittlement. A recent theory by Beachem⁵⁴, however, argues that hydrogen serves to promote locally any one of a number of fracture modes - intergranular, quasi-cleavage or micro-void coalescence - whatever deformation and fracture modes the matrix will allow. This in turn depends upon the value of K and the concentration of hydrogen in solution at the crack tip. Hydrogen allows or forces the normal fracture processes to become operative at unusually low macroscopic strains. Torsion tests on pipe revealed that the flow stress was lowered, and that hydrogen is trapped by plastic deformation. Such processes can be expected to occur on a microscopic level also. Observations of micro-void coalescence in steels under loading conditions of decreasing K showed unambiguously that hydrogen contributes to this type of fracture since this type of fracture occurred to lower values of K in hydrogen than in air and no distinction could be made between those formed in air and those in hydrogen.

This new model can be widely supported from the literature, e.g., the removal of the upper yield point in mild steel⁵⁵ and a general lowering of the stress/strain curve with increasing hydrogen content in mild steel also⁵⁶.

An attempt has been made to explain the phenomena observed. At high K values large volumes of material deform plastically if the hydrogen content is high enough. Inclusions in this material

serve as nuclei for voids resulting in micro-void coalescence. At lower K values the volume of material deformed is smaller and if it does not contain inclusions then the failure is by quasi-cleavage. At the lowest range of K values crack growth occurs by plastic deformation adjacent to the grain boundaries causing separation and grain boundary tear ridges. Where these are not observed some crack growth may occur by hydrogen in the grain boundary region providing sufficient pressure to provide a driving force to augment the force from the external loading. The occurrence of macroscopically flat 'brittle-type' fractures rather than necking down is not considered to be in contradiction of the proposed mechanism since it is argued that hydrogen causes severe deformation around the crack tip and consequent propagation before hydrogen can diffuse into the bulk of the specimen. This is the same requirement as for cracking in titanium alloys: hydrogen diffusion must be slow with respect to the amount of hydrogen absorbed otherwise it cannot accumulate on a localized scale to a damaging concentration. In the hot salt cracking referred to above the same requirement must hold and the much higher diffusion rates at elevated temperatures must be still too slow for what must be very high absorption rates.

Figure 17 summarizes the results obtained by Beachem.

Austenitic Steels. These materials are investigated mainly in the environment of $MgCl_2$ solutions boiling at 130-160°C. It has become clear⁴⁰ that a film exists on the surface of material exposed to this environment and a critical repassivation delay is an important feature of the cracking mechanism. Recently the velocity has been examined¹⁸ as a function of K and similarities to results obtained with high strength materials have been found. Branching occurs on the K-independent 'plateau' region as shown in Figure 18. Lowering K after branching results in one front being arrested as shown in Figure 19 since in a K-dependent region one front will predominate once it gets slightly in front of the other. The high activation energy in the plateau region of

23 kcal/mol, referred to above, is considerably higher than that reported for the similar region in aluminium and titanium alloys. It is not known what process is rate-controlling in this region. Morphologically there is a transition from intergranular to transgranular at low values of K but there is no noticeable change in kinetics at this stage. The transgranular fracture results in a fan-shaped fracture which has been described⁵⁷ as arising from a multiple crack front, giving rise to a striated surface and possibly shear along the length of propagation with bending and tearing at the same time. At room temperature austenite exhibits tunnelling⁵⁸ but the kinetics of cracking when they occur have not been determined and their mode of formation has been only tentatively explained.

Electrochemical Aspects. It has already been emphasized that alloys in aqueous solutions must undergo surface film breakdown before the reaction responsible for cracking can occur. Changes in electrochemical aspects can have therefore a two-fold effect. They will affect the filming characteristics, mainly the repassivation kinetics and they will affect the reactions occurring between the metal and the environment. The major determinant is the value of the potential. Cracking appears to occur where the film is either unstable or in a poor state of stability so that if broken it will repair over a period of time of a critical length, particular to the stress corrosion system under consideration.

It is only under non film-forming conditions that the effect of potential is most readily seen unambiguously and work in such environments has not been extensive because the simultaneously occurring general corrosion can render the experimental conditions difficult. In aluminium¹⁰ and titanium alloys^{13,59} region II velocity is mainly independent of the potential in strong acids over the ranges that have been investigated. Region I is shifted in aluminium alloys so that a given value of velocity is observed at a lower K value as the pH is lowered. In titanium alloys region I is observed as the pH is lowered (it is absent in some neutral solutions). Thus while film formation is important and can prevent cracking in some situations it is not responsible

for the exponential relationship in region I which is a relationship arising from the metal/environment interaction.

It has been demonstrated for aluminium¹⁰ and titanium alloys⁵⁹ that cracking is accelerated by the presence of Cl^- , Br^- and I^- ions and no others. Of all the other species examined in aqueous solutions, they either have no effect or exhibit some retarding effect. It remains unclear what is the unique characteristic of the three species that accelerate cracking. Adsorption of the species may have some particular feature about it and the exclusion of the F^- ion from this category may be related to the hydrolysis that metal fluorides readily undergo, unlike chlorides, bromides or iodides. It has been suggested that adsorbed chlorides promote hydrogen entry into titanium⁶⁰ and stainless steels⁶¹ although there is no direct proof for this. On iron surfaces such accelerated effects on hydrogen entry are apparently well-known⁶². Much remains to be determined in this area that is subject to widely varying speculative ideas. It would be surprising if single factors provided clarifying answers. It can be noted, for example, that fluorides, which do not cause stress corrosion crack acceleration, are known to cause hydrogen entry into titanium alloys. There are several ways of attempting to explain how this observation can be reconciled with the brief discussion above but currently it is not possible to distinguish between them.

Polymers. There is no single phenomenon occurring when polymers exhibit environmental stress cracking. Several descriptions of mechanisms have been proposed. Environments causing fracture in different materials include organic solvents, ozone, water and surface active liquids⁶³. Many organic solvents cause fracture, particularly in amorphous plastics, ozone in unsaturated hydrocarbons, especially elastomers, and surface-active media cause fracture in polyethylene. Cross-linking by radiation lowers susceptibility of polyethylene and polystyrene is immune. In ozone cracking very little energy is dissipated in plastic or visco-elastic deformation at the crack tip. The fracture surface energy determined⁶⁴ from equation (1) of 100 ergs/cm² is of the same order

as the surface energy and this does appear to be an example of fracture occurring by a lowering of surface energy, thus satisfying the original Griffith analysis. The chemical attack can be prevented by creating a surface phase inert to ozone or using chemical anti-ozonants⁶⁵. Phenomenologically the bonds are broken by the ozone. Ozone attack causes degradation of the surface layer which thickness increases as $(\text{time})^{\frac{1}{2}}$ and which has an oily consistency. The rate of crack propagation is directly proportional to the ozone concentration and the temperature. Work on rubbers of different mechanical hystereses suggests that the propagation rate is directly related to the mobility of the polymer molecules and the rate of diffusion of ozone into the polymer at the crack tip⁶⁵.

In specimens tested to failure many cracks are nucleated and the number of cracks which actually survive must be proportional to the stored energy density (W) in the specimen. If failure occurs by link up of the many cracks fracture can be expected⁶⁴ in a time (t_f) inversely proportional to the number of available cracks and therefore to the stored energy density:

$$t_f = aW^{-1} \quad (12)$$

At stresses below the yield stress the material can be treated as Hookean; therefore:

$$t_f = \beta \sigma_f^{-2} \quad (13)$$

and

$$\log t_f = \log \beta - 2 \log \sigma_f$$

Data by Gaube⁶⁶ for high density polyethylene immersed in water are shown in Figure 20 and below the point of yielding they appear to fit the elastic analysis of Braden and Gent.

In polyethylene the crystalline texture of the material is important in determining cracking. A large low molecular weight fraction has an extremely deleterious effect and slowly cooled material is much more susceptible than rapidly cooled material. Cracking is associated with the absorption of a monolayer of polar

molecules on the surface of a microfissure. Interspherulite boundaries crossed by only a few polymer chains would be weak in this respect. Phenomenologically, it has been suggested that the triaxial stressing system at the crack tip produces a dilation of the material in that region thus allowing rapid entry of solvent molecules. These plasticize the region around the tip and permit disentanglement of the chain molecules under relatively low stresses and with relatively little viscous dissipation of energy.

5. CONCLUSIONS

In choosing to concentrate upon three classes of materials and cracking in them under constant load conditions some large areas of interest in the general field of environmentally-assisted crack propagation have been omitted. Corrosion fatigue and environmentally-assisted creep and embrittlement in ionic solids can be included here. It is not clear that these types of failure include new or additional phenomena and it seems reasonable that a better understanding of the constant load phenomena discussed in this paper will aid these other forms of failure. Corrosion fatigue will include repassivation phenomena and has much in common with stress corrosion cracking except that it occurs in all alloys and many aqueous environments. The role of absorbed gases in promoting creep at elevated temperatures, e.g. helium in austenitic stainless steels⁶⁷, would appear to be a similar phenomenon to that advocated for hydrogen in high strength steels by Beachem⁵⁴ in so far as the process is accelerated by the absorbed gas but phenomenologically not changed. The capacity of a gas to enhance deformation and fracture processes in a metal in which it is dissolved may not always have been recognized because many gases that metals are in contact with react and form metal compounds. Another type of failure, the adsorption-induced embrittlement of ionic solids, is likely to have features in common with some of the processes discussed above. No separation therefore is intended in omitting these other processes from the general discussion.

Some have been less thoroughly studied than others and in concentrating upon one phenomenon which has been the object of a very large body of work it is hoped that a certain degree of simplicity has been achieved.

The complex phenomena that cause a crack to propagate as the result of being exposed to an environment can be reduced to several simple observed patterns which appear to apply to the three groups of materials discussed:

1. Crack velocity is commonly proportional to the exponential of the stress intensity at low values of K .
2. As K increases the velocity commonly exhibits a K -independent region in which the velocity is dependent upon diffusion processes within the environment, although the structural condition of the material may also be a determinant.
3. The reaction of the crack tip can be expected to depend upon the arrival of species to the tip rather than away from it.
4. The provision of reactive sites and the maintenance of a sufficiently high stress at the crack tip are structural factors which together determine the susceptibility of a material.
5. The nature of the surface at the tip of a crack is critically important and may be beneficial or detrimental in controlling fracture. In the simplest analysis, inert surfaces, formed perhaps of reaction products, may serve to localize chemical reactions by local rupture. A thick coating or diffusion layer which is never completely ruptured may produce non-susceptibility.
6. In metals and in some examples of polymeric fracture the rupture of protective surface films and their reformation may constitute an important ancillary reaction which may interfere with the kinetics of propagation by slowing or even arresting the crack front.

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REFERENCES

1. A.A. Griffith, Phil.Trans.Roy.Soc., A221, 163 (1920).
2. G.R. Irwin, Encyclopaedia of Physics, Vol. VI, Springer, Heidelberg (1958).
3. S.M. Wiederhorn, J.Am.Ceram.Soc., 50, 407 (1967).
4. E.G. Coleman, D. Weinstein and W. Rostoker, Acta Met., 9, 491 (1961).
5. E.H. Andrews and L. Bevan, The Physical Basis of Yield and Fracture, Institute of Physics, London, p.209 (1966).
6. H.W. Greensmith and A.G. Thomas, J.Polymer Sci., 18, 189 (1955).
7. The Theory of Stress Corrosion Cracking in Alloys (ed. J.C. Scully), NATO, Brussels (1971).
8. Stress-Corrosion Cracking in High Strength Steels and in Titanium and Aluminium Alloys (ed. B.F. Brown), Naval Research Laboratory, Washington, D.C. (1972).
9. S.M. Wiederhorn and L.H. Bolz, J.Am.Ceram.Soc., 53, 543 (1970).
10. W.B. Hillig and R.J. Charles, High Strength Materials (ed. V.F. Zackay), Wiley, New York, p.682 (1965).
11. M.O. Speidel, ref. 7, p.289.
12. J.C. Scully, Corros.Sci., 7, 197 (1967).
13. J.A. Feeney and M.J. Blackburn, ref. 7, p.355.
14. D.P. Williams and H.G. Nelson, Met.Trans., 3, 2107 (1972).
15. M.O. Speidel, ref. 7, p.345.
16. A.S. Tetelman and A.J. McEvily, Jr., Fracture of Structural Materials, Wiley, New York, p.53 (1967).
17. A.J. McEvily, Jr., and A.P. Bond, J.Electrochem.Soc., 112, 131 (1965).
18. M.J. Robinson and J.C. Scully, in preparation.
19. T.P. Hoar and J.M. West, Proc.Roy.Soc., A268, 304 (1962).
20. H.W. Liu, Trans. ASME J.Basic Engng., 633 (1970).
21. G.P. Marshall, N.H. Linkins, L.E. Culver and J.G. Williams, SPE J., 28,25 (1972).
22. A. Joffe, M.W. Kirpitschema and M.A. Lewitsky, Z.Physik, 22, 286 (1924).

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23. R.H. Doremus, Modern Aspects of the Vitreous State, Butterworths, London, Vol. 2, p.1 (1962).
24. R.J. Charles, J.App.Phys., 29, 1554 and 1949 (1958).
25. S.M. Wiederhorn, J.Am.Ceram.Soc., 52, 99 (1968).
26. A. Kelly, W.R. Tyson and A.H. Cottrell, Phil.Mag., 15, 567 (1967).
27. P.R. Swann, Corrosion, 19, 102 (1963).
28. G. Sanderson and J.C. Scully, Trans. AIME Met.Soc., 239, 1883 (1967).
29. H.A. Holl, Corrosion, 23, 173 (1967).
30. P.R. Swann and J. Nutting, J.Inst.Met., 88, 478 (1959-60).
31. R.M. Latanasian and A.R.C. Westwood, Office of Naval Research Report, Washington D.C. N:4162(00) (1969).
32. A.R.C. Westwood, Strengthening Mechanisms: Metals and Ceramics, Syracuse University Press, p.407 (1966).
33. T.L. Johnston, R.G. Davies and N.S. Stoloff, Phil.Mag., 12, 305 (1965).
34. C.M. Preece and A.R.C. Westwood, Trans. ASM, 61 (1969).
35. D.N. Fager and W.F. Spurr, Corrosion, 27, 72 (1971).
36. H.H. Uhlig, Physical Metallurgy of Stress Corrosion Fracture (ed. T.N. Rhodin) Interscience, New York, p.1 (1969).
37. J.C. Scully, Corros.Sci., 7, 197 (1967).
38. J.C. Scully, Corros.Sci., 8, 771 (1968).
39. H.-J. Engell, ref. 7, p.86.
40. R.W. Staehle, ref. 7, p.223.
41. J.C. Scully and D.T. Powell, Corros.Sci., 10, 371 (1970).
42. F.E. Watkinson and J.C. Scully, Corros.Sci., in press.
43. N.S. Stoloff, R.G. Davies and T.L. Johnston, Environment-Sensitive Mechanical Behaviour (ed. A.R.C. Westwood and N.S. Stoloff), Gordon and Breach, New York, p.613 (1966).
44. D.A. Meyn, Naval Research Laboratory, Washington D.C. Report, p.21 (1965).
45. D.T. Powell and J.C. Scully, Corrosion, 24, 151 (1968).
46. G.R. Lobley and J.C. Scully, to be published.
47. B. Cox, Corrosion, 28, 207 (1972).

48. E.N. Pugh, J.A.S. Green and P.W. Slattery, Fracture 1969, Chapman and Hall, London, p.387 (1969).
49. H.R. Gray, Corrosion, 25, 337 (1969).
50. J. Spurrier and J.C. Scully, Corrosion, in press.
51. D.T. Powell and J.C. Scully, Corrosion, 25, 483 (1969).
52. T.R. Beck, ref. 7, p.64.
53. B.F. Brown, ref. 7, p.186.
54. C.D. Beachem, Met.Trans., 3, 437 (1972).
55. H.C. Rogers, Acta Met., 4, 114 (1956).
56. N.J. Grant and J.L. Lundsford, Iron Age, 175, 92 (1955).
57. J.C. Scully, ref. 7, p.127.
58. J.D. Harston and J.C. Scully, Corrosion, 25, 493 (1969).
59. M.J. Blackburn, W.H. Smyrl and J.A. Feeney, ref. 8, p.245.
60. G. Sanderson and J.C. Scully, Corros. Sci., 6, 541 (1966).
61. I.S. McCollough and J.C. Scully, Corros.Sci., 9, 707 (1969).
62. J. McBreen and M.A. Grenshaw, Fundamental Aspects of Stress Corrosion Cracking (ed. R.W. Staehle, A.J. Forty and D. van Rooijen), NACE, Houston, p.51 (1969).
63. E.H. Andrews, Fracture in Polymers, Oliver and Boyd, London (1968).
64. M. Braden and A.N. Gent, J.Appl.Polym.Sci., 3, 90 (1960).
65. E.H. Andrews and M. Braden, J.Polym.Sci., 55, 787 (1961).
66. E. Gaube, Kunststoffe, 49, 446 (1959).
67. K.R. Garr, C.G. Rhodes and D. Kramer, North American Rockwell Report N:A1-AEC-13009 (1971).

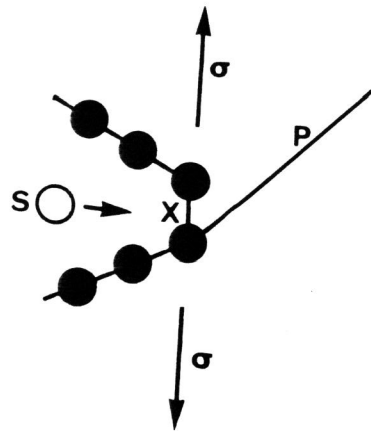


Figure 1. Schematic diagram of an atomically sharp crack under a tensile stress σ . Fracture occurs when the atom-atom bond X is broken. Inside the material shear may occur on the slip plane P. The strength of X may be lowered by the adsorption of a species S from the environment. Adsorption may raise the shear stress on P. Additionally, the surface may be covered with a film which is different in composition from the bulk, e.g. a passive film on a metal or an oxidized layer on a glass. The rupture of this film will be necessary before any environment-material reaction can occur. These aspects of fracture are discussed within the text.

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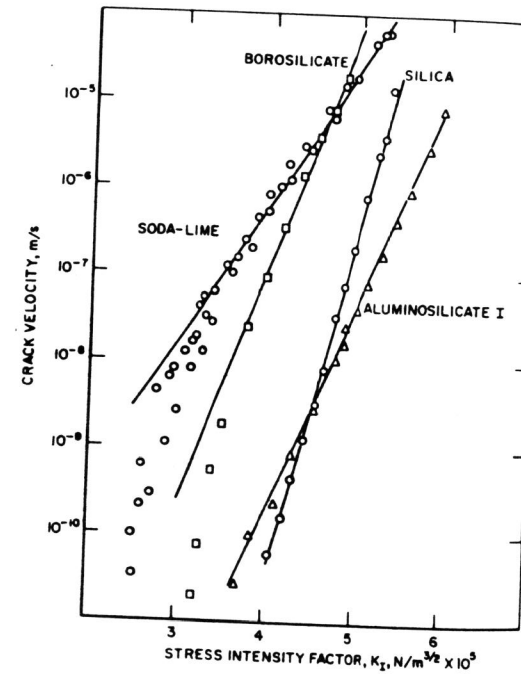


Figure 2. Fracture behaviour of glass in water at 25°C.⁹

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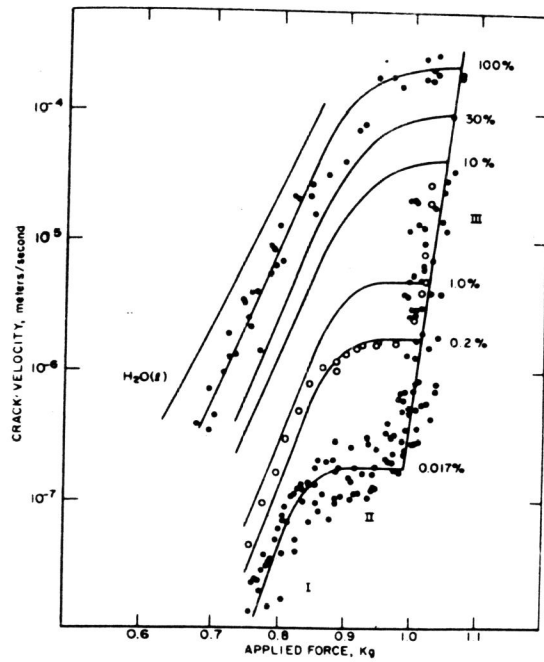


Figure 3. The relationship between crack velocity and applied force in soda-lime glass exposed to six environments of gaseous nitrogen at 25°C of different relative humidities and to full immersion in water.³

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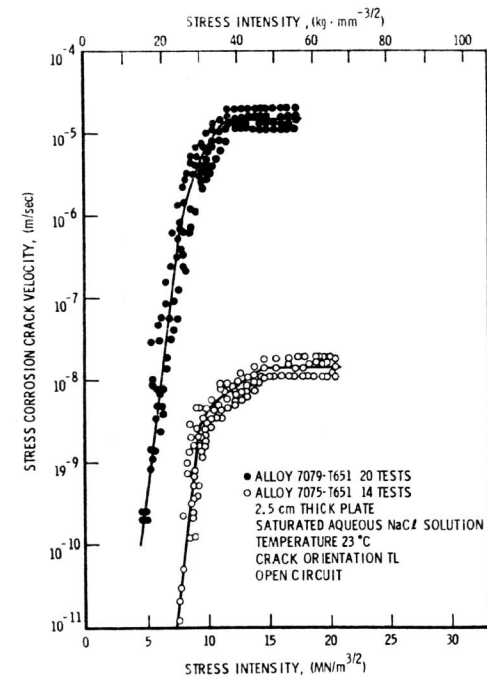


Figure 4. The relationship between crack velocity and stress intensity factor in two high strength aluminium alloys in NaCl solution.¹¹

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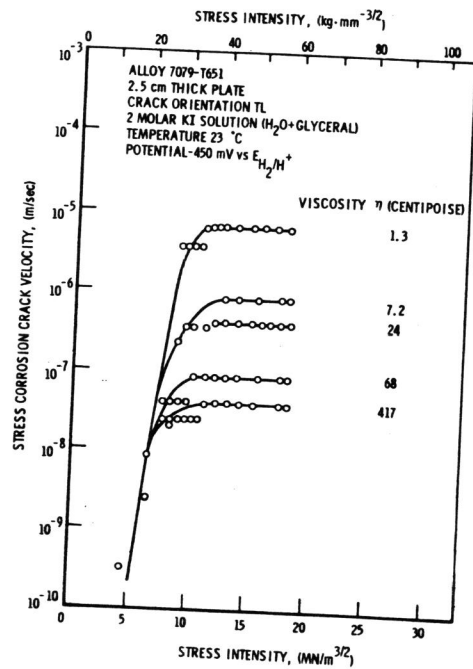


Figure 5. The relationship between crack velocity and stress intensity factor for an aluminium alloy immersed in water/glycerol mixtures of different viscosities.¹¹

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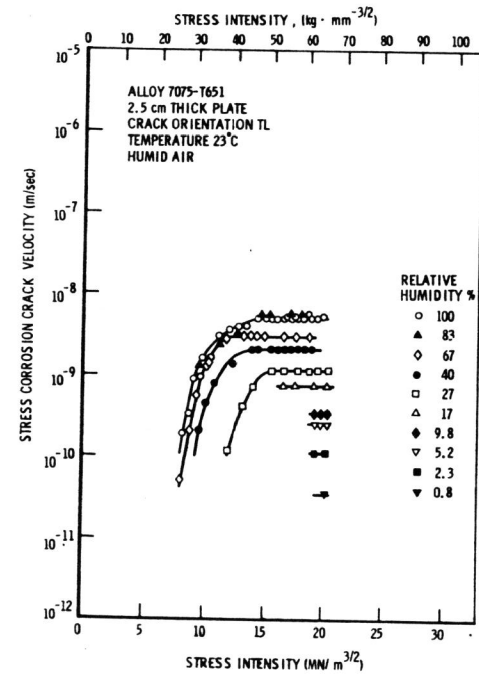


Figure 6. The effect of relative humidity on the relationship between crack velocity and stress intensity factor for a high strength aluminium alloy in air.¹¹

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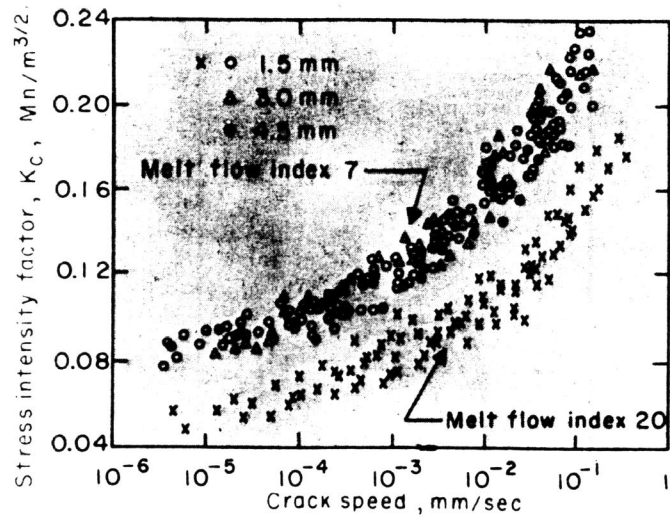


Figure 7. The effect of three different thicknesses and two different melt flow indices on the crack velocity in polyethylene in a methanol environment.²¹ The rate of increase in the velocity decreases as K increases for all conditions.

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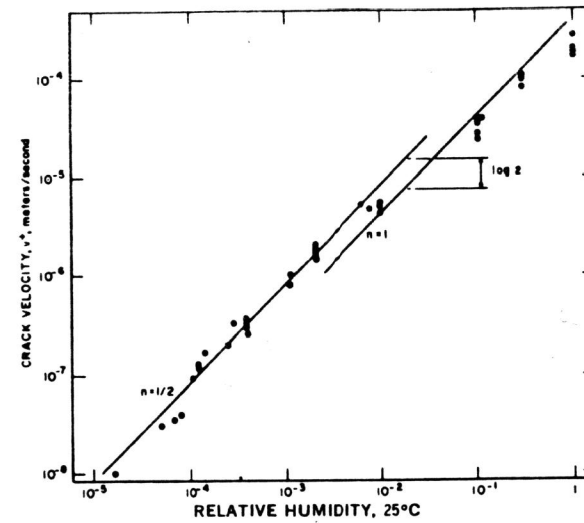


Figure 8. Relationship²⁵ between crack velocity in glass and water vapour concentration in region II. That at low concentrations $n=1/2$ and at high concentrations $n=1$ appear to yield the best agreement with experimental results.

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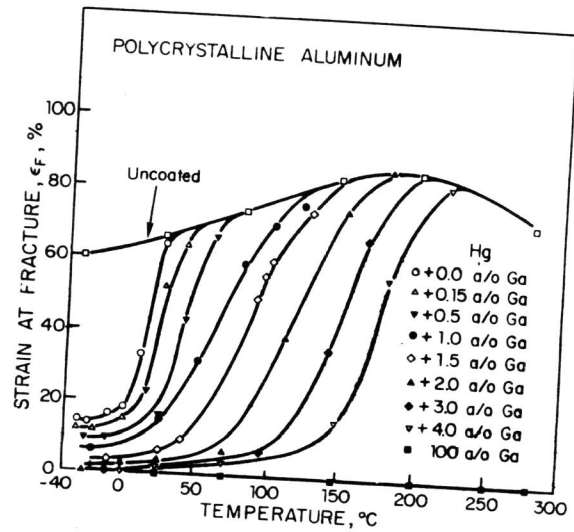


Figure 9. The temperature dependence of strain at fracture for polycrystalline aluminum specimens in mercury, gallium and mercury-gallium solutions³⁴. The results indicate that the ductile/brittle transition temperature is determined by the environment and not by the metal.

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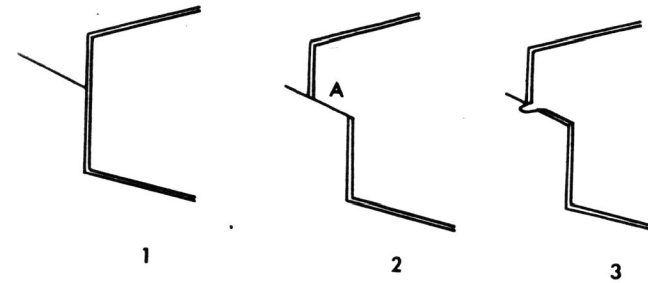


Figure 10. Schematic diagram depicting in three stages the creation of a slip step on an alloy surface covered with a passive film. The freshly created surface will be rapidly refilled but during the time in which this occurs corrosion attack and hydrogen entry are both likely to occur. Under very specific conditions the delay in repassivation will result in crack nucleation. Under a tensile stress the slip plane in (1) breaks the protective film creating unfiled metal surface (2) which repassivates except for a small part which undergoes dissolution and possibly exhibits hydrogen absorption (3).

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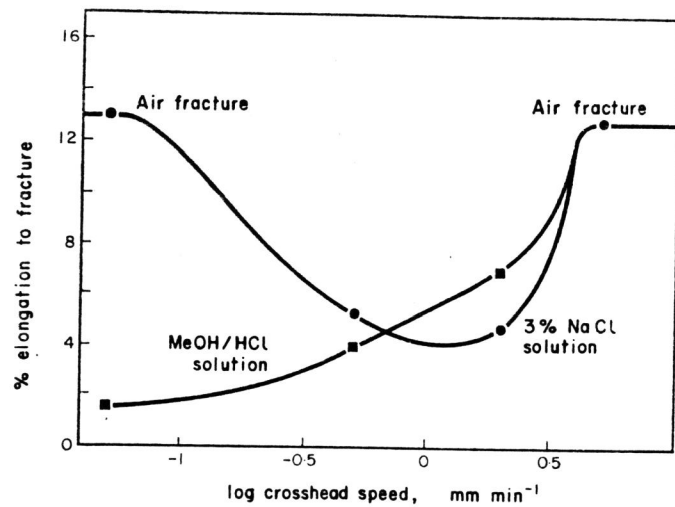


Figure 11. The elongation to fracture of tensile specimens of Ti-5Al-2.5Sn alloy of 3cm gauge length in 3% aqueous NaCl and in MeOH+1%HCl environments as a function of Instron crosshead speed.⁴¹

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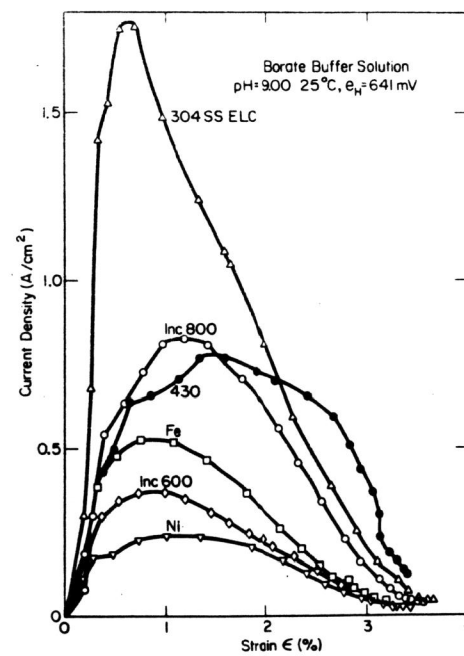


Figure 12. Current density as a function of strain for rapidly deformed wire electrodes potentiostatically controlled in a borate buffered solution⁴⁰. The alloy most susceptible to stress corrosion cracking develops the largest transient.

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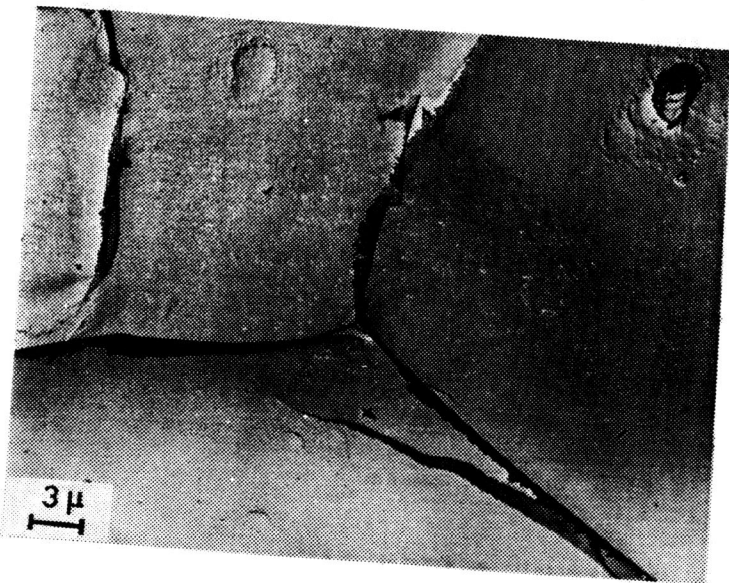


Figure 13. Carbon replica of the stress corrosion fracture surface of a high purity Al-6Zn-3Mg alloy after failure in distilled water. Very fine pitting and 'tongues' resulting from secondary cracking are visible but very little deformation. In air the same material exhibits transgranular dimple fracture.

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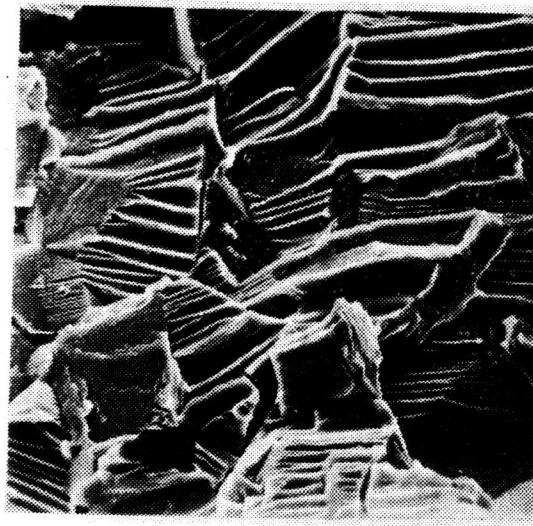


Figure 14. Scanning electron micrograph of the fracture surface of a Ti-0.29 O alloy after failure in a MeOH/HCl mixture. Areas of cleavage can be seen but much of the surface exhibits extensive fluting markings arising from a low energy tearing process. X590.

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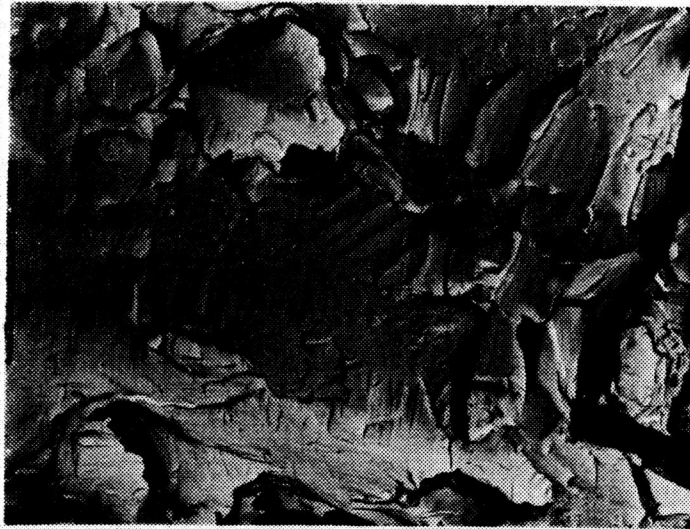


Figure 15. Carbon replica of the stress corrosion fracture surface of a Ti-6Al-4V alloy in the equiaxed condition after failure in a MeOH/HCl mixture. The cleavage facets have terminated in some instances by developing into a low energy fracture consisting of fluting markings, a process that represents a cleavage propagation arrest process.⁴⁶

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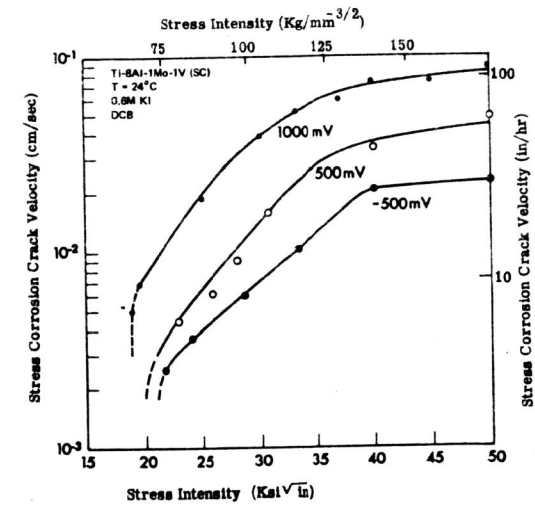


Figure 16. The effect of three different potentials upon the relationship between crack velocity and stress intensity factor for Ti-8Al-1Mo-1V alloy in 0.6M KI.⁵²

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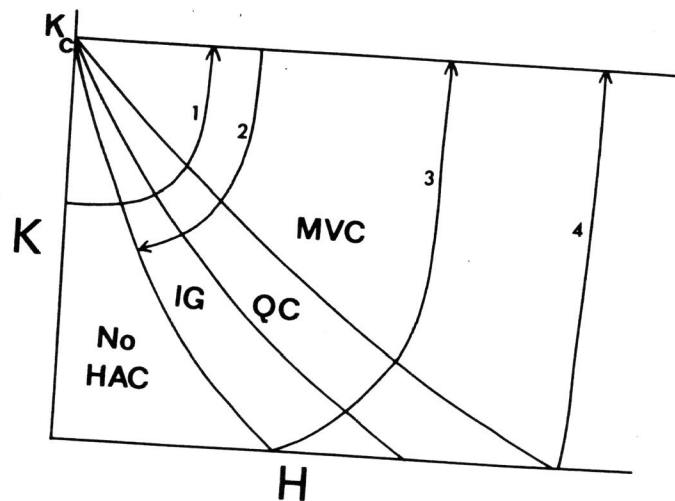


Figure 17. Suggested interrelationship between, K , dissolved hydrogen content (H) and hydrogen-assisted cracking (HAC) mode in microscopically small volumes of crack tip material to high strength steels (after Beachem⁵⁴). Three modes of cracking are observed: (a) micro-void coalescence (MVC), (b) quasi-cleavage (QC), and (c) intergranular (IG). Four of a number of conditions are indicated: 1. Constant K specimen: gradually absorbs hydrogen, three modes of fracture are observed. 2. Decreasing K specimen: three modes of fracture are observed before crack arrest. Increasing K specimens. 3. Three modes of fracture seen. 4. With a higher initial hydrogen content, only one mode of cracking is seen (MVC) but this is still hydrogen-assisted cracking.

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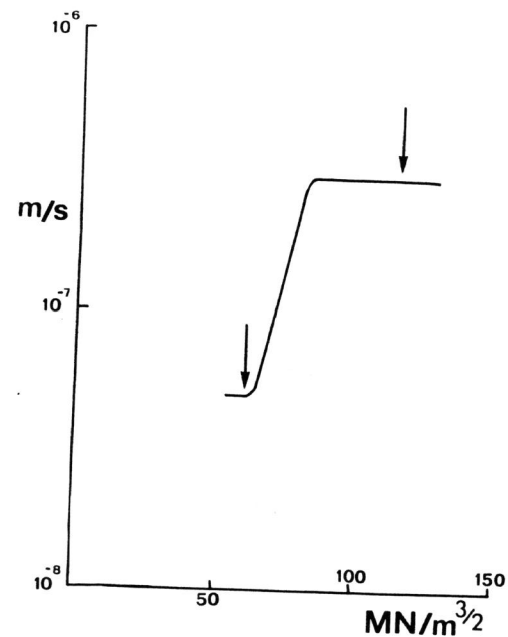


Figure 18. The relationship between velocity and stress intensity factor for stress corrosion cracks in an 18Cr-10Ni steel exposed to a $MgCl_2$ solution boiling at $160^\circ C$. Branching occurs on each plateau at values of K indicated by the arrows.

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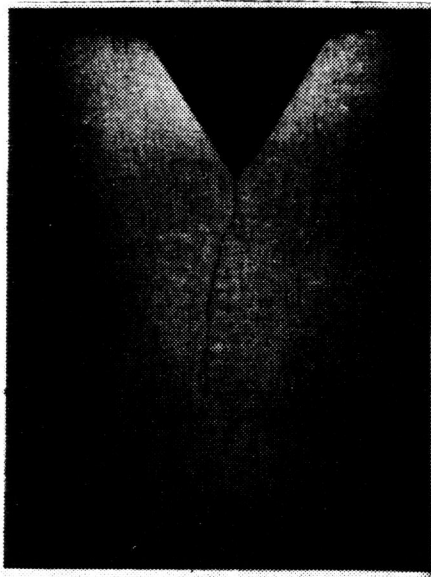


Figure 19. Optical micrograph of an austenitic stainless steel specimen initially stressed at a constant load in a $MgCl_2$ solution boiling at $160^\circ C$. Crack branching occurred at $28Kg/mm^2$. After this had occurred the stress was lowered to $25Kg/mm^2$ and kept constant. Only one front propagated under that condition. X20.

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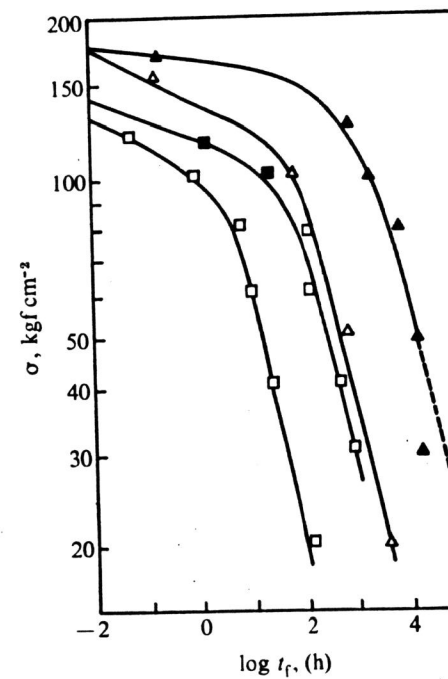


Figure 20. The relationship between time to fracture (t_f) and initial stress for various high density polyethylenes in water.⁶⁶

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