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Stress corrosion cracking of a titanium alloy in chloride-containing liquid environments

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Ti-8 Al-1 Mo-1 V was tested in solvents containing chloride, bromide or iodide ions. It was found that the region II plateau velocity could be correlated with the inverse of the viscosity for several solvents. It seems most likely that this reflects the influence of the viscosity on the diffusion coefficient of some species involved in a mass transfer process which limits the crack growth. Associated tests were performed in which the potential, pH and concentration of Cl^- were varied, in some of the same solutions as used for the viscosity tests. It is concluded from these tests that the *absence* of cathodic protection against cracking in solutions of low pH arises from an ohmic effect which isolates the crack tip from external potential control.

1. Introduction

Stress corrosion cracking (SCC) of titanium alloys, or any material, is a complex subject – for example, the scale (size) that may be examined ranges from the failure of large structures to atomistic descriptions of events at a propagating crack tip. In recent comprehensive reviews [1, 2] the range of the subject was demonstrated and it was shown that the myriad variables render any really complete and quantitative description of SCC unlikely at least in the near future. Thus, in selecting any aspect of the problem the constraints on experimental and theoretical analyses emerging from the investigation must be realized. The work which is described in this paper is an attempt to explain the controlling factors that determine the plateau velocity of a stress corrosion crack in some systems. The origin of this problem can be understood by examination of Fig. 1 which illustrates the extensive range of plateau velocities which may be observed in one alloy tested in various environments. It is noted that these environments contain liquids and gases, and in fact, if results for cadmium embrittlement [3] were present, could also include solid environments. Contemplation of Fig. 1 raised the obvious question of the factor(s) that control the plateau velocity and the point was selected as being worthy of further study. It was clear that one single physical property could not form the basis of an explanation of growth velocity – for example, it is difficult to see the connection (if any) between liquid mercury, molten halide salts and hydrogen gas. Thus, an initial restriction was placed on the range of these experiments and this paper only considers cracking in liquid environments.

It was considered that viscosity could at least provide a partial correlation in liquid environments. There was some evidence in the literature to support this hypothesis. Sedriks [4] had shown that the time-to-failure of smooth specimens of titanium tested in a series of alcohols containing iodine could be correlated with the viscosity of the solution. Beck *et al* [5] had also shown that the velocity of cracking in water-glycerol-HCl mixtures varied as the square root of the viscosity.

In order to investigate the influence of viscosity in ionic chloride (or bromide or iodide) solutions, it was necessary to study the effect of electrical potential, pH and concentration of chloride. That is, an excellent correlation of crack propagation rates with viscosity were obtained, but the absolute velocities depended on the solvent. Thus the influence of potential

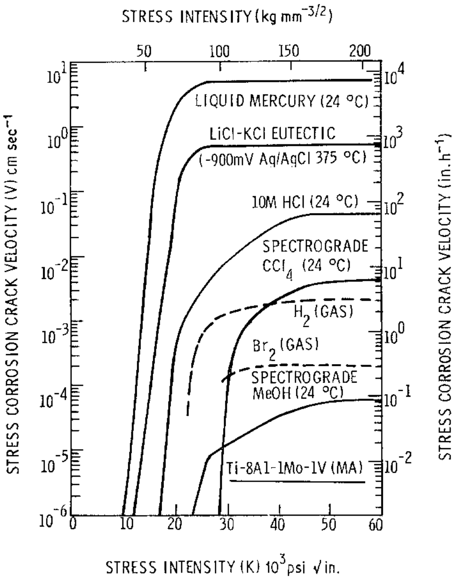

Figure 1 Crack velocity (V) versus stress intensity (K) for Ti-8 Al-1 Mo-1 V (mill annealed) tested in a variety of environments and illustrating the wide range of plateau (region II) velocities observed. Note that by using a different heat-treatment the velocity range could be extended to cover about eight orders of magnitude [1].

and concentration of ions were studied in an attempt to explain solvent and cation effects.

Previous work [1, 6-8] on the effect of concentration on crack velocity, demonstrated that several titanium alloys are susceptible to cracking in aqueous chloride solution, with the crack propagation velocity increasing with increasing chloride concentration. At high chloride concentrations, it has been shown [6-8] that the velocity of cracking varies as $C^{1/4}$ to $C^{1/2}$. The present work verifies this result for Na^+-containing solutions, but not for Li^+-containing solutions.

Previous work which determined the load to initiate cracking in neutral Cl^- solutions [9] demonstrated that there are two regions of potential where "protection" is exhibited – one anodic, the other cathodic. Initiation stress or initiation K both vary in a similar manner with applied potential [5, 10]. The velocity of cracking also varies in a complex manner with potential regions of anodic and cathodic protection being observed in neutral chloride solution at room temperature.* The terms anodic and cathodic protection are relative, at potentials more negative than -1300 mV (SCE) cracking rates are reduced to those observed in "inert" environments. At anodic potentials ($>$ 0 mV (SCE)) the cracking rates are reduced but in most cases are faster than those in inert environments, thus, in this case anodic crack retardation is probably a better description. It should be noted that such anodic retardation is a strong function of heat-treatment and probably preferred orientation, impurity content, etc, of any given alloy. For example, when the alloy studied in this investigation is heat-treated to precipitate the α_2 phase within the α phase, which increases SCC susceptibility, the anodic retardation region at room temperature is essentially eliminated. As discussed later, the anodic retardation region is also a strong function of halide ion type and temperature.

The results which will be presented are crack velocities as a function of stress intensity for several aqueous and non-aqueous solutions, at several temperatures. Associated viscosity and conductivity measurements were made and a general correlation between crack velocity and these variables will be demonstrated. The effect of concentration and applied potential on velocity of cracking will be reported also. Finally, crack propagation behaviour in a few non-ionic, chlorine-containing liquids will be described.

2. Systems investigated

2.1. Alloy

Titanium-8 aluminium-1 vanadium-1 molybdenum (Ti-8-1-1) was selected for these experiments as it had been widely studied. Also, many of the environmental effects on this alloy are observed in other titanium alloys, and it serves as a model system. A sheet 0.25 in. thick was selected which showed an extreme transverse (0002)α texture causing preferential crack propagation in the longitudinal direction. The heat-treatment selected was 820°C for 1 h and water quenched, as this resulted in the occurrence of crack extension over a wide range of K levels.

A complication in alloy selection became clear during the course of this study. The degree of susceptibility for any alloy is best demonstrated in practice by the position of a velocity (V) versus applied stress intensity (K) curve in the V:K plane, which defines both the plateau velocity in a given environment and the stress

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*See also [11], where similar results were found for this material, but in a slightly different metallurgical condition.

intensity value below which cracking will not occur, K_{ISCC}. It is well established that the presence of Cl^-, Br^-, and I^- ions in aqueous solutions either *induce* cracking or *accelerate* cracking with respect to any crack growth that occurs in an inert environment. The latter form of crack growth, first reported by Sandoz [12], may be due to residual hydrogen in the metal or a creep type failure. In the alloy, Ti-8 Al-1 Mo-1V, this (inert environment) form of crack growth is strongly dependent upon heat-treatment and the variation is represented semi-schematically in Fig. 2. It can be seen that in the lowest toughness condition, the difference between the salt solution and an inert environment is at a minimum but the difference increases as the rate of cooling from the solution-treatment temperature in the $\alpha + \beta$ region increases. The behaviour of the sheet of Ti-8 Al-1 Mo-1 V selected for this study was similar to that shown in Fig. 2. An earlier study (see [1]) indicated that after the 820°C water-quench treatment of a similar plate of Ti-8 Al-1 Mo-1 V, crack growth in inert environments at room temperature was extremely slow, $> 10^{-7}$ cm sec^{-1}. Crack growth in the Ti-8 Al-1 Mo-1 V sheet used in this study after the same heat-treatment occurred at $\sim 10^{-6}$ cm sec^{-1} in inert conditions, which obviously sets the lowest limit of crack growth in any environment at room temperature.

2.2. Solutions

The test solutions in the first part of the work described herein contained chloride or bromide ions added in the form of the lithium salt. These solutions were prepared with a constant mole ratio – 1:5, salt:solvent.

3. Experimental

The specimens used for this study were double cantilever beam (DCB) type, cut from the sheet in the WR orientation. These were loaded to a constant deflection using wedges of a Ti-11 % Mo alloy heat-treated to a strength level of 180 × 10^3 psi*. The applied stress intensity levels were computed from the standard equation for this specimen [13]. The specimen dimensions for these tests were 2.5 cm wide and 10 cm long, utilizing an initial crack length of 2.5 cm. Crack extension could be measured over a length of ~ 5.0 cm.

The properties of the alloy were as follows.

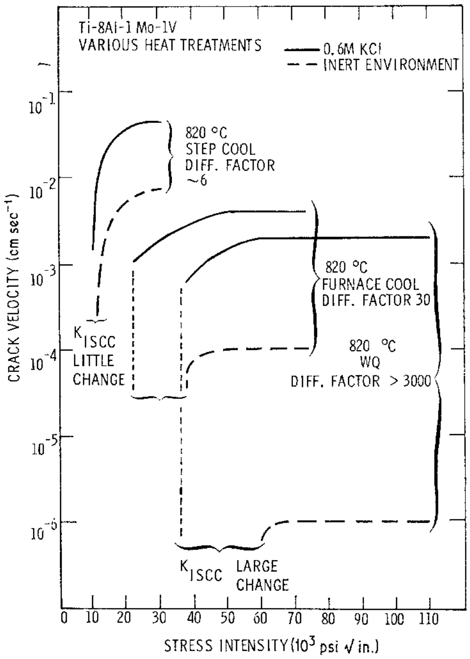

Figure 2 Crack velocity (V) versus stress intensity (K) relationships for Ti-8 Al-1 Mo-1 V tested in an aggressive (0.6 M KCl) and an inert (e.g. argon gas) environment. The relative displacements of the curve pairs is strongly dependent upon heat-treatment. Note that the lower (inert atmosphere) curve places a limit on the range of crack velocities that can be obtained in any series of experiments (at the same test temperature).

Mechanical properties – yield strength 124 × 10^3 psi (87.2 kg mm^{-2}), ultimate tensile strength 134 × 10^3 psi (94.2 kg mm^{-2}), 15% elongation. *Fracture toughness* – 90 × 10^3 to 100 × 10^3 psi $\sqrt{\text{in.}}$ (319 to 355 kg mm$^{-3/2}$), although this value is invalid as a plane strain fracture toughness value because the specimens did not comply with the thickness criteria of $t > 2.5\ (K/\sigma_Y)^2$. *Microstructure* – The heat-treatment results in the conventional equiaxed $\alpha + \beta$ structure. There was no evidence of the α_2-phase within the α-phase.

The physical properties of the solutions were either measured or taken from the literature. All solutions were made from analytical grade chemicals. The viscosity of many of the solutions used in this study was measured using calibrated falling-ball or Ostwald viscometers. The conductivity of each solution was measured using an a.c. bridge with the normal capacitance

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*10^3 psi = 0.703 kg mm^{-2} = 6.89 N mm^{-2}.

compensation [14]. The measurements were made at a fixed frequency of 1000 Hz. The conductivity cell was calibrated with a 1.0 demal solution of KCl. The electrodes of the conductivity cell were bright platinum because it is known that some non-aqueous solvents (e.g. DMSO [15]) decompose at platinized-platinum electrodes.

Tests were conducted at several temperatures between −70 and 220°C, and the general technique was as follows. The solution in which the test was to be conducted was held at the required temperature (± 4°C) in a constant temperature bath. Unloaded specimens were cooled or heated to approximately the same temperature, rapidly loaded and immersed in the solution. Crack extension was measured optically with reference to a grid scribed on the specimen surface. During the tests at open circuit the potential was monitored with reference to a room temperature saturated calomel electrode (SCE). In tests performed under a controlled potential a Wenking potentiostat was used in conjunction with a platinum counter electrode and a room temperature SCE.

4. Results

The results of the effect of potential will be presented first, followed by the correlations of plateau velocity and conductivity. Finally, the results of several supplementary tests will be presented.

4.1. Effect of potential on crack propagation velocity

4.1.1. Potential effects at different temperatures

A series of tests were performed at fixed potentials at +95, +23, −25 and −47°C. At +95°C, cathodic protection still occurs at potentials more negative than −1300 mV but there is little influence of potential in the range −1000 to +1000 mV. At +23°C both anodic crack retardation and cathodic protection are exhibited, as may be seen in Fig. 3. Reducing the test temperature below room temperature results in only minor modifications of the shape of the potential velocity curves.

4.1.2. Potential effects at different pH conditions

Several experiments related to those above were performed to check the influence of potential on crack growth in highly acidic environments.

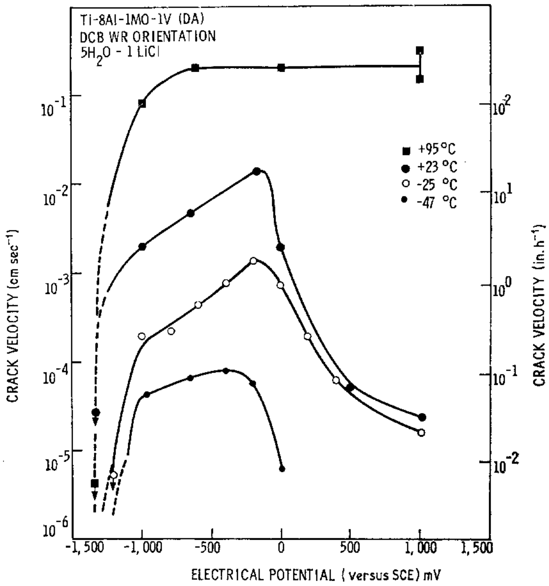

Figure 3 The region II (plateau) velocity versus potential for Ti-8 Al-1 Mo-1 V measured at several temperatures in 5:1 water:LiCl solutions. Note that cathodic protection occurs at all temperatures but anodic crack retardation does not occur at +96°C although present at lower temperatures.

Solutions of HCl:water with the same mole ratio (i.e. 1:5) were prepared and crack growth measured over a range of potential. The results are shown in Fig. 4 in the form of velocity (V) versus stress intensity (K) curves from which it can be seen that, as reported previously, the region of cathodic protection is eliminated in this solution [8]. The plateau velocity shows only a small variation between −1500 and −200 mV and there are indications that the V:K curve at +2000 mV is again similar. However, potentials in the range 0 to +1500 mV again result in rather slow cracking indicating another range of anodic retardation similar to that found in neutral aqueous chloride solutions. There is also evidence indicated in Fig. 4 that the velocity is strongly dependent on the test conditions in the anodic retardation region. Results for two tests at +500 mV are recorded, the lower V:K curve is for a test run at potential for the complete test (dynamic test) while the results at higher velocity were obtained by switching a crack propagating at −200 to +500 mV. The results from dynamic tests are used in subsequent figures.

The influence of potential on crack growth in 9 M HBr and 5.5 M HI was also studied and the results are shown in Fig. 5. In these solutions

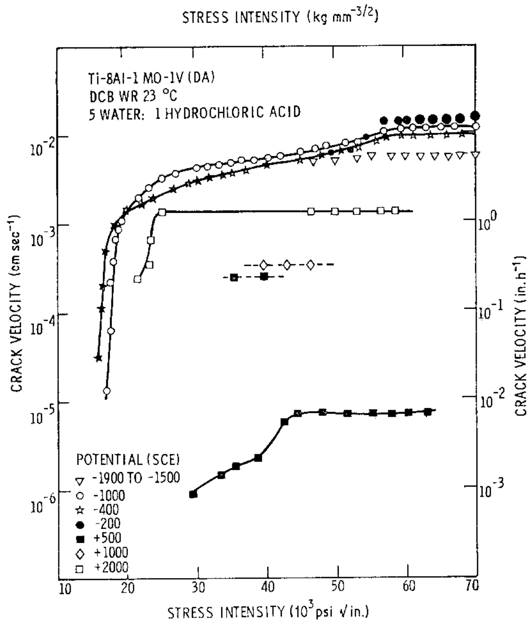

Figure 4 Crack velocity (V) versus stress intensity (K) relationships for Ti-8 Al-1 Mo-1 V tested in 9 M HCl solutions at various potentials at room temperature. The two results for a potential of +500 mV were obtained in a complete test at potential (lower curve) and changing the potential on a dynamic crack at −200 mV (upper points).

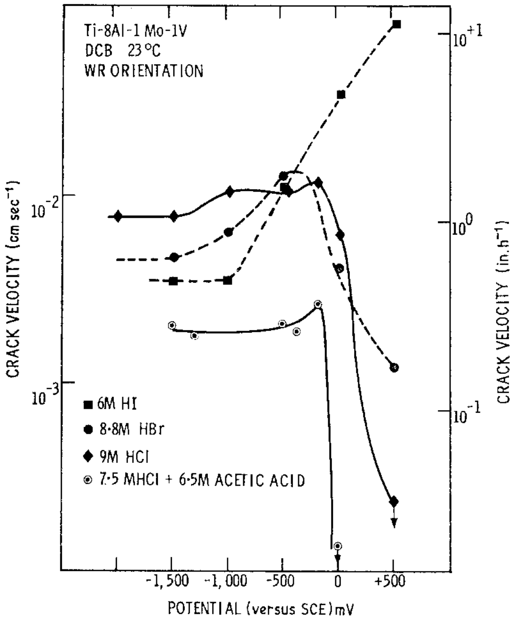

Figure 5 Region II (plateau) velocity variation with potential in three concentrated halogen acid solutions at room temperature. Note that cathodic protection does not occur in such solutions and that anodic potentials produce more complicated behaviour.

there was a more pronounced effect of cathode potentials in that the velocity of cracking was lower at −1000 mV than at −500 mV. However, further reduction of potential led to no further decrease of velocity. Thus in all three acids complete cathodic protection was impossible but the level of plateau (cathodic) velocities is in the order HCl > HBr > HI. (Note that the concentrations of the acids are slightly different.)

An attempt was made to extend the passive range in hydrochloric acid, especially to reduce the potential at which hydrogen was evolved to more negative values. This was accomplished by adding acetic acid to the HCl which reduced the potential for copious hydrogen gas evolution (controlled by the IR drop) on an oxide covered specimen from ∼ −400 to ∼ −800 mV. The results shown in Fig. 5 illustrate that the velocity of crack propagation is reduced in such solution mixtures but the general potential:velocity results are comparable with the results in hydrochloric acid.

Tests were performed in several solutions with pH between −1 and 7 to determine the pH at which cathodic protection would be possible. These solutions were made up of mixtures of LiCl and HCl such that the overall ratio of water to Cl^- was constant at 5:1. For HCl concentrations between 9 M and 0.5 M (the remainder of the Cl^- was added at LiCl), the effect of potential was identical to that for 9 M HCl, i.e. no cathodic protection. Cathodic protection first became possible in solutions containing 0.1 M HCl and 8.9 M LiCl, and the results are shown in Fig. 6.

From these and additional tests [16], it appeared that the influence of potential on crack growth is strongly temperature dependent, which complicates the establishment of any relationship involving velocity as a function of temperature at open circuit potential. It is of interest that the influence of potential decreases at elevated temperatures which is parallel to the behaviour observed in molten salt solutions where the plateau velocities are independent of the applied potential [17].

It had been suggested previously by proponents of both the anodic dissolution [18] and hydrogen embrittlement [19] postulates for the mechanism of SCC in aqueous solutions that the essential reason for cathodic protection is that OH^- ions are generated at the crack tip. The

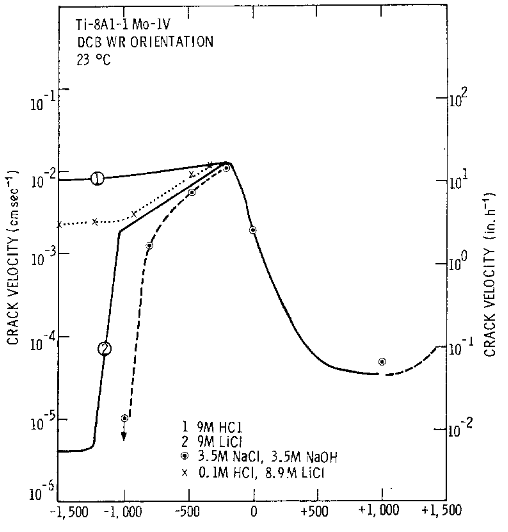

Figure 6 Variation of region II plateau velocity with potential in acidic neutral and basic solutions. Note the similarity of maximum velocities at -200 mV and that anodic crack retardation is observed in all solutions. Cathodic protection does not occur in the acid solution but is present in neutral and basic solutions.

arguments on the influence of such OH^- ions on crack propagation are obviously slightly different for the two cases but the details need not concern us here. To study solutions with high pH and coupled high concentration of halide ion is rather difficult owing to the relatively low solubility of the hydroxide in the case of lithium and the low solubility of the chloride in the case of sodium and potassium. Thus a compromise solution containing 3.5 M sodium chloride and 3.5 M sodium hydroxide was used. The influence of potential on crack velocity in this solution is shown in Fig. 6 compared with those observed in acidic and neutral solutions. It can be seen that the behaviour is very similar to that in neutral solution. However, the region of cathodic protection is shifted from potentials more negative than -1300 mV (neutral) to more negative than -900 mV (basic).

4.2. Plateau velocity-viscosity correlations

4.2.1. Lithium chloride-water

This environment was selected because of the wide range of temperatures (and viscosities) over which tests could be performed. Using the 1:5 LiCl:H_2O mixture, it was found that tests could not be performed below ~ -70°C owing to precipitation of LiCl which occurred preferentially on the specimen. Tests were thus performed over the temperature range $+112$ to -70°C in this solution. Some viscosity data for these solutions was obtained from [20] and some from [21] and the two were in excellent agreement where they overlapped. The variation of plateau velocity with temperature is shown in Fig. 7 and shows a similar trend to the viscosity data. It is immediately apparent that the velocity

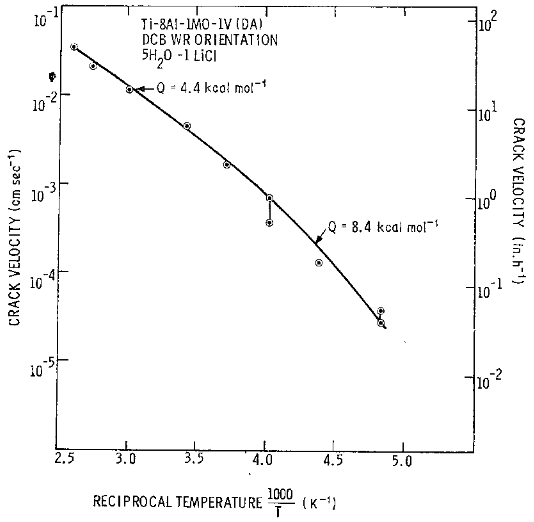

Figure 7 The variation of region II (plateau) velocity with reciprocal temperature (K) for Ti-8 Al-1 Mo-1 V tested in 5:1 water:LiCl mole ratio mixtures.

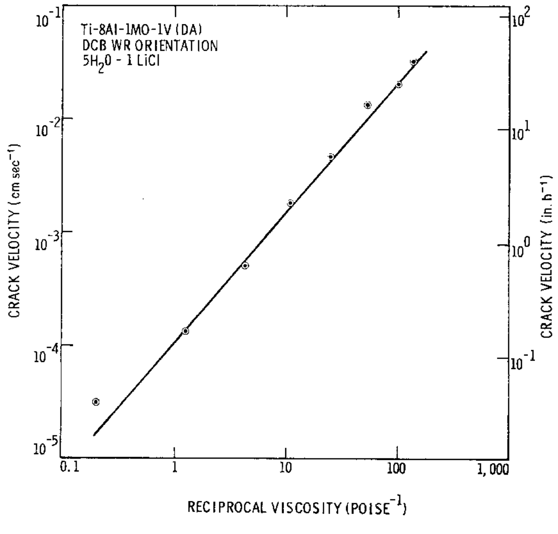

Figure 8 The variation of region II (plateau) velocity with reciprocal viscosity ($1/\eta$) for Ti-8 Al-1 Mo-1 V tested in 5:1 water:LiCl mole ratio mixtures.

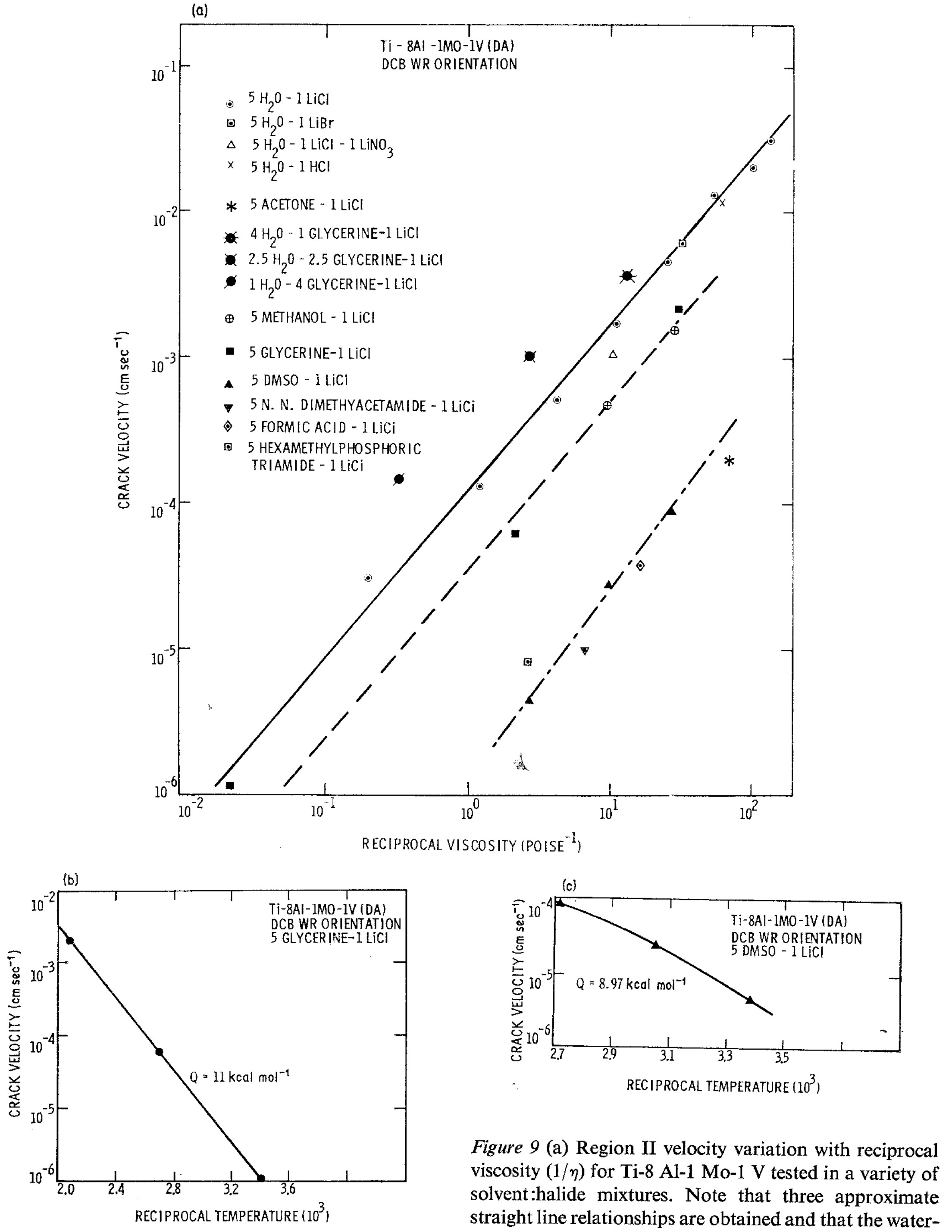

Figure 9 (a) Region II velocity variation with reciprocal viscosity ($1/\eta$) for Ti-8 Al-1 Mo-1 V tested in a variety of solvent:halide mixtures. Note that three approximate straight line relationships are obtained and that the water-glycerine-LiCl results lie above the water and glycerine lines. (b) The variation of region II (plateau) velocity with reciprocal temperature (K) in glycerine:LiCl mixtures. Note the apparent activation energy is ~ 11 kcal mol^{-1}. (c) Similar results obtained in DMSO:LiCl mixtures which yield an apparent activation energy of ~ 9 kcal mol^{-1}.

does not show a linear relationship over this temperature range, and thus the apparent activation energy for the process is not constant – in fact, the value varies from 4.4 kcal mol^{-1} at the higher temperature (~ 80°C) to 8.4 at the lower temperatures (~ −50°C). The apparent activation energy of the viscosity exhibits both a similar variation and approximately the same numerical values over this range (see [20]). Fig. 8 shows the variation of the logarithm of the velocity of crack growth with the logarithm of the reciprocal of the viscosity which illustrates that a linear relationship is obtained with a slope of 1.14. A smaller number of tests were performed in which the halide ion or the cation were different. Fig. 9a includes data for LiBr-water and HCl-water solutions and it can be seen that these points are close to the LiCl-water results.

4.2.2. Other solutions

The choice of solvents other than water was restricted by the requirement that the solubility of LiCl or LiBr had to be sufficiently high to produce a 5:1 solvent:solute solution. The following solvents were found to fulfill this requirement.

methanol
glycerine
dimethyl sulphoxide
hexamethylphosphoric triamide
N, *N*-dimethyl acetamide
formic acid (9% H_2O)
} lithium chloride
acetone-lithium bromide (⩾ 60°C)

Before describing the results obtained in these solutions some of the experimentally imposed limitations should be noted. The methanol solutions could only be studied over a limited temperature range; the upper limit (~ 60°C) being dictated by the evaporation rate of the methanol and the lower limit (~ 20°C) by the rapid fall in solubility of LiCl. Glycerine solutions could be utilized over a wider range of temperatures although some decomposition appeared to occur at temperatures > 230°C. Some ambiguity was introduced using this solvent due to the absorption of water – this was minimized in these tests by using fresh glycerine (water content <0.1%) and by heating the solution to 210°C which appeared effective in removing water introduced with the LiCl. Dimethyl sulphoxide would not dissolve sufficient LiCl at room temperature to produce a 5:1 mole ratio and some tests were performed in 6:1 mole ratio solutions. However, it was found later that at temperatures above ~ 100°C, 5:1 mole ratio solutions could be prepared and the supersaturated solution was stable on cooling to room temperature. The acetone solution also had a limited temperature range available for study for the same reasons as the methanol:LiCl solutions. Tests in the other solutions were only performed at room temperature. Similar tests were performed in these solutions as those in the LiCl:water mixtures – stress corrosion tests in which the plateau velocity was the parameter of interest coupled with viscosity (and conductivity) measurements on the solutions. The results of these tests are summarized in Figs. 9a, b and c, and the following points can be made, although it should be recognized that the data are less numerous than those for LiCl-water mixtures.

1. The apparent activation energies for the plateau velocity crack growth are ~ 11 kcal mol^{-1} for glycerine, ~ 9 kcal mol^{-1} for DMSO and ~ 5 kcal mol^{-1} for methanol (not shown), and are constant over the temperature range investigated.
2. The apparent activation energies are similar to the activation energies of the viscosity in these temperature ranges (data not shown).
3. The log velocity-log reciprocal viscosity lie on two curves. Results in glycerine and methanol lie on the same curve which is parallel to but displaced downwards from the LiCl-water results. The results in acetone, DMSO, etc, lie on a line of similar slope displaced downward from the other curves.

4.2.3. LiCl: water: glycerine solutions

In the above experiments the viscosity of the solutions was changed by varying the temperature. It was considered that an investigation of solutions in which the viscosity was varied at a constant temperature would provide useful confirmatory evidence for the velocity-viscosity correlation. Thus, a series of tests were performed on LiCl-H_2O-glycerine mixtures. These results are included in Fig. 9a and it can be seen that these results do not conform with those obtained in other solutions. In fact, over the viscosity range 0.1 to 1 P* the relationship between viscosity and velocity is very similar to that obtained in an earlier investigation in which a $\eta^{1/2}$ relationship was obtained [5]. However, at very high viscosities the plateau velocity shows a much stronger viscosity dependence. Note that the water-LiCl and glycerine-LiCl points are the end points of this curve. It is also of interest that

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*1 P = 0.1 N sec m^{-2}.

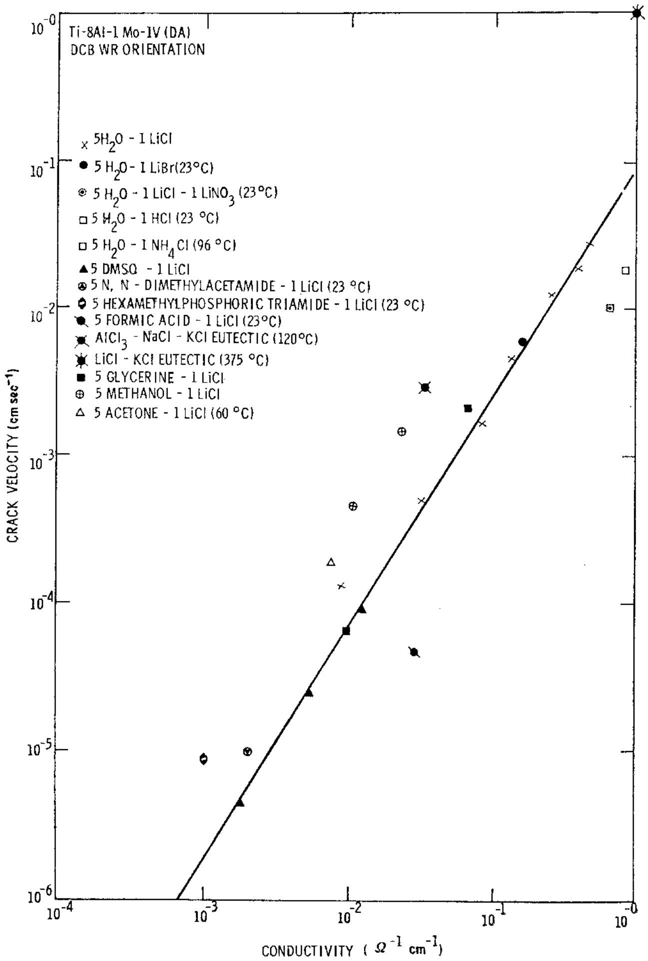

Figure 10 The variation of region II (plateau) velocity with conductivity of several solutions containing the halide ions (5:1 mole ratios). Results lie in a scatter band through which a line of slope 1 could be constructed. The line present on this figure is drawn through the LiCl:water and LiCl:DMSO points and has a slope of 3/2. Note that earlier results [9] obtained in molten salt mixtures lie near this line.

the points lie above both the glycerine-LiCl and water-LiCl mixtures which indicates a synergistic effect when comparison is based on *viscosity and molarity* (but not on an absolute velocity scale).

4.3. Plateau velocity-conductivity correlation

The conductivity of the test solutions was determined either from existing data or by direct measurement. Next the logarithm of the plateau velocities determined above were plotted against the logarithm of these conductivities with the resulting relationship shown in Fig. 10. It can be seen that, at least between velocities of 10^{-4} and 10^{-1}, a linear relationship is obtained in which velocity varies as conductivity$^{3/2}$. In passing, it could be noted that the results for two molten salt mixtures LiCl-KCl at 375°C and NaCl-KCl-AlCl$_3$ at 120°C also lie near, but somewhat above, the curves for the solvent: chloride mixtures. At velocities $<10^{-4}$ cm sec^{-1} the curves tend to deviate from the linear relationship at least in the aqueous and glycerine solutions. This immediately raises the question of why such deviations occur (assuming, of course, that the relationship observed is not fortuitous). Two possibilities which occurred to the authors were:

1. reaction products generated within a crack during its propagation produce local modifications of viscosity and conductivity and these changes assume more importance in high vis-

cosity solutions at low temperatures (low velocities). It is known that the H^+ ion is generated during the propagation of a crack [22] and thus it seemed pertinent to investigate the viscosity and conductivity of LiCl-HCl-water mixtures at low temperatures. Such solutions were prepared (keeping the $Cl^-:H_2O$ mole ratio constant at 1:5) and the measurements on the solutions at temperatures as low as −70° C indicated no significant differences from the LiCl:water solutions. This indicated that this hypothesis could not explain the deviation;

2. that potential has a much larger effect at low temperature (low velocities) and thus open circuit might not be the appropriate potential at which crack velocities should be compared. Measurement of the open circuit potential in the aqueous solution during SCC testing indicated a range of values for open circuit potential of -600 ± 150 mV and that during a specific test the value also varied over about the same range. The effect of potential on the plateau velocity was described above and does not appear to be of a sufficient magnitude to explain the deviations.

4.4. Solution containing non-ionic chlorine

A reasonable extension of these tests in liquid environments containing the chloride ion appeared to be a study of solutions which contain chlorine in other forms. It had been established that some titanium alloys are very susceptible to stress corrosion cracking in carbon tetrachloride (CCl_4). In order to see if the crack velocity in this solution varied with temperature (and thus viscosity), three tests were performed over the temperature range +50 to −25° C. These results indicated that in this solution the crack velocity does not depend on viscosity in any simple way. The approximate apparent activation energies determined from these SCC tests were ~ 4 kcal mol^{-1} above room temperature and ~ 9 kcal mol^{-1} below room temperature.

Two further tests were conducted in chloroform ($CHCl_3$) in order to evaluate the influence (if any) of replacing one −Cl by −H in the solvent. Both tests indicated that initially the crack grew at very slow rates, ~ 10^{-6} cm sec^{-1} but after induction times varying from 8 to 70 h the cracking accelerated and reached comparable values with those observed in CCl_4.

Finally, one test was performed in titanium tetrachloride ($TiCl_4$) which yielded the velocity stress intensity curve shown in Fig. 11. The velocity of cracking was relatively slow in this solution yielding a plateau velocity of ~ 7×10^{-5} cm sec^{-1} coupled with a low K_{ISCC} level (the existence of region I behaviour could not be excluded on the basis of this one test).

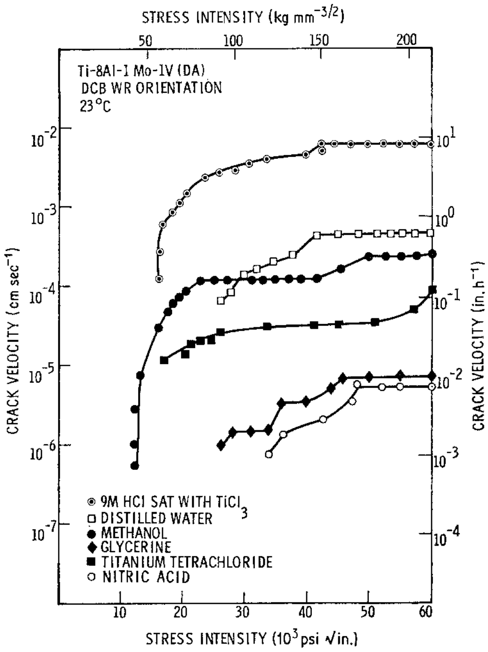

Figure 11 Crack velocity (*V*) versus stress intensity (*K*) for Ti-8 Al-1 Mo-1 V tested in several solutions. Note the similarity of the $HCl:TiCl_3$:water curve with the −400 mV curve in Fig. 4, with the exception of region I type crack growth. The velocity results in titanium tetrachloride are very similar to cracking rates observed in DMSO:LiCl type solutions (Fig. 9) and in the anodic crack retardation range (Figs. 4 to 6).

4.5. Supplementary tests

In this section we note two further groups of experiments that were conducted that certainly influence any interpretation of results but do not fall into any well-defined category.

4.5.1. Addition of Ti^{3+} ions

It has been proposed that dissolution of titanium is the critical step or at least forms part of the process of SCC [23]. The titanium species that forms in acid solutions (pH = 0) at potentials between −800 and 0 mV should be Ti^{3+} and thus it was considered that the presence of this ion in solution could influence SCC behaviour. The Ti^{3+} ion is unstable in neutral aqueous solutions and thus an acidic solution was utilized, specifically a solution of 9 M HCl saturated with $TiCl_3$. (The solubility of $TiCl_3$ in the solution is high,

$>$ 1 M in 9 M HCl.) A test was performed in this solution at open circuit (-350 mV) and the resultant V versus K curve is shown in Fig. 11. Comparison of this result with the V:K curve for 9 M HCl at -400 mV (Fig. 4) indicates the two curves are identical below a K value of 42×10^3 psi $\sqrt{\text{in.}}$ (149 kg mm$^{-3/2}$). The plateau velocity in the HCl:$TiCl_3$ solution was slightly lower than that in the HCl solution. One final point of interest is that a strongly stress intensity-dependent crack growth (region I type growth) is observed in concentrated HCl solutions at low K levels, but appeared to be eliminated in the $TiCl_3$:HCl solutions, as crack growth did not occur below a velocity of 10^{-4} cm sec^{-1}.

4.5.2. Inert environments

As mentioned in the introduction, results from any group of SCC tests can be complicated by the tendency of a very susceptible alloy to exhibit crack growth in any (and all) environments. The following is a list of aqueous environments in which crack growth was also observed but which did not contain any deliberate additions of the halide ion.

80% sulphuric acid
nitric acid (15.8 M)
saturated $AgNO_3$ ($\sim$ 10 M)

In all these environments crack growth occurred at rates between 1×10^{-6} and 5×10^{-6} cm sec^{-1} (a complete V:K curve for nitric acid is shown in Fig. 11). As cracking was observed to occur at the same rate in dry argon gas such crack growth appears independent of the environment and certainly of its viscosity. Crack growth in any solvent cannot occur at slower rates at room temperature which sets a lower limit on any relationship established (cf. glycerine: LiCl results).

Additions of chloride ions to nitric acid was briefly studied and it was found that crack growth was not accelerated in 3:1 and 2:1 mixtures of 15.8 M HNO_3 and 12.1 M HCl.

The variation in the crack growth in inert environments with temperature was also studied in detail although such data are of importance in the interpretation of the temperature dependence in more aggressive environments. One test in silicone oil at 100°C showed that cracks propagated slowly (velocity of 10^{-6} cm sec^{-1}) at high K levels ($\geqslant 65 \times 10^3$ psi $\sqrt{\text{in.}}$) which indicates that low or perhaps negative temperature dependence of cracking in such solutions and a large increase in threshold stress intensity with temperature.

4.5.3. Influence of concentration in "aggressive" solutions

Most of the data reported in the previous sections were for 5:1 molar ratio mixtures. In the course of this work several tests were run in which the chloride concentration and the cation was varied. It has been shown [10] that in 0.6 M solutions the nature of the cation has little influence on crack growth rate as long as the cation does not influence the potential of the system, e.g. Cu^{++} can lead to low velocities owing to the establishment of an anodic potential set up by the $Cu^{2+} \rightleftharpoons Cu^{+} \rightleftharpoons Cu$ couples. Tests in which chloride ion concentration was varied with the cation H^+, Na^+ and Li^+ indicated that at a constant potential (~ -200 mV):

(a) in H^+ solutions, velocity varied as the square root of the chloride concentration;
(b) in Na^+ solutions, velocity showed a somewhat low dependence especially in solutions with molarity $>$ 1 M;
(c) in Li^+ solutions, velocity remained essentially constant at molarities $>$ 0.1 M.

However, if the influence of viscosity is considered, these results can be at least qualitatively accounted for, since increasing the concentration of solute increases the viscosity most in LiCl and least in HCl. For example, the viscosity of a 9 M LiCl solution is $\sim$ 5 cP while that of a 9 M HCl solution is 1.8 cP.

Also, it may be noted that increasing the concentration of LiCl in glycerine to a mole ratio of 1.3 glycerine-1 LiCl, produced a solution of higher viscosity than the 5:1 mole ratio solution. The crack velocities in this solution also fall on the glycerine curve in Fig. 9a (not included).

4.6. The value of K_{Iscc}

For completeness, the values of K_{ISCC} determined in the above tests are listed in Table I. It should be noted that region I type behaviour was found in some solutions which are marked with a dagger (†) and the value of K_{ISCC} is quoted for a crack velocity of 10^{-5} cm sec^{-1}. As there is no really quantitative explanation of the value of K_{ISCC} at this time [1], the table is presented with no further comment.

5. Discussion

The results presented above have defined more

TABLE I Value of K_{ISCC} in several environments

(1) *Pure solvents*

Solvent	Water	Methanol	Glycerine	Carbon tetrachloride	Chloroform
K_{ISCC} (10^3 psi$\sqrt{\text{in}}$)	26 (23°)* 42 (96°)	13.8 (23°)†	26 (23°)	19.4 (−11°) 20.0 (23°) 19.5 (50°)	21 (23°)

(2) Solutions containing chloride or bromide ions, 5:1 solvent:solute ratio

(a) Open circuit

Solvent Solute	Water LiCl	Methanol LiCl	Glycerine LiCl	DMSO LiCl
K_{ISCC}, (10^3 psi$\sqrt{\text{in}}$)	>20.0 (−46°)*	13.0 (23°)†	19.0 (23°)	19.0 (23°)
	22.7 (−26°)		26.0 (96°)	>25 (55°)
	20.3 (−3°)	13.0 (58°)†		
	17.0 (+2°)		26.0 (210°)	
	14.7 (23°)			
	21.8 (60°)			
	20.8 (96°)			
	22.7 (113°)			

(b) Open circuit, room temperature,	23°C
Hexamethylphosphoric triamide	27.8
N, N-dimethylacetamide	30.6
Water-lithium bromide	19.5

(c) Open circuit – other temperatures

Acetone-lithium bromide	>30 (66°)*
Water-ammonium chloride	26 (95°)

(3) Mixed solvents containing chloride ions; 5:1 solvent:solute ratio, open circuit (room temperature 23°C)

Formic acid, water, lithium chloride	25.0
Water (3.4), DMSO (1.6), lithium chloride (1)	19.5
Water (4), glycerine (1), lithium chloride (1)	19.0
Water (2.5), glycerine (2.5), lithium chloride (1)	18.0
Water (1), glycerine (4), lithium chloride (1)	24.5

(4) Solutions containing chloride ions, 5:1, solvent:solute ratio various temperatures and potentials (mV versus SCE)

Solution	Temperature (°C)				
Water:LiCl	23	23.2 (−1000)	19.9 (−200)		20.0 (+2000)
	95	29.0 (−1000)	22.2 (0)	21.3 (+1000)	23.9 (+2000)
Water:HCl	23	17.0 (−1000)†	15.5 (−200)†	27.7 (+500)	20.8 (+2000)

(5) Miscellaneous

Water, 0.1 M lithium chloride, open circuit 23.1 (2°), 24.8 (23°), 30.2 (90°)

Water, 0.6 M sodium chloride (−500 mV)	20.0 (23°)
Water, 3.5 M NaOH, 3.5 M sodium chloride	21.4 (23°)
Water, HCl, 1 M LiCl_3, open circuit	16.3 (23°)
Water, 9 M LiNO, 9 M lithium chloride, open circuit	23.2 (23°)

(6) Inert environments

Room temperature (23°C)	36-45
100°C (silicone oil)	~65

*Temperatures are given in °C.

†Stress intensity for crack velocity of 10^{-5} cm sec^{-1}.

accurately some of the factors that influence region II crack propagation in a titanium alloy in certain environments. Incorporation of these results into any meaningful theory of SCC is much more difficult, however, owing to the lack of any base on which to build and our inability to find any relatively simple explanation of the results. It should be emphasized that the following discussion relates only to the controlling factors of region II crack velocity and is essentially chemical in nature. The metallurgical and mechanical factors are accepted as necessary conditions for stress corrosion cracking with no further attempt to explain them.

5.1. Influence of potential

The effect of potential on region II cracking is shown in Figs. 3 to 6 for aqueous halide solutions at several pH conditions and several temperatures. The maximum velocity was observed at about −300 mV (versus SCE) with both cathodic and anodic retardation found in neutral and basic solutions especially at low temperatures. The potential of the maximum velocity did not change much with temperature, but both cathodic and anodic retardation effects were smaller at higher temperatures.

At the same time as the data were taken for Fig. 6, it was noted that hydrogen evolution on the bulk surface of the specimen was quite vigorous in 9 M HCl at −400 to −600 mV (versus SCE) and more negative, while it was necessary to attain −1200 mV to achieve the same level of hydrogen evolution in neutral solutions, and even more negative potentials were required for the basic solution. This is consistent with the expected shift in equilibrium potential with pH of the $H^+ - H_2$ reaction. Polarization curves (cyclic voltammograms) were then run on specimens of identical size and in an identical geometrical arrangement as used in the stress corrosion tests. It was found that hydrogen evolution became *IR* controlled (for the particular geometrical arrangement used) at about −500 mV for 9 M HCl, −1200 mV for neutral solutions, and −1800 mV for the 3.5 M NaCl −3.5 M NaOH. Therefore, we propose that the *absence* of cathodic protection in acidic chloride solutions (and HBr and HI) is related to ohmic-control of the hydrogen evolution reaction. Ohmic-control of this reaction on the outer surface would essentially "isolate" the crack tip from external control. The crack velocity should then be independent of the externally-applied potential in the range of ohmic control. Also, the crack velocity in the SCC tests run in 0.1 M HC − 8.9 M LiCl levelled out at −1000 mV, where the hydrogen evolution reaction also became *IR* controlled.

The results in neutral and basic solutions are obviously consistent with the above proposal, although we still do not know why cathodic protection *does* occur. We have not attempted to determine whether the crack velocity becomes independent of potential in the ohmic region. Since the velocities are approaching those in the absence of an environment, results in this region would be ambiguous. On the other hand, anodic (dissolution) mechanisms would be consistent with these cathodic protection results.

"Anodic protection" is observed in chloride solutions independent of pH. Bromide solutions exhibit it also, but to a lesser extent, and iodide solutions do not exhibit anodic protection at room temperature.

There is the additional experimental observation that anodic protection is not observed (even in chloride solutions) for alloys and heat-treatments which exhibit SCC velocities faster than 2×10^{-2} cm sec^{-1} at a potential of −200 mV.

From these results the extent of the anodic protection region is thus obviously dependent upon the ion type. However, the extent is also dependent upon metallurgical structure and temperature. For example the present alloy, if heat-treated to a more susceptible condition (800° C, step cool), shows no anodic protection in chloride solution at room temperature but shows such protection at −23° C. In all cases, an approximate rule that defines the presence or absence of an anodic protection region can be stated as follows: if the region II plateau velocity at −200 mV is $> 2 \times 10^{-2}$ (alloy heat-treatment, solution constant), then no anodic protection will occur. This suggests that competing processes are responsible for the behaviour.

We conclude that it is unnecessary to consider the hydrogen reaction in explaining anodic protection since the effect is independent of pH. In order to use the hydrogen reaction in explaining anodic retardation, one would have to postulate that the crack tip pH is independent of the pH of the external solution, and this seems untenable when considering a pH range of −1 to 14.5 in the bulk solution. The formation of a four-valent titanium species such as TiO^{2+} could be associated with the anodic retardation, except that there should again be a dependence on pH for the formation reaction.

In both glycerine and methanol solutions, the open circuit potentials were ~ −500 mV and cathodic protecton was possible at −1500 mV. In DMSO solutions the open circuit potential was ~ −200 mV and there was little influence of potential although at high temperatures (96° C) there was some evidence of cathodic protection.

5.2. Influence of viscosity and conductivity

Essential points established by the experimental work described above are that region II or plateau velocities can be correlated with the viscosity and conductivity of the solution. This discussion is divided into two parts in which we examine possible influences of these physical properties on processes that could occur in stress corrosion cracks.

Hydrogen diffusion in the metal plays no role in limiting the crack velocity, based on these observations. That is, at a constant temperature, e.g. 25°C, the plateau velocity of cracking is 1.5×10^{-2} cm sec^{-1} in H_2O-LiCl, 5×10^{-4} cm sec^{-1} in CH_3OH-LiCl, 5×10^{-6} cm sec^{-1} in DMSO-LiCl, and 10^{-6} cm sec^{-1} in glycerine-LiCl. There should have been no difference in these velocities if hydrogen diffusion in the metal were the dominant process controlling cracking.

5.3. Fluid flow

The fluid flow characteristics in a propagating crack have not received much attention in the past. Some attempts have been made to treat the hydrodynamics in liquid metal embrittlement [23], but have employed models which are not generally useful. The problem is of importance for two reasons: (1) the fluid flow could limit the velocity of cracking by the onset of "cavitation" in the crack, and (2) even if cavitation is not important in limiting the crack propagation, the fluid characteristics may be important in determining concentration distributions in a crack where mass transfer is critical to crack extension (see next Section).

For a wedge-shaped crack propagating through a material immersed in a liquid, the hydrodynamics may be shown [24] to depend on the crack geometry, the physical properties of the fluid, the total pressure drop down the crack, and the velocity of crack propagation. The low velocities in the present study make it unlikely that cavitation is important in limiting these crack velocities [24]. Also, the lack of a correlation with the absolute viscosity makes it unlikely that cavitation is occurring in all these systems.

5.4. Convective diffusion (mass-transfer)

In this section it will be assumed that the viscosity of the solution controls the rate of stress corrosion crack propagation by influencing the rate of mass transfer.

Diffusion will occur as the result of a nonuniform concentration distribution and convective flow usually determines the distances over which the concentration changes. Therefore, the viscosity of the solution can influence the rate of a diffusion controlled reaction in two ways:

1. the diffusion coefficients of salts are changed by the viscosity and for many systems may be expressed by the empirical correlation

$$D \propto \frac{T}{\eta}$$

where T is the absolute temperature and η is the viscosity;

2. the diffusion layer thickness, δ, is also influenced by the viscosity and by the prevailing hydrodynamic conditions. For flow past a flat plate and flow to a rotating disk, for example, δ varies as viscosity$^{1/6}$.

It is, therefore, concluded that the influence of viscosity on a mass transfer controlled SCC reaction will be predominantly through changes in diffusion coefficients.

Returning now to the assumption that the velocity of cracking is controlled by a mass transfer limited chemical reaction, it is obvious that our results are consistent with this hypothesis. The linear viscosity:velocity relationships shown in Fig. 9a also shows three separate curves are obtained for the individual solvents. Plotting the results as log V versus log (T/η) changes the pattern very slightly, making the slopes nearer unity but leaving separate curves for different solvents. This, in turn, could be explained if the absolute values of the diffusion coefficients were different for the various solvents. Unfortunately, appropriate data on diffusion coefficients are not available for comparison. However, using the values for a single ion at infinite dilution (a situation far removed from these solutions), one would predict that the diffusion coefficients would fall in the order

$$H_2O > MeOH > DMSO\,.$$

The SCC velocities fall in the same order. The absolute values (for the dilute solutions) do not correspond to the relative displacement of the curves especially in the case of the DMSO solutions, but this could be due to different mass transfer processes involving different species in the three groups of solvents.

Having shown a general correlation it is pertinent to examine which processes in a stress corrosion crack could be mass transport limited, and more specifically consider the species that may be involved in the rate limiting step. For the systems investigated, it is considered that the solvent molecules may be excluded due to their high concentrations which leaves:

the Li^+ ion
the H^+ ion
the Cl^- ion

the Ti^{3+} ion derived from a chemical reaction
the $(TiO)^{2+}$ ion again formed in a chemical reaction.

Since there is no consumption of Cl^- ions to form Cl_2 under the conditions of our tests, we exclude it from further consideration. However, chloride ions could be involved in mass transport limited processes through solubility or complexation reactions which would also involve titanium ions. The lithium ion is not consumed under the conditions of our tests as well. Only the hydrogen ion and titanium ion(s) appear to be reasonable possibilities as the mass transfer limited species under the conditions of our tests.

The hydrogen ion has been suggested as a critical species in SCC of titanium alloys by analogy with other hydrogen embrittlement processes [19]. The limitation of crack extension could be due to a diffusion-limited reduction of hydrogen ions. Also, the formation of hydrogen bubbles might be viewed as another way of limiting the cracking rate, through "blocking" access of the liquid to the crack surface [25]. These two processes appear to be unlikely for the following reasons.

1. Unless the hydrogen ions and solvent molecules were reduced in separate processes, there would be no limiting rate for the reduction process in the potential range appropriate here.
2. There should be no influence of (cathodic) potential on crack velocity, contrary to our and other results.
3. It is unlikely that hydrogen bubbles could be formed *inside* the cracks because of surface tension limitations.* Since these liquids "wet" the solid (even the external, oxidized surface), it is unlikely that bubbles could be formed at the liquid-solid interface either.
4. Hydrogen was probably not generated in the tests conducted in DMSO, acetone, *N*,*N*-dimethylacetamide, and hexamethylphosphoric triamide solutions. No bubble formation was ever observed in these systems.

The first three arguments are applicable to all the systems, while the last is especially critical for those solvents listed.

Sedriks and Green [11] have also investigated SCC in DMSO and H_2O solutions. They have attributed the faster crack velocities in water to the ease of hydrogen reduction, and further argued that the low velocities in DMSO indicate that the chloride ion played a minor role in the cracking process. They use the concept of unsolvated anions (i.e. Cl^-) in DMSO proposed by Parker [26] as support for the argument eliminating Cl^- as playing a role in SCC. Several factors probably make their analysis an oversimplification; for example, although the chloride ion is solvated to a lesser degree in DMSO, and thus could be considered "freer," the mobility of the ion on an absolute scale is lower than in water (see Conductivity results). Also, the concept of unsolvated anions was developed for low solution concentrations [26].

Ti species could be involved in mass transfer limited processes such as: (1) the formation of a solid salt film which would also involve the chloride ion [27] and (2) the oxidation or reduction of a soluble Ti species at a diffusion limited rate on the crack walls. The first process appears to be inconsistent with our results in aqueous solutions in three ways.

1. Cracking rates should be inversely proportional to the chloride ion concentration owing to the influence of solubility~ This is inconsistent with earlier results [6-8] and some data reported here.
2. Separating the bulk solution with $TiCl_3$ should have decreased or even stopped cracking, which it did not (see Fig. 11).
3. The temperature influence reflected only changes in viscosity. The solubility of the salt would have to be temperature invariant (heat of solution equal to zero) in order to be consistent with this result.

Controlling the cracking rate through a mass transfer limited reaction of titanium ions on the crack walls appears unlikely for the following reasons.

1. The only stable species in aqueous (and methanolic) solutions are Ti^{3+} and $(TiO^{2+})_x$ (in alcoholic solutions, the four valent species is probably an alcoxy-chloride complex [28]). It is improbable that potentials within the crack deviate from the applied potential sufficiently to allow the oxidation or reduction of these species for the range of potential over which cracking is observed. For example, potentials of 0 to + 200 mV would be required to oxidize Ti^{3+} to $(TiO^{2+})_x$ and cracking occurs in neutral solutions at −1000 mV (see Fig. 6).
2. In DMSO, formic acid, and *N*,*N*-dimethyl-

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*The hydrogen current needed to support a bubble of the small size demanded in these small angle cracks would be on the order of tens of amps per square centimetre in aqueous solutions, because the hydrogen pressure inside the bubbles must be high (of the order of 10^3 bar).

acetamide, apparently only one species of titanium is stable, i.e. (TiO^{2+}) (or a species similar to the methoxy species formed in methanol), which can neither be oxidized nor reduced. The solvent in each case is reduced more easily than four valent titanium.

We conclude that these simple mass-transfer limited processes cannot be rationalized as the limiting process for SCC in these solutions at present. In many chemical reactions at current levels lower but at appreciable fractions of the mass-transfer limited current, kinetic and ohmic contributions can be substantial. Diffusion effects may still be contributed and be sensitive to viscosity, stirring, etc. Therefore, although we find none of the above processes to control cracking, they could make a contribution to overall control. It may prove that a more complex model is appropriate but at present insufficient data exist to aid in its formulation. The model due to Beck and Grens [29] may indicate the direction which such a formulation should take but in its present form is probably an oversimplification of the processes occurring in SCC.

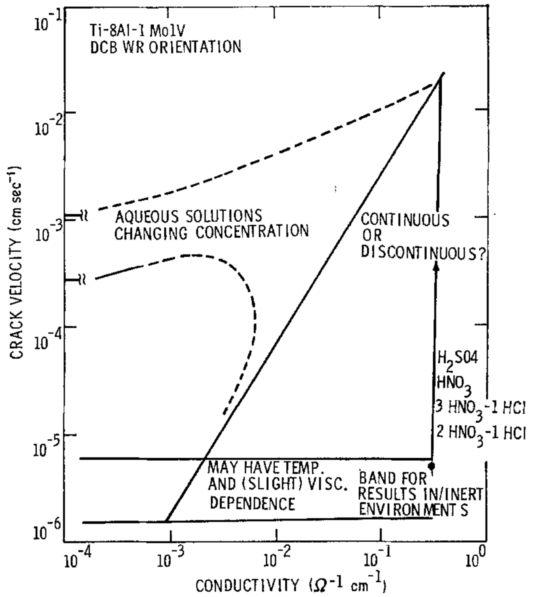

Figure 12 Semischematic diagram of the changes in the velocity:conductivity relationship (Fig. 10) produced by varying the halide ion concentration. Reducing this concentration in aqueous (and other solutions) produces points above the line for the 5:1 mole ratio solutions. It may be possible to produce points below the line by the addition of halide ions to high conductivity inhibitor solutions (e.g. HNO_3, H_2SO_4, etc).

5.5. Conductivity

The correlation between SCC velocity and conductivity of all solutions tested is surprisingly good – in fact, a line with a slope of 1 could be constructed through the scatter and the conclusion that SCC occurs by an ohmically controlled chemical reaction would seem quite convincing. However, this implies that: (a) the same reaction occurs in all solvents – which is most unlikely; (b) the reaction occurs at a constant overpotential; (c) the effect of concentration (of Cl^-, Br^- of I^-) could be accounted for by their influence on the conductivity of the solution.

In connection with this last point, it should be emphasized that we have only considered crack growth in solutions with 5:1 mole ratios of solvent-salt. Changing the concentration of the Cl^- ion produces large deviations from the velocity-conductivity relationship established in these solutions as illustrated semi-schematically in Fig. 12, which shows that the more dilute solutions produce points that lie above the curve. It is possible (but not proven) that points below the curve could be obtained by mixing chloride with high conductivity "inhibitors" such as nitric or sulphuric acid. A final point on mixing solutions is that deviations can also be produced by mixing solvents at a constant chloride ratio, as illustrated for water-glycerine-LiCl mixtures in Fig. 9a. None of these observations support an ohmically controlled reaction hypothesis.

6. Conclusions

For the conditions investigated, i.e. Ti-8 Al-1 Mo-1 V (820°C WQ) tested in solvents containing chloride, bromide or iodide ions, it was established experimentally that:

1. the region II plateau velocity varies inversely with the viscosity;
2. the activation energy for the region II plateau velocity shows the same temperature dependence as that for viscosity;
3. the plateau velocity in the several solvents may be correlated with the solution conductivity;
4. mixing the solvents gives non-additive results both on a viscosity and a conductivity basis.

Theoretical consideration of these results has shown that no simple explanation of the limiting propagation velocity can be proposed based on:

1. hydrogen diffusion in the metal;
2. limitation of the velocity by fluid flow cavitation during crack extension;

3. Limitation by a process involving a mass transfer controlled chemical reaction;

4. limitation by a chemical reaction under ohmic control.

A combination of all or a part of these processes may together limit the rate of cracking, but such a mechanism cannot be advanced at this time. It is proposed that:

1. the absence of cathodic protection in acidic aqueous solutions is due to ohmic control of the hydrogen discharge reaction which "isolates" the crack tip from external potential control;

2. anodic protection may be due to a relative kinetic effect.

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References

1. M. J. BLACKBURN, J. A. FEENEY and T. R. BECK, Stress Corrosion Cracking of Titanium Alloys, in "Advances in Corrosion Science and Corrosion Engineering", Vol. 3, edited by M. G. Fontana and R. W. Staehle (Plenum Press, New York, 1972).
2. M. J. BLACKBURN, W. H. SMYRL and J. A. FEENEY, Engineering Aspects of Stress Corrosion Cracking of Titanium Alloys, in "Status of SCC of High Strength Alloys", edited by B. G. Brown (Government Printing Office, Washington, D. C., 1973).
3. D. N. FAGER and W. F. SPURR, *Corrosion* **26** (1970) 409.
4. A. J. SEDRIKS, *ibid* **25** (1969) 207.
5. T. R. BECK, M. J. BLACKBURN and M. O. SPEIDEL, Contract NAS7-489, Quarterly Progress Report 11, March 1969.
6. J. D. BOYD, P. J. MORELAND, W. K. BOYD, R. A. WOOD, D. N. WILLIAMS and R. I. JAFFEE, Contract NASr-100(09), 26 August 1969.
7. T. R. BECK, *J. Electrochem. Soc.* **115** (1968) 890.
8. D. T. POWELL and J. C. SCULLY, *Corrosion* **24** (1968) 151.
9. T. R. BECK and M. J. BLACKBURN, *AIAA J.* **6** (1968) 326.
10. T. R. BECK, Boeing Doc. D1-82-0554 (1965).
11. J. A. SEDRICKS and J. A. S. GREEN, *Corrosion* **28** (1972) 226.
12. G. SANDOZ and H. NEWBEGIN, Report of NRL Progress, May 1968, p. 31.
13. S. MOSTOVOY, E. J. RIPLING and P. B. CROSLEY, *J. Mats.* **2** (1967) 661.
14. R. A. ROBINSON and R. H. STOKES, "Electrolyte Solutions", 2nd Edn. (Butterworths, London, 1965).
15. H. L. SCHLAFER and W. SCHAFFERNICHT, *Angew. Chem.* **72** (1960) 618.
16. M. J. BLACKBURN and W. H. SMYRL, Stress Corrosion Cracking of Titanium Alloys – A Review of Recent Developments, in "Titanium Science and Technology", Vol. 4, edited by R. I. Jaffee and H. M. Burte (Plenum Press, New York, 1973).
17. W. H. SMYRL and M. J. BLACKBURN, in Proceedings of Conference on Stress Corrosion Cracking Mechanisms in Titanium Alloys, Atlanta, 1971, to be published.
18. T. R. BECK, in "The Science, Technology and Application of Titanium", edited by R. Jaffee and N. Promsel (Pergamon Press, New York, 1970) pp. 239-45.
19. J. C. SCULLY, in Proceedings of the International Conference on Stress Corrosion Mechanisms in Titanium Alloys, Atlanta, 1971, to be published.
20. C. T. MOYNIHAN, N. BALITACTAC, L. BOONE and T. A. LITOVITZ, *J. Chem. Phys.* **55** (1971) 3013.
21. T. W. CHAPMAN and J. NEWMAN, UCRL-17767, University of California, Berkeley, 1967.
22. B. F. BROWN, C. T. FUJII and E. P. DALBERG, *J. Electrochem. Soc.* **116** (1969) 218.
23. W. ROSTOCKER, J. M. MCCAUGHEY and H. MARKUS, "Embrittlement by Liquid Metals" (Reinhold, New York, 1960).
24. J. NEWMAN and W. H. SMYRL, *Met. Trans.* **5** (1974) 469.
25. TENNYSON SMITH, *Corrosion Sci.* **12** (1972) 45.
26. A. J. PARKER, *Quart. Rev.* (1962) 163.
27. T. R. BECK, in "The Theory of Stress Corrosion Cracking of Alloys", edited by J. C. Scully (NATO, Scientific Affairs Div., Brussels, 1971).
28. R. J. H. CLARK, "The Chemistry of Titanium and Vanadium", Elsevier, New York, 1968).
29. T. R. BECK and E. A. GRENS, *J. Electrochem. Soc.* **116** (1969) 177.

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