
THE EFFECT OF ENVIRONMENT ON CRACK GROWTH IN A STAINLESS MARAGING ALLOY

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INTRODUCTION

The behaviour of a high-purity Fe-20%Co-15%Cr-5%Mo alloy when subjected to certain potentially-aggressive environments will be described; these environments have been varied systematically to provide an insight into the mechanisms affecting crack growth.

This composition is one of a series included in a study of the influence of certain metallurgical factors on fracture toughness [1-4]. Thus an age-hardened condition (38hrs at 500°C) was used which aided comparability with other alloys in that series and which also provided a favourable combination of fracture toughness and tensile strength in its own right.

EXPERIMENTAL METHOD

The alloy was prepared from high-purity base materials, melted and cast under vacuum into 9 kg ingots, then hot-rolled into strips, 14mm × 40mm. Specimens were machined and then solution treated at 1150°C, air-cooled to 100°C and quenched into liquid nitrogen for 12 hrs (M_s temp., 68°C) before ageing at 500°C for 38 hrs. The chemical analysis, together with the yield strength and K_{Ic} for this steel, in this condition, are as follows:

Co	Cr	Mo	C	S & P	Ni	Others	
20.2	14.4	4.93	0.006	0.002 each	0.09	≤ 0.03	wt%

0.2%PS 1.97 GPa K_{Ic} 50 MPa·m$^{1/2}$

For stress-corrosion testing, pre-cracked, wedge-opening loaded specimens [5,6] of 5mm thickness were used.

Immediately after stressing the specimens were placed in the test environment. The tests were arranged so that variations in chloride concentration, pH and humidity (in air) could be studied systematically. A potentiostat, accurate to ± 5mV, was used where appropriate.

The reference electrode was a commercial saturated calomel electrode in potassium chloride solution. Crack length was measured by travelling microscope.

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RESULTS

Crack growth

The alloys showed subcritical slow crack growth in all the environments used, except for humid air. In this latter case no crack growth was recorded at humidities of up to 70% in 10^7s, any crack growth must therefore have occurred at less than 10^{-5}μm/s. This contrasts with a similar alloy in which nickel substituted for the chromium and for which a systematic dependence of crack growth on relative humidity was observed.

All the results were plotted as crack velocity against stress intensity curves (Figures 1 and 3), which characteristically consisted of two, or sometimes three, stages. At low and at high stress intensities there was a strong K-dependence (stages I and III respectively). Crack velocity in the intermediate (stage II) region did not always form a true plateau in as much as there was often a slight dependence on K. In some cases the individual stages are not well defined.

Crack growth in solutions of three pH's (1, neutral and 12) showed that pH had no effect. Intermediate pH's may have produced different growth rates but if this were the case, it is unlikely that the growth pattern would have returned to identical form and values at the extremes studied.

Potential had a strong influence on the crack growth as can be seen from Figure 1. Free corrosion (about -0.4V SCE) produced the slowest growth and, as the cathodic polarisation increased, so did the crack growth rate at a constant stress intensity. At the two most active potentials, -1V and -1.2V, the stage I growth has apparently been shifted to the right, to higher stress intensities. This is because extensive crack branching and grain boundary penetration at these potentials reduced the effective stress intensity [7]. The curves for the -0.5V and -0.6V specimens show only a point of inflexion (a repressed plateau) between stage I and stage III, in which there is a reduced K-dependence.

Figure 2 shows crack velocity against potential for a constant value of K and also summarises the influence of potential on plateau velocity. At the lower K the occurrence of branching at active potentials ~ -0.8V probably explains the decrease in crack velocity observed. The effect of anodic polarisation could unfortunately not be studied because corrosion product masked the crack.

Testing in solutions of various chloride concentrations produced some unexpected results. It was found that as the chloride concentration was decreased the velocity for a given K increased, as Figure 3 shows. At 0.3 and 0.03% NaCl the growth characteristics are different. Crack growth at intermediate stress intensities is quite strongly K-dependent, whilst stage I was either not present, or else was depressed to very low stress intensities. Figure 4 shows crack velocity vs chloride concentration. Extrapolation to the crack growth rate in deionised water gives a sodium chloride concentration of 10^{-4}%, or about 10^{-5}M, which is reasonable for chloride content arising from contamination. The crack growth is strongly dependent on temperature as can be seen from Figure 5. The apparent Q_a values obtained from this Arrhenius plot are 42.2 KJ/mol and 44.8 KJ/mol for the 24.5 MPa•$m^{1/2}$ and 14.0 MPa•$m^{1/2}$ lines respectively. These values are characteristic of hydrogen diffusion in bcc iron.

Fractography

Both micro-branching and macrobranching could clearly be seen at the surface by light microscopy. Scanning electron microscopy showed the stress corrosion crack path to be predominantly intergranular with respect to the prior austenite grain boundaries, a mode of fracture which is typical of hydrogen embrittlement.

DISCUSSION

Significance of the shape of the SCC curves

Generally the crack growth vs stress intensity plots conformed to the three-stage pattern found by Speidel [6] and Carter [8].

The threshold, K_{ISCC}, has not been well shown by these experiments because the tests were started at a high stress intensity in order to study the crack velocity - stress intensity curve as fully as possible.

It may be that K_{ISCC} measured by this technique is different from that measured using a pre-cracked cantilever beam specimen [9]. Obviously the measured threshold will be dependent to some extent on the time allowed before a crack is considered non-propagating. In our case, assuming a resolution of 0.1mm in crack length measurement, then increasing this time from 10 h to 1000 h would reduce the threshold by about 2 MPa•$m^{1/2}$. Furthermore the cantilever beam specimen considers stress-corrosion started from a uniform fatigue crack, whereas the WOL specimen relies on the arrest of a (probably intergranular) stress-corrosion crack. A difference may result if there is a hysteresis between the stress intensity required for crack propagation and that required for crack arrest. More importantly, micro-branching could cause crack arrest at an apparent stress intensity considerably higher than the true threshold. Thus great care is necessary when measuring or using threshold values.

In stage I the crack velocity is strongly dependent on the stress intensity. Miller et al [10] have suggested that the crack growth here is indeterminate because of scatter in the data; this may be a manifestation of the inaccuracy of measuring stress intensity. Certainly it is not clear how the stress intensity is related to the crack growth rate in this region.

The plateau region is the most studied region of the stress-corrosion curve, probably because the stress intensity independence allows this factor to be disregarded. Nevertheless, the growth-limiting factors have not been identified positively. Our results show that the plateau velocity can be affected by the environment. There are several possibilities for the rate-limiting step. It could be the electrochemical reaction in which hydrogen is generated, the diffusion of hydrogen through a surface film or perhaps the adsorption of hydrogen to bare metal exposed by yielding at the crack tip. It may be that different factors are limiting under different circumstances.

Stage III of the crack growth curve is another region of rapidly changing velocity and it is probable that there is a strong mechanical component in this part of the fracture. Josephic and Oriani [11] found that at high stress intensities the intergranular facets showed signs of extensive ductile tearing: no similar evidence was found in this present work.

This region is difficult to study in self-stressed WOL specimens because the stress intensity range it covers is relatively small, the growth rate is initially high and the solution chemistry inside the crack will have little time to equilibrate. Hence, again, the results from this type of specimen may be different from those produced from a constant load specimen.

Environmental variables

(a) Potential - a strong dependence of crack velocity on the cathodic polarisation was found. The plateau velocity increased exponentially with polarisation in the range studied, as Figure 2 shows. Such a dependence might be expected if the growth rate varies directly with the amount of hydrogen generated. Thus when charge transfer through a surface film is rate-controlling, the hydrogen evolution reaction exhibits haviour with anomalously high slopes of the order of -0.5V. This is, in fact, the observed slope of the 'plateau' line in Figure 2. (Note that the equilibrium hydrogen activity in the inner Helmholtz plane also varies exponentially with cathodic polarisation, but this would give a slope of -0.06V).

Figure 1 suggests that increasing the cathodic potential slows down the crack growth rate by moving the stage I region to higher stress intensities. This anomalous effect is most likely to result from the micro- and macro-branching which was seen to become more prevalent at higher cathodic over-potentials: the use of single edge notch specimens loaded in tension may be beneficial.

(b) pH - variation of the pH produced no variation in the crack growth characteristics for the pH's studied. This was not unexpected, as Brown [9] showed that the electrochemical conditions at the crack tip adjust themselves to equilibrium conditions regardless of the bulk values.

(c) Chloride concentration- it is often found in high strength steels that many aqueous environments have very similar effects on growth rate (eg. [12]) in contrast to the selective nature of stress corrosion in many other alloys. In view of this, the effect of chloride concentration on the crack growth of this alloy was somewhat surprising (Figure 3), especially as deionised water, which would conventionally be regarded as the less aggressive environment, has produced a growth rate much faster than that produced by 3% sodium chloride solution. The log-log plot of Figure 3 indicates a power dependence of exponent -1/3, i.e. da/dt is proportional to $[NaCl]^{-1/3}$. It might be argued that the chloride solutions, because they are more aggressive corrodents, blunt the tip of the growing crack either by general corrosion or by encouraging intergranular penetration: by comparison, in the deionised water the crack remains sharp and suffers no diminution of stress intensity. If this explanation were true, then one might expect that the acceleration due to distilled water would be observed generally. However, this is not the case.

The abnormal behaviour of this steel suggests that its composition may be important, especially with respect to the electrochemical conditions occurring on the metal surface. Chromium steels are known to passivate at potentials > -0.3V SCE. It seems unlikely that the crack tip region could be conventionally passive under the experimental conditions used here; instead it is possible that Cl-rich salts of Cr and Fe may precipitate. This would explain the high slope observed in Figure 2 and at the same time the apparently beneficial effect of Cl^-, since it may be inferred that the film interferes with the ingress of hydrogen. An explanation in

terms of electrochemical effects is therefore favoured.

CONCLUSIONS

For SCC of a Fe-20%Co-15%Cr-5%Mo maraging alloy in the "under-aged" (38 hrs at 500°C) condition:-

(1) The fracture appearance, the effect of cathodic polarisation and the activation energies observed are all consistent with a mechanism of hydrogen embrittlement.

(2) In chloride solutions the crack growth rate is inversely proportional to the cube root of the chloride ion concentration.

(3) Crack growth rate is insensitive to changes in pH.

(4) K_{ISCC} should be sensitive to the type of test employed and to the development of crack branching.

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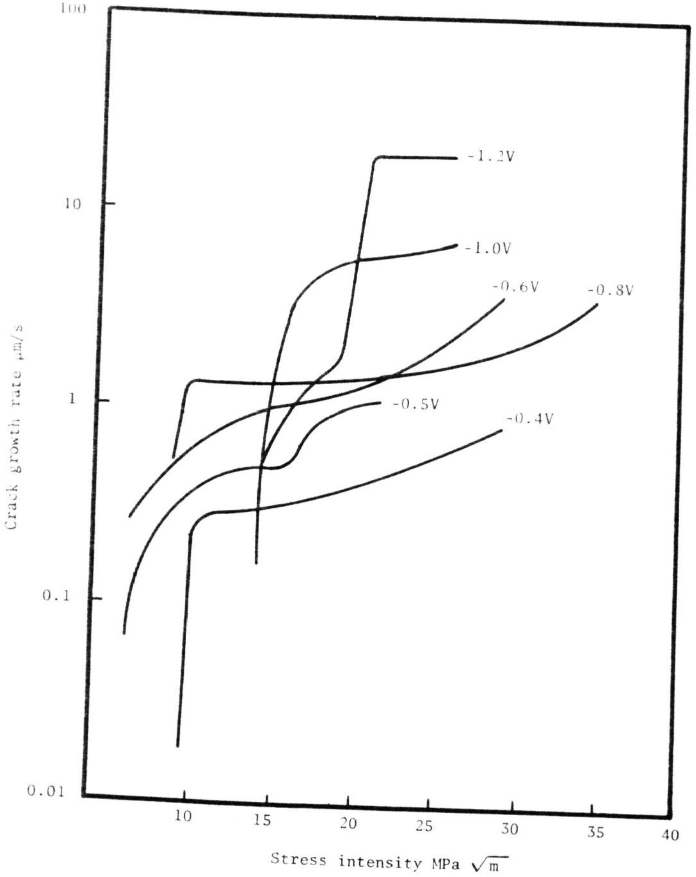

Figure 1 Influence of potential and stress intensity on crack-growth

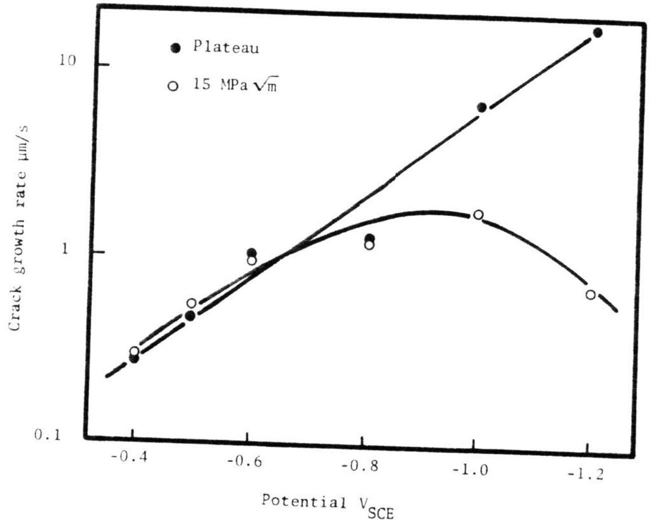

Figure 2 Crack velocity vs potential

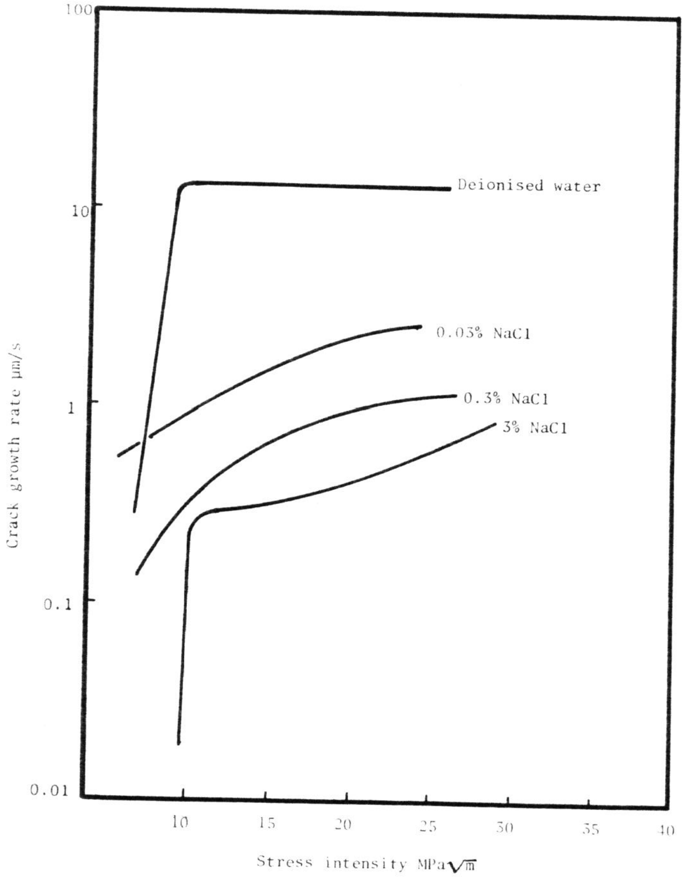

Figure 3 Influence of chloride concentration and stress intensity on crack growth

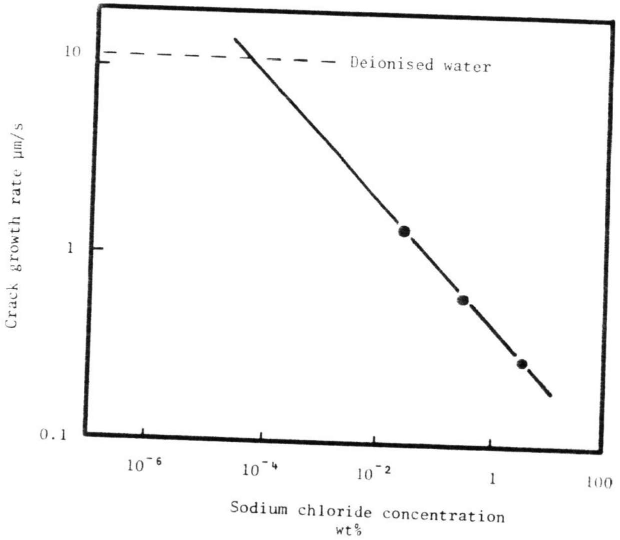

Figure 4 Crack velocity vs chloride concentration

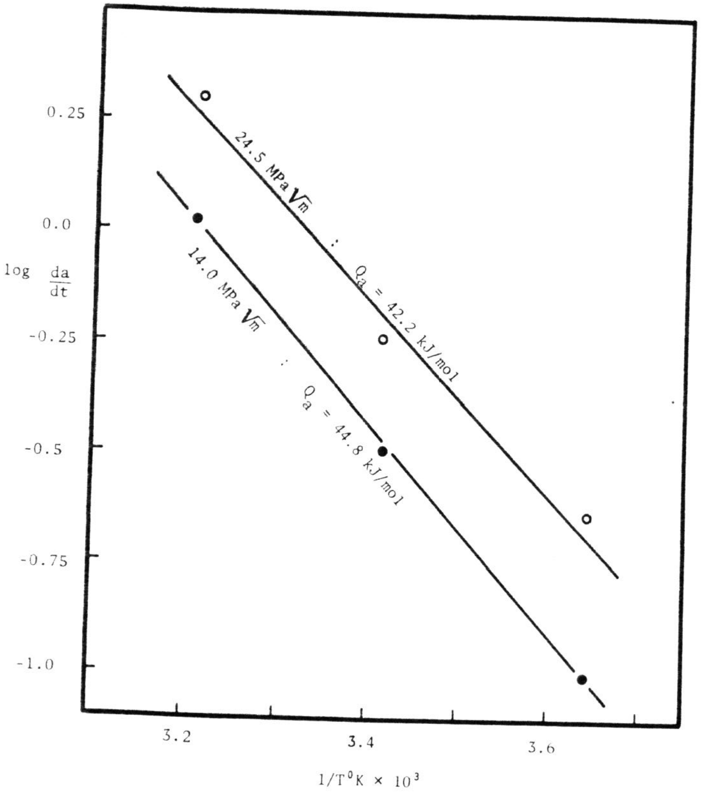

Figure 5 Crack velocity vs reciprocal temperature