ENVIRONMENT ASSISTED CRACKING OF METALS – ENGINEERING CHALLENGES

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ABSTRACT

A short overview is given of some of the key requirements in meeting the needs of industry with respect to testing and prediction of environment assisted cracking of metals. The primary challenge is to bridge the gap between laboratory testing based usually on simplified testing conditions and actual service experience where complex variations in environment, temperature and stress often determine the likelihood of failure. Examples from the offshore, power and chemical process industries will be used to illustrate the progress in responding to these demands.

INTRODUCTION

Limitations in service prediction of environment assisted cracking (EAC) exist because of the complex dependence of initiation and crack growth on interacting operational variables and uncertainty in the mechanism of cracking. Although engineering design will be optimised to minimise the probability of occurrence of cracking, or to provide an acceptable life using appropriate design codes, there are several reasons why cracking may still be of concern.

- The operating conditions may be altered to improve the process.
- Welding may not be ideal and may introduce defects and change the material characteristics.
- Transient variations in stress, temperature or environment chemistry may occur, either from scheduled excursions (e.g. shutdown) or from unintentional fluctuation in system control (e.g. contamination).
- Concentrated solutions may be generated by evaporation or boiling.
- The character of the metal surface may change with time of operation (e.g. precipitation of a scale or deposit) or the material may “age” (e.g. irradiation effects).
- Localised corrosion processes, such as pitting, crevice corrosion or intergranular corrosion may be initiated and become precursors for EAC.
- Laboratory testing and modelling assumptions may not be realistic; e.g. the surface state may not be representative of service conditions.

The risk that cracks will initiate and grow to the critical size for unstable fracture has to be identified and linked to a risk-based inspection (RBI) protocol. For most practical situations this is an empirical process, being based on a probabilistic assessment of crack size evolution using service or laboratory data. The reliability of that process depends on the quality and relevance of experimental data. Quantitative mechanistic models of cracking are used to-date in only limited industrial applications, primarily in the nuclear industry or in long-term waste containment. The challenge for the research and testing community is to develop an extensive and reliable EAC database and to provide an accessible framework for application of data and models to engineering prediction. However, most testing is carried out under conditions of constant temperature and environmental conditions and often stress without sufficient allowance for the varying nature of service conditions. Extensive standardisation of laboratory test methods[1] now exists but guidance in dealing with such transient conditions is largely absent, yet is probably the most critical requirement for the engineer. Much of our recent work has focused on this issue and this paper will give examples from work in progress in relation to the offshore, power and chemical processing industries.

OFFSHORE PIPELINES

Offshore pipelines are used to transport oil and gas with the selection of alloy being determined by how sour (level of H_2S) the oil or gas is and whether inhibitors are used. In the latter case, carbon-steels would be used but for many applications it is more economical and practical to use corrosion resistant alloys such as duplex stainless steels for sour applications and 13 Cr martensitic steels for sweet (essentially no H_2S) environments and thereby avoid the use of inhibitors. The new super 13 Cr martensitic stainless steels, containing about 2 % Mo, are now being considered and used for applications where some H_2S is present but at a relatively modest level. Indeed, the challenge is to identify those conditions for which its use is acceptable. This underpins the major issue of what testing protocol should be adopted to certify a material as being acceptable for service. Recent documents[2,3] published by the European Federation of Corrosion provide an important framework for a test programme but are not all-embracing.

A pipeline sitting on the seabed will experience bending stresses on the external surface due to pipe movement that will transiently induce some dynamic plastic strain. Cathodic protection will generate hydrogen and there is a risk of failure due to hydrogen embrittlement. In addition to the severe stresses, dynamic plastic strain is very important for corrosion resistant alloys as it enhances hydrogen atom ingress by rupturing the passive film, which normally limits hydrogen uptake of corrosion resistant alloys. It also enhances redistribution of absorbed hydrogen through mobile dislocations. On the internal surface of the pipe exposed to the oil or gas the source of stress is primarily residual but essentially static. It is the role of dynamic plastic strain and how best to accommodate it in testing which is still a topic of debate. Slow strain rate testing to failure is often regarded as unrealistic and useful only for comparative purposes. Nevertheless, dynamic plastic strain is important. For that reason, the use of the interrupt technique was evaluated as a means of assessing the performance of duplex stainless steel[4]. The principle involves applying dynamic plastic strain at a controlled slow strain rate but stopping the test at a particular strain or stress. The specimen is then section and examined for cracks. The strain or associated stress at which no cracking is observed can be regarded as the threshold, which then can be used for material selection or design.

An example of the results for a duplex stainless steel cathodically protected in a simulated seawater environment is shown in Figure 1. This material has the added complexity of a ferritic-austenitic structure. Cracks start in the ferrite but will often stop at the ferrite-austenite interface. Hence, the threshold for cracking is best defined as when cracks extend through both phases. The most important feature of these results is the dependency of the threshold on strain rate with the value at the lowest strain rate lying between about 2 % and 4 %. This result lies close to plastic strains that might be experienced in service. A similar type of sensitivity to strain rate has been observed when measuring the K_{ISCC} of a high strength steel in seawater using fracture mechanics specimens[5].

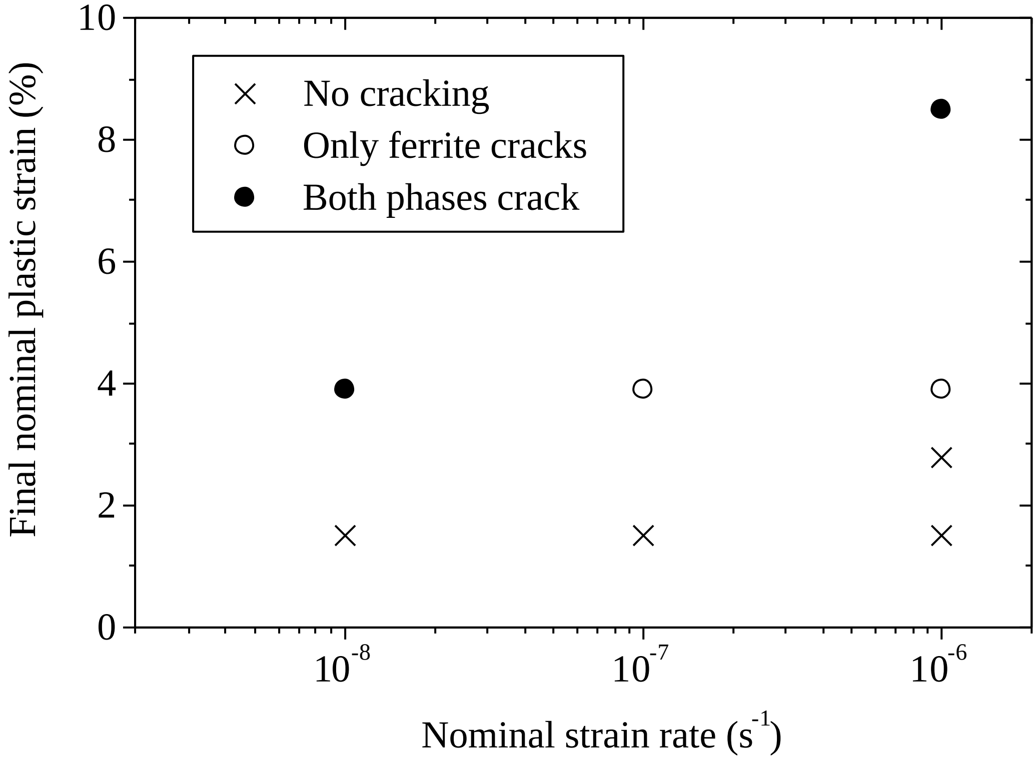

Figure 1. Application of the interrupted slow strain rate technique to measurement of the threshold strain for 22Cr duplex stainless steel in deaerated 3.5 wt.% NaCl solution (pH 8.5) at 20 °C, under cathodic polarisation of 30 mA cm^{-2}.

Further work is ongoing in relation to pipeline testing with the present focus on the performance of the super 13 Cr martensitc stainless steels. A key element of this study will be to test welded specimens under dynamic plastic strain but with the surface of the specimen in the as-welded state.

STEAM TURBINES IN POWER GENERATION

The power industry worldwide has experienced failures over the last 30 years from corrosion fatigue and stress corrosion cracking initiated from pits in steam turbine blades, discs and rotors. The blade material is mainly 12% Cr stainless steel whilst the discs and rotors are typically 3% Ni steels. The most notable failure was that at the Hinckley Point 'A' Power Station in 1969 that involved stress corrosion cracking of the disc[6]. More recently in 1996, at the Aberthaw Power Station, a single pit resulted in failure of a turbine blade and eventually to damage to the power station estimated in excess of £10m[7]. The circumstances leading to these failures are well understood and in the case of Aberthaw were specific to the operational conditions of that plant, since modified. Nevertheless, changes in operating practice of UK coal-fired plant practice are posing new challenges in life prediction of components. For economic reasons, the UK power industry is now operating its 500 MW coal-fired plants on a two-shift cycle in which the turbines are on-load for 16 hours per day and off-load overnight and at weekends. Ideally, more regular start-ups and shut-downs would be desirable in response to power demand, and are being introduced, but there are limitations to the rate at which the system can be brought to operational temperature. The concern with 'two-shifting' is the impact on cracking of the associated transients in stress, water chemistry and temperature.

On load, the inlet steam temperature of low pressure turbine varies depending on the water treatment. It is about 300 °C for phosphate treatment steam reducing to about 50 °C at the outlet. The inlet steam is dry but, as the temperature decreases and the pressure changes, droplets can form and condensates containing salts separate out on the discs, blades and rotors. The inlet steam chemistry is tightly controlled with a low initial conductivity of about 0.1-1.0 μS/cm and the oxygen content is less than 5 ppb under steady operating conditions. Off load, gland-sealing steam may be switched off and the water will gradually saturate with oxygen due to ingress of air; the stresses will be insignificant. When the system is restarted, the solution will be initially aerated. The temperature and stress will rise to their operating levels in about 20 minutes. However, it can take 1-2 hours to deaerate. Hence, there will be a complex transient in environment, temperature and stress whose interaction will determine crack growth. In addition, pitting corrosion is most likely to develop under aerated conditions but in service may take several years to get to a significant depth.

Our approach has been to develop electrochemical methods for pre-pitting specimens that control the number and depth of pits enabling focused probe attachment for short crack growth measurement[8]. Test times are very long and this work is still in progress. In addition, pre-cracked fracture mechanics specimens are being used to assess the significance of transient loading representing start-up and shut down. The details of these are described elsewhere[9]. An example of the impact of transient loading equivalent to 4 cycles per day is shown in Table 1. The load cycle involved 1 hour at zero load, 20 minutes rise to maximum load, hold for 4 hours and unload over 20 minutes.

Table 1 Effect of transient loading on the crack rate growth of 3 % NiCrMoV disc steel in aerated 1.5 ppm Cl^- solution at 90 °C (test duration: 299 days)

Loading form	Initial K (MPa $m^{1/2}$)	Crack extension (mm)	Growth rate (m/s)
Transient	0 - 40	0.81	4.0×10^{-11}
Constant	40	0.23	8.9×10^{-12}
Constant	50	0.26	1.0×10^{-11}

The growth rates are low, which is a necessary feature for plant management and inspection but the critical aspect is the factor of 4 increase in growth rate due to the transient loading. Further investigation is being undertaken to establish the relative contributions to growth associated with the rise time and hold time, taking into account the limited period of aeration in service, as distinct from the continuous aeration so far employed in testing.

CHEMICAL PROCESSING

The possibility of inducing stress corrosion cracking in stainless steel process plant due to an uncontrolled incursion of chloride ions into the process stream is of major concern to the chemical and petrochemical industry. The most susceptible period is during outages. Although normal chemistry should be restored in a relatively short timescale, certainly within a few days, there is considerable uncertainty as to the impact of the incursion on crack initiation and the extent to which cracks would continue to propagate following recovery of normal system chemistry. A system of relevance would be a teraphthalic acid plant for which 316L stainless steel in known to be satisfactory for the nominal environment, concentrated acetic acid (up to 90%) containing 1000-3000 ppm bromide and other chemicals (metal ion catalysts, inhibitors). For more aggressive environments, duplex stainless steels or more highly alloyed materials would be selected. The challenge is to establish the likelihood of cracking of the 316L stainless steel following a temporary system upset, such as a chloride incursion. An investigation of the impact of chloride ions on stress corrosion cracking susceptibility was undertaken using acetic acid (70%-90%) with bromide additions at 90 °C as being typical or reasonably representative of process plant conditions.

Testing was carried out under constant load using proof ring, and under dynamic straining using the slow strain rate method. The fill details are described elsewhere[10]. The results from the proof ring (gauge length 25 mm) tests illustrate the key features (Table 2).

Table 2. Summary of results of proof ring testing of 316S11 in acetic acid (HAc) solutions at 90 °C.

Environment				Time/ hours	No. cracks in gauge length	Deepest crack/ mm	'Average' da/dt (from deepest crack)/ mm s^{-1}	Adjusted crack depth/ mm	Adjusted da/dt / mm s^{-1}
HAc/ %	Br^-/ ppm	Na^+/ ppm	Cl^-/ ppm						
90	1500	200	-	719	0	-		-	-
90	1500	200	400	648	0	-		-	-
90	1500	200	1500	19	**	0.08	1.1×10^{-6}	0.08	1.2×10^{-6}
90	1500	200	1500	90	**	0.14	4.2×10^{-7}	0.17	5.4×10^{-7}
90	1500	200	1500	507	87	0.25	1.4×10^{-7}	0.46	2.5×10^{-7}
90	1500	200	1500	530	97	0.33	1.7×10^{-7}	0.55	2.9×10^{-7}
90	1500	200	1500*	650	72	0.09	3.9×10^{-8}	0.31	1.3×10^{-7}
70	1500	200	-	739	0	-		-	-
70	1500	200	1500	717	0	-		-	-

* Cyclical chloride incursion; ** not measured

In this particular system the corrosion rate is high and this loss has to be accommodated when calculating the crack growth rate (da/dt) for long exposures as the position of the surface is moving along with the position of the crack tip. Hence, the use of the term 'adjusted'. No crack growth was observed in the absence of chloride or in 70 % acetic acid, even with a chloride concentration of 1500 ppm. Tests were conducted with the environment constant in time with one exception. To examine the impact of an incursion in chloride concentration, complete refreshment of the initial, chloride-free, solution was made using preheated solution. This was undertaken on a cycle of 5 days, no chloride, then 2 days with chloride, such that there were 4 incursions over the 650 hour test duration. Assuming crack growth occurs only during chloride exposure (about 7 days) the adjusted crack growth rate of Table 5 would be recalculated to give a growth rate in the presence of chloride of 5.1×10^{-7} mm s^{-1}. When account is taken of crack size, the growth rate would appear to be somewhat slower than the value associated with continuous exposure to chloride. The observation is reasonably compatible with the view that growth occurs *only* during chloride exposure but some blunting may occur when the normal chemistry is restored.

Taking account of the relatively slow growth rate in chloride solutions for the deeper cracks, about 24 μm/day ($2.8x10^{-7}$ mm s^{-1}), based on the adjusted values, and the short period of exposure to chloride in a service excursion it would be reasonable to infer that crack advance in service would be modest and a short duration incursion could be readily tolerated. This is of particular value to the industry but further refinements in testing would be necessary to account for the greater complexity of specific service environments and the possibility of surface cold-work regions on the materials used in service.

CONCLUSIONS

Whilst standardisation of environment assisted cracking tests is well advanced, with numerous standards in place, there is a lack of guidelines on how best to test and predict cracking under the transient conditions which often lead to failure in service.

Extensive research on this theme is now ongoing at NPL. The illustrative examples in this paper have highlighted the importance of accounting for dynamic straining, transient loading, and excursions in chemistry when evaluating materials for service application.

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