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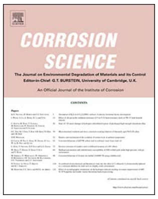

Modelling the electrochemical crack size effect on stress corrosion crack growth rate

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ABSTRACT

A model has been developed to predict the crack-tip potential and local chemistry in a stress corrosion crack in a steam turbine blade steel as a function of crack size and bulk chloride-ion concentration. The model incorporates mass transport and chemical and electrochemical reactions in the crack, with the potential drop in the bulk solution outside the crack calculated from the solution to Laplace's equation. The implications for crack-tip electrochemistry of full immersion vs a thin liquid layer are explored. The model predictions provide support for the concept of a solution conductivity dependent crack size effect on crack growth rates.

1. Introduction

The chemical crack size effect on environmentally assisted crack growth was first demonstrated experimentally by Gangloff [1] and supported on a more robust theoretical framework by Turnbull et al. [2,3]. It is probably better referred to as the electrochemical crack size effect since the potential drop in the crack is a critical factor in determining the solution chemistry and the sensitivity to crack size. Since that early work by Gangloff there have been further studies (review by Turnbull [4]) investigating the electrochemical crack size effect on corrosion fatigue crack growth [5–11] with far less on stress corrosion crack growth [12–14], with the latter relatively old. In recent experimental studies [15] we have focused on the growth rate of small and long stress corrosion and corrosion fatigue cracks in 12Cr steam turbine blade steels in low conductivity water containing 300 ppb[1] Cl^- and 300 ppb SO_4^{2-} (corresponding to normal steam condensate chemistry) and 35 ppm Cl^- (simulating an upset steam condensate chemistry). Depending on the loading conditions and solution conductivity a large effect of crack size on growth rate could be observed for the same mechanical driving force.

A conceptual framework was presented based on the idea that in very low conductivity solutions the crack tip would be electrochemically isolated from the bulk environment because of the combined effects of potential drop in the crack and in the bulk solution external to the crack. However, with increasing bulk solution conductivity and with decreasing crack size it would be projected that electrochemical polarisation of the crack tip would progressively ensue and that the crack growth rate would correspondingly change, albeit there would be no simple correlation. While the underlying principle would generally be accepted, there is a need to provide a fundamental foundation for the concept; in particular, to establish the degree of sensitivity of crack-tip electrode potential and chemistry to crack size and solution conductivity. A further feature of relevance to the steam turbine application is the value in exploring the implications for testing in full immersion conditions when condensing conditions prevail in service.

To address these requirements a model of crack chemistry has been developed with input parameters specific to the steam turbine application. The model focuses on stress corrosion cracks only. In principle, application to corrosion fatigue cracks and inclusion of advective flow induced by cyclic opening and closing of the crack would be feasible. However, cyclic loading means that time stepping is constrained to a fraction of the cycle period and since loading frequencies are very low for the application (4×10^{-4} Hz, corresponding to regular start-up and shut-down) attainment of a quasi-steady cyclic loading state would require inordinately long computing times.

2. Description of the model

2.1. Primary features

The model represents to a limited extent an extension of previous modelling work in relation to steam turbine crack chemistry, for example that of Liu and Macdonald [16] (though limited by lack of consideration of cathodic reactions within the crack) and subsequently of Turnbull [17]. The latter model was based on a more rigorous

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[1] All ppb (parts per billion) and ppm (parts per million) values reported are with respect to mass.

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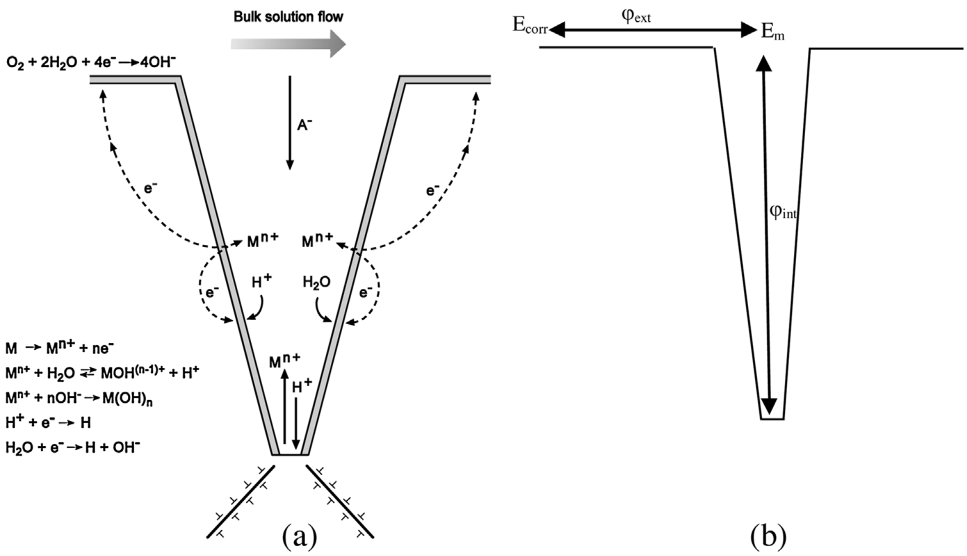

Fig. 1. (a) Schematic illustration of crack geometry and reactions; (b) components of potential drop external to crack (ϕ_{ext}) and internal to crack (ϕ_{int}).

treatment but applied only to a low alloy disc steel. Here, the focus is on a 12Cr martensitic stainless steel in aerated sodium chloride solution, which would be expected to show distinctly different crack chemistry because of the greater chromium content in particular. At 90 °C the bulk oxygen concentration would be 1.7-1.8 ppm. The model developed parallels that of previously published work [2,18,19]. The main features of the model for the crack geometry of Fig. 1a and b are:

i anodic (Fe and Cr atom dissolution) and cathodic (H^+ and H_2O reduction) reactions in the crack;
ii hydrolysis of ferrous ions and of chromium ions based on first hydrolysis constants;
iii solubility limit for Fe^{2+} in relation to $Fe(OH)_2$;
iv crack tip active or passive; crack walls passive;
v oxygen reduction external to crack but not internally because of very rapid depletion;
vi steel in passive state on external surface;
vii potential drop external to the crack calculated from solution to Laplace equation, as described elsewhere [19].

Two key features of steam turbine applications are the low conductivity of the service environment and the condensate layer. A significant potential drop will be expected external to the crack in low conductivity solutions. This will tend to be accentuated in the presence of a condensate because of the associated confinement of the ionic current to a thin liquid layer. Nevertheless, most laboratory testing is conducted under fully-immersed conditions. In view of this, calculations were performed primarily for the latter conditions but the impact of the condensate layer and of varying thickness of that layer is assessed.

2.2. Crack geometry

As implicit in Fig. 1, a Mode I crack was assumed with the width of the crack tip defined by [20]

$$\delta_t = 0.6\frac{(1-\nu^2)K^2}{\sigma_{0.2}E_{\mathrm{mod}}} \tag{1}$$

where δ_t is the crack-tip opening displacement (CTOD), ν is Poisson's ratio (taken to be 0.3), K is the stress intensity factor, E_{mod} is the elastic modulus and $\sigma_{0.2}$ is the 0.2% proof stress. For the 12Cr steel, FV 566, a value for $\sigma_{0.2}$ of 841 MPa was adopted. In the more general expression for δ_t the value of 0.6 is a variable depending on the work hardening characteristics of the material, ranging from 0.3 (high work hardening) to 0.8 (low work hardening) [21]. The value used is for a low to medium work hardening material. This expression for δ_t is based on elastic–plastic analysis but stress corrosion cracks are usually observed to be much sharper. However, an expression for the CTOD as a function of stress intensity factor in that situation is not available. For this reason, we have used Eq. (1) as the default and then assessed in specific cases the impact of reducing the crack-tip opening displacement. As will be shown later the impact is not significant in relation to crack-tip potential and crack chemistry compared with other uncertainties in modelling, for example from input data.

The crack mouth opening displacement (δ_m) was determined using standard linear elastic fracture mechanics expressions [20], assuming a SENT geometry but with the notch depth zero and with the specimen width, b, equal to 3.3 cm. For a crack length, a (measured from the surface), the crack width (2 h) at any distance (x) from the crack tip (trapezoidal crack) with crack angle θ can be defined by:

$$h(x) = \frac{\delta_t}{2} + x\theta \tag{2}$$

where

$$\theta = \frac{\delta_m - \delta_t}{2a} \tag{3}$$

2.3. Mass conservation equations

The close proximity of the walls of the crack means that concentration and potential profiles between the walls can be reasonably assumed to be flat. This allows averaging of the two dimensional transport equations across the crack. Thus, reactions on the walls, which would be boundary conditions in a full dimensional analysis, then appear as source or sink terms in the conservation equations although scaled on the half-width of the crack. Neglecting through-thickness variations in concentration and potential (fracture mechanics specimens should really be sealed along the sides), which is a reasonable assumption, leads to the generalised one-dimensional mass conservation equation for dilute solutions:

$$\frac{\partial C_i}{\partial t} - C_i\frac{\partial v}{\partial x} = -\frac{\partial J_i}{\partial x} + \underset{\text{solutionreaction}}{k_f C_k - k_b C_i C_j} - \underset{\text{precipitationreaction}}{\frac{k_p}{h(x,t)}\{C_i C_p^q - K_{so}\}^m} + \underset{\text{electrodereaction}}{\frac{i_w}{nFh(x,t)}\exp\left\{\frac{\alpha F\varphi}{RT}\right\}} + \frac{\theta(t)}{h(x,t)}D_i\frac{\partial C_i}{\partial x} + z_i\frac{D_i F}{RT}\frac{\theta(t)}{h(x,t)}C_i\frac{\partial \varphi}{\partial x} \tag{4}$$

where J_i is the flux of species i, i_w in this case is the current density for