Modeling of Corrosion Fatigue Chemistry in Steels in NaCl Solutions

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A mathematical model has been developed to describe the chemistry and potential distribution in a corrosion fatique crack in steels over wide ranges of temperature and NaCl bulk concentration. Mass transport by diffusion, ion migration, and convection (due to cychlical movement of crack walls) is considered. Anodic and cathodic processes, hydrolysis, oxide solubility, and water dissociation are also included in the model. In the previous models, it was postulated that the metal on the sides of the cavity is in a state of active anodic dissolution, i.e. in the same state as that at the tip of the crack. A consequence of this assumption is that the electrochemical reactions at the crack tip do not visibly influence the potential and concentration distributions, because the area of crack tip is much smaller than the area of crack sides. The current model recognizes the fact that, in general case, the specific rate (rate per area unit) of metal dissolution at the crack tip can be much greater than the rate of dissolution on the crack sides. Additionally, the model takes into account transport and charge transfer processes that occur in the external environment, which couple the crack internal and external environments.

Calculations show that, in many cases, the anodic current that is produced at the crack tip is consumed on the crevice sides near the crack tip. At larger distance from the crack tip, a “balanced charge transport” region, with zero net current density in the solution and on the crack sides occurs. Finally, near the crevice mouth, there exists a region of non-zero net current density that is compensated for outside of the cavity. Clear criteria of the existence of one, two or three concentration and potential regions in the crack were obtained.

Numerical simulations show that, for sufficiently low cyclic loading frequencies, $f (f < 10^5$ for the case in Figure 1), it is possible to neglect the influence of fluid flow (induced by the movement of the crevice walls) on the potential and concentration distributions in the crack. Contrariwise, for sufficiently high frequencies (f $\geq 1$ Hz), the solution in the crevice is well mixed and the concentrations of species in the crevice coincide approximately with their bulk values.

Transport and charge transfer processes occurring in the external environment do influence the kinetics of stress corrosion fatigue for the low and moderate frequencies ($f < 0.1 – 1$ Hz, for the case on Figure 2) and hence must be incorporated into any general, quantitative model for corrosion fatigue chemistry.

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