THE KINETICS OF OXYGEN REDUCTION ON TYPE 403 STAINLESS STEEL AT ELEVATED TEMPERATURES

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Type 403 SS is used extensively as blade material in low-pressure (LP) steam turbines in power generating systems. In many LP turbines, part of the system operates downstream of the Wilson line, which corresponds to the conditions of temperature and pressure at which condensation first occurs on the alloy surface. Thus, the affected blade and disk surfaces are covered with a thin layer of electrolyte that is concentrated in steam impurities, including salts such as NaCl, NaOH, and Na_2SO_4. The presence of these salts predisposes the blades and disks to localized corrosion, including pitting corrosion, stress corrosion cracking, and corrosion fatigue, with pitting commonly acting as the nucleation process for the latter two forms of attack.

According to the Coupled Environment Pitting and Fracture Models (CEPM and CEFM, respectively) [Ref.1 and citations therein], which are both based upon the differential aeration hypothesis for localized corrosion, the separation of the local anode, which resides in the corrosion cavity, from the local cathode (on the external surfaces adjacent to the crack or pit mouth) results in the flow of positive current from the cavity through the solution to the external surface, where it is consumed by appropriate cathodic reactions, including the reduction of H^+, H_2O, and O_2. In oxygenated environments, such as those that exist during shut down and start up or when the plant is operating under an oxygenated chemistry protocol, the most important cathodic reaction is oxygen reduction. Accordingly, an experimental study has been carried out to determine the kinetic parameters for the oxygen electrode reaction (Equation 1) on Type 403 SS.

$$\frac{1}{2}O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O \qquad (1)$$
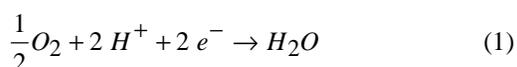
The apparatus used in this study consists of a high temperature/high pressure controlled hydrodynamic test cell contained within a once-through/recirculating flow loop. The test cell comprises an autoclave, a magnetic drive, a thermocouple, a working electrode, a counter electrode, a silver/silver chloride reference electrode, and an annular flow channel. Three borate buffer solutions were formulated to represent condensates on the steel surface in the field and to provide control over the pH of the solution (pH=9, 11, and 13 at 25ºC). The oxygen concentration in the high temperature test cell was calculated using Henry's law from the known partial pressure of oxygen in the reservoir. Experiments were carried out at temperatures 25, 50, 100 and 150ºC and at oxygen partial pressures up to 2.85 atm. Quasi-steady state polarization curves were obtained at a scan rate of 0.1 mV/s and at a range –1 V to +0.4 V vs. the open circuit potential. Electrochemical impedance spectro-scopic (EIS) measurements were carried out at 10 mV rms around the open circuit potential and at frequencies from 5,000 Hz to 0.02 Hz. The anodic polarization curves obtained at the different pH values are shown in Figure 1 for 25ºC.

The polarization curves for Type 403 SS in the selected buffer solutions display typical passive behavior at low anodic potentials, comprising a barely discernable active-to-passive transition, a region over which the current more-or-less remains constant with potential, and a region of transpassive dissolution and/or oxygen evolution at high potentials. With regard to the cathodic region, the polarization curve displays two waves, which are associated with the reduction of oxygen and the reduction of water (hydrogen evolution) as the potential is made increasingly more negative. In the case of oxygen reduction, the exchange current density, as determined from the cathodic polarization curve, can be expressed in the form of Equation (2).

$$i_0 = i_0^0 \left[H^+\right]^n \left[O_2\right]^m \cdot \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

where i^0_0 is the standard exchange current density, n and m are reaction orders with respect to H^+ and O_2, respectively, and E_a is the activation energy. On the other hand, for the reduction of water, the reactant activity is fixed (essentially equal to one), so that the kinetic expression becomes

$$i_0 = i_0^0 \left[H^+\right]^n \cdot \exp\left(\frac{-E_a}{RT}\right) \qquad (3)$$

where the kinetic parameters have the same definitions as those defined above, but, of course, they have different values. Once the kinetic parameters (n, m, E_a, and i^0_0) have been determined over the desired range of conditions for each reaction, they will be inserted into various "coupled environment" models for deterministically predicting the accumulation of localized corrosion damage to turbine blades in operating low pressure steam turbines [1].

1. D. D. Macdonald, Pure Appl. Chem., **71**, 951 (1999).
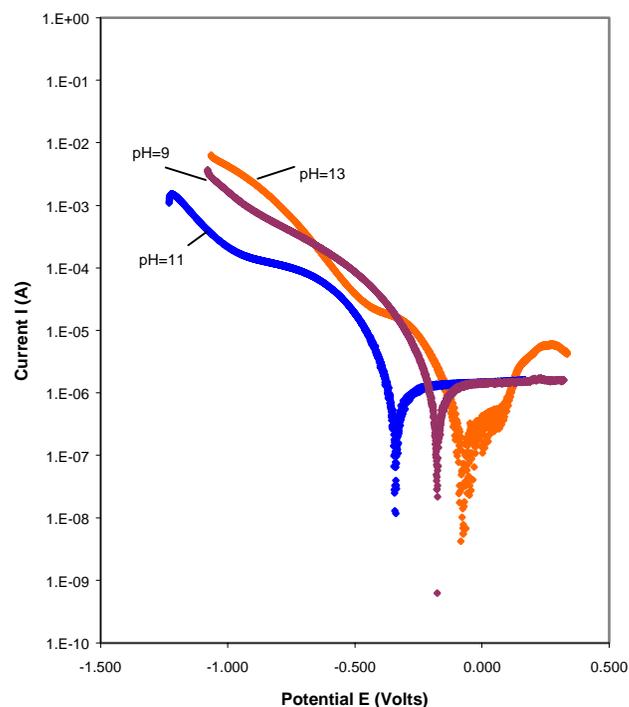
Figure 1. Anodic polarization curves obtained for 403 SS at different pH values, at 25ºC and oxygen concentration 100 ppm.