

Evaluation of the maximum pit size model on stainless steel under atmospheric conditions

M. T. Woldemedhin, J. Srinivasan, M. E. Shedd, M. J. McGrath, R. G. Kelly

Center for Electrochemical science and Engineering
Department of Materials Science and Engineering

University of Virginia
395 McCormick Rd., Charlottesville, VA

Thin oxide films formed naturally on the surface of engineering alloys such as stainless steels prevent or reduce the rate of corrosion of the alloys when exposed to the atmosphere. Breakdown of this passive oxide film by aggressive ions such as chloride ions from the atmosphere leads to pitting corrosion.

Knowledge of the maximum size of pits formed under such atmospheric conditions where the material is covered by a thin film of electrolyte is important in corrosion damage prediction. The aggressiveness of the thin film environment depends on the nature of the salts(s), the temperature and the relative humidity of the atmosphere to which the steel samples are exposed.

Previous reports on the pit sizes from long-term atmospheric exposure of stainless steel samples show a limiting pit size where the pit size becomes invariant after four years of exposure [1, 2]. Based on the galvanic couple involved in the pitting process, Chen and Kelly [3] recently developed a predictive analytical model to determine and explain the maximum or limiting pit size under atmospheric conditions. The galvanic couple consists of anodic current from an actively dissolving pit and cathodic current supplied to the pit from the surrounding surface covered with a thin electrolyte film as shown in Figure 1. For a pit to remain active, it must maintain the critical chemistry of the aggressive solution within the pit. The maintenance of the critical chemistry within the pit is given by the stability product (i) based on the work of Galvele [5], where i is the anodic dissolution current density from an active pit surface and x is the pit depth for a 1D pit. In order for the pit to continue growing, the surrounding cathode must provide sufficient cathodic current. However, the cathodic current supplied to a pit is limited by the inherent ohmic resistance of the thin electrolyte film. Thus, calculation of the maximum cathodic current possible under given atmospheric conditions based on the model by Chen and Kelly [3] coupled with the minimum anodic current which maintains the critical chemistry within the pit allows a physical limit to be determined for the size of a pit under thin film conditions. Calculation of the maximum cathodic current possible depends on corrosion potential, repassivation potential as well as the conductivity and thickness of the thin electrolyte film which were determined from physical chemistry data and cathodic polarization scans.

The present work thus involves the evaluation of the model in predicting the maximum pit size under controlled laboratory conditions on 316L, 304L, 17-4 PH and Custom 465 steel samples. The surfaces of the steel samples were first cleaned with an Ar/O₂ plasma and then covered by a thin film of ferric chloride solution of different concentrations and thickness before being placed in humidity chambers for different periods of time. The maximum pit size formed on the steel samples from the exposure tests in the humidity chambers was determined by optical profilometry and compared to that predicted by the maximum pit size model. Ferric chloride was chosen for these experiments due to its highly corrosive nature

which leads to rapid pitting.

Moreover, the influence of alloy composition, chloride concentration and pH on critical kinetic parameters such as the pit stability product and repassivation potential were also included in this work. The chloride concentration effects were studied in sodium chloride and ferric chloride solution with chloride concentrations varying from 0.6 M -10 M and the pH range from -0.36 to near neutral for the samples mentioned above.

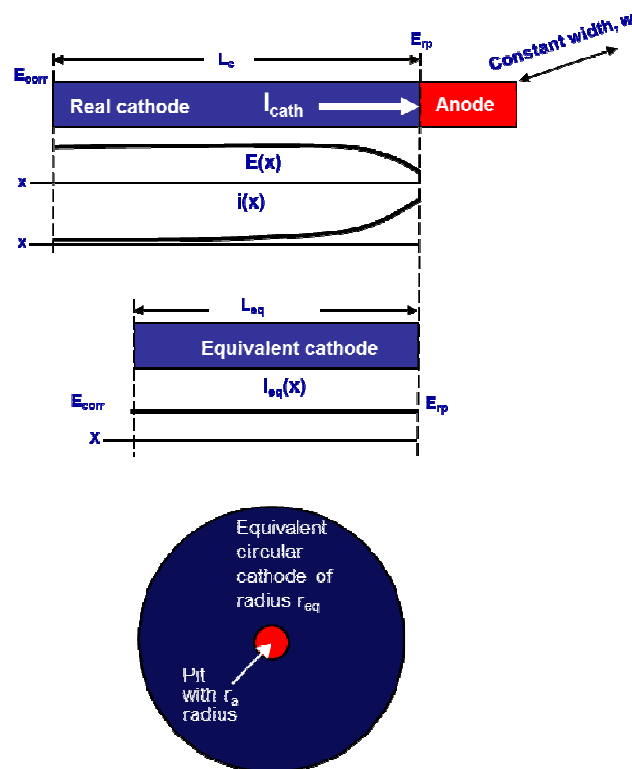


Fig. 1. Reduction of the real cathode to an equivalent cathode of length L_{eq} with uniform current density distribution across potential gradient ($E_{corr} - E_{rp}$) [4]. For a circular equivalent cathode, the treatment would be in polar coordinates, resulting in a uniform radial current density distribution from E_{corr} at the circumference of the cathode to E_{rp} at the circumference of the pit [3]

References

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