Mass Transport and Electrochemical Factors Influencing Stainless Steel Pitting and Repassivation in Neutral Chloride Media

J. Srinivasan, M. J. McGrath, R. G. Kelly
Center for Electrochemical Science and Engineering
Department of Materials Science and Engineering
University of Virginia
395 McCormick Road, Charlottesville, VA 22904

The critical conditions of mass transport and localized chemistry required for a 1-D pit to grow stably in an aggressive environment were first examined by Galvele [1], resulting in the establishment of the pit stability product $(i.x)_{crit}$ as the key parameter of interest. Experimentally determining this parameter has generally involved using artificial pits to examine steady-state conditions related to pit stability [2]. The pit stability product measured in this manner is that under a salt film and the potential corresponding to the appearance of this salt film has been termed the transition potential (E_t) [3]. However, pitting is known to proceed stably at potentials much lower than E_t. This result implies that $(i.x)_{salt\ film}$ overestimates the $(i.x)_{crit}$. Better estimates of $(i.x)_{crit}$ also result in a more accurate measurement of the repassivation potential, E_{rp}. Examining mass transport kinetics crucial to maintaining $(i.x)_{crit}$ can help determine local reaction mechanisms that affect repassivation. Applying this idea to different stainless steels in a range of chloride media allows mapping of electrochemical conditions for pit stability and repassivation in terms of metallurgical, chemical, and diffusional parameters.

1-D artificial pits constructed from wires of 4 stainless steel alloys – 430, 304L, 316L, and 17-4 PH – in different concentrations of neutral chloride media were used in this study to determine the effect of alloying and environment on repassivation and pit stability. Anodic dissolution kinetics experiments to determine $(i.x)_{salt\ film}$ were performed on the artificial pit samples using a modified version of the method outlined by Laycock and Newman [3]. E_{rp} measurements were also obtained from the same experiment using a variation of the technique employed by Sridhar and Cragnolino [4]. This approach enabled the direct correlation of the E_{rp} to pit depth, allowing the examination of its dependence on diffusive transport. Additionally, using artificial pit electrodes avoided any significant change in the bulk chemistry of the solution becausethe volume of corrosion product is very low. E_{rp} was obtained in this manner as a function of q, the charge density passed, and using Faraday's law, the pit depth d.

This relationship between E_{rp} and d was utilized to develop an indirect, graphical method of estimating the pit surface concentration at the edge of stability. This method involved comparing two measurable quantities dependent on pit depth d – a) Δt, the difference between t_{act}, the time taken to scan cathodically to E_{rp} from E_t and t_f, the time taken for the pit surface concentration to naturally diffuse to different fractions of saturation (i.e., $\Delta t = t_{act} - t_f$), and b) E_{rp}. Fig. 1 illustrates these relationships for 316L in 0.6 M NaCl, overlaying the E_{rp} versus pit depth plot on the Δt versus pit depth curves obtained for different values of f, the fraction of saturation. The concentration of ions at the pit surface C_s at the edge of stability can then be read from the graph and subsequently, $(i.x)_{crit}$ can be evaluated as $f*(i.x)_{salt\ film}$.

The effects of alloying elements on the repassivation potential were studied by testing the 4 alloys in 0.6 M NaCl (E_{rp} vs. q plots displayed in Figure 2). The influence of chloride content in the bulk solution on pit repassivation was studied using 316L wires in NaCl (0.6 M, 1.5 M, 2.8 M, 3.9 M) and LiCl (4.3 M, 5.3 M, 7.9 M, 10.6 M) solutions of pH ≈ 6. The data generated were utilized to develop a better comprehension of the conditions leading to pit stability and repassivation [5, 6], allowing for improved estimates of the critical parameters involved, which may then be used as bounding values in corrosion mitigation strategy and design.
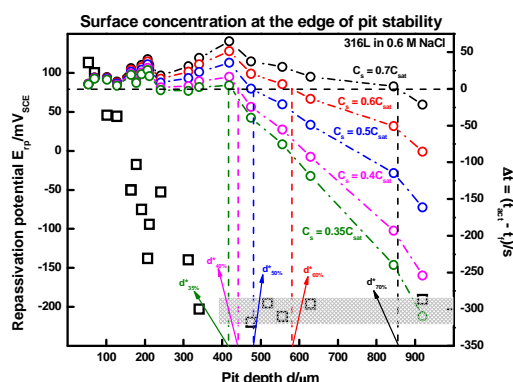

Figure 1: *Graphical method of determining pit surface concentration C_s at the edge of stability. Shaded region shows the constant value to which E_{rp} settles at high charge densities/large pit depths.*
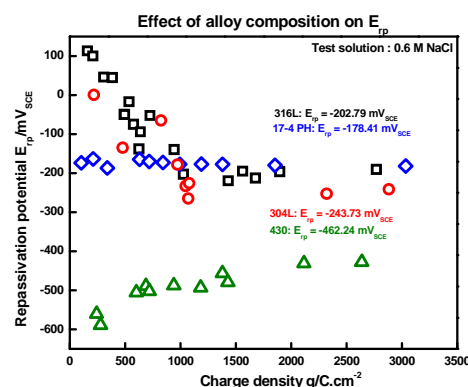

Figure 2: *E_{rp} vs. q behavior for stainless steels in 0.6 M NaCl.*

References

[1] J.R. Galvele, Journal of The Electrochemical Society, 123 (1976) 464-474.
[2] G.T. Gaudet, W.T. Mo, T.A. Hatton, J.W. Tester, J. Tilly, H.S. Isaacs, R.C. Newman, Aiche J., 32 (1986) 949-958.
[3] N.J. Laycock, R.C. Newman, Corrosion Science, 39 (1997) 1771-1790.
[4] N. Sridhar, G.A. Cragnolino, Corrosion, 49 (1993) 885-894.
[5] J.R. Galvele, Corrosion Science, 21 (1981) 551-579.
[6] S.M. Gravano, J.R. Galvele, Corrosion Science, 24 (1984) 517-534.