Future Frontiers in Corrosion Science and Engineering, Part II: *Managing the Many Stages of Corrosion*

Dr. John R. Scully, Technical Editor in Chief

As a follow up to my January 2018 editorial outlining some of the National Academy of Science engineering challenges facing us in the 21st century, the next editorial in this series[1] explores the challenges faced in corrosion modeling. Corrosion is a highly complex process involving coupled chemical, electrochemical, sometimes biological, and solid-state reactions. Both thermodynamic and kinetic factors incorporating materials science, surface science, and environmental and materials chemistry govern corrosion susceptibility and the associated outcomes.[2] Building on Part I of this editorial series' focus, on the multi-scale and multi-physics nature of corrosion processes, we now explore the incorporation of those processes with different stages of corrosion.

The difficulty in distilling complex corrosion behavior into key descriptors of corrosion susceptibility that engineers can use to guide materials selection, such as a pitting resistance equivalency number applied to corrosion resistant alloys (PRE_N)[3-6] or the chloride-to-sulfate mass ratio in the context of lead pipe (CSMR),[7-8] occurs because of the complexity of corrosion and the many mechanisms, triggers, drivers, and dependencies that control corrosion processes.[9-10] In some cases, there are no simple descriptors or there are too many exceptions to make due with simple correlations (e.g., the "Copson curve"[12-13]) reliably.[14-16] Fortunately, it is no longer necessary to rely on empirical parameters as descriptors of corrosion. The corrosion field has developed and gone well beyond "look and see" forensic type characterizations that can guide rules of thumb. Sufficient theory and knowledge has developed over the last 40 years to conduct modeling and simulation of corrosion, which has occurred in many cases.

A recent survey showed 114 modeling and simulation papers in *CORROSION* with 2 in the 1950s and about 10 per year from 2016-2018.[17] However, early models focused on the details of corrosion at one or two length scales in isolation without much attention to connection or integration across length and time scales. This type of modeling has dominated the corrosion field to date. The assumption (or hope) was made in early models that factors elucidated at the scales of choice governed overall corrosion behavior. Such an a priori assumption is no longer necessary given advances in computing power and the plethora of thermodynamic and kinetics models now available that can consider various phenomena at various length and time scales. The materials community has successfully bridged length scales, embracing integrated computational materials design (ICME), but this accomplishment is largely limited to static material properties[18] that can be targeted and only have to consider a few material tradeoffs.[18-20] There are many examples today of materials discovery and materials-by-design using such approaches. However, capturing the *time-based evolution of properties* remains a challenge at the frontier in corrosion science and engineering.[18,21] The corrosion field can advance at an accelerated pace by further connecting and integrating information at each scale to inform the next scale. ***However, this alone is not enough***.

A daunting challenge that still remains is incorporating the **stages of corrosion** in modeling and simulation of every form of attack. These stages mark the time dependency of corrosion and must be considered to conduct successful ICME directed toward both corrosion-oriented design as well as life prediction. Further advances in both ICME and life prediction require that materials, surface, and environmental attributes be reassessed at each time step based on material-environmental interactions. These stages and the material, environmental, and physical factors that regulate them define damage evolution seen in service and help find materials weaknesses pertinent to design.

For years, corrosion scientists have recognized initiation and propagation are distinct stages of most corrosion processes and that there also exist special conditions for "transition" between them. Often it has been stated that a lab or field test is dominated by one stage or another. Such recognition is desirable but by itself is inadequate. While an obvious question is *which stage dominates the useful lifetime or extent of damage after a given time such as in a corrosion resistant alloy (CRA)*? There is no single answer.

The many stages of local corrosion, such as in the case of pitting, are illustrated in Figure 1, which describes the possible pathways of corrosion damage evolution for this mode of corrosion. Each other mode of corrosion also has numerous linked stages, much like those shown in Figure 1. Each stage, in turn, has its own multi-scale physics laws (and mechanisms, triggers, drivers, and dependencies).

One challenging aspect in this new frontier is to develop models that can capture all of these stages. In other words, in order to accurately model, predict, and simulate incubation time and pit propagation, the best approach is to develop the theories and governing physics to describe each process along the critical path in appropriate detail to capture corrosion. If the model correctly captures the essential elements and laws, it could be "exercised" in a sensitivity analysis to identify the critical factors causing progression through the necessary stages under a given set of conditions.

Consider a CRA that forms a passive film and is susceptible to undergoing local corrosion. CRAs first form passive films based on alloy composition and surface structure, which form as island nuclei that coalesce, thicken, age, and break down.[22] Initiation can thus be further redefined in detail including oxide formation, growth, and alteration by interaction with the environment starting with Cl^- adsorption and leading to the development of defects and instabilities that are prone to passive film "trigger" or breakdown events.[23-32] Any one of these processes could define the overall incubation time for local corrosion indicated by the dotted lines encompassing several closely related stages in Figure 1. Incubation time may change with drivers such as potential and temperature. Increasing incubation times toward infinite values as a function of decreasing potential could define a potential threshold. Newly formed pits may also be metastable and repassivate quickly or instead satisfy the conditions to enable the transition to stable propagation and enable more severe forms of attack. In this case, the growth conditions and criteria for stability based on reaction kinetics and a plethora of other parameters are what determine pit survival.[33-39] If a pit "survives and grows up," a range of consequences may follow. This is shown in Figure 1 by the split in paths leading to repassivation and pit "death" versus transition to stability and "pit growth" subsequently growing into other modes of damage.

A current perspective is that highly resistant alloys and/or exposure in less aggressive environments lead to situations where oxide film breakdown is slow and rare, whereas pit propagation is fast (often because of the high driving force required to bring about breakdown and initiation).[40] In contrast, less resistant alloys with more defects in harsh environments promote conditions where initiation occurs quickly and frequently, enabled by many weak sites for initiation. The rate-controlling step in this case is pit growth, controlled by reaction rate behavior in pits. While there is general agreement on existence of these stages, the importance of each stage is still under debate, and no one model captures everything in a quantitative working model.

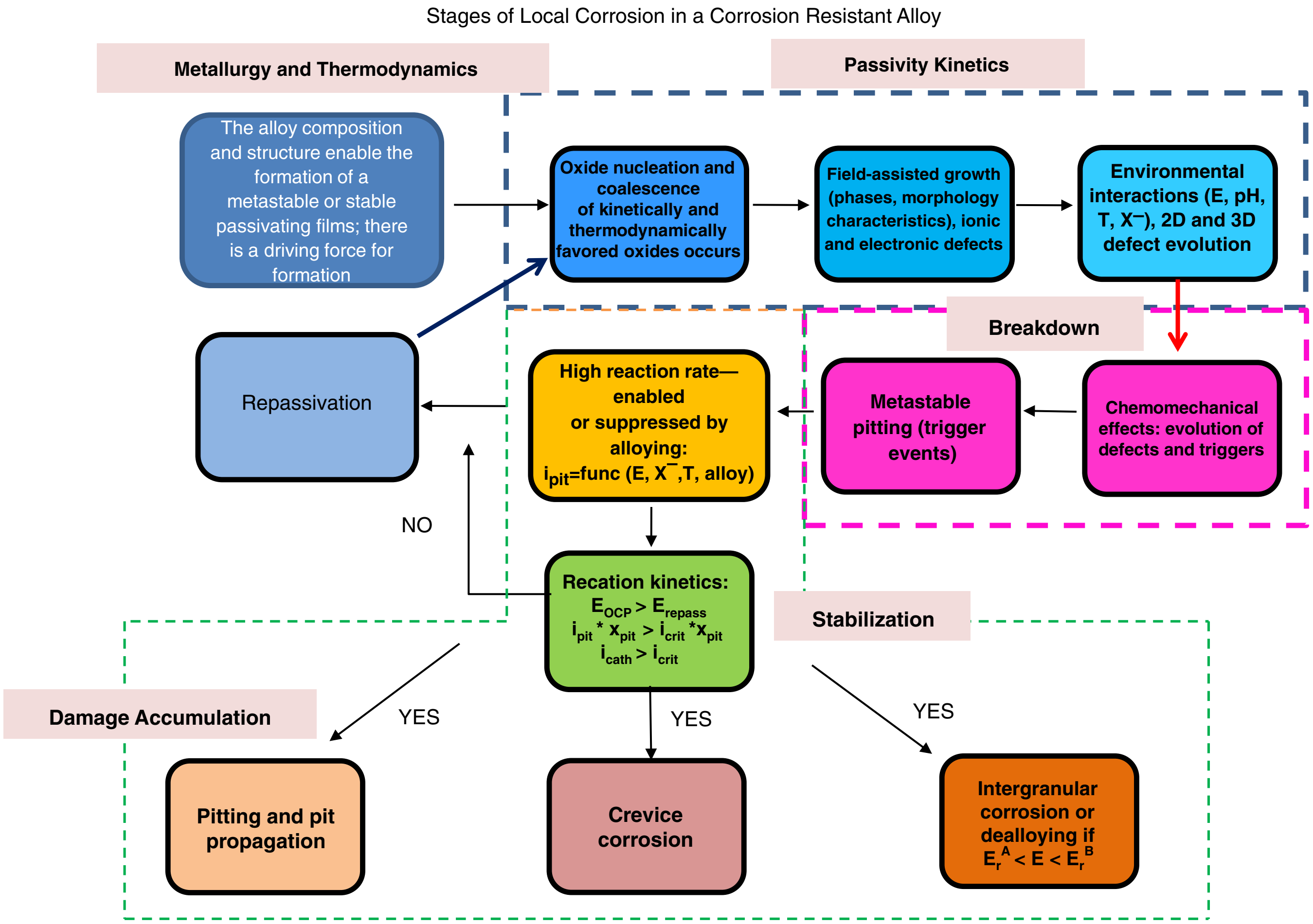

FIGURE 1. *Example of the many complex stages of corrosion, demonstrated in the case of localized corrosion of a corrosion resistant alloy (CRA), where a passive film protects the alloy and local breakdown and localized corrosion occurs. The metallurgy and thermodynamics establish the possible identity of the passive film and the thermodynamic driving force for its formation. The (blue) stages in the top row involve passive film growth and interaction with the environment starting with Cl^- adsorption, and leading to a variety of phenomena such as Cl^--induced changes in surface energy, defect creation, and coalescence, which eventually enable breakdown events. Breakdown and metastable pitting occur in certain environments, while certain high-rate corrosion processes occur, that either transition to stable pit growth or become limited by metastable pitting and subsequently repassivation. At this point, the process starts over again with oxide film growth and possible breakdown. However, if propagation continues and mature pits grow, then even more advanced modes of corrosion are possibly triggered that can lead to other kinds of damage accumulation.*

The complexities of modeling CRAs provides a snapshot of "where we are today" in terms of corrosion modeling. It is difficult to predict component lifetime from theories, tests, and models that only consider one stage or another. Additionally, there is a critical need to deal with variations or statistical distributions in the input factors and values utilized in governing laws and physics at each stage. Essentially, corrosion lifetimes may be regulated by rare events of low probability that create extreme circumstances instead of the average properties. Moving forward, the challenge for the corrosion community is to address these sorts of issues in a rational way.

The future potential for corrosion research lies beyond the frontier—it waits for us in areas like predictive modeling that encompasses time-based evolution of properties, stages of corrosion, and the variation in data, among others. Let's continue to explore these frontiers together with *CORROSION*.

ACKNOWLEDGMENTS

John R. Scully was supported in part by the Center for Performance and Design of Nuclear Waste Forms and Containers, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0016584. He was also supported by ONR MURI "Understanding Atomic Scale Structure in Four Dimensions to Design and Control Corrosion Resistant Alloys" on Grant No. N00014-16-1-2280, and by the National Science Foundation under Grant No. DMR-1309999.

References

1. J.R. Scully, *Corrosion* 74, 1 (2018): p. 3-4.
2. J.R. Scully, *Faraday Disc.* 180 (2016): p. 577-59.
3. K. Lorenz, G. Medawar, *Thyssenforschung* 1 (1969): p. 97-108.
4. R. Jargelius-Pettersson, *Corrosion* 54, 2 (1998): p. 162-168.
5. N.J.E. Dowling, Y.-H. Kim, S.-K. Ahn, Y.-D. Lee, *Corrosion* 55, 2 (1999): p. 187-199.
6. U. Steinsmo, T. Rogne, J. Drugli, *Corrosion* 53, 12 (1997): p. 955-964.
7. C.K. Nguyen, B.N. Clark, K.R. Stone, M.A. Edwards, *Corrosion* 67, 6 (2011): p. 065005-1 to 065005-9.
8. J. Hu, F. Gan, S. Triantafyllidou, C.K. Nguyen, M.A. Edwards, *Corrosion* 68, 11 (2012): p. 1037-1048.
9. C.D. Taylor, P. Lu, J. Saal, G.S. Frankel, J.R. Scully, *npj Mater. Degradation* 2, 1 (2018): article 6.
10. L. Marks, *Corrosion* 74, 3 (2018): p. 295-311.
11. H.R. Copson, W.E. Berry, *Corrosion* 16, 2 (1960): p. 79t-85t.
12. H.R. Copson, "Effect of Composition on Stress Corrosion Cracking of Some Alloys Containing Nickel," in *Physical Metallurgy of Stress Corrosion Fracture*, ed. T.N. Rhodin (New York, NY: Interscience Publishers, 1959), p. 247.
13. B.M. Gordon, G.M. Gordon, *Corrosion*, ASM Handbook, vol. 13, 9th ed. (Metals Park, OH: ASM International, 1987), p. 927.
14. D. Feron, C. Guerre, F. Martin, "Historical Review of Alloy 600 Stress Corrosion Cracking: from the "Coriou Effect" to the Quantitative Micro-Nano Approach," *Corrosion* in press (2019): https://doi.org/10.5006/2942.
15. H. Coriou, L. Grall, Y. Le Gall, S. Vettier, "Corrosion fissurante sous contrainte de l'Inconel dans l'eau à haute temperature," Proceedings of the 3rd "colloque annuel de métallurgie - corrosion" (Saclay, France: North Holland Publishing Co., 1959), p. 161-169.
16. H. Coriou, L. Grall, C. Mahieu, M. Pelras, *Corrosion* 22, 10 (1966): p. 280-290.
17. *CORROSION* journal, 2018, www.corrosionjournal.org (Dec. 12, 2018).
18. *Integrated Computational Materials Engineering: A Transformative Discipline for Improved Competitiveness and National Security* (Washington, DC: National Research Council, 2008).
19. C.J. Kuehmann, G.B. Olson, *Mater. Sci. Technol.* 25, 4 (2009): p. 472-478.
20. G.B. Olson, *J. Computer Aided Mater. Design* 7 (2001): p. 145170.
21. *Research Opportunities in Corrosion Science and Engineering* (Washington, DC: National Research Council, 2011).
22. K. Gusieva, K.L. Cwalina, W.H. Blades, G. Ramalingam, J.H. Perepezko, P. Reinke, J.R. Scully, *J. Phys. Chem. C* 122, 34 (2018): p. 19499-19513.
23. V. Maurice, W.P. Yang, P. Marcus, *J. Electrochem. Soc.* 141 (1994): p. 3016-3027.
24. V. Maurice, W.P. Yang, P. Marcus, *J. Electrochem. Soc.* 145 (1998): p. 909-920.
25. P. Marcus, *Electrochim. Acta* 43 (1998): p. 109-118.
26. P. Marcus, V. Maurice, H.H. Strehblow, *Corros. Sci.* 50 (2008): p. 2698-2704.
27. G.P. Halada, D. Kim, C.R. Clayton, *Corrosion* 52, 1 (1996): p. 36-46.
28. A. Kolics, J.C. Polkinghorne, A. Wieckowski, *Electrochim. Acta* 43 (1998): p. 2605-2618.
29. P.M. Natishan, W.E. O'Grady, E. McCafferty, D.E. Ramaker, K. Pandya, A. Russell, *J. Electrochem. Soc.* 146 (1999): p. 1737-1740.
30. S.Y. Yu, W.E. O'Grady, D.E. Ramaker, P.M. Natishan, *J. Electrochem. Soc.* 147 (2000): p. 2952-2958.
31. P.M. Natishan, W.E. O'Grady, *J. Electrochem. Soc.* 161 (2014): p. C421-C432.
32. P.M. Natishan, *Corrosion* 74, 3 (2018): p. 263-275.
33. R.C. Newman, *Corros. Sci.* 25 (1985): p. 341-350.
34. N.J. Laycock, R.C. Newman, *Corros. Sci.* 39 (1997): p. 1771-1790.
35. R.C. Newman, *Corrosion* 57, 12 (2001): p. 1030-1041.
36. G.S. Frankel, R.C. Newman, C.V. Jahnes, M.A. Russak, *J. Electrochem. Soc.* 140 (1993): p. 2192-2197.
37. D.E. Williams, J. Stewart, P.H. Balkwill, *Corros. Sci.* 36 (1994): p. 1213-1235.
38. G.S. Frankel, *Corros. Sci.* 30 (1990): p. 1203-1218.
39. R. Huang, D.J. Horton, F. Bocher, J.R. Scully, *Corrosion* 66, 3 (2010): p. 035003-01 to 035003-15.
40. G.S. Frankel, T. Li, J.R. Scully, *J. Electrochem. Soc.* 164, 4 (2017): p. C180-C181.