

2015 Research Topical Symposium Proceedings— “Environmentally Assisted Cracking”

Environmentally assisted cracking (EAC) is a form of corrosion that occurs when three concurrent factors are present: mechanical stress, environmental species that produce a crack tip interaction that alters the mechanical behavior of the material, and a susceptible material itself. Mechanisms for EAC may include hydrogen embrittlement, liquid metal embrittlement, and a variety of stress-induced anodic dissolution based corrosion cracking mechanisms such as sulfide stress corrosion cracking and halide-induced stress corrosion cracking. Because of the diversity in conditions and materials that EAC affects, almost all industries experience this form of corrosion to some extent, often resulting in failure. For this reason it is a vigorous area of active research. This special issue reflects this diversity and the concomitant challenges it brings, as well as reviews both fundamental research topics and industry-specific cases where EAC is a problem. The papers were based on the excellent presentations at the Research Topical Symposium held at the NACE International CORROSION 2015 conference in Dallas, TX.

The keynote speaker for the Research Typical Symposium was Professor Richard P. Gangloff, who presented a lecture titled “Probabilistic Fracture Mechanics Simulation of Stress Corrosion Cracking Using Accelerated Laboratory Testing and Multi-Scale Modeling.” This paper describes the theory and experimental support underlying the *SCCrack*TM fracture mechanics code, and its relationship to multi-physics hydrogen embrittlement models. By coupling the *SCCrack* code with the Monte Carlo method, probabilistic distributions for the time to failure and other EAC parameters of engineering usefulness can be assessed. Applications of the method to high-strength steels, nickel-based alloys, and sensitized aluminum alloys are presented. Issues associated with correctly providing the experimental inputs through detailed fracture testing are addressed, and a perspective is provided on research opportunities needed to advance the *SCCrack* model.

Dr. Suraj Persaud and Professor Roger Newman contributed a paper to this special issue on the topic of “A Review of Oxidation Phenomena in Ni Alloys Exposed to Hydrogenated Steam Below 500°C.” This paper explores the internal oxidation at grain boundary sites in nickel-based alloys exposed to hydrogenated steam, a scenario of relevance to nuclear power systems. Oxidation of reactive elements in the alloys at the sites along the grain boundary will generate internal stresses and possibly create an embrittling effect. Various possible materials responses to the internal oxidation are considered, including the development of vacancy gradients, dislocation pipe diffusion, and mechanical action. The selective oxidation of reactive elements (for example, Cr in Alloy 600) leads to the expulsion of metallic nickel. Experiments in primary water suggest similar phenomena may be occurring, and that internal oxidation could be a significant contributor to embrittlement mechanisms.

Professor Jian Luo’s paper, “A Short Review of High-Temperature Wetting and Complexation Transitions with a Critical Assessment of Their Influence on Liquid Metal Embrittlement and Corrosion,” explores new findings in the area of grain boundary segregation and wetting associated with the EAC failure mode of liquid metal embrittlement. Highly resolved microscopic measurements at grain boundaries have revealed the formation of atomic bilayers of Ni-Bi and Cu-Bi, which are a root cause for liquid metal embrittlement. Similar phenomena occur such as triple-grain-line wetting at high temperatures, which can contribute to liquid metal embrittlement, as well as liquid metal corrosion. The development of grain boundary λ -diagrams as a new means to assess grain boundary segregation and wetting phenomena is presented. Interactions between co-dopants in the alloy and the embrittling agents are also discussed and recommendations made for future research on this topic.

Professor Jenifer Locke presented a comparison of age-hardenable aluminum alloy corrosion fatigue crack growth susceptibility experiments and the effects of variations in the testing environment. This paper reviews fatigue crack growth kinetics in aluminum aerospace alloys with a focus on the disparities that emerge due to the differences between testing environment and in-service conditions. The fatigue response introduced by alloying elements, particularly copper, is considered as one specific example of how

experimental testing may lead to considerably different phenomena compared to in-service conditions. The paper argues for a renewed exploration of management strategies for research into the effects of corrosion fatigue induced by variables such as temperature, atmospheric conditions, changes in local pH, and chloride concentration.

The storage of legacy radioactive material at the Hanford site has necessitated studies of the fundamental role of chemistry in either provoking or inhibiting EAC. Dr. Narasi Sridhar's article "Stress Corrosion Cracking and Localized Corrosion of Carbon Steel in Nitrate Solutions" provides a review of the significant body of literature that has been produced on the topic of nitrate cracking of steel in the last 100 years. Original data that challenges some of the conventional thoughts regarding the role of $\text{NO}_3^-/\text{NO}_2^-$ redox potentials pointed instead toward the roles of passivity and the formation of surface films. Knowledge gaps surrounding the roles of pH, cations, and anions in promoting or inhibiting cracking, influencing the corrosion potential, and creating distinctive surface chemistries are identified as future fertile research topics.

Professor Milos Djukic, et al., presented a modeling approach that can be applied to industrial boiler tube systems, in a paper titled, "Hydrogen Embrittlement of Industrial Components: Prediction, Prevention, and Models." This paper focuses on predictive models for the hydrogen embrittlement of plain carbon steels used in industrial boiler systems. Correlations between microstructure, fractographic observations, and macro-mechanical testing data are used to propose a model enabling enhanced predictive maintenance of industrial component systems. Crack formation and growth due to hydrogen embrittlement (HE) and high-temperature hydrogen attack (HTHA) are both addressed.

Environmentally assisted cracking has resulted in in-service and hydrostatic test stress corrosion cracking and failures in the pipeline industry for over 40 years. Dr. Weixing Chen's paper describes the important roles of cyclic loading on crack initiation, dormancy, and growth-to-failure and presents potential mitigation strategies based on pipeline design, the control of pressure fluctuations, and the development of predictive models to help manage this form of stress corrosion cracking. Environmental effects are also important at various stages of the cracking process, with high rates of dissolution a feature of the initiation process while hydrogen is found to play a key role in crack growth. This paper demonstrates how knowledge obtained from basic research and development can be transferred to address a real industrial problem. This manuscript is an excellent example of the intent of the Research Topical Symposium in bringing together practitioners and researchers in a single forum.

Finally, Drs. Christopher Taylor and Matthew Rossi contributed an article to this special issue titled, "Multiphysics Modeling of the Role of Iodine in Environmentally Assisted Cracking of Zirconium via Pellet-Clad Interaction." This paper reviews the development of a multiphysics approach to studying the EAC of zirconium as induced by iodine, an environmental cracking mechanism pertinent to the degradation and failure of clad materials encasing nuclear fuel rod assemblies. Phenomenological models are reviewed, and then the development of a multiphysics model by the authors is presented that includes quantum chemistry, density functional theory, and molecular dynamics calculations. The authors then survey recent trends in modeling that they expect will lead to the next steps in the multiphysics simulation of iodine-induced stress corrosion cracking of zirconium and Zircaloy materials, and potentially other systems in which intergranular corrosion cracking is a key mechanism.

The 2015 Research Topical Symposium also included presentations by Professor Thomas Devine, who presented on "The Role of Stress and Synergistic Stress-Chemical Effects on Stress Corrosion Cracking," and Drs. Ting Chen and Indranil Roy, who presented on "Coarse Grain Polycrystalline to Nano: Addressing Environmental Cracking and Hydrogen Damage in Extreme Environments for Oil and Gas Applications."

In assembling this special issue of *CORROSION* journal, we have been impressed by both the breadth and the depth of research that spans atomistic modeling of interfacial chemical/mechanical interactions that lead to cracking through to post-failure investigations of microstructure and the experimental investigation on the effects of solution chemistry on EAC. The use of highly-resolved analysis techniques, such as transmission electron microscopy, to probe and characterize materials susceptible to EAC in detail, as shown in Professor Luo's paper, points the way toward connecting the length-scales at which methods applied from theory, modeling, and simulation and those from experimental investigation can operate. The increasing incorporation of materials informatics technologies that provide advanced strategies for making inferences from large data sets will also assist, for example, in identifying thresholds for the safe-operation of materials in complex chemical environments.

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