Carnegie Mellon
Materials Science and Engineering Seminar Series

Digby D. MacDonald

Department of Materials Science and Engineering
Pennsylvania State University

"The Electrochemical Nature of Stress Corrosion Cracking"

Friday, September 24, 2010
10AM Seminar in Baker Hall 136A

Stress corrosion cracking of metals and alloys in aqueous environments is primarily an electrochemical phenomenon falling within the realm of the differential aeration hypothesis (DAH). As such, the local anode and the local cathode are spatially separated, with the former existing within the crack enclave (on the crack flanks and at the crack tip) and the latter existing on the bold, external surfaces that have greatest access to the cathodic depolarizer (e.g., O_2). The resulting current that flows from the local anode to the local cathode implies strong electrochemical coupling between the crack internal and external surfaces and this coupling, which has been experimentally probed in a variety of systems, including intergranular stress corrosion cracking, contains a great deal of information on events occurring at the crack tip. Furthermore, the crack length is predicted theoretically to exert a strong influence on crack growth rate, because, as the crack grows, a larger fraction of the potential drop between the crack tip and the external surface appears as IR potential drop down the crack and hence less potential drop is available to drive the cathodic reactions that consume the coupling current on the external surfaces. Consequently, the magnitude of the coupling current drops as the crack lengthens and hence so does the crack growth rate. The dependence of the crack growth rate on the electrochemical crack length has profound implications for the accumulation of SCC damage, including: (1) All cracks must eventually die (repassivate) when the potential drop available at the external surface becomes insufficient to maintain the separation between the local anode and local cathode. (2) The rate of accumulation of damage, as determined by the crack growth rate, decreases with time, such that a model that postulates a crack growth rate that is constant with time would significantly over-estimate the accumulated damage (crack length). The above relationships are illustrated with reference to intergranular stress corrosion cracking (IGSCC) in sensitized Type 304 SS in BWR primary coolant environment, IGSCC in sensitized Type 304 SS in thiosulfate solution at ambient temperature, and IGSCC in AISI 4340 steel in concentrated caustic at 70 ^{o}C. It is shown that, in all three cases, crack propagation is due to hydrogen-induced cracking. Finally, it is concluded that the crack growth rate is controlled by the kinetics of the cathodic reaction occurring on the external surface.

Born in Thames, New Zealand, December 7 1943, Distinguished Professor Macdonald gained his BSc and MSc degrees in Chemistry at the University of Auckland, New Zealand, and his Ph.D. degree in Chemistry from the University of Calgary in Canada. He has served as Assistant Research Officer at Atomic Energy of Canada Ltd., Lecturer in Chemistry at Victoria University of Wellington, New Zealand, Senior Research Associate at Alberta Sulfur Research, Honorary Associate Professor at the Chemistry Department of the University of Calgary, Director and Professor of the Fontana Corrosion Center, Ohio State University, Vice President, Physical Sciences Division, SRI International, Menlo Park, California and has been Professor and later Distinguished Professor of Materials Science and Engineering at Pennsylvania State University since 1991. Professor Macdonald has received numerous awards and honors, including the 1991 Carl Wagner Memorial Award from The Electrochemical Society; the 1992 Willis Rodney Whitney Award from The National Association of Corrosion Engineers for "contributions to the science of corrosion"; the W. B. Lewis Memorial Lecture from Atomic Energy of Canada, ltd., for his "contributions to the development of nuclear power in the service of mankind"; the H. H. Uhlig Award from The Electrochemical Society; the U. R. Evans Award from The Insitute of Corrosion; the 20th Khwarizmi International Award in fundamental science; and the Wilson Research Award of Pennsylvania State University. He is an elected fellow of NACE-International; The Electrochemical Society; the Royal Society of Canada; the Royal Society of New Zealand; ASM International; the

World Innovation Foundation; the Institute of corrosion (UK); and the International Society of Electrochemistry. From 1993 to 1997 he was a member of the US Air Force Science Advisory Board with the protocol rank of Lieutenant General. He was awarded the US Air Force Medal for Meritorious Civilian Service in 1997. In 2006/2007 he led a congressionally-mandated team of experts to assess the corrosion control practices of BP in the wake of oil leaks at the Prudhoe Bay field on the North Slope of Alaska. Dr. Macdonald is a Trustee of ASM International and has recently been appointed Honoris Causa by the Government of France. He is also a Chair Professor at the King Fahd University of Petroleum and Minerals in Dhahran, Saudi Arabia, where he teaches for three months per year and is a Adjunct Professor at Massey University, New Zealand, and at the University of Nevada at Reno. He is a recent recipient of the Lee Hsun Research Award of the Chinese Academy of Sciences. Dr. Macdonald has published nearly 800 papers in scientific journals, books, and conference proceedings, plus four books, one of which ("Transient Techniques in Electrochemistry") established an important area of electrochemical research, and has 10 patents and numerous invention disclosures credited to his name. His professional competence lies in the fields of electrochemistry, corrosion science, battery science and technology, thermodynamics, chemical kinetics, high temperature aqueous chemistry, nuclear power technology, energy conversion technology, and physical chemistry. Finally, under his tutelage, more than 140 students have graduated with advanced degrees in Chemistry and Materials Science and Engineering over the past four decades.