

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: Gordon Conference on Aqueous Corrosion 2002
Project Number 20.01402.571; AI 01402.571.028

DATE/PLACE: July 14–19, 2002
New London, NH

AUTHORS: Gustavo A. Cragnolino and Narasi Sridhar

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AUTHORS: Gustavo A. Cragolino and Narasi Sridhar

PERSONS PRESENT: List of attendees attached

BACKGROUND AND PURPOSE OF TRIP:

Gordon Research Conferences on Aqueous Corrosion are held on alternate years to bring leading researchers in the field together to discuss recent advances in various aspects of corrosion. The conferences emphasize informal interactions, and in this spirit no formal proceedings or abstracts are issued. In addition to oral presentation by invited speakers, a number of poster presentations are given. The purpose of the trip was to participate in the discussions and obtain an understanding of the state of corrosion science in topics of relevance to high level waste repository performance. One of the authors, N. Sridhar, was invited to present the advances in the understanding of localized corrosion.

SUMMARY OF PERTINENT POINTS:

This year's conference included presentations on: (i) passive corrosion; (ii) initiation of localized corrosion; (iii) environmentally-assisted fracture; (iv) microbially-influenced corrosion; (v) advanced test methods based on the use of the Synchrotron radiation sources; (vi) effects of magnetic fields on corrosion; and (vii) use of magnetometry to detect corrosion.

The opening session focused on surface studies related to passive dissolution and early stages of localized corrosion by Philippe Marcus, University Pierre and Marie Curie, Paris, France. Marcus discussed growth mechanisms and structure of passive films on the basis of experimental work conducted on single crystals of pure metals, such as copper, nickel and chromium, and alloys, such as ferritic and austenitic stainless steel, using scanning tunneling microscope (STM) and X-ray photoelectron spectroscopy (XPS). He showed results indicating that adsorbed OH phases are precursors of the stable passive films which become more crystalline when aged.

The presentation of factors leading to stabilization of crevice corrosion, which is of engineering importance, by one of the authors (N. Sridhar) was well received. The talk was focused on predicting the occurrence of localized corrosion in multicomponent electrolytes that occur in the high-level waste repository near-field environment as well as in chemical process industries. Experimental results of repassivation potential in mixtures of chloride, bromide, nitrate, and acetate were presented. A competitive reaction model of repassivation was described and the agreement between model and experiments was demonstrated. The comments on the

experimental techniques we have used in studying crevice corrosion were valuable for further examination of the basis of our modeling efforts. A significant negative comment on the use of repassivation potential was related to the effect of prior pit growth on the repassivation potential.

Larry Thomas (Pacific Northwest National Laboratory) presented the results of a detailed study of stress corrosion crack tip microstructure on Alloy 600 and Type 304L SS. Both microchemistry using scanning electron microscopy and microstructure using Field Emission electron microscopy with a probe diameter of 0.5 nm were used in this study. Among the interesting observations were the presence of high nickel concentration near crack tips indicating selective dissolution and associated void formation. He presented evidences of lead accumulation at crack tips from failed Alloy 600 steam generator tubing of pressurized water reactors, as an indication of lead-induced stress corrosion cracking.

The presentation by Andrzej Anderko (OLI Systems, Inc.) on thermodynamic and kinetic modeling of corrosion processes drew many interested comments and interest in the use of their software.

The effect of past pitting events on the probability of future pitting was analyzed by John Scully (University of Virginia) using cluster analysis techniques. Three time frames were discussed in terms of the "memory" of a surface for a past pitting event. The short-term memory effect occurred because of ohmic potential drops and high chloride concentrations from growing pits, but these dissipated once pit growth stopped. However, the dissolution of manganese sulfide inclusions presented a relatively long-term memory, whereby the probability of pits increased at locations where past pitting events occurred.

The poster presentation by Claes Olsson of the Ecole Polytechnique Federale de Lausanne, Switzerland, was of interest. This group, headed by Dieter Landolt, uses an Electrochemical Quartz Crystal Microbalance to study passive film growth and compare the predictions of various literature models. This technique, in combination with XPS or electron microscopy techniques can shed important light on the long-term stability of passive film. Long-term stability of passive film is an important factor in the predicted long life of containers.

Investigators from the DOE's Yucca Mountain Project presented recent information on stress corrosion cracking of Alloy 22, studies on passive film of Alloy 22, methods for evaluating microbially-influenced corrosion, and potentiostatic test results. The stress corrosion cracking susceptibility of Alloy 22 in simulated concentrated water was evaluated using the slow strain rate technique. An important effect of temperature and applied potential was observed because cracking occurred at 0.4 V vs the Ag/AgCl/KCl_{sat} at 73 to 95 °C but not at room temperature. Also, the time to failure, used as a measure of stress corrosion cracking susceptibility, increase with decreasing potential and no cracking was observed at about 0.1 V. The studies on the passive film formed on Alloy 22 were focused mostly in the transitional potential range between passivity and transpassive behavior and a significant depletion of Mo in the passive film was detected associated with morphological changes in the oxide.

S. Dexter (University of Delaware) discussed the ennoblement in the corrosion potential of many alloys observed in natural sea water. He questioned interpretative concepts based in the microbial-enhanced kinetics for the cathodic reduction of oxygen and suggested that manganese oxidizing bacteria able to participate in the oxidation of Mn²⁺ to MnO₂ are involved. He presented experimental results of abiotic simulations using MnO₂ as a coating and

measurements using a Au-Hg microelectrode with a 25 μm tip to perform cyclic voltammetry to follow electrochemically the course of the postulated redox reactions.

M. Edwards (Virginia Polytechnic Institute and State University) made a very interesting presentation on corrosion problems in drinking water distribution systems. His presentation was mostly confined to pitting of copper. He discussed the role of humic acids as natural inhibitors and the effect of sulfides formed by the action of sulfate reducing bacteria in the initiation of pitting corrosion.

IMPRESSION/CONCLUSIONS:

The meeting was mostly attended by members of the academia and research laboratories. Representation from the industry was smaller than in the past. However, the discussions during and after the presentations were lively. These discussions provided ideas for future investigations related to container life that will enable NRC and CNWRA to improve the confidence in the models. Discussions with researchers representing DOE and the State of Nevada outside the presentations provided insights into their approach.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

None.

RECOMMENDATIONS:

The quartz crystalline microbalance technique used by Olsson et al. can provide important insights into the stability of passive films of chromium containing alloys. It is recommended that the use of this technique be investigated further to improve our confidence in passive dissolution models.

REFERENCES:

An agenda of the meeting and the list of attendees are attached.

SIGNATURES:



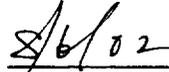
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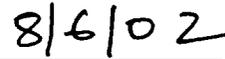


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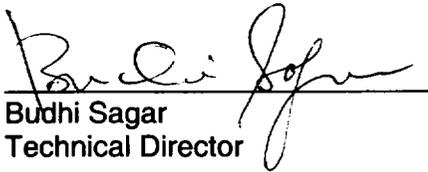
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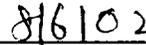
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Attachment

GC:jg

PROGRAM FOR THE 2002 GORDON RESEARCH CONFERENCE
ON AQUEOUS CORROSION
JULY 14-19, 2002
COLBY SAWYER COLLEGE, NEW LONDON, NEW HAMPSHIRE, USA

SUNDAY, JULY 14, 2002

7:30 - 9:30 PM, Session 1: OPENING SESSION

Discussion Leader: Patrick Moran, U.S. Naval Academy, Annapolis, Maryland, USA

Philippe Marcus, CNRS, Univ. P. M. Curie, Paris, France
Surface Structures, Passivity and Initiation of Localized Corrosion

30 One-minute Presentations by Poster Authors

9:30 - 11:30 PM, RECEPTION

MONDAY, JULY 15, 2002

9:00 AM - Noon, Session 2: RECENT PROGRESS IN LOCALIZED CORROSION

Discussion Leader: Barbara Shaw, Pennsylvania State Univ., State College, Pennsylvania, USA

Narasi Sridhar, Southwest Research Institute, San Antonio, Texas, USA
Initiation and Repassivation of Stable Pitting and Crevice Corrosion

Coffee Break and Picture Session

Michael Rohwerder, Max Planck Institut fuer Eisenforschung, Duesseldorf, Germany
High Resolution Studies of Delamination with SKPFM

4:00 - 6:00, POSTER SESSION ONE, Refreshments provided

7:30 - 9:30 PM, Session 3: ENVIRONMENTALLY ASSISTED FRACTURE

Discussion Leader: R. Staehle, Staehle Consulting, North Oaks, Minnesota, USA

Larry Thomas, Pacific Northwest National Laboratory, Richland, Washington, USA
High-Resolution Observations of Stress-Corrosion Crack Tips in Austenitic Stainless
Steels and Nickel-Base Alloys

~~En-Hou Han, Institute of Corrosion and Protection of Metals, Shenyang, P.R. China
Corrosion-Fatigue: Mechanisms and Lifetime Control~~

John Scully, University of Virginia, Charlottesville, Virginia, USA

TUESDAY, JULY 16, 2002

9:00 AM - Noon, Session 4: RECENT PROGRESS IN PROTECTIVE COATINGS

Discussion Leader: S. Ray Taylor, University of Virginia, Charlottesville, Virginia, USA

**Guido Grundmeier, Max Planck Institut fuer Eisenforschung, Duesseldorf, Germany
Plasma Polymerisation and Combustion CVD for the Deposition of Corrosion
Resistant Interfacial Thin Films for Polymer Coated Metals**

Coffee Break

**Rudy Buchheit, Ohio State University, Columbus, Ohio, USA
Developing and Evaluating Self-Healing and Corrosion-Sensing Functions in
Cr-Free Coating Systems**

30 One-minute presentations by Poster Authors

4:00 - 6:00, POSTER SESSION TWO, Refreshments provided

7:30 - 9:30 PM Session 5: PREDICTING CORROSION BEHAVIOR

Discussion Leader: Mike Graham, National Research Council, CANADA

**Andrzej Anderko, OLI Systems Inc., Morris Plains, New Jersey, USA
Simulation of Aqueous Corrosion Using Thermodynamic and Electrochemical Models**

**Robert Kelly, University of Virginia, Charlottesville, Virginia, USA
Linking Corrosion Phenomena Prediction to Corrosion Science & Engineering Fundamentals**

WEDNESDAY, JULY 17, 2002

9:00 AM - Noon, Session 6: SYNCHROTRON METHODS

Discussion Leader: H. Isaacs, Brookhaven National Laboratory, Upton, New York, USA

**Ian Robinson, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA
Interfacial Diffraction Methods for Investigating Chemical Reactions during Corrosion**

Coffee Break

**Paul Natishan, Naval Research Laboratory, Washington, DC, USA
Insights on the Role of Chloride in Oxide Film Breakdown**

WEDNESDAY, JULY 17, 2002 (CONTINUED)

7:30 PM - 9:30 PM Session 7: MICROORGANISMS AND CORROSION

Discussion Leader: Doug Hansen, Princeton Applied Research, Knoxville, Tennessee, USA

**Stephen Dexter, University of Delaware, Lewes, Delaware, USA
Oxygen vs. Bugs - Who Controls the Rate of Marine Corrosion?**

**Florian Mansfeld, University of Southern California, Los Angeles, California, USA
Microorganisms that Inhibit Corrosion**

THURSDAY, JULY 18, 2002

9:00 AM - Noon, Session 8: PASSIVITY AND LOCALIZED CORROSION

Discussion Leader: Shinji Fujimoto, Osaka University, Osaka, Japan

**Sanna Virtanen, Swiss Federal Institute of Technology (ETH), Zurich, Switzerland
Formation, Modification and Stability of Oxide Films on Ti and Ti alloys**

Coffee Break

**Marc Edwards, Virginia Polytechnic Inst. and State University, Blacksburg, Virginia, USA
Mechanisms of Pit Initiation and Propagation in Drinking Water**

7:30 PM - 9:30 PM, Session 9: CORROSION AND MAGNETIC FIELDS

Discussion Leader: John Scully, University of Virginia, Charlottesville, Virginia, USA

**Alison Davenport, University of Birmingham, Birmingham, UK
Corrosion in Magnetic Fields**

**John Wikswo, Vanderbilt University, Nashville, Tennessee, USA
Imaging Hidden Corrosion with Squid Magnetometry**

Conference Registration List

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