CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: CORROSION/2007 Annual Conference and Exposition
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DATE/PLACE: March 11–15, 2007, Nashville, Tennessee

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PERSONS PRESENT: X. He and G. Cragnolino, Center for Nuclear Waste Regulatory Analyses (CNWRA); K. Chiang and L. Yang, Geosciences and Engineering Division, and D. Dunn, Mechanical and Materials Engineering Division, Southwest Research Institute®; and about 5,000 attendees and 350 exhibitors from various countries and organizations.

BACKGROUND AND PURPOSE OF MEETING/TRIP:

The CORROSION/2007 Annual Conference and Exposition featured technical symposia, technical committee meetings, and an exhibitor show. The main goals of attending the conference were to

- Present papers authored by staff working on the CNWRA high-level waste program
- Attend presentations related to the high-level radioactive waste program
- Gain information on materials and test methods from exhibitors

In addition to presentations in the technical symposia, the CNWRA staff participated in symposia organization, technical committee meetings, and student poster session judging.

SUMMARY OF PERTINENT POINTS:

The following papers coauthored by the CNWRA staff were presented at the CORROSION/2007 conference:

(i) U.S. Nuclear Regulatory Commission (NRC)-funded papers

Crevice Corrosion Propagation Behavior of Alloy 22 in Extreme Environments authored by X. He and D.S. Dunn. Presented by X. He in the Corrosion in Nuclear Systems Symposium.

Corrosion Behavior of Alloy 22 in Concentrated Nitrate and Chloride Salt Environments at Elevated Temperatures authored by L. Yang, D. Dunn, G.A. Cragnolino, X. He, Y.-M. Pan, A. Csontos, and T. Ahn. Presented by G. Cragnolino in the same symposium.

(ii) Southwest Research Institute® Internal Research and Development-funded papers

Development of Crevice-Free Electrodes for Multielectrode Array Sensors for Applications at High Temperatures authored by K.T. Chiang and L. Yang. Presented by L. Yang in the Innovative Corrosion Sensor Technology Symposium.

A Nanostructured, Field Effect Transistor-Based Sensor authored by K.T. Chiang and B. Lanning. Presented by K.T. Chiang in the same symposium.

All papers were well received, prompted questions, and generated subsequent discussion.

Corrosion in Nuclear Systems

Eleven papers were presented in the Corrosion in Nuclear Systems Symposium: two from the CNWRA staff on pitting and crevice corrosion in the high level nuclear waste storage session; five papers on corrosion in the storage tanks, piping, and supporting components in the nuclear systems session; two papers on the special topics in corrosion in the nuclear systems session; and six papers on the stress corrosion cracking in the nuclear systems session.

Papers focused on the potential geologic repository at Yucca Mountain included one authored by P. Andresen (GE Global Research Center) and G. Gordon (Areva NP, Inc.); four from previous work conducted at Lawrence Livermore National Laboratory authored by R. Rebak, et al. and G. Ilevbare (currently at the Electric Power Research Institute); and four from several universities presenting research supported by the Science & Technology Program of the Office of the Chief Scientist, Office of Civilian Radioactive Waste Management, U.S. Department of Energy (DOE). The papers are discussed in the following section.

P. Andresen presented stress corrosion cracking of titanium alloys in compact tension, U-bend, and constant load specimens. DOE conducted this work after the structural support material of the drip shield changed from Titanium Grade 24 (Ti-6Al-4V-0.05Pd) to Titanium Grade 29 (Ti-6Al-4V-ELI-0.10Ru). The paper indicated that in the drip shield design, DOE may use Titanium Grade 28 (Ti-3Al-2.5V-ELI-0.10Ru) as the filler metal to weld Titanium Grade 7 to Titanium Grade 29 to make a transition from alpha-phase Titanium (Grade 7) to alpha plus beta phase titanium (Grade 29). The stress corrosion crack initiation and growth rate response was evaluated on Titanium Grades 7, 28, and 29 at 105–165 °C [221–329°F] in several aerated, concentrated groundwater environments. Time-to-failure experiments on actively loaded tensile specimens at 105 °C [221 °F] were used to evaluate the resistance to stress corrosion cracking and included specimens of stainless steel and Alloy 22. Long-term U-bend experiments at 165 °C [329 °F] were also performed. Long-term crack growth rate data showed stable crack growth under constant-K (no cycling) conditions in the titanium alloys. Creep tests in air at temperatures less than 200 °C [392 °F] suggest that the creep is the dominant mechanism of cracking. According to the authors, further work on mechanical tests and stress corrosion cracking of dissimilar titanium welds are also planned. In addition to the work on stress corrosion cracking, the general and localized corrosion in these and related environments are being studied in other programs at GE Global Research Center. Once all the information is available from DOE, CNWRA staff will review the data further to identify additional independent tests at CNWRA.

R. Rebak (Lawrence Livermore National Laboratory) presented one paper on long-term electrochemical behavior of creviced and noncreviced Alloy 22 in $CaCl_2$ plus $Ca(NO_3)_2$ brines and one paper on crevice corrosion repassivation potential of Alloy 22 in simulated concentrated groundwaters. Tests conducted in 18 m $CaCl_2$ + 9 m $Ca(NO_3)_2$ and

18 m $CaCl_2$ + 0.9 m $Ca(NO_3)_2$ brines at 155 °C [311 °F] with the as-welded and as-welded plus solution heat-treated specimens confirmed the localized corrosion initiation criteria (i.e., $E_{corr} > E_{crit}$), the inhibitive effect of nitrate for localized corrosion in highly concentrated brines and at high temperature, and the validity of repassivation potentials measured using cyclic potentiodynamic polarization in short-term tests as a representative measure of the repassivation potential values of Alloy 22 for 20-month immersion. The tests also showed that the presence of the black annealed film on the specimens seemed to offer additional protection from pitting corrosion under the tested conditions possibly because the oxide is rich in chromium and especially in molybdenum and tungsten. In the latter paper, tests on crevice corrosion susceptibility of Alloy 22 with different metallurgical conditions (mill-annealed, as-welded, and as-welded plus high-temperature aged) demonstrated that simulated concentrated groundwaters will not initiate crevice corrosion in Alloy 22 because (i) these electrolytes are rich in nitrate and (ii) the corrosion potential is always below a critical potential for crevice corrosion initiation. In addition, no effect of metallurgical conditions was observed.

G. Ilevbare presented one paper on the electrochemical behavior of Alloy 22 in extreme chloride and nitrate environments and another on the effect of temperature on the breakdown and repassivation potentials of welded Alloy 22 in 5 M $CaCl_2$. Results indicated that in these extreme environments, localized corrosion occurred by pitting even though specimens were tested using artificial crevice formers, and the susceptibility to corrosion increased with an increase in electrolyte temperature in both the wrought (in the mill-annealed condition) and the welded forms of the alloy. The weld metal was found to be less susceptible to localized corrosion under the conditions tested.

J. Payer (Case Western Reserve University) presented a paper comparing the effect of ceramic and polymer crevice formers on the crevice corrosion behavior of Alloy 22. Comparative tests showed that the polytetrafluoroethylene tape-covered ceramic was the most active crevice former on Alloy 22, solid polymer crevice formers that are polytetrafluoroethylene or polychlorotrifluoroethylene were less active, and ceramic crevice formers caused no crevice corrosion. Payer explained that the difference in crevice corrosion severity is a result of the different tightness of the crevice gap formed by different crevice formers with different mechanical properties. The ceramic crevice former has a relatively rough surface finish. However, when the ceramic crevice former is covered with polytetrafluoroethylene tape, the compressed tape can fill cavities both on the ceramic crevice former and the metal surface. This can greatly reduce the crevice opening and result in easier formation of crevice corrosion.

T. Devine (University of California-Berkeley) presented *in-situ* investigation of the passivation of Alloy 22 and of the passive films formed on Alloy 22 in 1 M NaCl + 0.1 M H_2SO_4 acidic electrolytes at room temperature and at 90 °C [194 °F] using a combination of cyclic polarization, electrochemical impedance spectroscopy, and Mott-Schottky analyses. The results indicate that the passive films formed on Alloy 22 exhibit semiconductorlike behavior. In particular, the passive films have n-type behavior and form an inversion layer at their free surface at potentials above approximately 0.45 $V_{Ag/AgCl}$. Measurements of capacitance suggest the passive films at room temperature and 90 °C [194 °F] of both Alloy 22 and chromium are very thin {approximately $\leq$ 1 nm [4 × 10^{-5} mil]}, even at potentials as high as 0.8 V_{SCE}. During the question and answer period, Cragnolino suggested that work should be conducted in more representative electrolytes such as chloride plus bicarbonate containing solutions, which are known to cause stress corrosion cracking of Alloy 22.

F. Bocher (University of Virginia) presented a paper on his investigation of crevice corrosion of AISI 316 Stainless Steel and Ni-Cr-Mo Alloy 625 using coupled multielectrode arrays. Because of the high corrosion resistance of Alloy 22, stainless steel and Alloy 625 were used instead to understand the spatial distribution of the crevice corrosion process.

D. Macdonald (The Pennsylvania State University) presented a paper on oxyanion inhibition of passivity breakdown and the nucleation of pits on Type 316L SS. Passivity breakdown of Type 316L SS (UNS S31603) in the presence of aggressive and inhibitive anions has been experimentally studied, and the results have been interpreted in terms of the Point Defect Model. Good agreement between the value obtained from experiments and those calculated from mechanistically derived parameters demonstrate, according to Macdonald, the validity of the model.

G. Cragnolino (CNWRA) presented the paper on corrosion behavior of Alloy 22 in concentrated nitrate and chloride salt environments at elevated temperatures. The corrosion rates and electrochemical behavior of Alloy 22 specimens in a system containing concentrated $NaCl$-$NaNO_3$-KNO_3 salt mixture in the temperature range between 150 and 180 °C [302 and 356 °F] at ambient pressure were studied. In this study, no significant localized corrosion was observed, and general corrosion was the main mode of attack. The corrosion rates of the Alloy 22 specimens were significantly higher in the liquid phase than in the vapor phase. It was also noted that large quantities of salt were used, and only small amount of salts mixed with insoluble dusts are expected under the repository condition.

X. He (CNWRA) presented the paper on crevice corrosion propagation behavior of Alloy 22 coupled to platinum or Titanium Grade 7 in 4 M $MgCl_2$ solution and in 5 M NaCl solution at 95 °C [203 °F] and 110 °C [230 °F]. Crevice corrosion propagation behavior strongly depends on the coupling material and the solution. Under very aggressive conditions, crevice corrosion initiated under open circuit conditions, and stifling or repassivation may not occur. However, it was observed that the penetration depth is limited, and the deepest penetration was confined to a small area. In addition, the possibility to develop such aggressive conditions is very small. The consequence due to crevice corrosion under these environmental conditions may be low.

In the stress corrosion cracking in nuclear systems session, S. Brossia (CC Technologies) presented the paper on inhibition of stress corrosion cracking of carbon steel storage tanks at Hanford. Stress corrosion cracking behavior of A537 tank steel was investigated in a series of environments designed to simulate the chemistry of legacy nuclear weapons production waste. Tests consisted of both slow strain rate tests using tensile specimens and constant load tests using compact tension specimens. Based on the tests conducted, nitrite was found to be a strong stress corrosion cracking inhibitor. Based on the test performed and the tank waste chemistry changes that are predicted to occur over time, the risk for stress corrosion cracking appears to be decreasing because the concentration of nitrate will decrease and nitrite will increase.

Research in Progress Symposium on Technical Basis for Long-Term Storage

J. Payer (Case Western Reserve University), as an invited speaker, presented an overview of the current corrosion research work being conducted at several universities as part of the Science & Technology Program of the Office of the Chief Scientist, Office of Civilian Radioactive Waste Management, DOE. He discussed the possibility of localized corrosion of Alloy 22 as a potential failure mechanism for the waste package covering the initiation, propagation, stifling, and arrest of crevice corrosion and emphasizing the electrochemical factors that may lead to arrest of crevice corrosion. Above all, he pointed out the need to evaluate Alloy 22 in the possible environment formed on the waste package through deliquescence of dust/particulates and the evolving seepage water due to evaporation, rather than fully immersed conditions. Assuming the persistence of the passive film, he concluded that the general corrosion rates of about 0.1 μm/yr [4×10^{-3} mil/yr] should be expected, but no new approaches or mechanistic concepts regarding this assumption were advanced to confirm its validity over the long term.

R. Kelly (University of Virginia) presented experimental data on the repassivation of crevice corrosion of Alloy 22 in 4 M NaCl solutions at 100 °C [212 °F] to support the discussion of the issues related to anode/cathode coupling, cathodic and anodic limitations, and electrolyte conductivity on sustained crevice corrosion propagation.

P. Keech (University of Western Ontario) presented a paper on the corrosion of nuclear fuel (UO_2) inside a failed nuclear waste container. UO_{2+x} of different stoichiometry ($0.002 < x < 0.1$) and simulated high burnup fuel (SIMFUEL) fabricated to simulate the chemical effects of different degrees of spent fuel burnup (1.5 to 6 percent) were used in this study. Scanning electron microscopy (SEM) and scanning electrochemical microscopy (SECM) were used to analyze topographic features and their anodic reactivity, respectively, as a function of UO_{2+x} stoichiometry. The distribution of the intermetallic ϵ-particles (stabilized metallic particles in the fuel lattice formed by the noble and other metal dopants such as Pd, Ru, Mo, and Rh) in SIMFUEL were studied by SEM and their composition analyzed by Secondary Ion Mass Spectrometry (SIMS). SECM measurements allowed the identification of the ϵ-particles as catalytic sites for the reduction of H_2O and O_2. It was found that the rate of the O_2 reduction reaction was proportional to the number and size of the ϵ-particles, and therefore, these particles can act as cathodes to accelerate spent fuel corrosion. However, the presence of H_2 can act as anodes for H_2 oxidation due to their electronic conductivity, therefore limiting fuel corrosion.

Research in Progress Symposium on Passivity and Localized Corrosion

This session had 13 presentations. Most of the presentations were focused on the correlation of localized corrosion resistance and passivity of materials.

P. Schmuki (University of Erlangen-Nuremberg, Germany), as an invited speaker, presented a paper of titanium and its alloys: from passivity breakdown to formation of oxide-nanotube layers. Titanium and its alloys are known to have high resistance to localized corrosion such as pitting corrosion due to their high passivity breakdown potential. However, by simple anodization of titanium alloys to high potential in fluoride-containing solutions, pitting processes can turn into highly organized titanium oxide nanotubes with a length of several micrometers. This simple approach to produce such highly defined nanoscopic form of titanium oxide nanotubes bears a high potential for technological exploitation.

M. Jakab (Southwest Research Institute®) made a presentation on the effect of torque and charge density on the crevice repassivation potentials of Ni-Cr-Mo-W alloys measured by modified "Tsujikawa-Hisamatsu Electrochemical" method. This work was performed under the round-robin testing for a proposed American Society for Testing and Materials standard test method for the measurement of crevice repassivation potentials of corrosion-resistant alloys. In this study, it was reported that the crevice corrosion repassivation potential of Alloy 22 decreased significantly with increasing torque ranging from 5–30 in·lb [0.6–3.4 N·m]. At torque greater than 30 in·lb [3.4 N·m], a lower-bound value of repassivation potentials was attained. In the case of Alloy 825, however, the applied torque has no statistically significant effect on the crevice corrosion repassivation potential. This finding does not affect the validity of the Alloy 22 crevice corrosion repassivation potentials measured at CNWRA. In the CNWRA measurements, polytetrafluoroethylene was used as a crevice former, which has been shown to be a more aggressive crevice former than that used by Jakab. In addition, previous work performed at CNWRA demonstrated that by using polytetrafluoroethylene as a crevice former, the measured repassivation potentials were not sensitive to the applied torque.

Research Topical Symposium on Advances in Environmentally Assisted Cracking

The objective of the Research Topical Symposium was to strengthen communications between corrosion science and engineering communities. This year's topic was advances in environmentally assisted cracking.

P. Andresen's (GE Global) presentation on emerging issues and fundamental processes in environmental cracking in hot water, although extremely comprehensive, did not provide any new concepts or ideas regarding mechanisms or models for stress corrosion cracking.

R. Staehle (University of Minnesota) made a very interesting presentation discussing the aspect ratio of the tight stress corrosion cracks observed in Alloy 600 steam generator tubing. The extreme acuity at the crack tip (a few nanometers wide) put in question some current mechanistic interpretations and models, such as the slip-step emergence/film rupture/repassivation model of Ford and Andresen that DOE adopted in the stress corrosion cracking model abstraction. Staehle made interesting and challenging calculations in relation to interatomic distances, molecular dimensions, etc., saying that three orders-of-magnitude difference exists between the domain of fracture mechanics (few micrometers for the crack opening displacement) and the atomic domain necessary to elucidate the crack advance process, suggesting the vacancies can play a critical role in the crack path and it is important to understand how vacancies can be generated.

Environmentally Assisted Cracking

R. Newman (University of Toronto) presented an interesting paper related to his stress corrosion cracking model in which a dealloyed layer can act as a material prone to cleavage, leading to fast fracture of the adjacent ductile matrix according to a discontinuous mechanism of crack advance. He discussed his ideas in terms of Fe-Ni-Cr compositional diagrams establishing limits for the occurrence of cracking versus passivation and parting limits for dealloying. This model is not in conflict with the ideas put forward by Staehle, but there are questions regarding its validity for different alloying systems, especially for high nickel alloys.

Innovative Corrosion Sensor Technology

K. Chiang presented a paper on a nanostructured, field effect transistor-based sensor. It was demonstrated that the knowledge gained is relevant to the NRC performance confirmation activities, especially in relation to online and real-time corrosion measurements, even during the thermal pulse period.

Student Poster Session

The Student Poster Session, sponsored by the NACE Research Committee, is the recognized technical conference forum for the youngest members of the corrosion field. This year there were 65 posters in the category of corrosion science, corrosion engineering, and applied corrosion technology from universities in various countries. Posters that focused on the potential geologic repository at Yucca Mountain are discussed in the following section.

P. Pharkya (Case Western Reserve University) presented a poster on repassivation behavior of crystalline Alloy 22 and Fe-based amorphous alloy (SAM 1651) in hot chloride solutions. This work was part of a multi-investigator study to determine the durability of passive films and localized corrosion processes in metal exposed to moist particulate and deposits. The objective of this study was to compare the repassivation behavior of Alloy 22 and SAM 1651 when the passive film is mechanically damaged. Repassivation behavior and kinetic of growth of the passive film were investigated by measuring current-time transients using a scratch technique at constant potentials. It was demonstrated that both Alloy 22 and SAM 1651 have strong repassivation ability.

B. Maier (Ohio State University) presented a poster on electrochemical measurements under thin electrolyte layers using a Kelvin probe. Kelvin probes are commonly used to measure volta potential distributions across surfaces exposed to atmospheric conditions or under polymeric coating. In this work, a new Kelvin probe design was utilized for electrochemical experiments under thin electrolyte layers. It was shown that the limiting current density for the oxygen reduction reaction on stainless steel varied with the electrolyte thickness. Lower layer thickness resulted in a higher limiting current density.

A. Mishra (Ohio State University) presented a poster on the effects of inhibitive anions on crevice corrosion resistance of Alloy 22 in chloride environments, which further demonstrated the inhibitive effect of nitrate on crevice corrosion of Alloy 22.

SUMMARY OF ACTIVITIES:

Technical Committee Activities

L. Yang chaired the TEG 316X committee meeting and a workshop on coupled multielectrode array sensors for corrosion monitoring and electrochemical studies. X. He and G. Cragnolino participated in the meeting of the NACE Research Committee where the subjects for the CORROSION/2008 Research in Progress Symposium and Topical Research Symposium were discussed and the chairs were appointed. X. He and G. Cragnolino also attended the Nuclear Systems Corrosion Technical Committee meeting. During the meeting, E. Shaber (Idaho National Laboratory) made a presentation on materials for our nuclear energy future. It is predicted that the materials demand for nuclear expansion will increase by 30 percent by 2030. G. Cragnolino attended the Environmentally Assisted Cracking Technical Committee meeting; the main subjects were the organization of next year’s symposia and the next International Conference on Environmentally Assisted Cracking.

IMPRESSIONS/CONCLUSIONS:

The conference provided an opportunity to follow the activities related to the potential geologic repository at Yucca Mountain. In addition, many symposia had papers that were relevant to the performance of engineered materials that are used in reactors and radioactive waste management, as well as those that may be used in the potential Yucca Mountain geologic repository. Relevant discussions on fundamental aspects of passivity, localized corrosion, and stress corrosion cracking were useful to assess advances in the application of new techniques and in mechanistic understanding of these corrosion processes.

PROBLEMS ENCOUNTERED:

The Research in Progress Symposium on Technical Basis for Long-Term Storage was scheduled at the same time as the Symposium on Corrosion in Nuclear Systems. This affected the attendance and the level of discussion at both symposiums.

PENDING ACTIONS:

None.

RECOMMENDATIONS:

Attendance and participation in selected committee meetings at the annual CORROSION conference are highly recommended.

REFERENCES:

None.