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14. ABSTRACT
We have completed our work on modeling pit initiation and repassivation following mechanical pit initiation in a chemically aggressive solution. We created a new model combining all of the chemical processes that influence pit evolution including dioxygen reduction, field-assisted aluminum oxide film growth and chemical dissolution of the oxide film. All of these elements have never before been included in such a model. The model successfully fits pit repassivation under a range of conditions. A manuscript is submitted on this effort. We also used molecular dynamics simulations to explore the influence of strain on the coalescence of pits. We believe this mechanism may be the origin of the transition from metastable pits to stress corrosion cracking. The simulation has successfully shown pit coalescence as a function of strain under tension. A manuscript on this has been submitted.

15. SUBJECT TERMS
corrosion, electrochemistry, aluminum alloy

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AFOSR Final Technical Report

Objectives

We conducted a study of the combined influence of mechanical and chemical stress on pit initiation for Al and high strength Al alloys of relevance to the USAF air fleet. The study wais motivated by two facts: 1) pitting corrosion is the most frequent cause of failure of high-strength Al alloys such as AA2024, a high strength, Cu-rich alloy used in the construction of older military and commercial aircraft, and 2) while some studies of pit initiation exist, no previous studies of pit initiation have considered well-defined samples under the "real world" conditions of combined mechanical and chemical stress. Mechanical stress is especially important in DoD aircraft applications; consider the flexing of a wing structure during take-off.

The impact of the work was significant in providing an understanding of how the combination of mechanical stress and chemical insult affect pit initiation in Al and its alloys under conditions of use. The long term goal was to provide information that will a) enhance DoD's ability to rationally schedule maintenance on its air fleet, b) provide a basis for design of environmentally compliant corrosion protection coatings, and c) move the science of corrosion forward into a new area.

The research also impacted the Nation's supply of qualified scientists and engineers by exposing at least three young people to a highly interdisciplinary research program geared toward solving a technologically important problem.

Status of effort

The research involved carefully intertwined experimental and theoretical components. The experimental component involved the preparation of Al and Al alloy samples with both native and synthetic defects. We exposed these samples to combined mechanical and chemical stress and monitor the formation of metastable pits, their evolution, and, especially, whether or not they transition to stable pits. Mechanical and (electro)chemical stress were applied using a unique in situ fluidic cell that allowed simultaneous application of mechanical stress, exposure to various solutions and imposition of an applied potential. Metastable pits were monitored using both in situ electrochemical and fluorescence measurements. Theory and simulations were used to predict and understand the mechanical behavior at the surface of the samples, with an emphasis on how stress induces breakdown in the protective surface oxide, thereby driving metastable pit formation.

Accomplishments/New Findings

We observed electrochemical transients that are signatures of metastable pit formation. We also developed a comprehensive mathematical model that encompasses major features of metastable pit repassivation, specifically including oxide film growth and dissolution. We also developed a molecular dynamics simulation for pit evolution to produce stress corrosion cracking. These simulations revealed the mechanism by which pit coalescence leads to stress corrosion cracks.

Personnel Supported

Graduate students supported: Dr. Eric Dufek (now on staff at DOE Idaho National Lab), Tom Dziedzic (MS in 2009), Dr. Poonam Singh (PhD 2010)
Postdoctoral fellow supported: Dr. Changwen Mi, now an academic professor in Department of Engineering Mechanics at the Southeast University in Nanjing, China.

Publications

1. "Inhibition of O2 reduction on AA2024-T3 using a Zr(IV)-Octadecyl phosphonate coating system"; Dufek EJ, Buttry DA; "Electrochemical and Solid State Letters, 2008, 11, C9-C12.
2. "Characterization of Zr(IV)-Phosphonate Thin Films Which Inhibit O-2 Reduction on AA2024-T3", Dufek EJ, Buttry DA; Journal Of The Electrochemical Society, 2009, 156(9), C322-C330.
3. "Repassivation Behavior of Stressed Aluminum Electrodes in Aqueous Chloride Solutions, Changwen Mi, Nishant Lakhera, Demitris Kouris, Daniel A. Buttry, submitted.
4. "Atomistic simulations of void cavitation by dislocation nucleation and propagation" Changwen Mia, Daniel A. Buttry, Demitris A. Kouris, submitted.

Interactions/Transitions

1. *Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories*. We worked with a small company in Charlottesville, Virginia called Luna Innovations, Inc. They had Phase 1 and Phase 2 SBIR funding for new corrosion protection pre-treatments based on chemical etching to remove IP's from AA2024 surfaces. This is a subject of a past AFOSR grant to our group. That technology was tested at the Coatings lab at Wright Patterson.
2. *Transitions*. Pending

New discoveries, inventions, or patent disclosures. None

Honors/Awards:

a) No recent honors during contract period
b) Previous honors: Japan Society for the Promotion of Science Senior Research Fellowship, Visiting Professor at Caltech and University of Colorado, Editorial Advisory board for *Langmuir*, member of Board of Directors for Society of Electroanalytical Chemistry, Member at Large for Physical Electrochemistry Division of the Electrochemical Society.