Understanding the Mechanism of Ennoblement of stainless steel: A multidisciplinary approach.

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Ennoblement is a phenomenon exhibited by stainless steel (SS) exposed to natural waters. It is characterized by an approximately 400 mV increase in corrosion potential. This increase in corrosion potential can aggravate pitting corrosion. Biofilms growing on SS surfaces are hypothesized to cause this phenomenon.

We expose SS to natural waters. After Ennoblement of the samples occurred, microbial deposits and inorganic surface chemistry were studied using XPS and other surface analytical tools.

The major accomplishments of this project were (1) to demonstrate that stainless steel Ennoblement in natural fresh water arises from manganic oxide mineralization, (2) to induce Ennoblement under laboratory conditions using pure cultures of the manganese-oxidizing genus *Leptothrix discophora*, and (3) to determine that microbially deposited MnO₂ can be electrochemically reduced to Mn²⁺ while Fe³⁺ is oxidized; manganese oxyhydroxide, MnOOH, is an intermediate product.

These findings open the door to assessing and controlling the corrosive impact of Ennoblement by providing a rational explanation for the phenomenon and by allowing the process to be manipulated under controlled conditions. It is the first step in developing new corrosion resistance strategies for stainless steel and other passive metals and alloys.

Ennoblement, corrosion, stainless steel, manganic, oxidizing bacteria, biofilm, eletrochemistry, *Leptothrix discophora*
Title of GRANT or CONTRACT
Understanding the Mechanism of Ennoblement of Stainless Steels: A Multidisciplinary Approach

Name(s) of Principal Investigators:
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Date Submitted
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PART I

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 96PR0-2849
Contract/Grant Number: N00014-95-1-0900
Contract/Grant Title: Understanding the Mechanism of Ennoblement of Stainless Steels: A
Multidisciplinary Approach
Principal Investigator: Dr. Zbigniew Lewandowski

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a. Number of papers submitted to refereed journals, but not published (YET): __2__

B.H. Olesen, R.Avci, Z. Lewandowski Manganese Dioxide as a potential Cathodic reactant in
Corrosion of Stainless Steels. Submitted to Corrosion Science

W.H.Dickinson, Z.Lewandowski Electrochemical Concepts and techniques in the study of
Stainless Steel Ennoblement. Accepted to "Biodeterioration" Will be published in Volume 9, Issue 1.

b. + Number of papers published in refereed journals (for each, provide a complete citation): __5__

Steel by the Manganese-Depositing Bacterium Leptothrix discophora. Applied and Environmental
Microbiology. 63, 2502-2506.

metal surfaces. Water Science and Technology. 36, 295-302

Ennoblement of Type 316L Stainless Steel: Dissolved Oxidant and Capacitance Measurements.
Corrosion. 52, 910-920.

Dickinson W.H., Lewandowski Z. (1996) Manganese Biofouling and the Corrosion Behavior of

Dickinson W.H., Caccavo F., Lewandowski Z. (1966). The Ennoblement of Stainless Steel by
Manganic Oxide Biofouling. Corrosion Science 38, 1407-1422.

c. + Number of books or chapters submitted, but not yet published: __0__

d. + Number of books or chapters published (for each, provide a complete citation): __1__

surfaces. Reviews in Mineralogy 35, 123-159.
e. **Number of printed technical reports/non-refereed papers (for each, provide a complete citation):** 5

f. **Number of patents filed:** 0

g. **Number of patents granted (for each, provide a complete citation):** 0

h. **Number of invited presentations (for each, provide a complete citation):** 3

i. **Number of submitted presentations (for each, provide a complete citation):** 6
j. **Honors/Awards/Prizes for contract/grant employees (list attached):**  
   (This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)

k. **Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:**  
   Graduate Students:  _1 FTE_ 
   Post-Doctoral Associates:  _0_ 
   including the number of, 
   Female Graduate Students:  _0_ 
   Female Post-Doctoral Associates:  _0_ 
   Minority* Graduate Students:  _0_ 
   Minority* Post-Doctoral Associates:  _0_ 
   Asian Graduate Students:  _0_ 
   Asian Post-Doctoral Associates:  _0_

l. **Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)**
   
   **Agency:** NSF  
   **Title:** Center for Biofilm Engineering, internal project ‘Biofilm Structure-Function’  
   **Fiscal 1997-1998 support (Pl Zbigniew Lewandowski):** $214,000  
   **Total Award:** $16,500,000  
   **Period of Performance:** 4/16/90 - 4/15/2001  
   **Relationship to ONR Grant:** Chemical, physical, and physiological heterogeneities within biofilms can influence the electrochemical processes occurring at the interface between a metal and its environment. This has well documented consequences for corrosion as exemplified by biologically produced oxygen concentration cells and iron sulfide deposits, and may influence the electrochemical phenomenon of Ennoblement. Research in the Biofilm Structure-Function project focuses on describing the heterogeneities within biofilms and has resulted in oxygen concentration maps, maps of the mass transfer coefficient, and physical models of advective transport within biofilms. An example of how this project can complement the ONR project: by mapping the location of aerobic/anaerobic boundaries, the concerted corrosive influence of aerobic bacteria involved in Ennoblement and anaerobic bacteria such as SRB can be investigated.

   **Agency:** DOE  
   **Title:** Acceptable Endpoints for metals and Radionuclides: Quantifying the Stability of Uranium and Lead Immobilized under Sulfate reducing Conditions.  
   **Fiscal 1998 - 1999 support:** $133,728  
   **Total Award:** $345,491  
   **Period of Performance** 11/1/98 - 10/31/2001  
   **Relationship to ONR Grant:** The creation of sulfate reducing conditions to immobilize metals will be tested to remove uranium and lead from dilute aqueous solutions. Relation to the ONR grant: use of microorganisms to control redox reactions involving metals

   **Agency:** SC Johnson Wax  
   **Title:** Chemical Methods of Improving Biocidal Activity of Hydrogen Peroxide and other Peroxides against Microorganisms in Biofilms  
   **Fiscal 1997 - 1998: support $51,000**  
   **Total Award:** $114,000
Period of Performance: 8/1/97 - 7/31/99
Relationship to ONR Grant:
The goal of the project is to identify means of increasing biocidal efficacy of hydrogen peroxide against biofilms. Relation to the ONR grant: none
PART II.

Principal Investigator: Dr. Zbigniew Lewandowski

Phone: (406) 994-5915

ONR Program Manager: Dr. Richard Carlin

Program Objective: To establish the mechanism(s) by which microorganisms alter the rate and/or nature of the electrochemical reactions underlying Ennoblement.

e. Significant results:
   As a result of the project we demonstrated:
   1) that the deposits accumulated on 316 L stainless steel exposed to natural waters contained 
      microbially generated manganese dioxide, MnO₂:
      \[ \text{Mn}^{2+} + \text{manganese oxidizing bacteria} \rightarrow \text{MnO}_2 \]
   2) that the microbially deposited manganese dioxide acted as a cathodic reactant, accepting electrons 
      from the underlying metal.
   3) that the microbially deposited manganese dioxide was ultimately reduced to divalent manganese, 
      and that manganese oxihydroxide, MnOOH, was the intermediate product of this reaction:
      \[ \begin{align*} 
      \text{MnO}_2 + \text{H}^+ + \text{e}^- & \rightarrow \text{MnOOH} \\
      \text{MnOOH} + 3\text{H}^+ + 3\text{e}^- & \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}. 
      \end{align*} \]
   4) that pure cultures of the manganese-oxidizing genus *Leptothrix discophora* induce Ennoblement 
      under laboratory conditions.
   5) that the following sequence of events is likely:
      a. manganese oxidizing bacteria deposit manganese oxide on the surface of the metal, according 
         to (1)
      b. manganese oxide is reduced to divalent manganous ions while the base metal serves as a 
         source of electrons, according to (3).
      c. divalent manganous ions, products of reaction (3), may serve as a source of manganese ions 
         for manganese oxidizing bacteria in reaction (1), generating a loop stimulated by the 
         oxidation/reduction of manganese.
      d. cathodic reaction (3) continuously consumes electrons provided by anodic dissolution of the 
         base metal and accelerates corrosion, pitting corrosion in case of passive metals.

f. Summary of plans for next year's work.
   N/A

g. Names of graduate students and post-doctoral(s) currently working on the project
   Dusty Tripp  
   Graduate Student  
   Department of Chemical Engineering  
   Montana State University  
   Bozeman, MT

   Bo Olesen  
   Ph.D. Candidate  
   Department of Environmental Engineering  
   Aalborg University  
   Aalborg, Denmark
Wayne H. Dickinson
PhD Candidate
Department of Chemistry
Montana State University
Bozeman, MT
PART III.

A Power Point file containing viewgraphs and supporting information is included as an attachment with this report. In addition, viewgraphs generated from the Power Point file are included. Additional supporting discussion material for the multi-part and supporting viewgraphs is included below.

Technology Issues:
- Noble shift of $E_{corr}$ to values exceeding +300 mV SCE
- Two to three decade enhancement in cathodic current density at potentials above -200 mV SCE
- $E_{corr} > E_{pit}$ increases the risk of pit nucleation
- Enhanced cathodic current impedes repassivation by holding $E_{corr}$ above $E_{prot}$

Objectives:
- Demonstrate that Ennoblement is caused by microbial deposits
- Define the nature of biofouling deposits on ennobled samples
- Determine the reaction responsible for Ennoblement

Approach:
- Expose stainless steels (SS) to natural waters and study the microbial deposits and inorganic surface chemistry.
- Use pure cultures of target bacteria to demonstrate that Ennoblement is caused by specific microbial-metal interactions
- Use XPS spectra to define the nature of biofouling deposits on ennobled samples

Accomplishments:
- Ennoblement can be induced by *Leptotrix discophora* under laboratory conditions
- The Ennoblement-causing mineral deposited on metal samples is MnO$_2$
- Microbially deposited MnO$_2$ can be electrochemically reduced to Mn$^{2+}$; manganese oxihydroxide, MnOOH, is the intermediate product

Impact:
- Manganese oxidizing bacteria may be responsible for an important example of microbially influenced corrosion. According to our hypothesis, microbially deposited manganese oxide is subsequently reduced to divalent manganese ions by electrons from the base metal. The anodic aspect of this reaction is metal oxidation; i.e., corrosion of the metal.