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0575

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13. ABSTRACT *(Maximum 200 words)*

This research program improved our understanding of how surface chemical reactions, surface stress, and atomic level microstructure influence materials oxidation/corrosion processes. Central to this effort was the construction of a new scanning probe microscopy facility which now houses a UHV-STM and a combined STM/AFM for operation in both air and electrochemical environments. It was demonstrated that applied stress fields can influence the electrochemical pitting corrosion chemistry of pure aluminum and 2024-T3 alloy. The role that surface defects play in oxidation reactions involving graphitic surfaces was also examined. Here it was shown that surface defects, including ones occurring on the atomic level, can dominate the reactivity and morphological evolution of such surfaces. Finally, high-impedance STM imaging was used to elucidate the structure and domain boundary characteristics for adsorbed self-assembling molecular films, providing information that will be needed if such films are to be used for interface passivation. The basic science opportunities addressed in this program were quite significant, and have technological implications given current interest in corrosion prevention and developing an improved fundamental understanding for stress-corrosion cracking, a topic of obvious importance to the aircraft industry.

14. SUBJECT TERMS
Surface oxidation; metallic corrosion; scanning tunneling and atomic force microscopies; surface electrochemistry; stress effects on surface chemistry; interfacial structure; reaction kinetics; aluminum.

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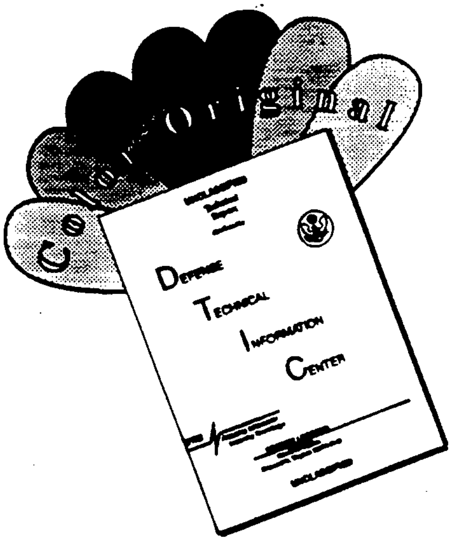
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Scanning Tunneling Microscopy Studies of the Morphology and Kinetic Pathways for Corrosion Reactions of Stressed Materials

AFOSR-F49620-93-1-0423

Final Technical Report for July 1, 1993 - June 30, 1996

Submitted by: Steven J. Sibener

Department of Chemistry and The James Franck Institute
The University of Chicago, 5640 South Ellis Avenue
Chicago, Illinois 60637

Contents

[Note that some portions of this program will be continued under the auspices of AASERT grant F49620-96-1-0268. Ongoing research associated with AFOSR F49620-96-1-0084 will also benefit from the scanning tunnneling and force microscopy laboratory that was constructed during the course of this URI grant.]

1. Introduction

This research program in the area of materials oxidation/corrosion placed emphasis on the important role that surface chemical reactions, surface stress, and atomic level microstructure play in such processes. Past work in this area clearly demonstrated that a wide variety of chemical and physical factors can influence the course of corrosion reactions, and that electrochemical processes can be of especial concern at both the microscopic and macroscopic level. In spite of this progress, there is still a great need to further improve our fundamental understanding of corrosion processes at the atomic level. Such understanding could have important ramifications for corrosion prevention, lead to improved methods of surface passivation, and possibly to the development of new surface-science-based diagnostics for materials evaluation. Such studies are of current interest to the DoD due to the widespread use of high performance engineering materials such as aluminum, nickel, hardened aluminum alloys, and superalloys of nickel and aluminum in corrosive environments, particularly in aging aircraft and naval vessels. Recent advances in surface science experimentation, including modulated molecular beam techniques, the advent of in-situ atomic imaging via scanning tunneling (STM) and atomic force (AFM) microscopies, and real-time monitoring of reacting surfaces with non-destructive neutral helium atom scattering, made this an opportune time to launch such such a research effort.

Central to this effort was the construction of a new scanning probe microscopy facility which now houses two new instruments: an UHV-STM and a combined STM/AFM for operation in both air and electrochemical environments. We have examined whether applied stress (including both compressive and tensile stress fields) can influence the electrochemical reactivity of various materials, including reaction pathways, kinetic rate constants, and the morphological evolution of oxidized interfaces. We have also examined the important role that surface defects play in oxidation reactions at surfaces. We have initiated electrochemical etching experiments on both pure aluminum and 2024-T3 alloy either with or without applied stress fields. AFM images demonstrate differences in the morphological evolution of etched samples, depending on their composition and for various levels of applied stress. In the future we hope to initiate higher resolution experiments to ascertain how atomic level microstructure is modified by the presence of externally applied stress fields. Moreover, *in situ* imaging during etching is also getting underway. This will allow us to examine the surface morphology's time-evolution during etching, and hence the kinetics for the etching process. The correlation of surface reactivity parameters with (i) topological features (such as steps, kinks, and grain boundaries) and (ii) local chemical environment, i.e, the influence that trace adsorbed species can have on either oxidation promotion or surface passivation, is needed to obtain a more complete understanding of such reactions.

The students and postdoctoral fellows who participated in this research program received unique training in areas bordering surface chemistry, electrochemistry, and materials science, furthering the URI's stated goal of developing human resources in important areas of scientific endeavor. This project complements other AFOSR supported activities that primarily use electron and neutral particle scattering probes to assess issues relating to interface reactivity, structure, stability, and bonding.

The basic science opportunities addressed in this effort are quite significant. Surface stress has recently been discussed as a key parameter in surface reactivity, but definitive measurements are lacking. Such effects due to stress are not unexpected given the observation that structural relaxation and surface stress field changes frequently accompany adsorption, especially including oxygen adsorption on metallic interfaces. We are in some sense turning this question around, seeing if we can influence surface oxidative chemistry by tuning the level of stress, including both compressive and tensile regimes. Further motivation for these studies comes from important technological issues such as stress-corrosion cracking, which is of obvious importance to the aircraft industry. Here we have conducted imaging measurements on stressed samples (induced by either macroscopic conditions such as bending the sample, or by microscopic phenomena such as chemical adsorption) in order to learn how the surface structure and forcefield at the atomic level is influenced by stress. This issue is of particular interest in the vicinity of load levels which lead to surface reconstruction and crystal facetting.

3. Facilities and Instrumentation

During the duration of this URI grant we designed and completed the construction of a new scanning probe microscopy laboratory in the basement of The James Franck Institute. This laboratory, whose $100K renovation costs were paid for by the university, now houses (1) a combined STM/AFM microscope which operates in both air and electrochemical environments, and (2) a custom-designed and air-levitated ultra-high-vacuum STM instrument. Note that these two microscopes will continue to play a crucial role in our continuing AFOSR and AASERT funded projects after the expiration of this URI grant.

Also note that in addition to the UHV-STM, our new air-levitated chamber houses instrumentation for low energy electron diffraction (LEED), Auger spectroscopy, thermal desorption, and has provisions for XPS and UPS photoelectron spectroscopies as well as other optical spectroscopies. The system is based on a modified "micro-STM" from Omicron Corporation. Graduate student Tom Pearl will next examine how stepped metallic surfaces restructure during the initial stages of metallic oxidation using this instrument, thereby providing a superb real-space complement to our previous scattering data. He will in particular use the STM to quantify step structure and atom mobility along step-edges during during interface oxidation. He will also use the STM as a spatially localized source of electrons, attempting to elucidate further information on how electrons synergistically enhance metallic oxidation. This will encompass both nucleation issues as well as the actual electron attachment process. These experiments will extend our work on electron stimulated oxidation, experiments which have received widespread attention in both the metallic oxidation and semiconductor patterning communities. The reader is referred to recent work from our group for more details.

4. Accomplishments/New Findings

During the course of this grant we focussed on two issues which we believe to be central to developing an improved understanding of surface reactivity. These are (1) whether, and if so to what extent, applied surface stress (including both compressive and tensile stress fields) can influence the electrochemical reactivity of various materials, including reaction pathways, kinetic rate constants, and the morphological evolution of oxidized interfaces, and (2) delineating the important role that surface defects play in oxidation reactions at surfaces. **Results are herein reported which demonstrate that tensile stress does influence the reactive behavior of aluminum, including Al-2024-T3.** Results are also presented for the oxidation of graphite in which the crucial role that step edges and point defects play in the nucleation phase of etch pit formation is demonstrated. In addition to the above topics we have also successfully conducted high-impedance STM imaging experiments involving molecular overlayers of alkanethiols. Understanding in detail the atomic level structure and domain boundary arrangement for such systems is important due to potential applications in interface passivation.

To summarize, highlights include: (1) First quantitative results on stress effects in electrochemical corrosion of aluminum and its alloys. Work has also begun with Prof. Burdett in our department on developing a theoretical basis for such effects; (2) Results which demonstrate the crucial role that step edges and point defects play in the nucleation phase of etch pit formation during the air oxidation of graphite; and (3) First results on the high-impedance imaging of molecular overlayers. These accomplishments are described below. Further details can be found in the Annual Progress Reports and Annual Technical Reports that have been previously filed for this program.

(4.1) Electrochemical Reactions with Applied Stress - First Quantitative Results
Electrochemical etching including the option of utilizing applied *in situ* stress is being accomplished using a newly built apparatus. Fig. 1 is a schematic representation of the experimental setup. Here we can apply a force which leads to buckling, or with more gentle compression, curvature of a sample. This curvature is most useful as one side of the sample is placed under compressive stress, Side 1 in Fig. 1, while the opposing side is placed under tensile stress, Side 2 in Fig. 1. In our experiments we have used force levels either under or above the plastic deformation limits for given samples. For example, we have used buckling force levels with thin 2024-T3 samples both under and over its plastic deformation limit, 196 and 491 dynes, respectively. In this report we restrict our discussion to sample curvatures during etching that were below the deformation limit. AFM images taken after etching indicate that etch pits on the tensile side are bigger and more dense (frequent) than on the compressive side. This can be more clearly seen in Figure 2 (one of 20 samples used in this study) which offers a wide-field (71 micron) comparison of surface mophology following electrochemical etching with Fig. 2a showing a surface under compressive stress, and Fig. 2b being for tensile stress. In the future etching experiments using systematically varied stress levels will be carried out.

Figure 3 is perhaps the best summary of our findings to date: it shows that the electrochemical pitting corrosion of 2024-T3 (summarizing data from approximately 4000 etch pits from 20 samples) proceeds more rapidly for the sample when tensile surface stress is present than for the complementary case of compressive stress. This "proof of concept" experiment suggests that a rich range of discoveries will flow from measurements such as these. Planned *in situ* STM/AFM experiments will be a most informative extension of these measurements as they will allow us to actually watch, in real-time, structural changes and the progress of corrosion reactions as experimental parameters such as stress level, chemical environment, and temperature are systematically varied. Such real-time experiments are now getting underway.

In conjunction with Prof. Burdett of our department, we are attempting to develop a theoretical understanding of such stress-induced changes in surface reactivity. As stated earlier, the basic science opportunities here are quite significant. Surface stress has recently been discussed as a key parameter in surface reactivity, but definitive measurements are lacking. Such effects are not unexpected given the observation that structural relaxation frequently accompanies adsorption. Moreover, these studies will become especially interesting in the vicinity of load levels which lead to surface reconstruction, bulk dislocation formation, and crystal facetting; it would be wonderful if we could correlate changes in corrosion kinetics with such structural transformations at the atomic level. In order to elucidate common trends in this work which can be traced back to basic issues of electronic structure, we will expand this work from its focus on Al to include metals located on the "left" and "right" sides of the periodic table, with Ti and Ni being two promising choices. This will allow us to ascertain whether simple rules associated with elemental electronic structure can be developed which will allow us to predict how the oxidation/corrosion chemistry of a given metal will respond to varying levels of compressive and tensile stress. Issues to be examined include how the bandwidth and band-center of the surface density of states varies as a function of interatomic spacing. Another issue is whether the experimental results will eventually be understandable in terms of a model, as above, where the basic structural and electronic picture is one where just the dimensions of the surface are changed. Does the stretching or compression of the surface lead to the generation of steps or other local sites where the structural-electronic problem is quite different. Some earlier work from Burdett's theory group has been associated with the adsorbate-induced reconstruction of metal surfaces. Here too it will be interesting to examine the local electronic description of these sites when stress is applied to the system.

(4.2) Role that Step Edges and Point Defects Play in the Nucleation Phase of Etch Pit Formation During the Oxidation of Graphite

Another issue we have examined is the crucial role that step edges and point defects play in the nucleation phase of etch pit formation during the air oxidation of graphite. Here we have oxidized samples of HOPG graphite in a high-temperature furnace at ca. 650° C. Figures 4 and 5 are post-oxidation STM images which clearly reveal that **all** of the etch pits nucleate along either step-edges (including monoatomic high steps) or localized point defects. This work demonstrates that atomic-size morphological defects can indeed govern the rate at which interfaces react in an oxidizing environment. Also note the nearly uniform size of the etch pits shown in Figure 5. This suggests that the morphological evolution of the pits can be predicted quite well after the initial nucleation event has occurred.

(4.3) High-Impedance STM Imaging of Molecular Overlayers

As part of our new atomic probe microscopy effort, we are also developing the capability to image molecular overlayers. This is technically difficult due to the high electrical "resistance" such molecules present to electrons involved in STM imaging. If care is not taken, images may actually be due to the substrate, or the tip may reside "within" the molecular overlayer. To avoid this, one wishes to detect very low tunneling currents - a situation in which the tip-overlayer interaction can be attributed to the wavefunctions of the molecule far from the surface. Figure 6 shows such an STM image which clearly reveals rotated domains of decanethiol on Au(111). The high-impedance and relatively fast response time electronics we have developed for this purpose are also cited in the Technology Transfer section of this document. We are most encouraged by these images, and look forward to many experiments which will probe the spatially relsolved reactivity of molecular overlayers.

Figure Captions

Figure 1: Conceptual diagram of an electrochemical cell for etching with/without applied stress.
Figure 2: 3D AFM images and topographic line measurements of electrochemically etched pure Al: Effect of tensile vs. compressive stress on etch pit size and frequency.
Figure 3: Proof-of-Concept! Demonstrated effect of surface stress on the electrochemical pitting corrosion of Al 2024-T3 (Preliminary Results).
Figure 4. STM image of oxidized graphite which shows that etch pits exclusively nucleate along point and extended defects, including step edges.
Figure 5. STM image of oxidized graphite which clearly shows that formation of oxidative etch pits can occur along monoatomic step-edges. Note also the nearly uniform size of the pits.
Figure 6. High-impedance STM image of decanthiol self-assembled monolayers adsorbed on Au(111). Different domain structures are clearly visible in this image.

Figures 1-6 appear on the next 9 pages of this document.

Figure I

Electrochemical Cell for Etching With or Without Applied Stress

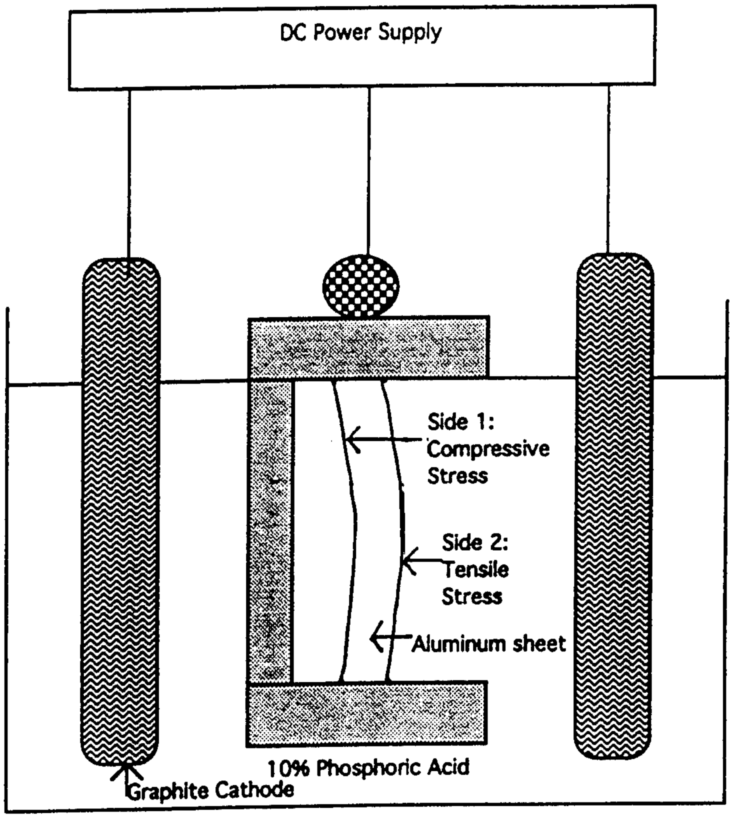


Fig.1. Experimental Setup for Electrochemically Etching Aluminum Samples either with or without Applied Stress.
Etching Condition: 4.13V DC,0.6A,in 10% Phosphoric Acid for 31 Minutes

Note that when the sample is elastically deformed (curved) it allows us to etch one side of the sample (side 1) under compressive stress and the other (side 2) under tensile stress

Figure 2

Wide-Range (75 micron) 3D AFM Images and Topographic Line Measurements of Electrochemically Etched Pure Al: Effect of Tensile vs. Compressive Stress on Etch Pit Size and Frequency

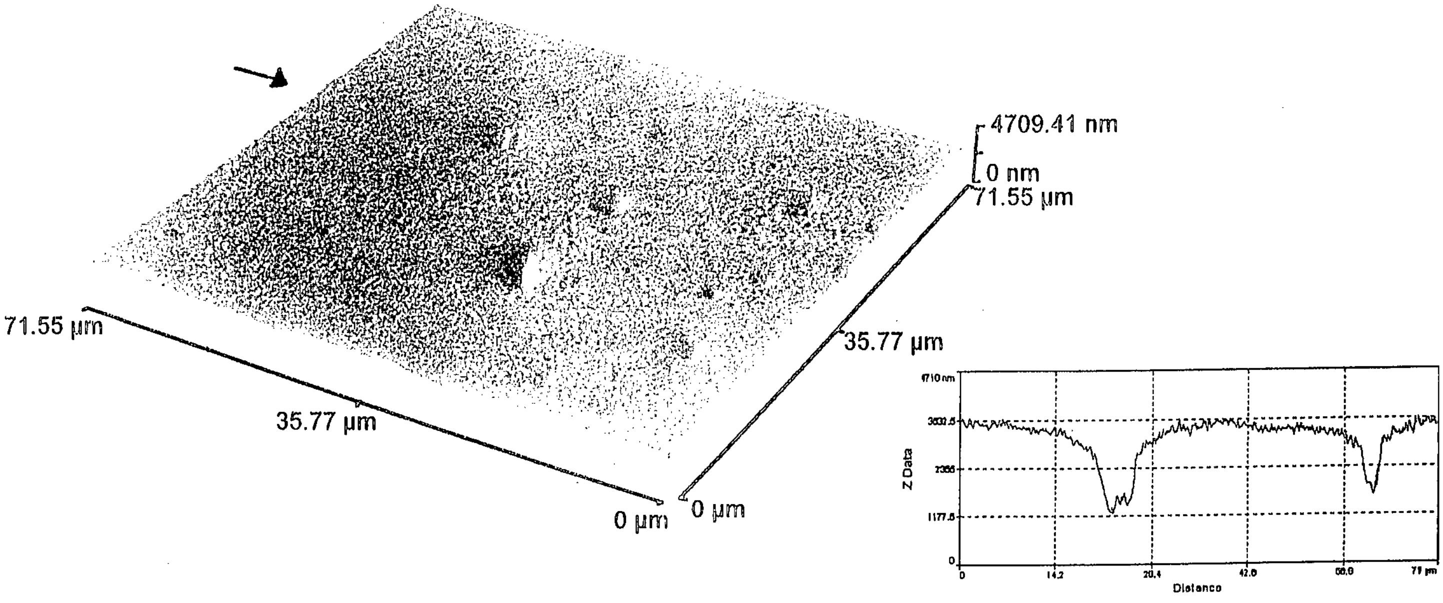


Fig.2a. Compressive Stress: Smaller Size and Lower Density of Etch Pits

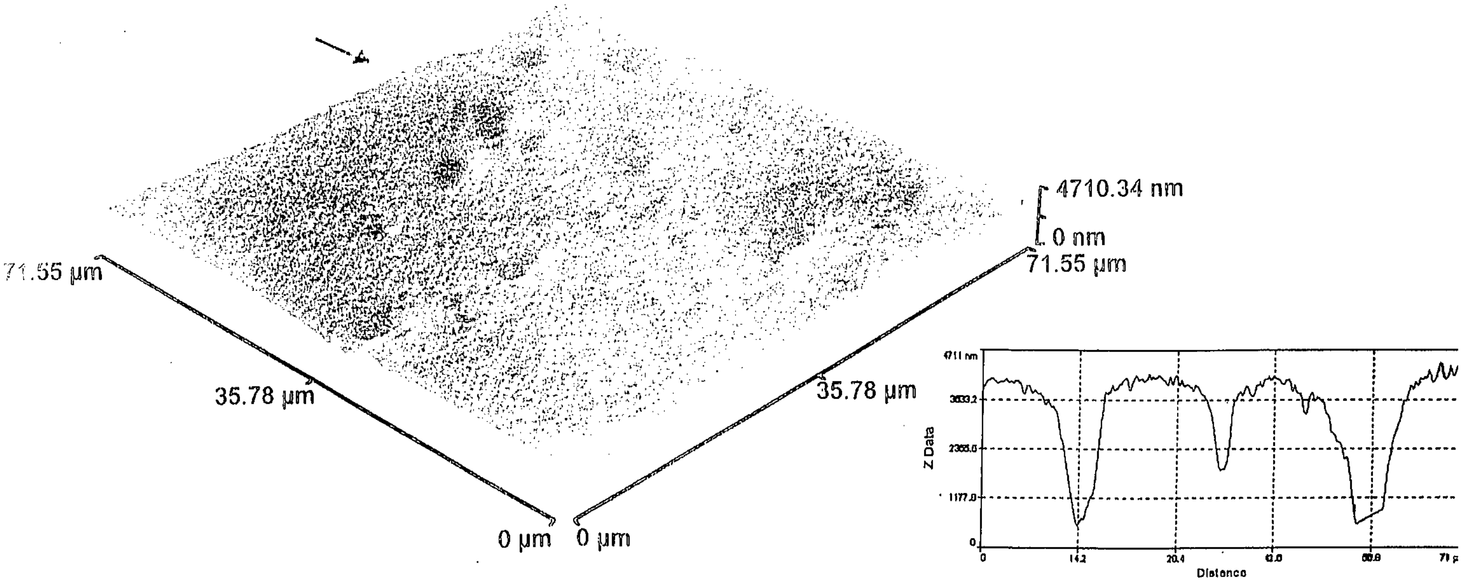
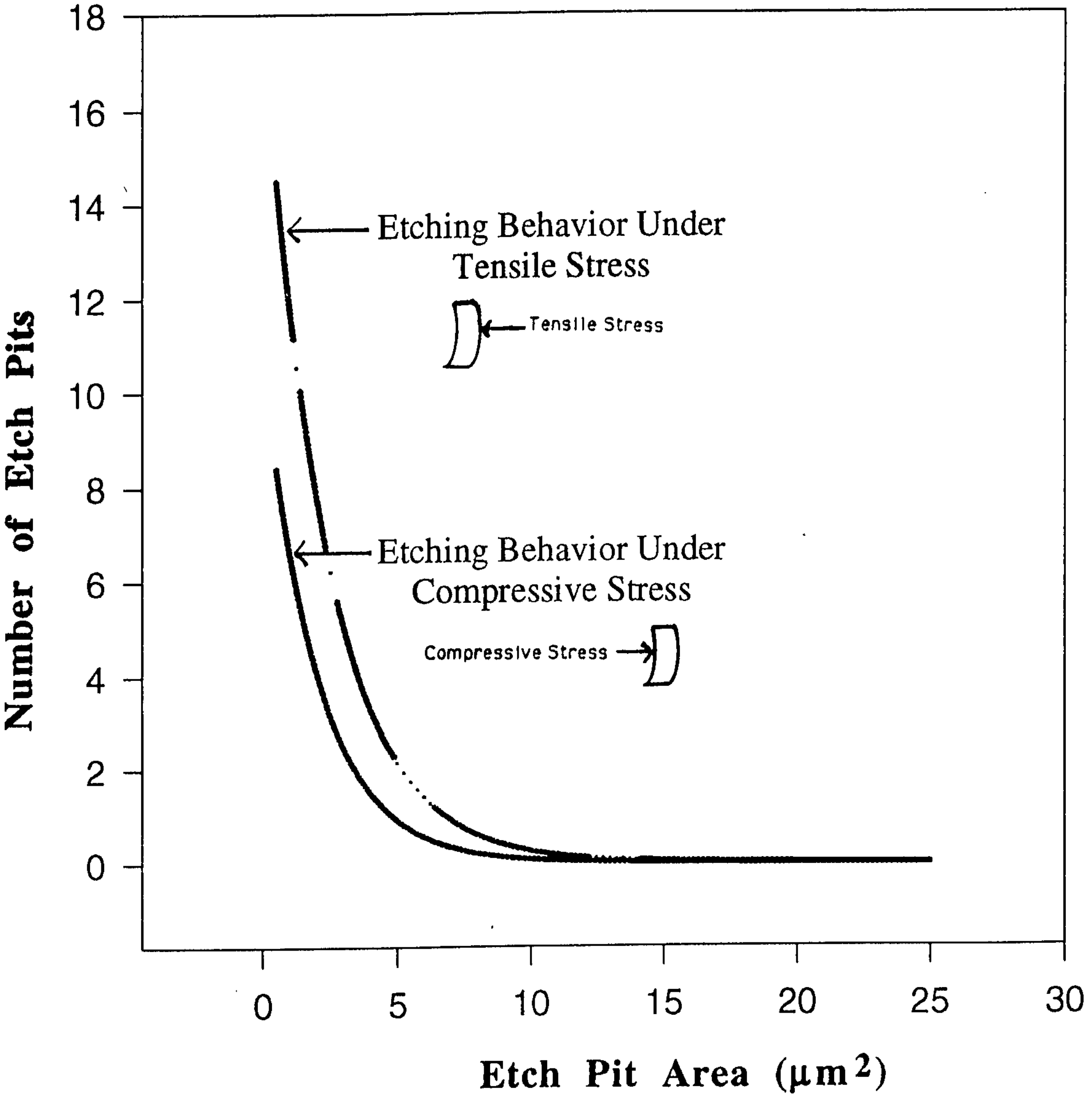


Fig.2b. Tensile Stress: Larger Size and Higher Density of Etch Pits

Figure 3

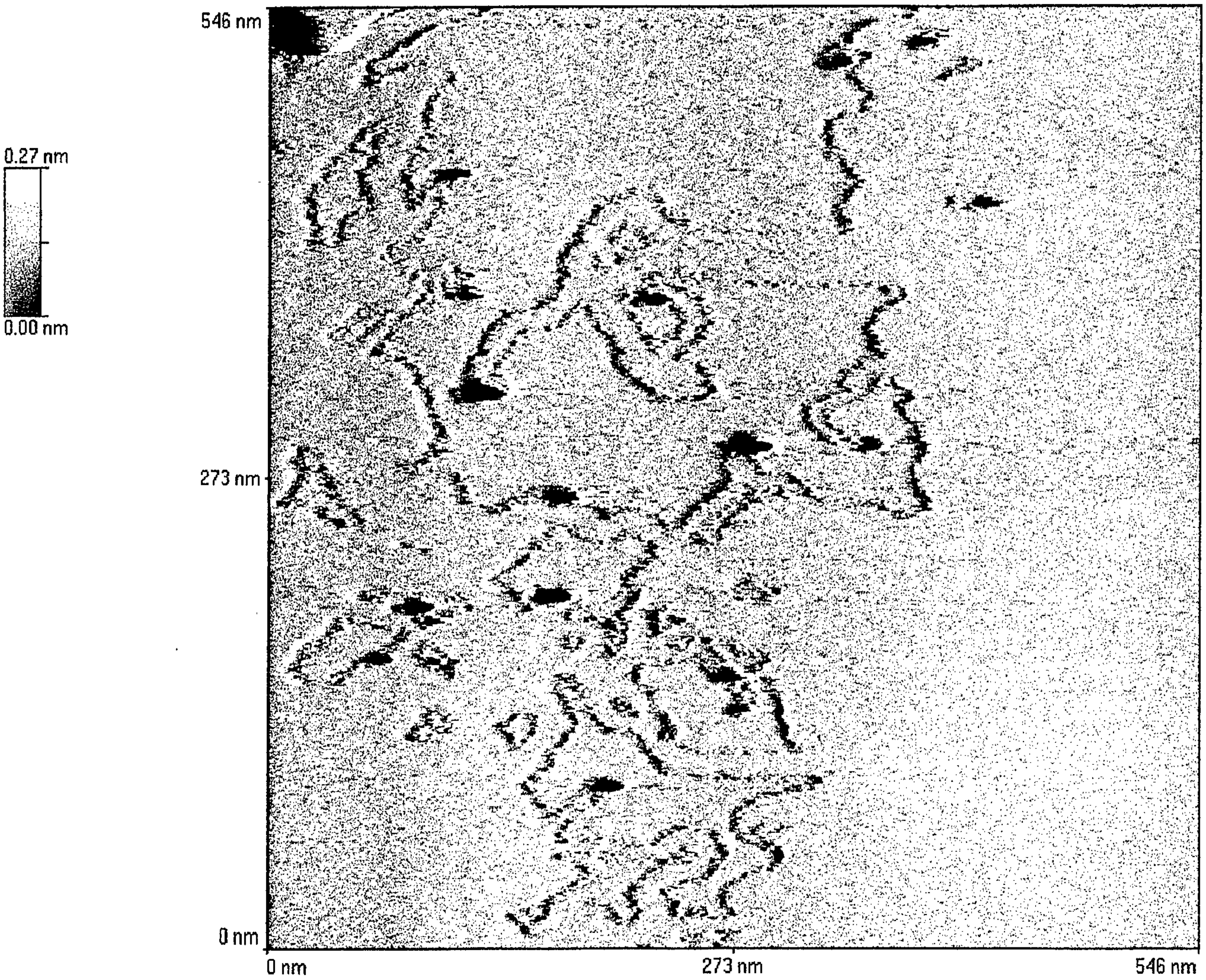
Effect of Surface Stress on the Electrochemical Pitting Corrosion of Al 2024-T3: Preliminary Results*
(Stress Level = 71.4 N/m)



Conclusion: Side with Tensile Stress is More Reactive than the Side under Compressive Stress

***Histograms are from twenty (75x75) micron samples, having approximately 200 etch pits measured per side**

HOPG Oxidation: Longer Heating Time Results in a Greater Number of Etched Pits Along Defects

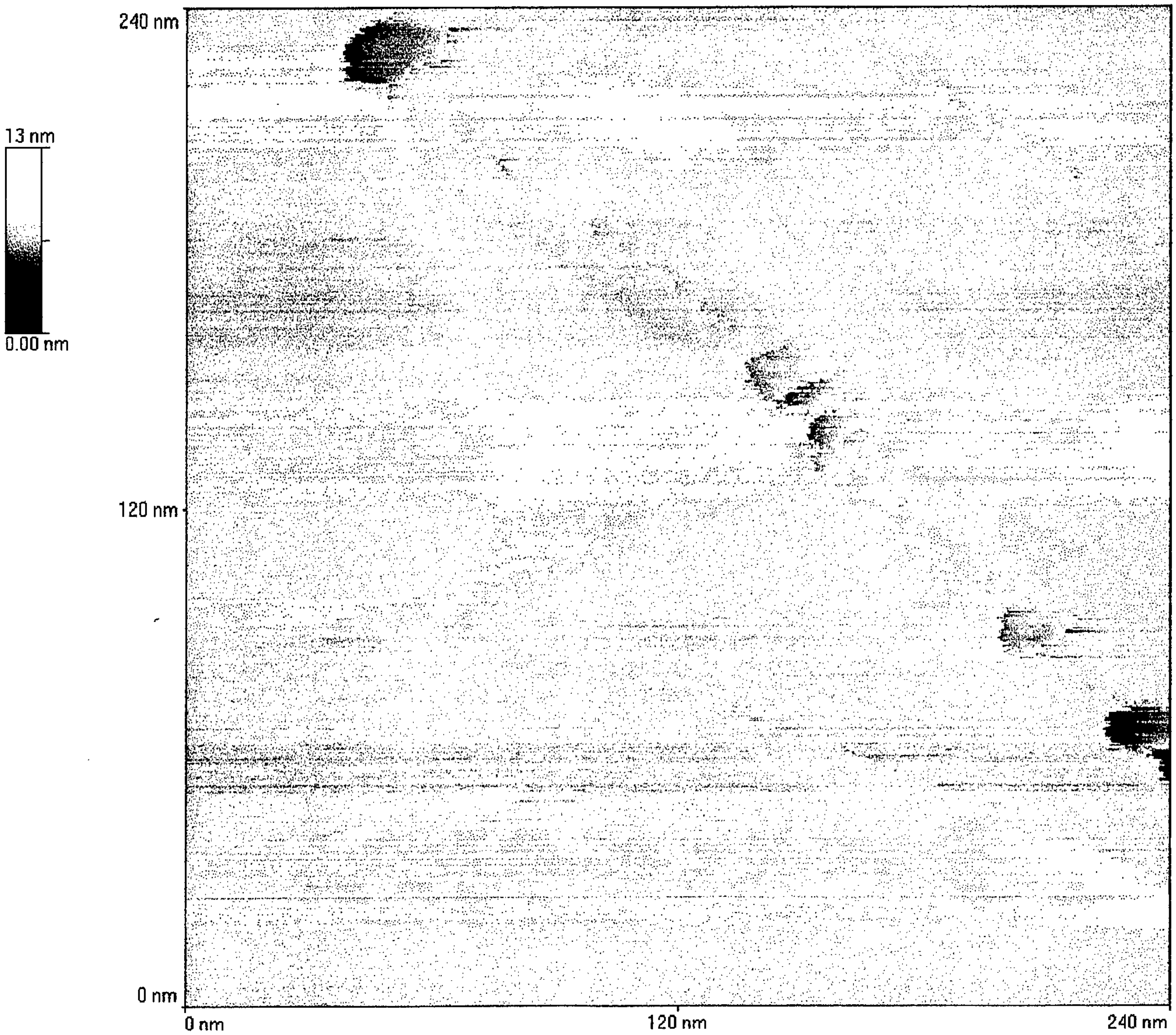


-Sample heated for 8 minutes in air at ~650 degrees Celcius

-Air STM acquisition setup:
tunneling current: 0.20 nA, sample bias: 85 mV

Figure 5

HOPG Oxidation: Formation of Etched Pits Along Monoatomic Step Edge

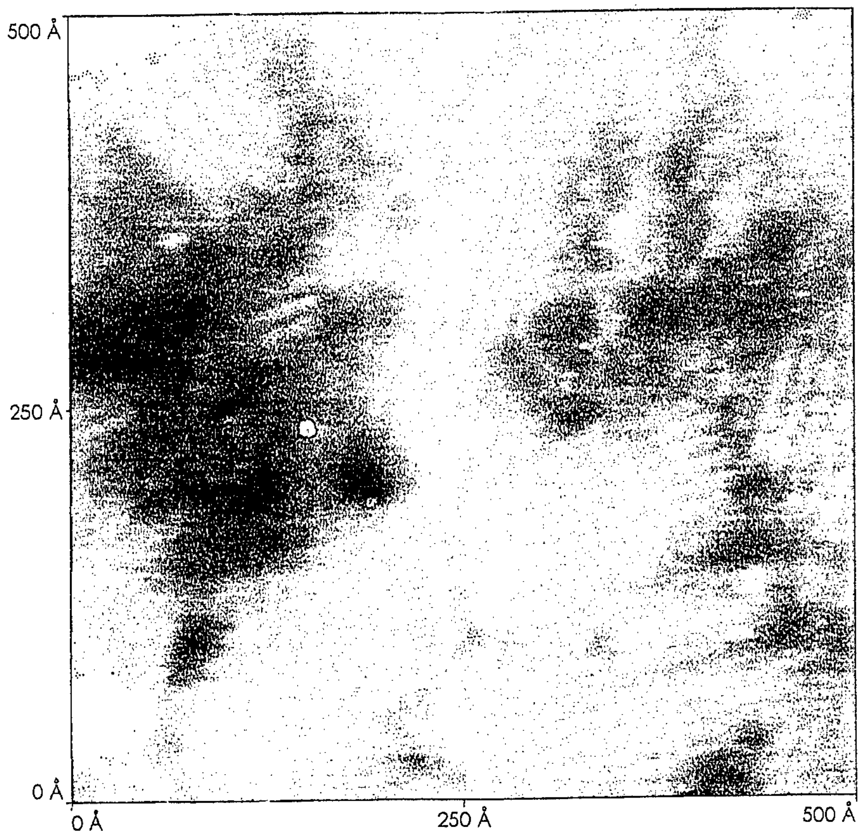


-Sample heated for 6 minutes at ~650 degrees Celcius

-Air STM acquisition setup:
tunneling current: 1 nA, sample bias: 100 mV

Figure 6

STM Image of Decanethiol Domains on Evaporated Au(111)
Tunneling Conditions: I = 100pA, V = 0.45 mV



5. Personnel Supported and Associated with This Program

Key: *Primary effort on air and electrochemical oxidation, **Primary effort on UHV-STM
Steven J. Sibener, Professor and PI
Jongin Hahm*, Graduate Student
Nabil Isa*, Graduate Student
Tom Pearl**, Graduate Student
Wenhai Liu, Postdoctoral Fellow
Daniel Gaspar, Graduate Student
Mike Stirniman, Graduate Student
Ben Zion, Graduate Student

6. Publications

Several publications are anticipated during the next few years from this new air/electrochemistry/UHV scanning probe microscopy effort. These papers will acknowledge support from this seed URI grant.

7. DoD Interactions/Transitions

7a. Connections with DoD

The PI and his group have attended several DoD meetings on the topic of corrosion and aging aircraft. For example:

- Graduate student Mike Stirniman participated in the "Joint AFOSR-AFMC/EN Aging Aircraft Conference" [Workshop on Aging Aircraft Research] that was held from 27-28 April 1993 at Georgia Tech in Atlanta, GA.
- Professor Sibener was an invited participant at the "Second Air Force Aging Aircraft Conference" that was held from 17 May to 19 May at the Oklahoma City Air Logistics Center, Tinker AFB, OK. His talk was entitled "The Initial Stages of Metallic Oxidation", and stimulated much discussion with the participants and sponsors.
- Professor Sibener was also an invited speaker at the AFOSR/URI Meeting on "Corrosion, Tribology, Lubrication, and Materials Fatigue Under Extreme Conditions" that was held from 17-18 August 1994 at the Beckman Institute at the University of Illinois/Urbana-Champaign. His presentation was entitled "The Initial Stages of Metallic Oxidation", and was presented at a much higher technical level than the overview talk presented earlier at Tinker AFB.
- As our electrochemical etching work advances, additional contacts with Tinker AFB and Wright-Patterson are envisioned.

7b. DoD Consulting of the PI

The PI was a charter member of the Defense Science Study Group of the Institute for Defense Analyses. He is currently a consultant for IDA.

7c. Transitions

1. Title: Electronics for high-impedance STM imaging
   Purpose: Circuitry needed for STM imaging of molecular overlayers
   Recipient: Mark Greenbaum, Topometrix Corporation (708-717-0566)

2. Title: Electron enhanced oxidation of materials
   Purpose: Improved oxidation and patterning of semiconductors
   Recipient: Dr. Wilson Li, Intel Corp., 408-765-2837

3. Title: Ultra-high vacuum technology for atomic traps
   Purpose: Generation of ultra-low temperature atomic beams for atomic/synchrotron physics and small-scale pattern deposition
   Recipient: Bruce Zabransky, Argonne National Lab (630-252-4046)

8. Biographical Information of the PI: STEVEN J. SIBENER

August 1996

Born

April 3, 1954; Brooklyn, New York

Education

1971-1975 University of Rochester, Rochester, New York.
Sc.B. in Chemistry awarded with High Distinction, 1975.
B.A. in Physics awarded with Distinction, 1975.

1975-1979 University of California, Berkeley.
M.S. in Chemistry, 1977.
Ph.D. in Chemistry, 1979.
Research with Professor Yuan T. Lee.

Professional Experience

Eastman Kodak Research Laboratories, Photographic Research Division, Summer 1974: Electrostatic properties of polymers and polymer-metal interfaces.

Eastman Kodak Research Laboratories, Physics Division, Solid State Physics Research Laboratory, Summer 1975: Oxide growth on GaAsP for MOS fabrication.

Bell Laboratories Postdoctoral Fellow, September 1979 - August 1980. Research with Dr. M.J. Cardillo involving molecular beam scattering from single crystal surfaces.

The University of Chicago, The James Franck Institute and The Department of Chemistry:
Assistant Professor, August 1980 - June 1985.
Associate Professor, July 1985 - June 1989.
Professor of Chemistry, July 1989 - .

Honors and Awards

Chairman, Div. of Chemical Physics, American Physical Society, 1996.
Visiting Fellow, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, 1992-93.
Marlow Medal of the Faraday Division of the Royal Society of Chemistry, 1988.
IBM Faculty Development Award, 1984-86.
Alfred P. Sloan Foundation Research Fellow, 1983-87.
Camille and Henry Dreyfus Young Faculty in Chemistry Award, 1980.
Gulf Oil Research Fellow, University of California, Berkeley.
American Institute of Chemists Award, University of Rochester.
American Chemical Soc. Div. of Colloid and Surface Chemistry Undergraduate Thesis Competition Honorable Mention: "The Shape of Liquid Interfaces," 1975.
Regional Scholar for New York City, University of Rochester.

Associations

Phi Beta Kappa, American Physical Society,
American Chemical Society, Royal Society of Chemistry,
Sigma Xi, AAAS, American Vacuum Society

Invited Lectureships

Physikalisches Institut der Universität Erlangen-Nürnberg, 1988
Chemical Physics Institute Retreat Speaker, U of Oregon at Eugene, 1992.
ACS Lecturer of the Analytical Chemistry Division, University of Wisconsin, Madison, 1992.

Consulting

Dow Chemical USA	(1982-1985)
Teltech Resource Network	(1985-)
Institute for Defense Analyses	(1985-)

Professional Activities

Vice-Chairman, 1985 Gordon Research Conference on the Dynamics of Gas-Surface Interactions
Member, Defense Science Study Group--Institute for Defense Analyses (1985 - 1988).
Member, Materials Research Laboratory Policy Committee, The University of Chicago (1987 -).
Chairman, 1987 Gordon Conference on the Dynamics of Gas-Surface Interactions.
Member, International Advisory Committee of the Vibrations at Surfaces V Conference (September 1987).
Member, Board of Trustee's Visiting Committee for the College of Arts and Science, University of Rochester (July 1, 1987 - June 30, 1993).
Member, Council of the University Senate, The University of Chicago (September 1989 - September 1992).
Member, IQEC '90 Program Committee (May 1990).
Member, Physical Electronics Conference Advisory Committee (1991).
Member, Physical Electronics Conference Committee (1991-1994).
Organizer, Symposium on "Surface Chemistry from Reaction Dynamics Through Materials Growth", August 1992, ACS National Meeting, Washington, DC.
Co-Chairman, Symposium on "Laser Techniques for Surface Science", January 1994, SPIE/OE LASE '94, Los Angeles, CA.
Chairman, ACS Irving Langmuir Prize Canvassing Committee (1995).
Division of Chemical Physics, American Physical Society: Vice-Chair (1994), Chair-Elect (1995), Chair (1996).

Research Interests

Surface Chemistry & Physics; Interfacial Kinetic Processes; Chemical Physics; Reaction Dynamics; Electrochemistry; Materials Growth and Thin Film Dynamics; Molecular Beam Scattering; Surface Metallurgy: interface oxidation, vibrational dynamics, alloys, phase transitions; Nanostructures; STM/AFM studies of surface phenomena.

DoD Consulting of the PI

The PI was a charter member of the Defense Science Study Group of the Institute for Defense Analyses. He is currently a consultant for IDA.

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