SYMPOSIUM H

Corrosion of Metals and Alloys

April 23 – 26, 2000

Chairs

Nancy Missert
Nanostructure and Semiconductor Physics
Sandia National Labs
MS1415
Albuquerque, NM 87185-1415
505-844-2234

Alison Davenport
School of Metallurgy & Matls
Univ of Birmingham
Birmingham, B15 2TT
UNITED KINGDOM
44-121-4145191

Rudy Buchheit
Dept of MS&E
Ohio State Univ
477 Watts Hall
Columbus, OH 43210
614-292-6085

Mary Ryan
Dept Materials
Imperial College
London, SW7 2BP
UNITED KINGDOM
44-171-5946755

* Invited paper

TUTORIAL

The implementation of Cu in the metallization process of integrated circuits has redirected many research and development projects in universities, research institutes, and industry. A vast amount of data is being collected on the physical and mechanical properties of Cu thin films and lines, on various aspects of its polycrystalline nature. The implementation of Cu also goes hand in hand with the changeover from the physical vapor deposition technique to electroplating of the metal and with the introduction of chemical-mechanical polishing instead of the classical metal dry etch process. The research related to these new process steps has created a need to get more insight into other aspects of materials science.

The aim of this tutorial is to provide an interdisciplinary introduction to the latest evolution in fields relevant to Cu interconnects. An overview will be given of the state of the art of Cu metallization for high-performance Si technology. The importance of electrochemistry for the understanding of electrochemical deposition will be highlighted, and possible mechanisms of Cu corrosion will be discussed.

Instructors:
Robert Rosenberg, IBM T.J. Watson Research Center
Tom Moffatt, NIST
Vlasta Brusic, Cabot Corporation

SESSION H1: CORROSION OF ALUMINIUM ALLOYS
Chairs: Alison J. Davenport and Nancy Missert
Monday Morning, April 24, 2000
Golden Gate C3 (Marriott)

8:30 AM *H1.1
GALVANIC AND CREVICE CORROSION WITH ALUMINUM/ COPPER COUPLES. H.S. Isaacs, Brookhaven National Laboratory, Upton, NY; C.S. Jeffcoate, The Ohio State University, Columbus, OH; G. Adzic, Brookhaven National Laboratory, Upton, NY; N. Missert, J.C. Barbour, Sandia National Laboratory, Albuquerque, NM.

Alloying aluminum with copper has a detrimental effect on the corrosion resistance. The initial poor corrosion resistance has been attributed to copper rich second phase particles and the effects of copper on increasing the corrosion potential. Subsequent corrosion is associated with the presence of pits or micro-crevices. In order to model the corrosion of these alloys and the varied effects of potential and current distribution, galvanic and crevice corrosion of aluminum in contact with copper has been studied using a range of in situ techniques including simple galvanic cells where the aluminum forms a crevice with copper or an inert material, scanning current density mapping, and pH mapping. Studies have also been carried out on copper/aluminum reaction zones formed by heating copper/aluminum couples.

9:00 AM H1.2
DEALLOYING AND COPPER REDISTRIBUTION DURING CORROSION OF ALUMINUM ALLOY 2024. Roger C. Newman, Thomas J.R. Leclere, UMIST, Corrosion and Protection Centre, Manchester, UNITED KINGDOM; Alison Davenport, School of Metallurgy and Materials, Univ. of Birmingham, Birmingham, UNITED KINGDOM; Nikolay Dimitrov, Jake Mann, Karl Sieradzki, Dept. of Mech. and Aerospace Engr., Arizona State Univ., Tempe, AZ.

The redistribution of metallic copper on the surface of 2024Al controls the cathodic reaction kinetics and thus the corrosion behavior. Previous descriptions of the copper redistribution process focused on S phase intermetallic particles and did not give enough attention to the events around these particles. We show that the dominant source of redistributed copper is the solid solution. The role of the S phase particles is to localize the cathodic reaction, thus generating alkalinity that selectively dissolves Al from the nearby solid solution, releasing copper that forms metallic nanoparticles. The original S phase particle becomes inactivated as a cathode by deposition of hydrous alumina, and eventually the redistributed copper takes over the role of the cathodic surface. There is little or no difference between the cathodic behaviors of 2014 and 2024 alloys except for an initial transient in the latter (due to de-alloying of S phase) which is only observed in specialized conditions and has limited long-term significance. The various processes responsible for the redistribution of cathodic activity have been displayed by surface analysis and coupled-electrode experiments, including 1-D analogs of the intermetallic particle and adjacent matrix.

9:15 AM H1.3
HOT STAGE TEM STUDIES OF Al_2Cu PRECIPITATION FROM THE MELT. J.J. Hren, North Carolina State University, Raleigh, NC; K.A. Son, N. Missert and J.C. Barbour, Sandia National Laboratories, Albuquerque, NM.

Films of Al_2Cu were studied during the melting and resolidification of Al/Cu bilayers deposited using electron beam evaporation onto SiO_x support films on copper grids. The depositions were performed at RT in the sequence Cu then Al with proportions of stoichiometric Al_2Cu and a thickness of $\sim$400 nm. Parallel depositions onto thermally oxidized Si (100) substrates were separately studied using XPS, SEM (with EBSD and EDS) and RBS(1). Bilayers were then heated to $\sim$580 C and recooled at $\sim$10 C/s. The TEM studies used a GATAN Model 628 Heating Holder in a JEOL 2000 FX TEM. Images were viderecorded, with additional images and SADP recoprded at fixed temperatures. During heating, several Al-Cu phases precipitated, with volume fraction and dimensions heavily dependent upon temperature and time. At temperatures >530 C, large grains of Al_2Cu predominated and grew sporadically. At the two-phase Al_2Cu-Liquidus boundary, melting took place first at triple points, then at other grain boundaries. As the liquid encircled grains, their shapes became rounded until they were surrounded by liquid Crystalline phases were easily distinguished from the liquid by differences in diffraction contrast. The melt appeared to remain uniformly thick, sandwiched between the substrate oxide (SiO_x) and the thermal Al oxide , residual from the initial deposition. Upon cooling, large single phase grains with {110} normals, and containing only low angle subgrain boundaries formed, so rapidly that the nucleation events could not be recorded. Similar experiments were conducted on four different, but presumably identical, specimens. The results were strikingly similar and consistent with the parallel studies on thermally oxidized Si., The key factor seems to be the thin uppermost layer of Al_2O_3, which is apparently strong enough to confine the melt between it and the SiO_x. (1) K.-A. Son, N. Missert, J.C. Barbour, J.J. Hren, R.G. Copeland and K.G. Minor, submitted to ECS.

9:30 AM H1.4
EFFECT OF OXIDE CONDUCTIVITY ON CORROSION INITIATION AT NANOENGINEERED Cu-RICH DEFECTS IN Al THIN FILMS. N. Missert, F.D. Wall, J.C. Barbour, K.A. Son, and J.P. Sullivan, Sandia National Laboratories, Albuquerque, NM; R.G. Buchheit, The Ohio State University; H.S. Isaacs, Brookhaven National Laboratory; J.J. Hren, North Carolina State University.

Localized corrosion in Al-Cu alloys is often initiated at second phase precipitates. A common precipitate in low Cu content alloys is the theta phase Al_2Cu. Corrosion initiation at these precipitates is thought to be driven by galvanic coupling, where the Al matrix is preferentially dissolved in the vicinity of the noble particle. The efficiency of the galvanic couple is thought to depend upon the conductivity of the oxide at the surface of the theta phase, where a more conducting oxide should produce a more efficient couple. The electron density and electronic conductivity of the (predominantly) Al_2O_3 layer at the surface of Al_2Cu thin films are much higher than those of the insulating Al_2O_3 layer on thin film Al. In order to determine the role of oxide conductivity in mediating corrosion initiation by galvanic coupling, we have investigated localized corrosion initiation at nanoengineered Cu-rich defects in an Al thin film matrix, where the surface oxide properties are varied from conducting CuO to insulating Al_2O_3. Arrays of Cu-rich defects are fabricated with diameters ranging from 2 - 10 μm and spacings from 10 - 360 μm by combining photolithography with thin film deposition. The conductivity of the surface oxide layers are varied by exposing either Al or Cu to an oxygen plasma generated by an electron cyclotron resonance source. A comparison of the open circuit potential fluctuations in 0.05 M NaCl and the morphology of Al dissolution as measured by energy dispersive spectroscopy will be discussed.

10:15 AM *H1.5
THERMOMECHANICAL PROCESSING INDUCED CORROSION OF ALUMINUM ALLOY SHEET. Geoff Scamans, Alcan International Limited, Banbury, UNITED KINGDOM; George Thompson and Xirong Zhou, Corrosion and Protection Centre, UMIST, Manchester, UNITED KINGDOM.

Thermomechanical processing of aluminum alloy sheet by hot and cold rolling or by surface grinding results in the development of electrochemically active surface layers. These layers control the corrosion performance of sheet alloys particularly for painted architectural and automotive products. Cleaning treatments that

remove the active layers prevent underfilm corrosion in almost every case except for alloys with a copper content of more than 0.5 wt%. The active layers have been investigated using TEM of ultramicrotomed cross sections for a wide range of alloys as a function of process step. The surface has been studied from the as-cast state through hot rolling, annealing and cold rolling. This has included both DC cast and continuously cast alloys. Hot rolling and annealing are the most significant treatments for creating and activating surface layers. High levels of surface shear are the key to the development of microstructurally distinct surface layers which can be several microns thick after hot rolling. The reactivity of the layers can be seen directly by their corrosion in the microtome water bath. The inherent susceptibilty of the processed surface has been assessed at each production step by a simple filiform corrosion test. This test has also been used to assess the efficacy of different cleaning methods. In situ observation of the development of corrosion attack from a scibe mark using time-lapse video techniques has also been used to study filament growth on rolled, annealed and ground surfaces. The observations have important ramifications for the thermomechanical processing, cleaning and pretreatment of aluminium alloy sheet products and for the development of realistic 'fit-for-purpose' test methods.

10:45 AM H1.6
LOCALIZED METAL ION DEPOSITION ON ALUMINUM 2024-T3 ALLOY. Artur Kolics, Univ of Illinois, Dept of Chemistry, Urbana, IL; Pal Baradlai, Univ of Veszprem, Dept of Radiochemistry, Veszprem, HUNGARY; Andrzej Wieckowski, Univ of Illinois, Dept of Chemistry, Urbana, IL.

The deposition of cations on Al 2024-T3 alloy is analyzed with specific attention to their effect on cathodic reactions that occurs at copper rich intermetallics. Cerium and zinc accumulation was followed in 0.1M NaCl solution under open circuit and controlled potential conditions in aerated solution. The scanning electron and scanning Auger electron microscopic results indicated that metal deposition is a strongly site-dependent process. After 45 minutes of solution exposure, cerium and zinc deposition was the highest on the $CuMgAl_2$ intermetallics, significantly lower on the cathodic ones ($CuFeMnAl_6$/$CuFe_2Al_7$) while practically no cerium and zinc was detected on the bulk matrix. Adsorption is considered to be the main pathway for cerium and zinc deposition on the cathodic intermetallics, while a cerium oxide/hydroxide film formation is likely on the S-phase particles. The mechanism of deposition under cathodic polarization is different for the cations. After cathodic treatment at -1.20 V, highly insulating cerium rich caps formed on the intermetallics. The coupled appearance of cerium and chloride on copper rich heterogeneities is due to the local precipitation of $Ce(OH)_{2-x}Cl_x$ with $Ce(OH)_3$. In contrast zinc covered the copper rich sites without forming thick deposits on them. It was found that neither cerium nor zinc exhibited any inhibiting action for hydrogen ion reduction in pH = 3.0 solution. However, their influence on water decomposition is markedly different, cf. zinc strongly inhibited while cerium catalyzed the hydrogen evolution.

11:00 AM H1.7
SURFACE FINISHING OF ALUMINUM AEROSPACE ALLOYS. Alison J. Davenport, Flavie A.M. Moulinier, Bin Liu, The University of Birmingham, School of Metallurgy and Materials, Birmingham, UNITED KINGDOM; Peter C. Morgan, British Aerospace Sowerby Research Centre, Bristol, UNITED KINGDOM.

Borax acid anodizing is being considered as a replacement for chromate conversion coatings for corrosion protection of high strength aluminum alloys, particularly those containing copper such as 2024. Anodizing behavior and subsequent corrosion performance can be enhanced by improvement of the metal cleaning steps prior to anodizing, which typically involve degreasing, an alkaline etch, then an acidic "deoxidizing" step, usually in nitric acid. The presence of copper in the alloy causes problems both during pretreatment and corrosion owing to the presence of large (micron-sized) intermetallic particles, which are far more reactive than the matrix for reduction of oxygen, leading to alkaline dissolution of the surrounding matrix and accumulation of more cathodically active copper on the surface. In 2024, there are two types of intermetallic particles, those containing Cu, Fe, Mn and Al, and those of approximate composition Al_2CuMg (S-phase). The latter are a particular problem for corrosion resistance as they can dealloy, giving high surface area copper. They can also be a problem during anodizing as they are sites where oxygen evolution can occur, leading to low film growth efficiency. It has been found that adding a rare earth cation to the deoxidizing bath leads to the removal of S-phase particles, but not the other type. This improves the corrosion resistance of the cleaned surface by decreasing the rate of the oxygen reduction reaction, which in turn is due to a decrease in the copper content of the surface. Quantification of copper content on very heterogeneous alloy surfaces is not straightforward with conventional surface analytical methods. An alternative method involves carrying out cyclic voltammetry of the Cu(0)/Cu(I) reaction

in an inert electrolyte (borate buffer) in which no copper dissolution takes place. Rare earth treatment also improves the efficiency of anodizing by decreasing the oxygen evolution efficiency on the alloy surface.

11:15 AM H1.8
SELF-HEALING CHROMATE-FREE CONVERSION COATINGS. R. Buchheit, H. Guan, V. Laget, S. Mamidipally, P. Schmutz, Dept. of Materials Science and Engineering, Ohio State University, Columbus, OH.

Chromate conversion coatings on Al alloys consist of an insoluble mixed Cr(III)-Al oxide that contains a soluble Cr(VI) component. The excellent corrosion resistance of these coatings is due to the barrier properties of the insoluble mixed oxide and active corrosion protection, or self-healing, provided by soluble Cr(VI). When a chromate conversion coated alloy surface is contacted by an aggressive solution, soluble Cr(VI) is leached into solution where it can migrate to incipient flaws and be reduced and precipitated to stifle further corrosion. We have used this model as the basis for devising chromate-free conversion coatings. In our chromate-free coatings, barrier protection is provided by hydrotalcite and active corrosion protection is derived from soluble Ce(IV) or Mn(VII) oxides introduced into the coating. The corrosion resistance of these coatings is equal to that of chromate coatings in both exposure and electrochemical testing. Solution and surface analysis show that the soluble transition metal components can be leached into solution, and that they migrate to and interact with defects in a manner similar to Cr(VI). Electrochemical tests show that corrosion is slowed by this interaction. The sum of these findings indicate that it is possible to produce conversion coatings with active corrosion without using chromates.

11:30 AM *H1.9
SCANNING KELVIN PROBE FORCE MICROSCOPY AND AUGER ELECTRON SPECTROSCOPY STUDIES OF PASSIVE SURFACES. P. Schmutz, V. Guillaumin and G.S. Frankel, Fontana Corrosion Center, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH.

Auger Electron Spectroscopy (AES) and Scanning Kelvin Probe Force Microscopy (SKPFM) can be used to characterize the surface film properties of various materials. AES gives information on the oxide film composition, whereas SKPFM allows mapping of the Volta potential of the surface with submicron sensitivity. A linear relation has been found for a range of pure metals between the corrosion potential of in aqueous solution and the Volta potential measured in air upon emersion, indicating that this potential is a measure of the practical nobility of the surface. However, various observations indicate that the interpretation of the Volta potential measured in air is much more complicated. For instance, both the Volta potential and the OCP are both offset along the calibration line depending upon the ions in the solution. Another example is that all of the intermetallic particles in as-polished AA2024-T3 have a Volta potential noble to that of the matrix, but the Volta potential of S phase particles after light sputter etching becomes active. In samples exposed to various conditions, some regions exhibiting potential differences show no difference in composition (at least at the resolution of Auger measurements) and regions with differences in composition do not always exhibit potential contrast. In order to understand better the meaning of the Volta potentials measured by SKPFM, experiments were performed on pure Ni and Pt samples emersed at open circuit or under potential control. The potential was found to be composed of a transient component that discharged slower in air than in solution at open circuit, and a more-permanent charge associated with adsorbed species. These measurements validate the use of SKPFM for the study of corroded samples. Other experiments on pure Mg and pure Al samples further highlight the value of Volta potential measurements made by SKPFM.

SESSION H2: CORROSION MONITORING AND MICROSTRUCTURE
Chairs: Robert G. Kelly and Rudy Buchheit
Monday Afternoon, April 24, 2000
Golden Gate C3 (Marriott)

1:30 PM H2.1
KELVIN PROBE STUDY OF ADSORPTION OF LUBRICANTS ON METAL SURFACES. Yeyuan Yang, Steven Danyluk, Georgia Institute of Technology, School of Mechanical Engineering, Atlanta, GA.

A non-vibrating Kelvin probe has been utilized in an immersed oil bath system to detect the interaction of oil additives with metal (Cu, Al, and 1030 steel) surfaces. The probe signals are used to determine

the influence of additive adsorption on the electrical (surface) charge at the interface between the metals. The additive has a significant effect on the adsorbed film as well as the surface potential, which causes contact potential difference (CPD) signal to be asymmetrical. The surface potential is also found to be time dependent. These results are modeled by adsorption and charge re-distribution at the metal interface. The relationship of these results to the initiation of corrosion will be discussed.

1:45 PM H2.2
SQUID MAGNETOMETERS FOR QUANTITATIVE MEASUREMENTS OF CORROSION IN ALUMINUM. <u>Afshin Abedi</u>, John P. Wikswo, Vanderbilt University, Dept. of Physics and Astronomy, Nashville, TN.

Superconducting QUantum Interference Device (SQUID) magnetometers can detect the magnetic fields associated with electrical currents from metal corrosion. In contrast to conventional electrochemical techniques, SQUIDs are ideal for observing the spatio-temporal characteristics of corrosion hidden within the lap joints of aluminum aircraft. However, the corrosion magnetic fields (CMF) are significantly weaker than would be expected from the electric current predicted by metal loss and Faraday's law, suggesting that some of the corrosion currents are either magnetically silent or randomly oriented at spatial scales below SQUID resolution. To explore the relationship between the CMF and mass loss, we used an automated, scanning SQUID within a magnetic shield to map every hour for 24 hours the vertical component of the magnetic field above 0.8-mm thick, 70-mm diameter disks of 7075-T6 aluminum while being exposed to various concentrations of NaOH at room temperature. Mylar and epoxy masks limited the corroding region to a circular area centered on the sample's top surface. In area-test experiments, we used 0.1M NaOH and varied the corroding area from 8% to 85% of the top-surface area. In pH-test experiments, the corroding area was 17% and we used 0.01 to 0.5 M NaOH. The cumulative magnetic activity for the area-test samples increased linearly with both mass loss ($r^2 = 0.74$) and corroding area ($r^2 = 0.76$). In the pH-test, the relationship between the cumulative magnetic activity and mass loss depended upon whether the corrosion attack was homogeneous or inhomogeneous, particularly at very high corrosion rates ($[NaOH] > 0.1M$). The masked metal outside of the corroding area served as an antenna to couple the secondary corrosion currents into a region where the currents obeyed Laplace's equation and hence could be attributed to effective current sources. The voltage gradients associated with these magnetically-imaged currents are about 10 nV/cm.

2:00 PM H2.3
MICROSTRUCTURE AND LOCALIZED CORROSION INITIATION ON Ni-BASED ALLOYS. <u>Peter J. Bedrossian</u>, Adam J. Schwartz, Wayne E. King and Mukul Kumar, Division of Materials Science and Technology, Lawrence Livermore National Laboratory, Livermore CA.

Using an combination of Atomic Force Microscopy (AFM) and Orientation Imaging Microscopy (OIM), we have observed preferential grain-boundary attack of several Ni-based alloys, including Inconel 600 (Ni/Cr/Fe), Alloy 22 (Ni/Cr/Mo/W), type 316 stainless steel, and commercially pure Ni Grade 201 in acidic environments. While these alloys have very different rates of general corrosion, they still show common microstructural dependence of their local corrosion. The relative degree of grain boundary attack on a particular specimen correlates strongly with grain boundary orientation, with the more aggressive attack occuring at random boundaries. Triple junctions of three or more random grain boundaries generally show enhanced attack compared with junctions of special boundaries. The degree of attack of individual, random grain boundaries is generally modulated by intersection with a special boundary such as a sigma-3 twin. The results are consistent with models of grain boundary energetics, which would predict the strongest susceptibility at random boundaries, and are relevant to the development of grain boundary engineering for corrosion control. The work was performed at LLNL under the auspices of the US Department of Energy under Contract W-7405-Eng-48.

2:15 PM H2.4
CORROSION OF PARTICULATE-REINFORCED TITANIUM-MATRIX COMPOSITES. <u>Bernard S. Covino, Jr.</u>, David E. Alman, U.S. Department of Energy, Albany Research Center, Albany, OR.

The corrosion behavior of a series of titanium-matrix composites reinforced with TiC and TiB_2 particles has been studied. The composites were produced via powder metallurgy methods by mixing Ti powder with either 0, 2.5, 5, 10 or 20 volume percent TiC or TiB_2 powder. Subsequent to mixing the composites were pressed and sintered in vacuum to produce near fully dense composites. The potentiodynamic polarization technique was used to assess active-passive behavior, to measure corrosion rate, and to prepare surfaces for further evaluation. All composites and alloys were tested in deaerated 2 wt% HCl at temperatures of 50, 70, and 90°C. The morphology of the corrosion attack was analyzed using analytical scanning electron microscopy. Results suggest that TiB_2 additions increase the corrosion rate of Ti but TiC additions have little to no effect. Higher temperatures generally lead to higher corrosion rates. The behavior of the composites was compared to a variety of commercial Ti alloys, including CP-Ti and Ti-6Al-4V.

2:30 PM H2.5
CORROSION RESISTANCE OF ION NITRIDED AISI 304 AND 316L STAINLESS STEEL. <u>R. Vallerio</u>, J. Chen, M. Landis, B.C. Giessen, Barnett Institute and Dept. of Chemistry, Northeastern University, Boston, MA; R. Hidalgo, Springfield Technical Community College, Springfield, MA; K. Marchev, Norton Diamond Film, Northboro, MA.

As the technology of ion nitriding stainless steels progresses, it becomes imperative to examine the effect of nitriding on the corrosion resistance of the surface treated steel. This work will give some insight into the relationship between the conditions of the nitriding and the corrosion resistance of the surface layer through the effect of structure. By varying the nitriding conditions, single or multi-phase layers can be obtained, leading to dramatic changes in the corrosion resistance. As reported earlier, a textured tetragonal martensitic phase (m phase) can be produced under mild conditions. The corrosion resistance of m phase was found to be superior to that of a mixture of phases (ϵ and γ')present after higher temperature treatments.

3:15 PM *H2.6
RECENT COMPUTATIONAL AND EXPERIMENTAL INVESTI-GATIONS OF CREVICE CORROSION. <u>R.G. Kelly</u>, J.S. Lee, M.L. Reed, X. Wang, School of Engineering and Applied Science, University of Virginia, Charlottesville, VA.

Studies to determine the mechanisms and controlling factors of crevice corrosion have been limited by size considerations; generally, experiments have had to have been performed with samples large enough to allow macroscopic measurement instrumentation to fit within the crevice gap. A method for constructing creviced samples with relevant gaps (0.1 to 10 microns) and relevant depths (0.1 to 10 mm) has been developed utilizing the fabrication techniques used in semiconductor device processing. These techniques involve the deposition and patterned etching of several layers of structural and sacrificial material on Si wafers. The crevice substrates contain arrays of electrodes of the metal to be studied separated by walls of oxide. The electrodes have individual electrical connections so that the current from each can be measured. The crevice substrates are coupled to crevice formers that contain oxide posts used to maintain a constant crevice gap. The fabrication techniques not only produce samples on a size scale comparable to practical crevices, but also result in excellent uniformity of the crevice dimensions, a critical need for comparison of these measurements to computational models. This uniformity is the key to comparisons because mathematical models, in the interest of coding complexity and speed, use relatively simple boundary conditions. The range of applicability of the crevice samples and crevice formers so produced will be discussed.

3:45 PM H2.7
THE SIGNIFICANCE OF THE TEMPERATURE CHANGE ON THE POTENTIAL PROFILE INSIDE CREVICE-CORROSION CAVITIES. <u>Mohammed Ismail Abdulsalam</u>, Chemical and Materials Engineering Department, King Abdulaziz University, Jeddah, SAUDI ARABIA.

Crevice corrosion is one of the common forms of localized corrosion that reduces the service life of metals. It is considered one of the most serious forms of corrosion that is still under investigation. However, most of these works have been done at ambient temperature. In this work the crevice corrosion in commercially pure Ni specimens was investigated in 225 ml 1N sulfuric acid at temperatures; 25, 45 and 70°C. For this purpose an effective artificial crevice cell was used which enabled the observation of active corrosion activity inside the cavity. The potential at the surface next to the crevice mouth was kept constant at 400 mV (SCE) in the passive region of the polarization curve. The crevice dimensions were; 10 x 5 x 0.3 mm. The crevice was designed with both ends open, and its mouth was positioned facing the electrolyte in a downward position. This setup allows mixing between the crevice and the bulk solutions. Important surface morphology of the crevice region was photographed. Potential distribution measurements inside the crevice, using a fine glass microprobe, showed a large potential drop inside the cavity with the potential more steep as the temperature of the electrolyte increased. A large potential drop of about 600 mV was measured at 70°C, while the potential at the bottom of the crevice was found to be around 200 mV more active than that recorded at room temperature. The crevice

corrosion current also increased as the temperature increased. The effect of increasing temperature on the anodic polarization behavior was investigated on a flat Ni specimen in the 1N sulfuric acid. From these results it was seen that crevice corrosion occurred when the potential dropped inside the crevice to potentials inside the active region of the polarization curve. These findings are shown to be in agreement with the IR theory of crevice corrosion.

4:00 PM H2.8
THE PITTING BEHAVIOR OF TYPE 321 STAINLESS STEEL IN SULFIDE CONTAINING CHLORIDE AQUEOUS ENVIRON-MENTS. H.C. Shih, Y.M. Liou, S.Y. Chiu, J.W. Hsu, National Tsing Hua Univ, Dept of Materials Science and Engineering, Hsinchu, TAIWAN.

The pitting behavior of type 321 stainless steel in sulfide-containing chloride aqueous environments was studied using cyclic potentiodynamic polarization. A well-established correlation between H_2S and $Na_2S_2O_3$ in the study of corrosion was applied, that is, H_2S was simulated by $Na_2S_2O_3$. The major factors affecting the pitting corrosion of type 321 stainless steel are the Cl^-- concentration, solution pH and temperature. The results clearly indicate that both E_{pit} and E_{pp} decreased with increasing Cl^- concentration and temperature, while I_{pass} is more sensitive to temperature variation. E_{pit} decreased with decreasing pH in the range $2 < pH < 7.5$. The surface morphology and chemistry of the corroded type 321 stainless steel resulting from anodic polarization in 0.01M $S_2O_3{}^{2-}$-containing Cl^- solution were analyzed by XRD, SEM, and EPMA. A higher concentration of sulfur was found in the pits, and the dark surface film was mainly composed of FeS and γ-Fe_2O_3. The results describe the pitting behavior of type 321 stainless steel in sulfide-containing environments.

4:15 PM H2.9
MICROSTRUCTURAL ANALYSIS OF CO_2 CORROSION PRODUCT IN CARBON STEEL UNDER MULTIPHASE FLOW CONDITIONS. Kedar Sapre, Sudipta Seal, Vimal Desai, University of Central Florida, Dept of Mechanical, Materials and Aerospace Engineering, Orlando, FL; Paul Jepson, Madan Gopal, Ohio University, Dept of Chemical Engineering, Athens, OH.

The objective of this study is to understand the effects of flow on the morphology of the carbon steel coupons exposed to two types of multiphase flow conditions: full pipe and slug flow. The interaction of carbon dioxide (CO_2) with carbon steel, during the transport of oil and gas though pipelines, is a common occurrence in the oil and petrochemical industries. The corrosion products, formed on the surface of the carbon steel coupons exposed to corrosion, underwent surface morphological and chemical analysis using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Energy Dispersive Spectroscopy (EDS), X-Ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). SEM revealed the nature of the corrosion product layer (CPL) and its thickness with flow. Microstructural analysis of the CPL provided insight to the topographical variations on the surface as a function of various multiphase flow conditions. A coupon exposed to full pipe flow has a smooth surface whereas that of the slug flow is more rough and patchy. These variations on the surface were also seen in high-resolution AFM images and were confirmed with the measurement of its surface roughness. The use of XPS and AES help us to understand the surface chemical interactions occurring at varying flow conditions. Thus, the use of these characterization techniques helps to analyze the effect of carbon dioxide corrosion on the surface of 1018 carbon steel by identifying various chemical species present in the corrosion product layer. (This work is funded by National Science Foundation Grant and NSF/IUCRC Ohio University)

4:30 PM *H2.10
SOME UNSOLVED PROBLEMS IN CORROSION SCIENCE (A PERSONAL AND HISTORICAL VIEW). Roger C. Newman, UMIST, Corrosion and Protection Centre, Manchester, UNITED KINGDOM.

Corrosion science needs new challenges and initiatives, particularly in the field of metal passivity, where a cost-benefit analysis might be embarrassing to those of us working in that field (compared, say, with polymer coatings). However for the purposes of this talk we shall revert to the foundations of the subject without prejudice as to utility, and address the major issues identified by pioneers such as Evans and Uhlig. Some of these, such as the physical nature of the passive film, have been answered at quite a deep level, while others of equal if not greater importance have been neglected. Anodic stress corrosion cracking of metals has almost died out as a research topic, but still contains rich challenges. As Evans said (I am quoting from memory since the deadline is imminent, and he probably said it more elegantly): The chief drawback of subsidised research is that one is apt to enquire too much after effects and not enough after causes.

SESSION H3: PASSIVE FILMS AND THEIR BREAKDOWN
Chairs: Mary P. Ryan and Paul M. Natishan
Tuesday Morning, April 25, 2000
Golden Gate C3 (Marriott)

8:30 AM *H3.1
SCANNING ELECTROCHEMICAL MICROSCOPY OF ELECTRON-TRANSFER ACTIVITY AT THIN OXIDE FILMS. Irina Serebrennikova, Solomon B. Basame, Henry S. White, Department of Chemistry, University of Utah, Salt Lake City, UT.

Electron-transfer reactions at native oxide films (approximately 2 nm thick) on titanium (hereafter designated as Ti/TiO_2), tantalum (Ta/Ta_2O_5), and aluminum (Al/Al_2O_3) have been investigated in aqueous and non-aqueous solutions using scanning electrochemical microscopy (SECM). SECM images demonstrate that electron transfer occurs at randomly distributed, microscopic defect sites on the oxide films. The electroactive sites have dimensions ranging from 1 to 50 micrometers. SECM-based analysis also allows quantitative evaluation of the current density of individual redox-active sites as well as the dimensions of the sites. The methodology is generally applicable to any heterogeneous surface containing an arbitrary number of randomly positioned sites, each of different size and/or displaying different electron-transfer kinetics. We show that a small number of microscopic electroactive sites, occupying a remarkably small percentage of the total exposed area, can dominate the overall electrochemical behavior of oxide film-covered electrodes. We also show that SECM imaging can be used to predict the position of oxide film breakdown.

9:00 AM H3.2
IN-SITU HYDRATION AND ELECTROCHEMICAL MODIFICATION OF TITANIUM/TITANIUM OXIDE. Jane Bearinger, Chris Orme, Lawrence Livermore National Laboratory, Medical Technology Program and Chemistry and Material Science, Livermore, CA; Jeremy Gilbert, Syracuse University, Dept of Bioengineering and Neuroscience, Syracuse, NY.

Titanium and its alloys are commonly used in naval, aerospace and biomedical applications due to their high strength, low density, and biocompatibility. Formidable lifetime issues arise from fatigue, tribological, electrochemical, and biological origins, all of which affect titanium's protective oxide coating. Traditionally, the oxide and its topography have been studied using vacuum-based techniques. However, the electrochemical environment in an aqueous solution influences the near-atomic structure of the titanium surface. The objective of this research was to image hydration, and electrochemically-induced oxide growth and reductive dissolution in-situ using atomic force microscopy (AFM). Sputtered and polycrystalline titanium were studied. Titanium was sealed in a flow cell, and configured in a three electrode system. The native TiO_2 film was first imaged dry. To study hydration, the fluid cell was filled with acetonitrile with 0.1M salt. A 10% (v/v) water solution was then pumped through the fluid cell. Continuous images and open circuit potentials were recorded. In other experiments, phosphate buffered saline (PBS) was injected into the fluid cell to investigate the TiO_2 surface in a more physiological setting. In-situ imaging proceeded while the voltage was potentiostatically changed from cathodic to anodic. Step Polarization Impedence Spectroscopy (SPIS) was used to characterize the electrical properties of the TiO_2 film. The results of these experiments show that vacuum techniques such as XPS and Auger are limited in studying the oxide in its native, hydrated state. Excursions in potential alter the dimensions of the surface oxide of titanium. The hydrated oxide domes grew laterally over time; cathodic potentials revealed a more plate like surface and anodic potentials led to nucleation of oxide domes . Oxide film resistance increased and capacitance decreased with increasing potential. ACKNOWLEDGEMENTS: This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng.48.

9:15 AM H3.3
THE EFFECTS OF ANIONS ON THE PASSIVE FILM AND PASSIVE FILM BREAKDOWN ON TITANIUM AT DIFFERENT pH - A CYCLIC VOLTAMMETRY AND SURFACE ANALYSIS STUDY. R. Schennach, A. Taiyabi and D.L. Cocke, Lamar University, Gill Chair of Chemistry and Chemical Engineering, Beaumont, TX.

Passive films on titanium were prepared by potentiodynamic polarization in the presence of a range of anions and at various pH values. Incorporation of anions is found to produce unique transpassive peaks in the cyclic voltammograms, that appear to be associated with an amorphous to crystalline transition and subsequent enhanced species transport along the resulting grain boundaries. With addition of molybdate to the electrolyte a new peak in the reverse cycle of the voltammograms was found, that indicates a change in the

Mo oxidation state. The onset of pitting corrosion in the transpassive region can be qualitatively described by $E_{np}=E_c+\eta+\Phi+E_{inh}$. Where E_{np} is the pitting potential, E_c the corrosion potential in acidified solution, η the polarization necessary to obtain a current density high enough to maintain acidity inside the pit, Φ the potential drop inside of the pit and E_{inh} the contribution to the pitting potential resulting from inhibitors present. The variation in the cyclic voltammetry scans along with the results from surface studies have been used to describe the passive to transpassive transition and to present a model that involves chemically bound water oxidation and local oxygen evolution. The effects of either ohmic drop and/or local acidification are presented as well.

9:30 AM H3.4
THE STRUCTURAL AND MECHANICAL CHARACTERISTICS OF PASSIVATING FILMS GROWN UNDER VARIOUS ELECTROCHEMICAL CONDITIONS. M. Pang, D.E. Wilson and D.F. Bahr, Mechanical and Materials Engineering, Washington State University, Pullman, WA.

Oxide films were grown on polycrystalline grade II titanium by electrochemical polarization methods. Electropolished titanium samples were polarized in aerated 0.1 M sulfuric acid from open circuit to a final potential of 9 V (vs. Ag/AgCl). Three different polarizing methods were used: (i) ramping at 1mV / s, (ii) ramping at 100 mV / s and (iii) step polarization. The anodized films exhibited distinctly different structures. The mechanical properties of three films were examined by nanoindentation testing while the films were growing. This allows transient and steady state information on the mechanical properties to be determined. The load - depth curves showed that the strengths of these three films varied. The slowly grown film was soft and loose. No film fracture event happened, but the film could also not support any substantial stresses. The rapidly grown film and the step-polarized film were harder and denser. The excursion phenomenon, which indicated film fracture happened, and the excursion loads were different for each film. Furthermore, the chemical structure of these three films were examined by XPS technique. The relationship of structural and mechanical properties in anodized passivating films is explored in detail. Additional testing on stainless steel alloys is presented, demonstrating that technique developed for determining the strength of passive films can be examined on a variety of engineering alloys.

10:15 AM H3.5
STRUCTURAL CHANGES IN THE PASSIVE FILM ON IRON DURING OXIDATION AND REDUCTION - AN X-RAY SCATTERING AND REFLECTIVITY STUDY. Mary P. Ryan, Department of Materials, Imperial College of Science Technology and Medicine, London, UNITED KINGDOM; Michael F. Toney, IBM Almaden Research Center, San Jose, CA; Lucy J. Oblonsky, DuPont CR&D, Wilmington, DE.

The structure of the passive film formed on iron at a high potential in near-neutral solutions has recently been elucidated by using X-ray scattering techniques [1]. The film is not identical to any bulk phase and is a nanocrystalline, highly defective spinel. The passive film that is formed at low potentials in the passive range is qualitatively similar to the high potential film but significant changes in the diffracted intensity are observed with time. Specifically, the change in integrated intensity (measured for the (404) peak) with time was found to exhibit a two stage increase. The total integrated intensity after several days was found to approach a limiting value that was independent of applied potential. The observed changes in diffracted intensity may be related to either a thickening of the film or to a slow crystallization of the low potential film. X-ray reflectivity measurements are being employed to distinguish between these postulates and preliminary results will be presented. X-ray scattering measurements have also been performed during cathodic reduction of the passive film in alkaline solutions. In this case the film is known to undergo a solid state conversion to a lower valent oxide or hydroxide film [2]. Our results indicate a sudden change in structure occurs as the potential is stepped below the Fe3+ / Fe2+ equilibrium potential and the species formed is similar to, but not identical to, Fe(OH)2. The structures formed during potential cycling in alkaline solutions will be briefly discussed. 1) M.F. Toney et al. Phys. Rev. Lett. 79, 4282 (1997). 2) see for example: P. Schmuki et al. J. Electrochem. Soc, 143, 574 (1996).

10:30 AM H3.6
PASSIVITY AND PITTING SUSCEPTIBILITY OF BULK AMORPHOUS AND CRYSTALLINE $Zr_{55}Al_{10}Cu_{30}Ni_5$ ALLOYS. K. Buchholz, J. Eckert, A. Gebert, L. Schultz, IFW Dresden, Institute of Metallic Research, Dresden, GERMANY.

Bulk amorphous $Zr_{55}Al_{10}Cu_{30}Ni_5$ alloy samples were prepared by die casting into a copper mould. The microstructure of the samples was investigated by X-Ray Diffraction (XRD), Optical (OM) and Scanning Electron Microscopy (SEM). Their electrochemical behaviour was studied by cyclic potentiodynamic polarization and current transient measurements in aqueous electrolytes in a wide pH-range (pH=0.5-13) at ambient temperature in comparison to the behaviour of the crystalline alloys and the main alloying element zirconium. Both alloys form strongly passivating films, similar to the valve metal zirconium. These films consist of oxides of all alloying elements. Auger Electron Spectroscopy (AES) reveals a gradient in composition in cross-sectional direction. Electrochemical Impedance Spectroscopy (EIS) was applied to characterize the electrode behaviour of the oxide covered $Zr_{55}Al_{10}Cu_{30}Ni_5$ samples. In weakly alkaline sulphate electrolyte (pH= 8) the nonpolarized and anodically polarized bulk amorphous and crystalline samples show a capacitive behaviour in a wide frequency range indicating a strong barrier effect of the grown surface films which act predominantly as dielectric material. In 0.001M and 0.01M NaCl electrolytes, the bulk amorphous alloy samples are susceptible to pitting corrosion. This was found to be due to the existence of micrometer-sized crystalline inclusions in the amorphous matrix. Detailed information of the shape of the pits were obtained by Atomic Force Microscopy (AFM). Investigations on hot water oxide layer formation on bulk amorphous alloy samples at 423 K and 523 K reveal a significantly lower barrier effect of these layers compared to that of passive films formed at ambient temperature. From AES investigations layer thicknesses are estimated to be about 30 nm and more than 3 μm for layers formed at 423 K and 523 K, respectively. SEM investigations reveal a coarse-grained structure of hydrothermally formed oxide layers.

10:45 AM H3.7
ON THE CORROSION BEHAVIOUR OF BULK GLASS-FORMING $Mg_{65}Y_{10}Cu_{25}$. A. Gebert, U. Wolff, J. Eckert, L. Schultz, IFW Dresden, Institute of Metallic Materials, Dresden, GERMANY.

The corrosion behaviour of Mg-based alloys strongly depends on their composition and on their microstructure. Amorphous samples of the bulk glass-forming $Mg_{65}Y_{10}Cu_{25}$ alloy were produced by rapid quenching using the single roller melt-spinning technique in an argon atmosphere. Furthermore, crystalline cylindrical bulk samples with 5 mm diameter were prepared by die casting into a copper mould. The alloy samples were characterized regarding their microstructure by X-ray diffraction (XRD), optical and scanning electron microscopy (OM, SEM) and regarding their thermal stability by differential scanning microscopy (DSC). The general corrosion behaviour of the amorphous alloy in comparison to that of the crystalline alloy and the pure magnesium was investigated in borate buffer solution (pH=8.4) and in sodium hydroxide solution (pH=13) by potentiodynamic and potentiostatic polarization measurements and by impedance spectroscopy. The pitting susceptibility is checked in chloride containing electrolytes (pH=8). Electrochemically treated sample surfaces were subsequently characterized by means of Auger electron spectroscopy (AES) and SEM combined with energy-dispersive X-ray analysis (EDX). In borate buffer solution, the free corrosion potential of the amorphous alloy was found to be about 1000 mV more positive than that of pure magnesium. Corrosion current densities and passive current densities as well as polarization resistances measured are two orders of magnitude lower than the values for magnesium. This indicates a significantly improved corrosion resistance for the amorphous alloy by formation of more protective surface films under participation of all alloying elements. In sodium hydroxide electrolyte, the electrochemical behaviour of the amorphous alloy is very similar to that of magnesium. In contrast, the crystalline alloy shows lower corrosion resistance. Oxide film formation processes are discussed in detail. In chloride electrolytes, amorphous $Mg_{65}Y_{10}Cu_{25}$ alloy samples are susceptible to pitting which mainly results from surface inhomogeneities.

11:00 AM H3.8
THE GENERATION AND ROLE OF SURFACE DEFECTS ON LOCALIZED CORROSION INITIATION ON AMORPHOUS ALUMINUM OXIDE FILMS. Kevin R. Zavadil, J. Charles Barbour, Sandia National Laboratories, Albuquerque, NM.

Ion adsorption at the surface of native aluminum oxide films is believed to impact corrosion initiation in aqueous environments. One approach to testing the role that ions play is to generate specific defects active to ion adsorption at the surface of the oxide and investigate the electrochemical expression of these defects. Controlled, reproducible, amorphous alumina films are grown by generating a 3 nm, self-limiting oxide on aluminum films by exposure of an evaporated Al film to an oxygen electron cyclotron resonance (ECR) plasma. Electron irradiation in vacuum is used to generate oxygen vacancies at the surface through an electron stimulated desorption mechanism. A combination of Ultraviolet (UPS), X-ray (XPS) and Auger (AES) photoelectron and electron spectroscopies are used to characterize the surface composition prior to and after defect generation, as well as after immersion. Films are transferred to a contiguous electrochemical cell to study the impact of immersion in

water and in dilute aqueous NaCl solutions at open circuit and under potential control. We find that irradiation results in a total dehydroxylation of the near-surface in the initial films. The defective surfaces are active toward atomic chlorine adsorption with surface concentrations reaching 10^{14} atoms/cm^2 or approximately 10% oxygen defect levels. Chlorine is hydrolyzed from the surface with immersion in water. Immersion on the order of hundreds of seconds is not sufficient to restore original hydroxide levels in the near-surface region of the film, indicating that sub-surface defects are not readily titrated and remain active in solution. We demonstrate that bulk defects generated at higher electron energies shift the pitting potential of these films to lower potential. We will discuss the activity and role of near-surface constrained defects as a function of potential. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

11:15 AM H3.9
THE ROLE OF PASSIVE FILM HYDRATION IN THE PITTING OF ALUMINUM. <u>Bruce Bunker</u>, Gerald Nelson, Doug Wall, Charles Barbour, John Sullivan, Sandia National Laboratories, Albuquerque, NM; Chuck Wendisch, Mark Engelhard, Don Baer, Pacific Northwest National Laboratory, Richland, WA; John Hren, North Carolina State University, Raleigh, NC.

Migration of defects such as aluminum vacancies through protective oxide films has long been thought to influence pit initiation in aluminum and other passive metals. However, the concentration and mobility of such vacancies are orders of magnitude too low to explain the kinetics of pit initiation. Alternate defects to consider in rationalizing film breakdown are hydroxyl groups incorporated into the oxide film. It is known that oxide films hydrate and can form oxyhydroxide or hydroxide phases in water. The concentration and mobility of defects associated with hydration are expected to be much higher than those of aluminum vacancies in pure alumina. Secondary ion mass spectrometry (SIMS) has been used to determine the concentration and mobility of hydrogen, oxygen, and chloride ions in thermal oxides exposed to isotopically labeled NaCl solutions under a range of cathodic and anodic polarizations. The results show that the native oxide contains several atomic percent hydrogen after exposure to water. Both hydrogen and oxygen from labeled water are readily incorporated into the oxide layer. Under anodic polarization above the pitting potential, thick layers of AlOOH form. Implications of the SIMS results to mechanisms for the pitting of Al are discussed. Some of the SIMS experiments were performed at the Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94Al8500. Work was funded by the Division of Materials Sciences in the Office of Basic Energy Sciences.

11:30 AM *H3.10
CHLORIDE UPTAKE BY POLYCRYSTALLINE ALUMINUM AND ALUMINUM SINGLE CRYSTALS AS DETERMINED BY X-RAY PHOTOELECTRON AND X-RAY ABSORPTION SPECTRO-SCOPY. <u>P.M. Natishan</u>, Naval Research Laboratory, Washington, DC; S.Y. Yu, Naval Research Laboratory, Washington, DC; D.E. Ramaker, George Washington Univ., Washington, DC; W.E. O'Grady, Naval Research Laboratory, Washington, DC.

The uptake of chloride by polycrystalline and aluminum single crystals polarized at potentials below (less positive than) the pitting potential in 0.1M NaCl solutions as determined using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy will be discussed. The X-ray absorption near edge structure (XANES) spectra were obtained using electron yield and fluorescence detectors at the NSLS. The spectra were obtained concurrently for samples polarized in chloride solutions. In the case of the polycrystalline aluminum, two distinct peaks were observed in the electron yield spectrum. The peak at 2833 eV was attributed to Cl- on the surface of the oxide, while the peak at 2836 eV was associated with Cl- within the oxide film. In contrast, the surface species, which is evident as a distinct peak at 2833 eV in the electron yield, appears as a slight shoulder in the fluorescence spectra. The electron yield results also confirmed the presence of two distinct chloride species as seen in XPS spectra. The electron yield and XPS results show that Cl- was incorporated into oxide film on aluminum prior to pit initiation and that chloride movement into the oxide film did not occur until a specific potential was reached. The XPS spectra also provided evidence that the oxide film was thinning before the pitting potential was reached.

SESSION H4: OXIDE FILMS
Chairs: J. Charles Barbour and Hugh S. Isaacs
Tuesday Afternoon, April 25, 2000
Golden Gate C3 (Marriott)

1:30 PM H4.1
MODELING OF THE PASSIVE FILM ON NICKEL-CHROMIUM-MOLYBDENUM ALLOYS. <u>Osvaldo Pensado</u>, Darrell Dunn, Gustavo Cragnolino and Narasi Sridhar, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX.

This paper presents the results of modeling the passive dissolution behavior of nickel-chromium-molybdenum alloys, in particular of Alloy 22, using a modified version of Macdonalds Point Defect Model (1). Alloy 22 (Ni-22Cr-13Mo-3W-5Fe) is a candidate material for the construction of disposal containers for high level radioactive waste, and therefore, accurate predictions of passive corrosion rates over a long time span (thousands of years) are needed. Since corrosion resistant alloys such as Alloy 22 display preferential dissolution of certain alloying elements (e.g., Ni, Mo), possible changes in the alloy composition are envisioned that could affect the long-term steady-state passive dissolution rates. Model calculations are presented and discussed in the context of experimental data obtained in short term potentiostatic measurements. Acknowledgments: The paper was prepared to document work performed on behalf of the Nuclear Regulatory Commission, Office of Nuclear Material Safety and Safeguards, under Contract No. 02-07-009 and does not necessarily reflect the views or regulatory position of the NRC. (1) Digby D. Macdonald, J. Electrochem. Soc., Vol. 139, (1992) p. 3434-3449.

1:45 PM H4.2
PASSIVATION MECHANISMS OF ION BEAM DEPOSITED Cr-Mo NITRIDE COATINGS. <u>J. Derek Demaree</u>, Wendy E. Kosik, Army Research Laboratory, Aberdeen Proving Ground, MD; Clive R. Clayton, Gary P. Halada, Dev Chidambaram, State University of New York at Stony Brook, Stony Brook, NY.

The aqueous corrosion behavior of metal nitrides is strongly affected by the presence of nitrogen at the interface between the passive layer and the solution. Hard nitride coatings, often considered candidates to replace electroplated chromium in tribological applications, can provide greater corrosion resistance than chromium through the development of a thin, highly bipolar passive film with significant incorporation of ammonium ions and cation-selective oxyanions. In this study, coatings of Cr-N, Mo-N, and Cr-Mo-N have been synthesized with ion beam assisted deposition (IBAD), using 1 keV nitrogen ions and e-beam vapor deposition, in an attempt to understand the synergisms involved in the production and incorporation of these protective oxyanions in the passive films formed on these alloys. The chemical and phase composition of the coatings were examined using Rutherford backscattering spectrometry (RBS) and x-ray diffraction, their aqueous corrosion behavior in dilute hydrochloric acid was studied by electrochemical techniques, and the chemistry of the passive oxides formed was examined using angle-resolved x-ray photoelectron spectroscopy (XPS). The effect of nitrogen and metal species on the passive film structure will be discussed, as will the consequences of this passive film formation on corrosion resistance.

2:00 PM H4.3
MECHANISMS OF PLASTIC DEFORMATION ARE RESPONSIBLE FOR THE METAL CORROSION. <u>Valery P. Kisel</u> and A.D. Styrkas, Inst. of Solid State Physics, Chernogolovka, Moscow Distr., RUSSIA.

The remarkable finding of this work is the new fundamental understanding of the oxide breadown and the subsequent metal corrosion (C) within the framework of oxide film-metal plastic deformation under current/piezo effect stresses. The current density, i, vs potential, U, curves can be examined as the mechanical strain-stress curves up to the fracture-damage (electrical break-down)[1]. In this case the anode C means its slow deformation - fracture, so the dependences of growing C-thickness on time, current density, temperature for various materials [2] are similar to the standard creep (the delay time, transient and steady stages) or strain-stress curves. Therefore the alternating current, half-wave rectified or direct anodic/cathodic current densities [2] play the role of alternating or half-wave pulsed/constant stresses which considerably increase dislocation motion/multiplication in crystals at low frequencies [3]. The intensification/reduction of C processes and the oxide breakdown may be concerned with compression-extension stresses in oxide films on the metal anode or with metal hardening/softening due to hard oxide film/film dissolution on the deformed metal under alternating current stressings. The deformation nature of C is confirmed by the C thickness - alternating current density hysteresis in soft metals and by the increase of microroughness as the current density increased [2] like it was for the development of dislocation microstructures under deformation [4]. The scaling of current densities at fixed electric fields for various voltammograms up to the fragmentation (fracture) of cathodic films and their correlation with grain sizes of corresponding films are similar to the correlations of the deformation stresses for atomic, micro- and macroscales of

observations in various crystal classes [4]. 1. Kisel V.P. MRS 2000 Spring Meeting, Symp. H, Abstract Book 2. Styrkas A.D. and Styrkas D., J. Appl. Electrochem.,1995,v.25, pp. 490-494. 3. Kisel V.P. and Erofeeva S.A., MRS 1999 Fall Meeting, Abstract Book 4. Kisel V.P., Physica Status Solidi 1995, v. 149 a, No 1, pp. 61-68

2:45 PM *H4.4
A COMBINATORIAL MICROLAB INVESTIGATION OF ATMOSPHERIC COPPER-SULFIDATION. <u>J.C. Barbour</u>, J.W. Braithwaite, J.P. Sullivan, N. Missert, W.G. Breiland, J.S. Nelson and K.R. Zavadil, Sandia National Laboratories, Albuquerque, NM.

An important aspect in developing a capability to predict the reliability of electronic components is a physics-based understanding of atmospheric copper corrosion. This topic has been investigated over the last few decades but debate continues concerning the mechanisms underlying even the initial stages of degradation. The difficulty being encountered is caused by the large number of coupled chemical reactions that depend on complex interactions of materials with the environment and the function of the copper-containing device. A solution to this multidimensional problem requires new experimental approaches that can quantitatively identify critical phenomena occurring in corrosion phase space. An effort is currently underway at Sandia to examine the usefulness of micro-combinatorial techniques as the basis for developing these needed efficient experimental approaches. The initial phase of this work is focusing on the specific topic of atmospheric copper sulfidation using H_2S as the sulfidizing agent. A combinatorial (parallel experimentation) matrix was made in which the copper oxide growth (oxide type and thickness), surface alloying, and point defect levels were varied systematically to test the mechanism of solid-state transport by vacancy mediated diffusion. Solid-state diffusion of vacancies and di-vacancies in Cu, Cu-alloys, Cu_2O, and Cu_2S may determine the kinetics of Cu sulfidation in one region of corrosion space. Advancements in the use of micron-scale probes, coupled into parallel experimentation, will be given. This work was supported by the U.S. DOE under contract DE-AC04-94AL85000.

3:15 PM <u>H4.5</u>
INITIAL OXIDATION OF Cu(210) STUDIED BY STM AND IV-LEED ANALYSIS. <u>Andrew T.S. Wee</u>, Y.P. Guo, K.C. Tan, H.Q. Wang, J.C. Zheng and C.H.A. Huan, Natl Univ of Singapore, SINGAPORE.

The oxidation of Cu is of great interest especially since the implementation of Cu in advanced IC interconnects. Although the chemisorption of oxygen on low index Cu surfaces has been the subject of a large number of studies, the technologically more important polycrystalline Cu surface is less amenable to model surface science studies. The Cu(210) surface may be a better model system for understanding the oxidation of complex polycrystalline surfaces since it has the maximum step density in the [001] zone comprising 100 terraces two atom rows wide separated by monatomic {110} steps. In this work, we present STM and IV-LEED data showing the formation of a Cu(210)-(2x1)O reconstruction as well as other (nx1) reconstructions after oxygen adsorption at various substrate temperatures. Quantitative IV-LEED analysis of the (2x1) structure confirms an added row model with oxygen sitting on the long bridge sites along the [001] direction. The stability of the (2x1) reconstruction at different oxygen partial pressures and temperatures is discussed. At higher temperatures and oxygen exposures, a range of faceting behaviour is also reported.

3:30 PM <u>H4.6</u>
SULFUR CHEMISTRY AT THE OXIDE-METAL INTERFACE: THE DESTRUCTION OF PROTECTIVE ALUMINUM OXIDE SCALES. <u>J.A. Kelber</u>, S.G. Addepalli, N. Magtoto and C. Niu, Department of Chemistry, University of North Texas, Denton, TX.

Results of surface science studies under controlled UHV conditions reveal the chemical mechanism whereby interfacial sulfur destabilizes protective alumina scales at metal substrates. The debonding of protective alumina scales from metal substrates is a long standing problem in aggressive corrosion environments, such as gas turbine blades. Auger studies of alumina films deposited on clean and S-modified Fe substrates show that at temperatures above 500 K, S will react with alumina to form metallic Al, which then diffuses into the Fe substrates. The concentration of metallic Al at the interface does not increase monotonically as the reaction proceeds, but achieves a steady-state concentration consistent with the following chemical reaction:

(1) Fe-S + Al-O → Al-S + Fe-O (ligand exchange)
(2) Al-S + 2 Fe → Al-Fe + Fe-S (formal reduction to Al^0)
(3) Al-Fe → Fe + (Al diffusion into bulk)

(No SO_2 formation is observed.)

Step (1) is quite endothermic, suggesting that the driving force for the overall reaction is (3), the diffusion of metallic Al into the bulk substrate. This is confirmed by performing the same experiment on a stoichiometric aluminide (e.g., $Al_2O_3/S/Ni_3Al(111)$). The experiment results in no interfacial reaction due to substrate aluminum inhibition of steps (2) and (3). The debonding of protective alumina scales from aluminide substrates in industrial practice is due to the formation of an aluminum-depleted layer beneath the oxide/metal interface during rapid oxidation. The above results provide a chemical mechanism for the observed effects of interfacial sulfur on protective alumina scales, and indicate that the effect can be inhibited by minimizing the Al depletion zone adjacent to the interface. The data also indicate that interfacial chemical reactions may occur counter to the apparent predictions of thermodynamics, due to the driving force of the diffusion of reaction products away from the reaction zone.

3:45 PM <u>H4.7</u>
EFFECTS OF DIRECTED VACANCY FLUX ON NUCLEATION AND GROWTH KINETICS OF CORROSION OXIDE LAYERS AT HIGH TEMPERATURE. <u>L.N. Paritskaya</u>, Dept. of Crystal Physics, Karazin Kharkiv National University, Kharkiv, UKRAINE; Yu S. Kaganovskii, Dept. of Physics, Bar-Ilan University, Ramat-Gan, ISRAEL.

The following two aspects of high temperature corrosion process have been studied: 1) nucleation and growth of oxide islands at local centers of oxidation at the crystal surfaces which are the sinks of vacancies; 2) layer oxide growth as a special type of reaction diffusion which includes interdiffusion of oxygen and metal atoms with unequal partial diffusion coefficients and accompanied with a vacancy flux directed towards the metal-oxide interface. The regularities of nucleation and evolution of oxide islands have been studied at $950°C$ in wet hydrogen atmosphere (dew point $\sim 25°C$) on Cu single crystal surfaces using two different sources of directed vacancy fluxes: 1) the Cu surface was a vacancy sink under Nabarro-Herring creep; 2) the vacancy flux was the result of interdiffusion in two layer Cu-Ni sample, and the Cu surface perpendicular to the Cu-Ni interface was a sink of vacancies. It has been found that the vacancy fluxes directed to Cu-surfaces in both cases increased the oxide island density and their growth rate. On the base of parabolic kinetics of oxide island growth the surface diffusion mechanism of this process has been proposed. The surface diffusion coefficients of Cu atoms have been calculated, which are in a good agreement with the literature data. The kinetics of Cu_2O and NiO layer growth in three layer samples Cu_2O-Cu-Cu_2O and NiO-Ni-NiO with inert marks between different layers has been studied in temperature ranges 600-1000°C for Cu and 900-1200°C for Ni oxidation in air atmosphere. Arrhenius equation for diffusion Cu in Cu_2O and Ni in NiO have been obtained and compared with the Arrhenius equations for tracer diffusion. Atomic mechanism for oxide growth under directed vacancy flux has been proposed.

SESSION H5/M5: JOINT SESSION:
GROWTH AND MORPHOLOGY AT THE OXIDE
SOLUTION INTERFACE
Chairs: Elias Vlieg and Karl Sieradzki
Wednesday Morning, April 26, 2000
Golden Gate C2/C3 (Marriott)

8:30 AM *H5.1/M5.1
INTERPRETATION OF MODEL CAPACITANCES IN TERMS OF THE STRUCTURE OF THE ELECTRIC DOUBLE-LAYER AT THE OXIDE-WATER INTERFACE. <u>Dimitri A. Sverjensky</u>, Johns Hopkins Univ., Dept. Earth and Planetary Sciences, Baltimore, MD.

Systematic analysis of surface charge as a function of pH and ionic strength for a wide range of metal oxides and 1:1 electrolytes in water has resulted in a set of internally-consistent model capacitances (C1) referring to the inner layer of the triple-layer model (TLM). The values of C1 show systematic trends with electrolyte cation radius that can be interpreted using electrostatic theory. The TLM assumes that a layer of electrolyte cations lies at an unspecified distance (b) from the 0-plane. It is hypothesized here that the distance b is determined by two layers which may interpenetrate: a layer of water molecules and the layer of electrolyte cations. It follows that the TLM capacitances can be regressed in terms of the cation radius yielding an interfacial dielectric constant equal to 37 and values of b characteristic of different solids. On rutile, anatase, magnetite and manganese dioxide, b is equal to 1.9A plus the crystallographic radius of the electrolyte cation: for the series Li, Na, and Cs, C1 decreases because b is equal to 2.6, 2.9 and 3.6A, respectively. On these solids, the alkali cations appear to be dehydrated and very close to the 0-plane, possibly forming inner-sphere complexes. In contrast, on hematite, b is equal to 2.1A plus the radius of the hydrated electrolyte cation. Consequently, for the series Li, Na, and Cs, C1 increases because b is equal to 4.6, 4.0 and 3.8A, respectively. Similar

considerations apply to goethite, silica and alumina, where Li and Na also appear to be hydrated, possibly forming outer-sphere complexes.

9:00 AM H5.2/M5.2
EVOLUTION OF CORROSION PROCESS ON METALLIC THIN FILM MEDIA. Andrei V. Mijiritskii, Frans C. Voogt, Dik O. Boerma, Groningen University, NVSF, Materials Science Centre, Groningen, THE NETHERLANDS.

Understanding the oxidation mechanism for multi-layered metal films is of high importance for preventing metal-based storage media from failure due to corrosion. In this work, the oxidation of epitaxial Ag/Fe and Ni/Fe bi-layers was studied by x-ray photoelectron spectroscopy (XPS), Rutherford back-scattering spectroscopy (RBS), nuclear reaction analysis (NRA), x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and conversion electron Mössbauer spectroscopy (CEMS). The epitaxial Ag/Fe and Ni/Fe bi-layers were grown on MgO(100) by molecular beam epitaxy (MBE) or laser ablation deposition (LAD) and subsequently subjected to *in situ* or *ex situ* oxidation in O_2 at elevated $(200-300°C)$ temperatures. Different O_2 pressures were applied in the range from 1×10^{-6} mbar to 100 mbar. In both Ag/Fe and Ni/Fe cases the oxidation of Fe was found to initiate through the structural defects present in the Ag or Ni overlayers. The defects consist of domain boundaries and pin-holes formed due to lattice mismatch. The further development of the Fe-oxide growth was found to depend on the overlayer material. Models explaining the observed large difference in oxidation behaviour of the two types of bi-layers are proposed. The dependence of the oxide growth on the O_2 pressure is also discussed.

9:15 AM H5.3/M5.3
EPITAXIAL ELECTRODEPOSITION. Julie K. Barton, Eric W. Bohannan, Run Liu, Mark G. Shumsky, Alexey A. Vertegel and Jay A. Switzer, Univ of Missouri-Rolla, Dept of Chemistry and Graduate Center for Materials Research, Rolla, MO.

The traditional synthetic routes to epitaxial films involve deposition from the gas phase. Epitaxy usually requires similar structures for the film and the substrate, as well as a good match of their lattice parameters. Recently, we reported electrodeposition of epitaxial δ-Bi_2O_3 [1], Cu_2O [2] and PbS [3] on single crystal Au substrates. Here, we extend this work to other oxide materials, including ZnO, Tl_2O_3 and α-PbO_2. These systems are characterized by either very high lattice mismatch (158% in the case of Tl_2O_3), or different lattice symmetry (hexagonal ZnO and orthorhombic α-PbO_2 on cubic Au). Epitaxy is achieved by forming coincidence lattices, in which the structure of the film is rotated with respect to the substrate. We also show the possibility of electrodepositing epitaxial semiconductor heterojunctions, such as Cu_2O/PbS(100) on single crystal Au(100). 1. J.A. Switzer, M.G. Shumsky and E.W. Bohannan, Science 284, 293 (1999). 2. E.W. Bohannan, M.G. Shumsky and J.A. Switzer, Chem. Mater. 11, 2289 (1999). 3. A.A. Vertegel, M.G. Shumsky and J.A. Switzer, Angew. Chem. Intl. Ed., in press.

9:30 AM H5.4/M5.4
MODELING THE COUPLED EFFECTS OF INTERFACIAL AND BULK PHENOMENA DURING SOLUTION CRYSTAL GROWTH. Yong-Il Kwon, Bhushan Vartak and Jeffrey J. Derby, Department of Chemical Engineering and Materials Science, Army HPC Research Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN.

Solution crystal growth processes are governed by complex interactions of bulk transport phenomena, surface diffusion, and crystal growth kinetics. Of critical practical importance is the stable growth of discrete facets of large crystals at fast rates. However, crystal quality is often compromised during fast solution growth by a host of morphological flaws including macrosteps, step bunches, and inclusions. These instabilities arise from the complex interplay between transport and kinetic factors. We present a novel model for the growth of a vicinal facet from solution, which couples surface phenomena and bulk effects. The surface kinetic model, based on the theory of Burton, Cabrera, and Frank (BCF), rigorously accounts for the interactions of discrete growth steps through surface diffusion fields, adsorption and desorption events, ledge growth kinetics with Schwoebel effects, and convective transport due to step motion. This model is self-consistently coupled with a bulk transport model which describes bulk diffusion to terraces, direct bulk diffusion to growth steps, and bulk convective transport due to step motion and applied flow fields. No analytical approximations are made, rather the simultaneous governing equations are solved numerically by an efficient, moving-boundary finite element method. The coupled transport-kinetic model is applied to elucidate mechanisms responsible for step growth dynamics which occur during solution crystal growth. Effects of solution hydrodynamics, different bulk and surface

diffusivities and incorporation rates, and the rate of generation of growth steps on the stability of a step train will be discussed.

10:15 AM *H5.5/M5.5
THE CRYSTAL-SOLUTION INTERFACE. Leslie Leiserowitz, Meir Lahav, Dept. of Materials and Interfaces, The Weizmann Institute of Science, Rehovot, ISRAEL.

Nucleation, growth, habit and composition of solution-grown molecular crystals are strongly affected by the nature of the solvent and the presence of molecular additives in the solution. This influence is primarily a result of interaction between the "foreign" molecules and the crystal faces. The structural nature of such interactions was, and still is, generally deduced from a knowledge of the crystal structure and from macroscopic properties, such as the morphology and symmetry of the resulting crystal.
Recently, molecular dynamics simulations and experimental methods such as atomic force microscopy, nonlinear optical spectroscopy, neutron and X-ray reflectivity, and grazing incidence X-ray diffraction (GIXD), have been applied to probe the structure of the crystal-fluid interface at the subnanometer scale. GIXD has matured on studies of metal and semiconductors surfaces and used for interfacial systems such as thin molecular films on water. The technique has begun to be applied to characterize the surfaces of minerals and the molecular crystal-solution interface.
The interplay between crystal nucleation, growth, morphology, twinning and the crystal-liquid interface shall be addressed where techniques such as GIXD have been applied to help elucidate the structure of the solid solution interface.

10:45 AM H5.6/M5.6
THE ACIDIC AND REDUCTIVE DISSOLUTION OF γ-MnOOH DURING THE SORPTION AND OXIDATION OF CR(III). Robert Weaver, Michael Hochella, Jr., Virginia Polytechnic Institute, Dept. of Geological Sciences, Blacksburg, VA.

The interaction of $Cr(III)_{aq}$ with Mn-oxide surfaces is complex, characterized by the simultaneous reductive dissolution of the Mn-oxide surface and oxidation of Cr(III) to the more toxic Cr(VI) species. Our experimental approach to understanding these reactions has been 3-fold: 1) to directly observe these surface reactions using fluid-cell AFM, 2) to identify and quantify the reaction products using XPS, and 3) to measure the aqueous concentrations of Cr_T, Cr(III) and Mn(II) using ICP and colorimetric analysis. Our in situ fluid-cell AFM observations show the growth of Cr microprecipitates and the dissolution of the manganite (110) and (100) surfaces to be spatially heterogeneous. Because of this heterogeneity, it is difficult to measure the rate of Cr-bearing microprecipitate growth or manganite dissolution. However, with exposure to a pH 4.5, $100\mu M$ Cr(III) solution for one hour, we have observed simultaneous growth and dissolution at the mineral-water interface. The Cr-microprecipitates cover existing hillocks to a thickness of up to approximately 2nm and do not appear to nucleate with preference along step edges. Observations of surfaces reacted for up to 30 hours show these precipitates to undergo continued growth or dissolution. SEM images of these reacted surfaces have revealed highly eroded, kinked steps in some areas. However, immediately adjacent step edges may appear undisturbed. These AFM and SEM observations suggest that the solution conditions are locally more aggressive at certain topographic or structural sites. XPS results from cleaved surfaces and powders reacted under conditions analogous to the AFM experiments show a progressive increase in Cr with time up to 8 hours, then remaining constant suggesting surface saturation. The oxidation states of the Cr and surface Mn, as determined from multiplet splitting, remain throughout the experiment as Cr(III) and Mn(III), respectively. Ongoing experiments are focused on measurement of Mn(II) and Cr(VI) concentrations produced as a function of time and initial [Cr(III)].

11:00 AM H5.7/M5.7
MISORIENTED ATTACHMENT: PREFERENTIAL DISSOLUTION IN HETEROGENITE (CoOOH). R. Lee Penn, Department of Earth and Planetary Sciences; Alan T. Stone, Department of Geography and Environmental Engineering; David R. Veblen, Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD.

High Resolution Transmission Electron Microscopy (HRTEM) results show a strong crystal-chemical and defect dependence on the mode of dissolution of synthetic heterogenite (CoOOH) particles. As-synthesized heterogenite particles are micron-size plates (aspect ratio ~1/30) constructed of crystallographically oriented ~3-nm primary particles or are single ~21-nm unattached heterogenite platelets (aspect ratio ~1/7). Reductive dissolution; using 10 μM to 2

mM hydroquinone, acetate buffer (pH ~4.6), and 0.4 mM total Co as heterogenite particles; was examined in order to evaluate morphology evolution as a function of reductant concentration. Two end-member modes of dissolution were observed: 1) non-specific dissolution of macroparticles and 2) preferential dissolution along misoriented boundaries. In the case of non-specific dissolution, average macro-crystal size and morphology is not altered as building block crystals are consumed. The result is web-like particles with similar breadth and shape as undissolved particles. Preferential dissolution involves the formation of channels or holes along boundaries of angular misorientation. Such boundaries involve only a few degrees of tilt, but dissolution occurs almost exclusively at such sites. Energy Filtered TEM thickness maps show that the thickness of surrounding material is not significantly different from that of undissolved particles. For comparison, unattached ~21-nm heterogenite particles underwent partial reductive dissolution using hydroquinone, and HRTEM results show dissolution primarily at the {101} and {102}, or edge, crystal faces and no significant dissolution at the (001), or basal, crystal faces. This suggests that the reactive surface area is dominated by edge faces and that basal faces are essentially non-reactive under these conditions. Finally, natural heterogenite from Goodsprings, Nevada shows morphology and microstructure similar to that of the synthetic heterogenite macroparticles.

11:15 AM H5.8/M5.8
HALOGEN CORROSION OF TiO$_2$: A FIRST-PRINCIPLES STUDY. Andrew A. Quong, Babak Sadigh, C.M. Schaldach and W.D. Wilson, Lawrence Livermore National Laboratory, Livermore, CA.

The corrosion of Ti shows an unusual dependence on which halogen anion is in solution. Cl, Br, and I are expected to have increasing pitting potentials, yet it observed that Br has a significantly lower pitting potential. In order to get a clearer understanding of the surface chemisty that governs this reaction, we have performed first-principles density functional calculations of the interaction of these anions on a TiO$_2$ surface. We consider the adsorption of these anions at different surface sites and address the role of surface defects. The influence of the electrochemical double layer is also considered.

11:30 AM *H5.9/M5.9
TOTAL ENERGY CALCULATIONS OF IRON AND ALUMINUM OXYHYDROXIDE BULK PHASES AND SURFACES. James R. Rustad and Kevin M. Rosso, Pacific Northwest Natl Lab, Richland, WA.

The intrinsic stabilities of the oxyhydroxide polymorphs constitute an important set of controls on the structures of hydroxide/oxyhydroxide precipitates on mineral surfaces. For example, as CrOOH grows on magnetite through chromate reduction, the fact that CrOOH has only been characterized in the heterogenite and manganite structures would suggest that other possible structures, such as the diaspore/ goethite structure may not be exhibited by CrOOH. On the other hand, it is possible that the structures are more a function of kinetics than of intrinsic lattice stability, with intrinsic equilibrium structural preferences playing only a minor role in which type of structure forms. To shed some light on this issue, plane-wave pseudopotential methods are used to investigate the structures and total energies of AlOOH and FeOOH in the five canonical oxyhydroxide structures: diaspore (goethite), boehmite (lepidocrocite), akaganeite, guyanaite, and grimaldiite. The local density approximation was used in conjunction with ultrasoft pseudopotentials in full optimizations of both AlOOH and FeOOH in each of these structures. Structures are in reasonably good agreement with experiment, with lattice parameters and bond lengths within 3 percent of the experimental ones. Neither AlOOH nor FeOOH have been identified in the grimaldiite or guyanaite structures, however we find that total energies for AlOOH and FeOOH in these structures are comparable to or lower than the total energies of the commonly observed polymorphs. The near equality of the total energies of each of the different polymorphs suggests that kinetic factors are more important in determining the structure of these polymorphs than intrinsic stabilities.

SESSION H6/M6: JOINT SESSION:
DISSOLUTION OF METALS AND ALLOYS
Chairs: Olaf M. Magnussen and Leslie Leiserowitz
Wednesday Afternoon, April 26, 2000
Golden Gate C2/C3 (Marriott)

1:30 PM *H6.1/M6.1
FUNDAMENTAL ASPECTS OF ALLOY DISSOLUTION. K. Sieradzki, Dept. of Mechanical and Aerospace Engineering, Arizona State Univ., Tempe, AZ.

Conventionally, the critical potential marks the onset of bulk

dealloying and the development of a bi-continuous solid/void microstructure. The current density below the critical potential is only weakly dependant on potential and the physical processes responsible for this passive-like behavior are poorly understood. We will present experimental data connecting the surface morphology evolution to the current density in each of these regions, and discuss analytical models that have been developed to describe this complex behavior.

2:00 PM *H6.2/M6.2
3D PATTERN FORMATION AND POROSITY IN BINARY ALLOY CORROSION. Jonah Erlebacher, Michael J. Aziz, Harvard University, DEAS, Cambridge, MA; Karl Sieradzki, ASU, Tempe, AZ.

Electrochemical dissolution of the less noble component of a binary alloy has long been known to result in extended three-dimensional nanoporous structures of the more noble species. We used a kinetic Monte Carlo model to examine the microscopic origin of such pore formation. We have found that a model that incorporates only (1) diffusion of all species and (2) dissolution of the less noble species exhibits the entire range of current/voltage behavior seen in real experiments. In particular, the model is quantitatively compared to dissolution data of Ag-Au alloys.

2:30 PM *H6.3/M6.3
DEALLOYING OF LOW INDEX Au$_3$Cu AND Cu$_3$Au SINGLE CRYSTALS: AN IN-SITU STM STUDY. Gerald A. Eckstein, Andrea S. Dakkouri, Hermann Kaiser, University of Erlangen-Nuremberg, Department of Corrosion Science and Surface Technology (LKO), Erlangen, GERMANY; Martin Stratmann, Max Planck-Institute of Iron Research, Dusseldorf, GERMANY.

Alloys are of great technological importance because their properties can be tailored by changing the chemical composition. Detailed information about the surface properties of alloys is essential for a deeper understanding of complex interfacial reactions in fields like selective corrosion and heterogenous catalysis. At present a detailed understanding of the selective corrosion of binary alloys is still lacking. We present a detailed study of UHV experiments, classical electrochemical results and in-situ STM investigations on low index Au$_3$Cu and Cu$_3$Au single crystals. The results were used to evaluate the mechanism of selective copper dissolution and formation of the Au-rich protective layer in the low current (E<E$_c$) potential region during anodic polarization of Au$_x$Cu$_y$ alloys.
The stability of binary alloys in aqueous environments depends on the alloy composition at the surface, their surface preparation and the electrolyte. For this reason the single crystals were prepared under UHV conditions and characterized by LEED, UHV-STM and surface X-ray diffraction (SXRD). These surface studies revealed new structural models for the topmost surface region and represent an ideal starting point for electrochemical and in-situ EC-STM studies on defined surfaces. Electrochemical studies in sulfate media by cyclic voltammetry and current-time transients enabled us to get a deeper understanding on different electrochemical behavior of low index single crystals. The Au$_3$Cu and Cu$_3$Au surfaces showed different critical regimes dependent on the netplanes. Kinetic data have been obtained which describe the early stages of dealloying. In comparison to sulfate media, chloride caused a decrease in E$_c$ which is also dependent on the netplanes.
In situ EC-STM was used to study the nature of surface morphology during dealloying of Au$_3$Cu and Cu$_3$Au at potentials below the critical potentials. The electrochemical behaviour was correlated with alteration of surface morphology observed by in situ EC-STM. The results demonstrate also the necessity of careful electrode preparation under UHV conditions to get reproducible data.

3:30 PM *H6.4/M6.4
IN-SITU STUDIES OF THE ATOMIC-SCALE DYNAMICS OF COPPER DISSOLUTION. Olaf Magnussen, Universität Ulm, Abteilung Oberflächenchemie and Katalyse, Ulm, GERMANY.

The anodic dissolution of a bare metal surface is one of the most basic processes in electrolytic corrosion, however, a detailed picture of the underlying microscopic mechanisms and dynamics is only emerging. The kinetics of metal dissolution are determined by the removal of atoms at atomic kinks in the steps on the crystal surface. We demonstrate here that the local rate of these atomic-scale processes, which can not be obtained from electrochemical measurements due to the generally unknown kink density, can be measured directly using methods based on in-situ scanning tunneling microscopy. As an example the anodic dissolution of Cu single crystals in acidic electrolytes was investigated, with particular emphasis on Cu(100) in HCl solution. The latter system is especially well suited for these studies, since the Cu surface is covered in the dissolution regime by an ordered c(2x2) Cl adlayer, which induces a pronounced facetting of the steps. This results in straight {001}-oriented steps with a very low density of structurally well defined kinks, facilitating the separation of individual kinks. Various approaches for the study of the fast dynamic

processes at individual kinks by in-situ STM are discussed. First we show that the motion of kinks along the step, which by far exceeds the temporal resolution of conventional scanning probe microscopes, can be directly observed by a novel high-speed electrochemical STM, recently developed in our group. Atomic resolution studies by this instrument with acquisition rates of up to 30 images per second confirm that local dissolution as well as the reverse local growth processes proceed via subsequent removal/addition of atoms at kink sites starting at the corners of the terraces. Better suited for quantitative studies is a second type of experiments, where STM scan lines are alternately recorded at two positions along the step, which allows to measure the propagation time of kinks between these positions. From a statistical analysis and a simple random-walk model detailed data on the kink dynamics can be obtained. Both methods indicate high local rates and pronounced local dissolution/redeposition fluctuations at the individual kinks even at the onset of Cu dissolution with average kink propagation and reaction rates in the range of 10^3 and 10^5 atoms s^{-1}, respectively. In addition, they reveal a second, unexpected collective process, where not one but two rows of the elementary cells are removed.

4:00 PM H6.5/M6.5
COMPUTER MODELING OF CORROSION PROCESSES. MOLECULAR DYNAMICS AND HARTREE-FOCK CALCULATIONS. R.I. Eglitis, Institute of Materials Research and Engineering, Singapore, SINGAPORE; M.R. Philpott, Institute of Materials Research and Engineering and Departments of Chemistry and Material Science, National University of Singapore, SINGAPORE; S.V. Izvekov, Institute of Materials Research and Engineering, Singapore, SINGAPORE.

It is extremely important to understand the fundamental mechanisms involved in corrosion and find ways for its inhibition. The dissolution of metal is an important step in corrosion. Taking into account that the predictive power of first principles quantum electronic structure calculations due to increased speed of computers and recent developments of a new and powerful computational methods that allow one to model aspects of corrosion processes we have explored features of the potential energy surface (PES) of a metal atom (ion) leaving a hydrated metal surface using quantum electronic structure calculations for a model that retains the key physics of the dissolution process. In separate calculations aspects of dissolution/deposition dynamics are followed using ab initio molecular dynamics. Scenarios for dissolution include adatom detaching from kink, step or terrace site. Comparisons between (001) and (111) are described as well as for atom in the (001) surface plane.

4:15 PM H6.6/M6.6
Transferred to H5.3/M5.3