

PRESENTATION ABSTRACTS

MONDAY

Overview

L.D. Marks

Department of Materials Science and Engineering, Northwestern University

The intent of this project funded by the Office of Naval Research is to bring the full power of twenty first century experimental and theoretical tools to bear on corrosion at the atomic scale to unravel how the nanoscale structure influences the properties in 4D. We hypothesize that the near-surface selvedge region microstructure at the nano to mesoscale plays a critical role. Our specific target is to understand in detail the early-stage oxidation and aqueous corrosion in three selected model systems, looking specifically at the formation of unusual oxides by nonequilibrium solute capture, the role of morphological instabilities and the electronic semiconductor physics of the doped oxides that are formed. We believe that a comprehensive experimental and theoretical attack on the details will enable us to understand what matters, what does not, and lay the basis for a paradigm shift in improvements of corrosion-resistant materials. This talk will overview recent progress.

Nonequilibrium Solute Capture Overview

J.H. Perepezko

Department of Materials Science and Engineering, University of Wisconsin-Madison

Nonequilibrium Solute Capture in Corrosion

J. Scully and P. Reinke

Department of Materials Science and Engineering, University of Virginia

In this talk, supporting evidence of non-equilibrium solute capture during aqueous passivation of Ni-Cr, Ni-Cr-Mo, and Ni-Cr-Mo-W alloys is presented. The types of aqueous corrosion processes that are likely to result in solute trapping due to high metal/film interface velocities during corrosion are discussed. Following this brief introduction, methods enabling fast or slow oxide growth during passivation are exploited to produce either strong or limited non-equilibrium solute capture (and other effects) during oxide growth. Corrosion electrochemistry behavior is then investigated focusing on passive film attributes and the early stages of local breakdown of passive films grown in such a manner. Repassivation kinetics, electrochemical impedance, nano-scale oxide morphology, and breakdown of oxide films followed by the early stages of pitting are monitored. All methods reveal that fast oxide growth results in more extensive corrosion (passive dissolution and breakdown) especially in Ni-Cr alloys without a minor element. Moreover, alloying with Mo and W attenuates the observation of enhanced corrosion after fast oxide growth. The possible role(s) of minor alloying elements are addressed in a second talk.

Thermodynamics of Non-Equilibrium Solute Capture

P.W. Voorhees

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In classical theories of the oxidation of metals it is assumed that the interface between the oxide and metal is in thermodynamic equilibrium. However, in many cases this is not true. We present a thermodynamic and kinetic analysis of the deviations from local equilibrium during the early stage oxidation of metals, and apply this to the oxidation of Ni-Cr alloys. We focus on the growth of oxides with the rock salt crystal structure, the first phase to nucleate at high temperature on dilute Ni-based Ni-Cr alloys. A thermodynamic assessment of the Ni-Cr-O system is used to provide the free energies of the metal and rock salt oxide. Classical solute trapping theory is modified to describe the interfacial chromium concentrations in the alloy and rock salt as a function of interfacial mobility, interfacial velocity, and oxygen partial pressure. We find that the interfacial compositions that govern solute capture can be strong functions of the interfacial velocity and the composition of the oxide can approach that of the metal for sufficiently high velocity.

Real Space Imaging of Nonequilibrium Solute Capture

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Current models for oxidation and corrosion involve sequential formation of oxides, with the most stable thermodynamic phases forming first. Within the MURI project detailed analysis of the early stages of both oxidation and corrosion have revealed something completely different: oxides with unexpected combinations of structure and composition. To date extensive TEM and APT evidence has revealed oxides with a rocksalt structure but compositions of about 50:50 Cr:Ni, and similar compositions for corundum structured materials. This talk will overview these results, connecting them to thermodynamic calculations of non-equilibrium solute capture.

Role of Minor Alloy Elements in Solute Capture

J. Scully

Department of Materials Science and Engineering, University of Virginia

In this talk, the effect of non-equilibrium solute capture promoted during fast passivating oxide growth, as previously presented for Ni-Cr, Ni-Cr-Mo, and Ni-Cr-Mo-W alloys, is expanded to both 304 and 316L stainless steels as well as Ti alloyed with Mo and Nb. Methods enabling fast or slow oxide growth during passivation were again exploited to produce either strong or limited non-equilibrium solute capture (and other effects) during passivation. Corrosion electrochemistry behavior in the passive range was then investigated. The trends produced in SC are shown to apply to all the alloy systems tested. Certain minor alloying elements are capable of mitigating the detrimental effects of solute capture in all systems. The talk ends as time allows with speculation on the beneficial role of the selected minor elements functioning as oxide dopants. Broad applicability of the concept to a variety of alloys systems is suggested; alloys containing selected elements as minor solute may function in a similar role in each.

Role of trapped solutes at the water/oxide interface

J.M. Rondinelli

Department of Materials Science and Engineering, Northwestern University

During the fast oxidation of Ni-based alloys, e.g., Ni-Cr and Ni-Cr-Mo, the solute species (Cr and Mo) are often trapped in the majority oxide, NiO. These trapped solute atoms will influence various physical and chemical properties of the oxides. Using density-functional theory (DFT), we studied the stabilities of Cr and Mo solutes trapped in bulk and nanofilms of NiO and their effects on the oxide-water binding energies. Our DFT results show that the thermodynamic stability for the solute trapping in the bulk NiO lattice decreases upon substitution of Cr with Mo. We also examined the stability of the solute atoms as a function of depth-within the oxide (below the oxide-water surface) and find that the solutes highly favor segregation to the surface layer of the NiO nanofilm. The surface preference arises because the solutes are more easily able to distort the lattice structure at surface with lower elastic energy costs. The structural distortion also significantly influences the NiO-H₂O binding strength, because the hydrogen and chemical bonds at the NiO-H₂O interface are largely dependent on the NiO-surface geometry. The NiO-H₂O binding strength and the underlying mechanism will be important to predict/understand the electrochemical behaviors of bulk and nanofilm NiO with trapped solutes, and our future work aims to calculate the effect of trapped solutes on the electrochemical phase diagrams of NiO.

Time and Space Resolved Oxidation of NiCr Alloys

J.H. Perepezko

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Oxidation of Ni-Al-Cr alloys that are the basis of many superalloys is dependent upon composition (i.e. Al/Cr ratio) and often yields a multilayer oxide microstructure with alumina, chromia and spinel phases. The evolution of the oxide structure is controlled by competitive nucleation and growth kinetics since the thermodynamically most stable oxide is alumina. To elucidate the initial stage of the kinetic competition an oxide nucleation map has been developed based upon the relative driving free energies of the competing oxide phases for comparison to the final steady state oxide structures. In companion experimental examination oxide nucleation has been measured with a pulse oxidation technique for comparison to the calculated oxide nucleation map.

In order to examine the early nucleation stage a pulse oxidation facility has been constructed that allows for accurate and reproducible control of oxidation exposures. As a test of the pulse oxidation facility the initial efforts are focused on the oxidation of N and Ni-Cr alloys. Sample preparation procedures have been optimized to achieve large grain sizes that allow for the examination of the orientation dependence of oxide nucleation and clean surfaces. An image analysis protocol has been implemented to permit the quantification of the oxide island size distribution. By monitoring the evolution of the oxide island size distribution with exposure time we have developed an analytical kinetics analysis that will yield nucleation rates and elucidate the growth and coarsening behavior.

From nanoscale TEM examination of cross sections on samples after pulse oxidation of Ni xCr (x = 1, 5, 30 %Cr) the initial oxide layer is identified as NiO with evidence for Cr capture. These results are consistent with a developing model of nonequilibrium solute capture and provide a new perspective on the initial stage of oxidation.

In complimentary studies the earliest oxide island development has been followed by STM measurements. For a Ni-5%Cr alloy the initial NiO islands develop with unit cell height that is maintained as the islands exhibit lateral growth and then coalescence. Measurements of the island number density and growth have been analyzed to determine the nucleation rate.

PRESENTATION ABSTRACTS TUESDAY

Morphological Instabilities Overview

P.W. Voorhees

Department of Materials Science and Engineering, Northwestern University

It is well known that oxides on metals grow with interfaces that are non-planar. By contrast, most theories and simulations for oxide growth assume one-dimensional growth, or planar interfaces. An introduction to morphological instabilities will be given in the context of oxide growth. The drivers for these instabilities will be discussed, as well as how these instabilities lead to well known corrosion behavior such as the loss of passivity and pits formation.

The Role of Cl⁻: Theory

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The consequence for aqueous corrosion of chloride ions in an aqueous environment on the surface structure and thermodynamics of hydroxylated magnesia (001) and alpha-alumina (001) and (100) is analyzed using density functional methods. It is shown that there is competitive chemisorption between hydroxide and chloride, with the chloride disrupting the hydrogen bonding network on the surface. There is a significant crystallographic dependence, as well as dependencies upon the environment in terms of the pH and chloride molarity. An analysis of the results in terms of existing, competing models in the literature for the effect of chloride indicates that rather than the existing models being competitors, most are correct but incomplete. Rather than the different models being viewed as competitors, or each being rate determining for some specific set of conditions, the majority are simultaneously correct. Conventional oxide surface science extrapolation of the results yields qualitative conclusions for the effects of, for instance, alloy dopants which are consistent with existing experimental data. The analysis also indicates the existence of a number of new phenomena in corrosion, for instance local galvanic couples due to the work-function change with chloride chemisorption, as well as thermodynamic dewetting of the oxide film.

The Role of Cl⁻: Experiment

J. Scully

Department of Materials Science and Engineering, University of Virginia

Some effects of Cl⁻ on passive film formation, repassivation, steady state passive current density and early stages of breakdown were investigated on polycrystalline Ni-Cr, Ni-Cr, Ni-Cr-Mo, and Ni-Cr-Mo-W alloys. Results in Cl⁻ are compared to Cl⁻ free sulfate solutions. Single grains of dilute Ni-Cr and Ni-Cr-Mo alloys, prone to Cl⁻ induced corrosion effects, were also investigated and showed large differences in corrosion behavior depending upon the grain orientation exposed. Nano-scale morphological characterization was combined with global electrochemical corrosion measurements as well as atomic emission spectro-electrochemistry to provide new insights regarding the effects of Cl⁻ on the early stages of breakdown regulated by minor alloying elements.

Phase-field Modeling

P.W. Voorhees

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Phase field methods are routinely used to follow the evolution of morphologically complex interfaces during phase transformations. A phase-field model of an oxide relevant to corrosion resistant alloys for film thicknesses below the Debye length, where charge neutrality in the oxide does not occur, is formulated. The phase-field model is validated in the Wagner limit using a sharp interface Gouy-Chapman model for the electrostatic double layer. The phase-field simulations show that equilibrium oxide films below the Wagner limit are charged throughout due to their inability to electrostatically screen charge over the length of the film. The character of the defect and charge distribution profiles in the oxide vary depending on whether reduced oxygen adatoms are present on the gas-oxide interface. The Fermi level in the oxide increases for thinner films, approaching the Fermi level of the metal in the limit where the ratio of the film thickness to Debye length goes to zero, which increases the driving force for adsorbed oxygen reduction at the gas-oxide interface. Simulations of growing oxides will also be discussed.

Electronic Overview

J.M. Rondinelli

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Local Electronic Structure and Chemistry of Oxides

P. Reinke

Department of Materials Science and Engineering, University of Virginia

The electronic structure, chemical bonding environment and composition of oxides formed in the thermal oxidation of NiCr and NiCr(Mo,W) alloys changes dramatically during the evolution of the oxide layer. This covers the initial steps within the Mott-Cabrera regime of oxidation. We focus on the very early stages of this reaction process when the alloy surface is transformed to an oxide up to several nanometer thickness. NiCr and NiCr(Mo,W) alloys with 5 at% to 30 at%Cr and 6at%(Mo or W) were studied with Scanning Tunneling Microscopy at the atomic scale and X-ray photoelectron spectroscopy at near-ambient $p(\text{O}_2)$. The latter experiment allows us to monitor the alloy, oxide, and oxide surface simultaneously. Note that in the assessment of XPS core level data a comparison is made between the pure compound such as NiO or Cr_2O_3 and the observed peak positions and shapes seen in the oxide layer. This does not imply that, for example, Ni(IV) is only present in NiO – the same oxidation state can be realized in different configurations where Ni is a dopant atom within another oxide matrix, and subtle variations in bonding environment might not be resolved in XPS.

On the NiCr(100) surface Cr acts as a promoter to NiO nucleation which is kinetically hindered for pure Ni due to the presence of a $c(2 \times 2)$ -O reconstruction. The growth of oxide islands is correctly described in a surface diffusion model with a very small capture radius for the reactant. This behavior is specific to the (001) surface and illustrates the significant differences to be expected on different surfaces. The impact of Cr on the defect population and thus growth rate of NiO is well studied, but its role in the initial reaction steps is yet to be fully understood. This work illustrates the impact of relatively small Cr concentrations in the alloy on the kinetics of oxide nucleation which is relevant to future alloy development.

DFT Probes of Nonequilibrium Solute Capture Effects

L.D. Marks

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Nonequilibrium solute capture leads to unexpected valence states, for instance the possibility of Cr^{2+} trapped in a rocksalt structure, or Ni^{3+} trapped in a corundum structure. An important, very open question is what are the valence states of these anions, and what role do they play in oxidation, corrosion and breakdown. One method to start to probe this is via DFT calculations of different model structures, computational experiments. This talk will overview some results, showing how the variation of the Fermi energy (which changes with band bending and applied fields) will lead to different oxidation states. More complex calculations where cations are embedded into thin oxides on a metal substrate will also be described.

Heterogeneity of Interfaces and Band-offsets in Thin Oxides

P. Reinke

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The study of oxidation of NiCr and NiCr(W/Mo) alloys with XPS and STM affords not only information on chemical bonding and progression of the oxidation reaction but also delivers insight in the local electronic structure of the oxide layer. The local variation of the Fermi level within the ultrathin oxide layer are already seen within the first oxide layer, and are likely attributable to local defects and the onset of dopant incorporation in the oxide.

The oxide layer growth up to a thickness of 5 nm measured in an operando mode shows that a Cr (VI) related bonding configuration develops rapidly concurrent to Cr depletion in the alloy. NiO (Ni IV) growth on the other hand is not limited by the Ni-supply and dominates the oxide at later stages of the process. The oxide-specific rates can now be deconvoluted and we will show a direct comparison for alloys from Ni5Cr to Ni30Cr. For Ni15Cr6W the W(VI) accumulates at the alloy interface and the W-concentration is greatly diminished at the oxide surface. The oxide surface is oxygen terminated and in addition covered by a likely physisorbed layer of O₂. The feasibility of extracting band bending information, and contact potentials between the different oxides, and a direct comparison between the experimental and theoretical data from J. Rondinelli/Laurence Marks will be discussed.

Tribocorrosion of Aged 2507 Super Duplex Stainless Steel

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U.S. Naval Research Laboratory

The phenomenon of tribocorrosion is created when the surface degradation processes of wear and corrosion are combined. The tribocorrosion-induced material losses may greatly exceed those of either individual process combined. Surface probe microscopy techniques, notably the AFM, provide an attractive opportunity to study the links between local microstructural features, the electrochemical response before and during abrasion, and the material loss. Such *in situ*, microscale tribocorrosion studies in the AFM present a further opportunity in that local material losses can be quantified spatially and in real time, rather than the *ex situ* characterization required for conventional tribocorrosion testing. In the present study, an *in situ* tribocorrosion testing method was developed by using a commercial potentiostat in combination with an AFM fitted with a diamond coated fluid cell tip. By abrading the surface with the AFM tip and monitoring the corrosion current in real time, the electrochemical changes can be mapped along with the changes in height, and can thus be linked to microstructural features. In doing so, an understanding of the spatial and temporal material loss rates and electrochemical activity was developed that complements the information gained from conventional, macro-scale tribocorrosion testing.

Doped Molybdenum Silicides

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The challenges of a high temperature environment impose severe material performance constraints in terms of melting point, oxidation resistance and structural functionality. In metallic systems the multiphase microstructures that can be developed in the Mo-Si-B system based upon the coexistence of the high melting temperature ($>2100^{\circ}\text{C}$) ternary intermetallic Mo_5SiB_2 (T_2) phase with Mo and the Mo_3Si phases offer useful options for high temperature applications. The early stage of oxidation behavior of Mo-based alloys has been studied at the microstructure scale where a transient period was identified involving the Mo_3Si phase before the onset of steady state oxidation. To elucidate the transient period mechanism a nanometer scale investigation of the initial oxidation was conducted based upon direct observation by means of *in-situ* environmental TEM. A nanometer size porous SiO_2 develops at very early stage of the oxidation of Mo_3Si between $600\text{--}800^{\circ}\text{C}$ (i.e. the pesting range) as a competition between loss of volatile MoO_3 and the growth of SiO_2 . Based upon the insight from the nanometer scale observations we have developed a strategy to minimize the transient stage and the degradation due to pesting. By using minor element doping additions that do not alter the alloy microstructure but act to reduce the viscosity of the silica scale we have been able to inhibit the nanoporous structure formation.

Pourbaix Diagrams from Bulk to Nanoscale Films

J.M. Rondinelli

Department of Materials Science and Engineering, Northwestern University

The thermodynamic stabilities of materials at various electrochemical environments may be predicted and understood using Pourbaix diagrams. To that end, we have advanced a strategy to compute ab initio Pourbaix diagrams, which is improving our understanding of electrochemical phenomena in complex materials. First, we identified that available Pourbaix diagrams constructed from published experimental thermodynamic energies of solid compounds are frequently inconsistent with many direct electrochemical phenomena. To address this issue, we designed an approach based on density-functional theory (DFT) calculations without ad hoc corrections to obtain more reliable Pourbaix diagrams and demonstrated its utility in Ti- and Ni-based systems. Our results for the Ni Pourbaix diagrams are consistent with most direct experimental observations in decades, including measurements by the Scully Group at UVA. Second, apart from the inaccuracy and uncertainty in existing experimental thermodynamic energies for various compounds, the experimental thermodynamic and structural data of many compounds is often missing. We designed a first-principles high-throughput approach to screen a large range of structural-magnetic configurations using efficient DFT methods (e.g., GGA and metaGGA functionals), calculate the thermodynamic energies of solid compounds using accurate DFT methods (e.g., hybrid functional), and finally generate Pourbaix diagrams using the DFT thermodynamic energies. We applied this approach to obtain reliable Pourbaix diagrams for magnetic transition metals and their compounds (oxides, hydroxides, and

oxyhydroxides). Third, because various passivating species (e.g., oxides and hydroxides) grown on metal surfaces are always present in nanoscale thicknesses, we calculated the energetic corrections due to the nanoscale geometries for the aforementioned Ni-based Pourbaix diagrams.

Nanoscale Mechanism of Pesting and Oxidation in MoSi₂

P. Reinke

Department of Materials Science and Engineering, University of Virginia

The use of Mo-silicides in technical applications depends on their unique resistance to corrosion once the formation of a SiO₂ scale has been achieved. At lower temperatures the oxidation process is destructive a pesting reaction leads to rapid disintegration of the material. The interplay between mixed oxide formation in the pesting regime and the transition out of this regime to SiO₂ scale formation due to the volatilization of MoO₃ govern the oxidation of MoSi₂ prior to protective silica formation. This work presents a study of the oxidation of nanometer-scale MoSi₂ crystallites with the use of Scanning Tunneling Microscopy/Spectroscopy (STM/STS). Oxidation is initiated by a nascent period with subtle modulations of the surface electronic structure due to oxygen adsorption. This is followed by a rapid onset of pesting recognized by a dramatic increase in crystallite density. The O-adsorption destabilizes the silicide surface and opens reaction pathways to MoO_x formation – or vice versa – O-adsorption stabilizes the surface at a temperature where thermodynamics already favors MoO_x formation. Pesting is a non-local reaction and diffusion of MoO_x drives the rapid spread of the destructive reaction. This is followed by transition to SiO₂ for T > 750°C. Direct observation of pesting can be combined with DFT modeling of surface reactions, and contribute to develop and understand strategies to mitigate pesting and advance scale formation.