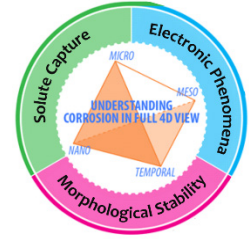


Corrosion in 4D: The Future

The Hive (Room 2350), Ford Motor Company Engineering Design Center
(2133 Sheridan Rd).



Thursday 17th March

- 9:30-10:30 Registration and Breakfast
- 10:30-11:00 L. D. Marks *Corrosion in 4D: The Future*
- 11:00-11:40 J. Scully *Formation and Long-Time Exposure Aging of Oxides on Ni-Cr and Ni-Cr-X (Mo, W) Alloys in Acidic Chloride Solutions and Ramifications Towards Local Corrosion Resistance*
- 11:40-12:20 P. Voorhees *Solute and Vacancy Capture During Oxidation: Theory and Experiment*
- 12:20-1:30 Lunch: Cohen Commons (Room L482), the Technological Institute (2145 Sheridan Road)
- 1:30-2:10 K. Wahl *Tribocorrosion processes in sliding contacts to stainless steel*
- 2:10-2:50 P. Reinke *Initial Steps in Alloy Oxidation for Ni-Cr, Ni-Cr-Mo, and Ni-Cr-W alloys*
- 2:50-3:30 A. Samin *An analysis on the bulk and surface oxidation of refractory alloys using Density Functional Theory and Monte Carlo calculations*
- 3:30-5:00 Coffee & Posters
- 6:30 Conference Dinner at Farmhouse Evanston (703 Church St.)

Friday 18th March

- 8:00-9:00 Registration and Breakfast
- 9:00-9:40 P. Marcus *Passive Films on NiCr and NiCrMo Alloys: Thickness, Composition, Stratification, Ion Transport*
- 9:40-10:20 J. Perepezko *Initial Oxidation in Ni-Cr Alloys and Enhanced Oxidation Resistance in Mo-Si-B Alloys*
- 10:20-11:00 Coffee
- 11:00-11:40 C. Wren *Nonlinear Dynamics of Corrosion: Why Butler-Volmer Kinetics and Equivalent Electric Circuit Analysis Fail*
- 11:40-12:20 B-C Zhou *Modeling preferential dissolution in corrosion of multi-principal element alloys using non-equilibrium thermodynamics*
- 12:20-1:30 Lunch: Cohen Commons (Room L482), the Technological Institute (2145 Sheridan Road)
- 1:30-1:50 J. Zhang *Morphological stability of electrostrictive thin films*
- 1:50-2:10 E. Romanovskaia *Exposure Aging of Oxides on Multi-Principal Element Alloys and Ramifications Towards Local Corrosion Resistance*
- 2:10-2:30 J. Cavin *Flexoelectricity and Morphological Stability in Nickel-based Alloys*

Corrosion in 4D: The Future

^{1*}Marks, L.D., ²Perepezko, J., ³Reinke, P., ¹Rondinelli, J.M., ³Scully, J.M. & ¹Voorhees, P.W.

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When the MURI started back when I was young, we made the rather bold statement, to quote:

We believe that a comprehensive experimental and theoretical attack will enable us to understand what matters, what does not, and lay the basis for a paradigm shift in improvements of corrosion-resistant materials.

Looking back, I will argue that we have achieved at least some of this, although at times the road has been complicated. Among our achievements has been:

1. The discovery of a new type of nonequilibrium, solute capture, which is common if not dominant in oxidation and corrosion.
2. Delineating the difference between Drivers, Mechanism, Trigger and Dependencies which have often been confiscated.
3. Determination of the connection between key dependencies such as chloride concentration with surface energy drivers and morphological instabilities.
4. Demonstration of the role of semiconductor physics and heterogeneity contrast in understanding oxide films.
5. Pointing out that many assumptions have been made in both oxidation and corrosion, some of which are inappropriate.

However, much remains to be done. This talk will set the stage for the meeting, briefly covering some of the prior achievements as well as unknowns, both known and unknown ones.

Formation and Long-Time Exposure Aging of Oxides on Ni-Cr and Ni-Cr-X (Mo, W) Alloys in Acidic Chloride Solutions and Ramifications Towards Local Corrosion Resistance

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Ni-Cr-based alloys are considered amongst the most corrosion-resistant when utilized in aqueous marine applications. The superior corrosion resistance of these alloys is known to depend on the presence of a homogeneous solid solution and the desirable attributes of their oxide films. However, the scientific basis for excellent passivation and protection against localized corrosion initiation remains uncertain and insights are often based on short term laboratory testing under limited conditions even though exposures are long-term. The engineering basis for alloy choice relies on empirical metrics such as the PREN that do not even consider exposure time. Both highly engineered legacy and emerging alloys lack information on the precise attributes of protective passive films after long-time exposures. However, relevant field exposure periods are nearly infinite in time.

The focus of the current work was on solid solution Ni-22Cr, Ni-22Cr-6Mo, and Ni-22Cr-6Mo-3W. Potential step passivation studies in 0.1 NaCl pH 4 solutions in the passive range were investigated over 10s to 10 days and at select potentials. Improvements in passive films protectiveness was correlated Cr³⁺ enrichment, minimal morphological roughening, and dopants promoted by aliovalent cations brought about by alloying with Mo and W. Ni²⁺ rich oxides and hydroxides were preferentially dissolved with time. The most corrosion resistant alloys possess passivating films that are efficacious not only just after formation, but that self-heal and improve over long exposure times as evident from impedance spectroscopy. Such alloys were observed to be the most resistant when interrogated for local corrosion compared to other alloys whose impedance response degraded over time. The latter alloys eventually arrived at conditions for breakdown.

Oxide exposure aging time, potential, and oxide “transformation” diagrams are introduced and shown to provide valuable insights. Passivated films may form as solute captured solid solutions after short term passivation or when grown quickly but are gradually enriched in Cr, Mo and W over long time. Can such Cr enrichment continue during exposure without limits? Factors affecting and limiting Cr enrichment are discussed.

Solute and Vacancy Capture During Oxidation: Theory and Experiment

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During oxidation of metals and alloys, it is usually assumed that local equilibrium is established at the oxide interfaces, and as a result equilibrium oxide phases form on the surface. However, during the earliest stages of oxidation, the fluxes across the metal-oxide interface can be sufficiently large that a deviation from local equilibrium exists at that interface, leading to the formation of metastable oxides that are supersaturated with alloying elements, a process that has been termed "solute capture." An irreversible thermodynamics analysis of this process has been developed for the growth of both AO binary oxides and ABO oxides. We show that trapping naturally accounts for cation vacancy concentrations that can deviate from the usual values obtained from equilibrium considerations, and thus measuring non-standard exponents can indicate a nonequilibrium effect. For the ABO oxides we focus on the capture of trivalent B atoms in a rocksalt oxide AO during the oxidation of binary A-B alloys, which has relevance to the oxidation of Ni-Cr and Co-Cr alloys. Through the analysis, we identify the conditions under which significant capture of B atoms in the rocksalt oxide occurs and show that it is possible to form pure rocksalt oxide $B_{2/3}O$ or pure AO oxide, thus allowing one to control the oxide composition and, eventually, design protective oxide films. A comparison between this theory and recent results on oxide film growth and dissolution of Ni-Cr alloys will be given.

Tribocorrosion processes in sliding contacts to stainless steel

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Mitigating the risk of wear and corrosion damage caused by operation in seawater environments typically requires the use of highly-alloyed metals with passivating surface oxides that protect the material from corrosion. Materials that may perform well under corrosive or wear conditions separately can experience significant damage from synergistic processes collectively termed ‘tribocorrosion.’ We have explored the tribocorrosion behavior of duplex and austenitic stainless steels, both wrought and prepared by additive manufacturing (AM) at scales ranging from single asperity to macroscopic. Experiments were performed in 0.6M NaCl under anodic potentiostatic conditions. At the single asperity level, we are able to spatially resolve both material loss and corrosion current, and correlate the electrochemical response to sliding as a function of contact pressure and microstructure. We demonstrated that an interfacial film growth model could account for oxide growth across a range of conditions on austenite, and we fit this to an Arrhenius model to assess the overall pressure-dependent response observed in the nanoscale experiments. We are also examining the role of chloride-ions in manipulating the material removal rates and wear mechanisms of 2205 duplex stainless steel in NaCl, Na₂SO₄ with and without trace chlorides, and chloride-free Na₂SO₄ under linear reciprocating sliding. Finally, we are contrasting the tribocorrosion behavior of wrought and AM 316L stainless steel in unidirectional sliding conditions.

Initial Steps in Alloy Oxidation for Ni-Cr, Ni-Cr-Mo, and Ni-Cr-W alloys

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Ni-based superalloys have excellent mechanical properties and can form a chromia rich layer which mitigates the load imparted by environmental stressors. We specifically study the transition from clean alloy surface to the first few nanometers of the oxide layer with dry oxidation experiments in a highly controlled environment. This marks the transition between pristine alloy surface and the validity of the Mott-Cabrera description of oxide film growth. The initial reaction steps on the alloy reflect the competition between formation of chromia, which is thermodynamically preferred but kinetically hindered, and the rapid nucleation of NiO aided by an epitaxy, and limited Cr transport. We will discuss the oxidation of a wide range of alloys, and crystallographic orientations and put them into context of models developed within the MURI project, and include insights from surface chemistry and structure.

To access the initial oxidation steps we combine high spatial and temporal resolution experiments with scanning tunneling microscopy (STM), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and x-ray photoemission electron microscopy (XPEEM). The parameterspace for oxidation is 500-600 °C and $p(\text{O}_2)=10^{-6}$ to 10^{-9} mbar (< 200 L). The narrow selection of processing conditions is complemented by the use of binary alloys Ni-15at%Cr, Ni-22at%Cr, and alloys with minor alloying elements Ni-15at%Cr-6at%W, and Ni-22at%Cr-6at%Mo. We include large grain samples (up to 1 mm in diameter) with crystallographic orientations of grain surface from (100), (111), (314) and (213) which alters the overall oxidation rate by about 15% nearly entirely due to a change in the chromia contribution. The crystallographic orientation severely impacts the surface topography, and nanofaceting, which can be related to morphological instabilities, is observed after reduction of the native oxide.

We will discuss the role of surface chemistry in the comparison of binary and ternary alloy oxidation. Our results indicate that the presence of preferential W(or Mo)-Cr adsorption sites in the ternary alloys lowers the nucleation barrier for chromia formation. The XPEEM experiment directly shows the role of crystallographic orientation by comparison of (212) and (104) which differ in terrace structure but not width. If time permits, the quantitative data on the evolution of chromia particles on both surfaces will be discussed. The complex interplay of kinetic factors leads to chemical, compositional, and structural heterogeneity across the alloy surface and oxide layer formed in the early stages of oxidation are proposed to be at the core of failure mechanisms which limit protective function.

An analysis on the bulk and surface oxidation of refractory alloys using Density Functional Theory and Monte Carlo calculations

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Emerging technologies in jet propulsion have led to increased demand for materials that are able to withstand extreme conditions, including high temperatures, large stresses, and harsh, oxidizing environments. One of the principal limiting factors in the development of new materials for jet turbine engines is high-temperature oxidation. Refractory high entropy alloys (RHEAs) are candidate materials for high temperature applications due to their exceptional physical properties. In this work, we used density functional theory-based methodologies to examine the early stages of oxidation of a bulk MoNbTaW alloy, and an AlNbTaTiZr surface and to conduct a full analysis on the oxidation thermodynamics of a binary Nb-Ti alloy as a step towards improving our general understanding of the oxidation behavior in complex refractory alloys.

Isothermal-isobaric sampling of the interstitial oxygen in the MoNbTaW alloy indicated the tendency towards the formation of O-rich ordered clusters which slightly improved mechanical behavior consistent with experimental literature. Moreover, the interstitial oxygen solubility in the alloy was found to decrease as a function of temperature implying a thermodynamic drive towards the formation of the bulk oxide at lower oxygen concentrations in high temperature environments.

The multi-cell Monte Carlo algorithm which is based on the Gibbs Ensemble Monte Carlo was utilized to find the relevant phases and phase fractions of an AlNbTaTiZr alloy at 1000 °C. Bulk structures were then sampled from equilibrium and their properties were in agreement with the available experimental literature. Surface slabs were then generated from these bulk structures and analyzed. It was determined that the (011) surface was the energetically favored surface and oxygen adsorption was studied on this surface up to 2 ML. The oxygen adsorbed with a strong preference towards sites with Ti and Zr and avoided sites with Nb-Al and Nb-Ta. A thermodynamic analysis indicated that the surface was extremely reactive to oxygen. Inward oxygen diffusion at low coverage was preferred in regions rich with Zr, but slowed with the addition of Ti and Al and diffusion rates slowed dramatically after 1 ML.

Finally, a complete analysis of the oxidation thermodynamics of the Nb-Ti binary alloy was conducted by considering the Gibbs free energy for the alloy and for 24 oxide phases (including mixed oxides) at different temperatures and pressures. As the oxygen chemical potential increased, the most stable oxides to form were first Ti₂O₃ followed by TiO₂, and then Nb₂O₅. These oxides were found to be more stable than mixed oxides for all temperatures and pressures considered in agreement with the experimental literature. By studying the thermodynamics of oxidation of titanium and niobium separately, it was determined that the presence of Ti favored the formation of TiO₂ over Nb₂O₅ in a large region of the stability diagram that would otherwise be dominated by Nb₂O₅. This may help explain the role that titanium plays in enhancing oxidation resistance in Nb-containing alloys from a thermodynamic point of view since the formation of Nb₂O₅ is generally undesirable due to its susceptibility to spallation and pore formation.

Poster Session

The Effect of Solute Capture on Chlorine Chemisorption, Cavin, J.D.

Microstructure and Electrochemical Behavior of Conventional and Additively Manufactured Orthopedic Components Made of Ti6Al4V, Neto, M.Q.

Composition and Thermal Stability Analysis of Passive Films on NiCr and NiCrMo Alloys, Orson, K.

Correlation of the chemical signature of periprosthetic macrophages with CoCrMo wear of corresponding hip implants, Liu, S.

The Combined Effect of Ti ions, Hydrogen Peroxide and Lactic Acid on Implant Corrosion, Alhamad, M.

Fretting-corrosion apparatus with low magnitude micro-motion ($<5 \mu\text{m}$) to study the hip implant taper degradation, Sun, Y.

The Effect of Solute Capture on Chlorine Chemisorption

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Environmental factors can threaten the stability of a passivating oxide, e.g. degradation of protective surface oxides by aqueous Cl⁻ ions [1]. The consideration of this phenomenon is necessary for aqueous applications where NaCl is dissolved (e.g., sea water). Previous first-principles studies have suggested that the chemisorption of Cl⁻ can lower the surface energy of passivating surfaces, causing runaway growth of physical perturbations in the passivating film, leading to breakdown [2]. Additionally, the non-uniformity of Cl chemisorption leads to inhomogeneous local work functions, indicating the presence of local electric fields that can drive instabilities in passive oxides [1]. Therefore, it is critical to understand the effects of Cl chemisorption on oxides when attempting to engineer corrosion-resistant alloys.

Solute capture describes the phenomenon of nonequilibrium concentrations of minority alloy elements being trapped into a surface oxide [3]. The discovery of such non-equilibrium passivating oxides opened a vast phase space of possible protective oxides that can be accessed by tuning alloy composition and oxidation conditions. Here, we present our work on the effects of solute-captured elements on chlorine chemisorption in passive oxides corresponding to Ni-Cr alloys. Primarily, we examined the influence of captured Cr on (111) surfaces of NiO. Because the phase and composition of passive oxides on Ni-Cr alloys show significant crystallographic dependence, the reverse situation of Ni-doped Cr₂O₃ will also be discussed [3]. Lastly, because the inclusion of Mo and W in nickel-based alloys has been experimentally shown to inhibit Cl⁻ chemisorption on passive oxides, Mo and W are also examined as possible minor alloying elements [2,4].

Using density functional theory, we show that only Cr dopants near or at the surface play a significant role in changing Cl chemisorption energies. Furthermore, we show that the presence of Cr at the surface significantly reduces the favorability of Cl chemisorption compared to pure NiO. While NiO is predicted to begin exhibiting finite Cl coverage below a pH of 9 in a 10⁻³ M solution of NaCl, the inclusion of Cr at the surface reduces this threshold to a pH just under 2, well below the pH of sea water. In fact, this threshold is below the analogous quantity of about 3 for pure Cr₂O₃. This indicates that under certain conditions, NiO with captured Cr can resist corrosion in Cl⁻-rich environments better than either pure NiO or Cr₂O₃. This work serves to guide future attempts to tune alloy composition and oxide treatment for improved corrosion resistance.

Acknowledgements: The authors were sponsored by the Department of Navy, Office of Naval Research, under ONR Award number N00014-16-1-2280.

[1] L. Marks, *Corrosion* **74**, 295 (2017).

[2] K. Lutton Cwalina, C. R. Demarest, A. Y. Gerard, and J. R. Scully, *Curr. Opin. Solid State Mater. Sci.* **23**, 129 (2019).

[3] X.-X. Yu, J. H. Perepezko, and L. D. Marks, *Acta Mater.* **198**, 223 (2020).

[4] C. D. Taylor, P. Lu, J. Saal, G. S. Frankel, and J. R. Scully, *npj Materials Degradation* **2**, 6 (2018).

Microstructure and Electrochemical Behavior of Conventional and Additively Manufactured Orthopedic Components Made of Ti6Al4V

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Ti6Al4V is the most used alloy in orthopedic implants such as total hip, knee and shoulder replacements due to its low density, superior corrosion resistance, good osseointegration and lower elastic modulus. Implants are conventionally made by cast or wrought alloys, but additively manufactured (AM) implants are increasingly used. The emergence of additive manufacturing (AM) provides interesting new perspectives by enabling the affordable and quick production of custom-made implants to fit specific patient needs and anatomy to increase the implant longevity and reduce the revision surgery risk. Although Ti6Al4V is known for its great corrosion behavior, there are increasing reports of corrosion and fretting-corrosion related implant failures. Currently, it is unknown if conventionally traditional implants have a varied microstructure, and how different it is from AM components, and how this variation impacts the electrochemical behavior of Ti6Al4V, and its implication on in-vivo corrosion. Therefore, this study aimed to compare the microstructure of Ti-6Al-4V alloy of additive manufactured and the conventional retrieved orthopedic implants such as acetabular cups, tibial trays, femoral stem and modular necks by means of electron backscatter diffraction (EBSD). Six types of microstructure were found (Fig. 1): wrought alloys with A) fine equiaxed grains, B) coarse equiaxed grains and C) bimodal grain; D) lamellar cast alloys; AM alloys with E) lath-type grains and F) needle-like grains. Then, we performed a corrosion test on those six frequently occurring microstructure types occurring in Ti6Al4V implant components. Our hypothesis was that, despite identical chemical composition, differences in microstructural features can dictate the corrosion behavior of implant alloys. While A-E exhibited varying degrees of β phase within an α matrix, F exhibited a α' martensitic structure. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were performed within simulated joint fluid (30 g/L protein) at pH 7.6 and 37°C to determine the corrosion behavior. We observed differences in corrosion current (I_{corr}), polarization resistance (R_p) and capacitance (Q), but not in the corrosion potential (E_{corr}) (Fig. 2). The needle-like group had the worst corrosion behavior attributed to the metastable nature α' and the presence of built defects (local crevice corrosion), followed by equiaxed coarse and lath-type groups attributed to the galvanic coupling between α and β phase, specifically when a difference in Ti and V content of >10% occurred between both phases. Therefore, the microstructure does influence the corrosion behavior of Ti6Al4V implants, however, the distribution of alloying elements across phases also played a role.

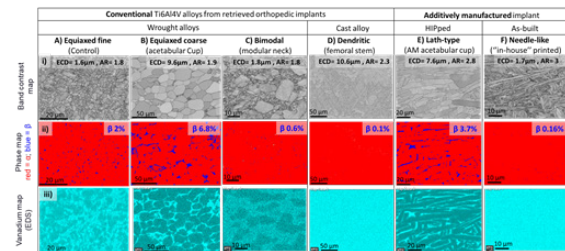


Fig. 1 Contrast map, phase map and vanadium map of six different Ti6Al4V implant alloy microstructures

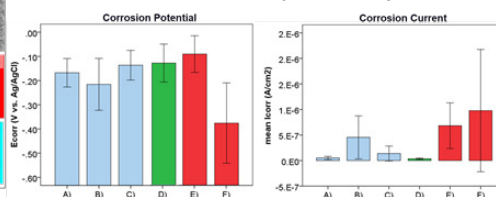


Fig. 2 Corrosion potential and current density corresponding to the six microstructures (A-F)

Composition and Thermal Stability Analysis of Passive Films on NiCr and NiCrMo Alloys

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The Ni-Cr based super-alloys are coveted technical alloys in part because of their corrosion resistance, which is generally attributed to a chromia-rich passive layer. During aqueous corrosion a complex surface layer comprised of $\text{Ni}(\text{OH})_2$, $\text{Cr}(\text{OH})_3$, and Cr_2O_3 forms and is accompanied by a modulation of the alloy composition in the sub-surface region. Angle Resolved X-Ray Photoelectron Spectroscopy (AXPS) measurements were used to study the oxide and hydroxide species in passive layers on NiCr and NiCr-Mo alloys followed by stepwise annealing to 400 °C to test layer stability and explore the solid-state reaction pathways. The oxide and hydroxide contributions were analyzed using a constrained XPS fitting procedure, which affords information on composition, thickness, and layering of the passive layer.

A wide range of electrochemical parameters were studied for two alloys - Mo22wt%Cr, and Mo22wt%Cr6wt%Mo. To investigate the aqueous corrosion process these alloy samples were exposed to a wide range of conditions including “high” and “low” current density (e.g. 100-1 $\mu\text{A}/\text{cm}^2$) to achieve fast and slow passive layer growth, and 10 ks at +0.2V(SCE) potentiostatic hold with the potential correspondingly adapting to maintain constant oxidation rate. At high current densities, a fast-moving oxidation front is expected to promote solute capture.

Our poster illustrates the correlation between passive layer and alloy characteristics in the context of passivation conditions, and their response to annealing. In electrochemically corroded samples, the passive layer is significantly enriched in Cr with chromia and Cr- hydroxides as the dominant species. In contrast, Ni-hydroxide is detected, but no NiO is observed. The sub-surface region of the alloys tend to be moderately enriched in Cr with few exceptions. At elevated temperatures (>200°C), $\text{Ni}(\text{OH})_2$ is reduced and at 400°C only Ni(0) can be detected. Under all conditions and temperatures, Cr is present as oxide as well as hydroxide. While the contribution from chromia increases with temperature, evidence for the persistence of $\text{Cr}(\text{OH})_3$ is found in both the O 1s and Cr 2p core levels. For Mo-containing alloys MoO_x and Cr_2O_3 coexist at low temperatures and MoO_x is reduced by the endpoint of the annealing experiment. In agreement with prior work on dry oxidation, chromia is more prevalent in ternary alloys.

Overall, the detailed passive layer analysis, and the progression of oxide and hydroxide reduction during annealing offers insight on passive layer stability and a direct comparison between ternary and binary alloys, fast and slow growth, short and long potentiostatic holds. In combination with information from the electrochemical experiments we can now use statistical and machine learning methods to quantify complex mechanistic relations.

Correlation of the chemical signature of periprosthetic macrophages with CoCrMo wear of corresponding hip implants

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AIM: The goal of this work was to 1) characterize differences in the IR spectra of periprosthetic tissue samples, specifically of debris-laden macrophages/foreign body giant cells, from patients with failed meta-on-metal (MoM) hip resurfacings (HR), and 2) determine the relationship between CoCrMo alloy wear, macrophage chemistry, and in vivo chemical alteration of CoCrMo debris.

METHODS: Surgically retrieved hip pseudo-capsule tissue samples from 15 MoM-HR patients were analyzed. Wear of the metal heads of the corresponding implants was assessed using an optical coordinate-measuring machine. Two serial, 5- μm sections of FFPE tissue were made. One section was stained for histological evaluation, and the other was placed on a BaF₂ window and analyzed using a FTIR microscope. Spectral data were collected at a resolution of 4 cm^{-1} with the range of 3750-850 cm^{-1} in transmission mode. For each single point measurement, 64 interferograms were averaged and ratioed against a 128 co-added background scans. Ten macrophage spectra and five adjacent connective tissue spectra were recorded from each sample. Data were vector normalized within the 1725-1596 cm^{-1} range, and the extended multiplicative signal correction was performed on the entire spectra dataset. The calculated value of wear rate and total wear volume were incorporated into the spectral datasets to perform PCA and further data visualization using Python-based home-made programs.

RESULTS: The mean wear volume and wear rate of the femoral heads were 17.73 mm^3 (0.16, 77.97) and 4.76 mm^3/year (0.06, 24.64). The marked presence of debris-laden macrophages exhibited a strong absorbance in the phosphate region ($\nu(\text{PO}_4^{3-})$: 1101-950 cm^{-1}) and exhibited a similar dome-shaped peak as previously described for the main corrosion products, CrPO₄. The first two PCs account for 94.7% of total variance. Cases with higher wear rates and/or higher total volumetric loss tended to have a higher PC1 and lower PC2 scores. PC1 had positive loadings on the spectral range associated with $\nu(\text{PO}_4^{3-})$. PC1 score had a linear correlation with the $\nu(\text{PO}_4^{3-})$ peak height ($r=0.96$) and area integral ($r=0.98$). We found that the chemical signature of periprosthetic macrophages associated with MoM-HR correlated well with the wear rate of the CoCrMo femoral heads. There are a few outliers which include two low wear cases clustered with the excessive wearing ones. These specific cases exhibited gross implant loosening and numerous necrotic bone particles within macrophages.

CONCLUSIONS: This study strongly indicates that chromium-phosphate is the dominant byproduct of the phagocytosis process of CoCrMo particles. Also, we demonstrated how FTIR can complement the pathological assessment with specific chemical information on intra-cellular corrosion.

The Combined Effect of Ti ions, Hydrogen Peroxide and Lactic Acid on Implant Corrosion

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Background: Peri-implantitis is a substantially prevailing condition. A potential risk factor for peri-implantitis is titanium (Ti) implant corrosion. During an inflammation, substantial quantities of oxygen reactive species (ROS) secretion and local acidification occur. Little is known about the interaction between inflammatory products and corrosion products on Ti surface corrosion. Therefore, the objective of the current study is to evaluate the synergistic effect of hydrogen peroxide (H₂O₂), lactic acid, and Ti ions on dental implant corrosion.

Methodology: Twenty-seven grade-4-commercially-pure-Ti samples were polished (Ra≈40nm) and divided into 9 groups as a function of electrolyte; 1) artificial saliva-(AS) as control (C), 2) AS+Ti-ions 20ppm (Ti), 3) AS+lactic acid (pH= 5.5) (L), 4) AS+lactic acid+Ti-ions 20ppm (TiL), 5) AS+H₂O₂ 0.5mM (HP_{0.5}), 6) AS+H₂O₂ 1.0mM (HP_{1.0}), 7) AS+H₂O₂ 0.5mM+Ti-ions 20ppm (HP_{0.5}Ti), 8) AS+H₂O₂ 0.5mM+lactic acid (HP_{0.5}L), and 9) AS+H₂O₂ 0.5mM+Ti-ions 20ppm+lactic acid (HP_{0.5}TiL). Electrochemical tests were performed following ASMT guidelines. Based on Tafel's method, current density (*i*_{corr}) and corresponding potential (E_{corr}) were acquired from potentiodynamic curves. Using electrochemical impedance spectroscopy (EIS), Nyquist and Bode plots were derived. Using a modified Randle's circuit, polarization resistance (R_p) and capacitance (C_{dl}) were estimated.

Results: The combination of Ti-ions, lactic acid, and H₂O₂ significantly decreased R_p (p<0.05). AS with H₂O₂ (groups 5 and 6) show significantly increased corrosion density (p<0.05).

Conclusions: The concurrent presence of Ti ions, lactic acid, and H₂O₂ in the vicinity of the Ti surface increased the corrosion kinetics. More corrosion in the peri-implant tissues, therefore more Ti products, is a potential risk factor for peri-implantitis.

Fretting-corrosion apparatus with low magnitude micro-motion (<5 μm) to study the hip implant taper degradation

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Although the modern design of hip implants with multiple components offers a better flexibility, it can also assist fretting corrosion to happen, which may lead to the early failure of the prosthesis. It is necessary to simulate the in vivo fretting behavior to overcome this issue, however, the current fretting test devices are not accurate enough to portray the micromotions occurring at the modular head/neck junction.

This study describes the development of a fretting-corrosion apparatus with low micromotion ($\leq 5 \mu\text{m}$) that can simultaneously monitor the corrosion process. Initial experiments with Ti6Al4V-Ti6Al4V in 0.9% saline were conducted to validate the system. During the fretting stage, a normal load of 83 N was applied, then the pin was controlled to oscillate $2 \mu\text{m}$ with a frequency of 1 Hz for 3600 cycles. After the testing, fretting loops were generated based on the friction force and displacements, and the sample surface was examined under the white-light profilometer and scanning electron microscopy (SEM) to obtain the surface morphology and wear loss.

As a result, the energy dissipated in a single cycle is approximately $2 \mu\text{J}$, and the energy ratios remained below 0.2 throughout the entire fretting stage, which is a direct indicator of a partial slip fretting regime. Regarding the electrochemical aspect, the open-circuit potential (OCP) drop in one cycle is around $30 \mu\text{V}$, and the local polarization resistance decreased after the fretting phase according to the electrochemical impedance spectroscopy (EIS) results.

Passive Films on NiCr and NiCrMo Alloys: Thickness, Composition, Stratification, Ion Transport

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Time-of-Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy were applied to characterize the passive films formed in acidic solution on two Ni-based alloys containing chromium and molybdenum (Ni-20Cr and Ni-20Cr-10Mo (wt.%)). The passive film on Ni-20Cr has a bilayer structure comprising a Ni and Cr outer hydroxide layer and a Cr inner oxide layer. The Ni-20Cr-10Mo alloy presents a similar bilayer structure, but with Mo oxide located at the outer layer/inner layer interface. Cr enrichment is observed after passivation for both alloys. The electrochemical data show that the corrosion resistance in acidic solution containing chlorides is enhanced by Mo, and by electrochemical pre-passivation in Cl⁻ free solution. This behavior is well explained by the spectroscopic data. Ion transport was studied with ¹⁸O isotopic tracer and revealed a significant role of Mo oxide.

Initial Oxidation in Ni-Cr Alloys and Enhanced Oxidation Resistance in Mo-Si-B Alloys

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Although extensive studies have been conducted on the oxidation behaviors of Ni-based alloys and their dependences on the alloy composition, temperature, and oxygen pressure, the microstructure effects such as grain size, grain boundary, and crystallographic orientation are known to be important but are usually not given much attention. For example, the dependence of oxidation rate on crystallographic orientation has been found in Ni, Cu, Fe, and Cr alloys where the character of the grain boundaries in the passive oxide film plays an important role in the differences of oxidation rate. However, in these studies the oxidation was examined in the late stages after exposure time of many hours. More importantly, there are even fewer studies on the effects of grain orientation and native oxide, which act as the initial states for the later stage oxidation. We have developed a novel pulse oxidation facility with the capability to detect the onset of oxidation on samples with a native oxide within the first few seconds of exposure¹. With this facility we have measured the nucleation of oxidation in Ni-15wt%Cr and Ni-30 wt%Cr alloys over a range of temperatures from 300 to 600°C. These measurements have allowed for the construction of TTT curves for oxide nucleation (the first to be reported) and the analysis of the nucleation kinetics.

Building on our previous MURI work on enhancing the oxidation resistance of Mo₃Si with selected dopants at the 2 at% level we have extended this strategy to multiphase Mo-Si-B alloys. Moreover, based upon our other research we have selected an alloy Mo-6Si-12B which is in the Mo_{ss} + Mo₅SiB₂ (T₂) + Mo₂B three phase field that allows for a significant reduction in the Si solubility in the Mo_{ss} phase that leads to an improvement in the ductility and toughness with a similar oxidation performance to the Mo_{ss} + Mo₃Si + T₂ alloys. Both the isothermal and cyclic oxidation behavior of Mo-6Si-12B-(1, 2, 4, 8)Al samples have been studied from 800 to 1300°C. With an increase of the Al content, the isothermal oxidation resistance is enhanced while the cyclic oxidation resistance is degraded. Moreover, the Al substitutions also suppress the pesting behavior at 800°C that is a typical issue for Mo alloys. On the Mo-6Si-12B-4Al sample the oxide layer consists of both an Al-doped borosilicate glass phase and a mullite phase. This composition has the best overall oxidation performance with about a factor of five improvement compared to the base without Al addition. The low viscosity of the Al-doped borosilicate glass provides a self-healing effect which contributes to the good cyclic oxidation performance. An oxidation kinetics model was developed based upon the independent contributions of the individual phase oxidation rates weighted by their relative phase fractions and sizes that provides a good account of the observed oxidation behavior.

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Nonlinear Dynamics of Corrosion: Why Butler-Volmer Kinetics and Equivalent Electric Circuit Analysis Fail

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Aqueous corrosion is an electrochemical process, in which a metal oxidation half-reaction is coupled with an oxidant reduction half-reaction via the exchange of electrons through a conducting medium (electrode), the metal. For this reason, most existing corrosion rate analyses are based on the chemical dynamics originally established for electrochemical half-reactions occurring in conventional electrochemical cells. A typical electrochemical cell consists of two electrodes, the anode and cathode, which are separated by an ion-conducting medium, the electrolyte. The electrodes are electronically conducting (or semi-conducting) but chemically inert. The overall process in each half-cell occurs in a number of elementary chemical steps, including *reversible* electron transfer reactions of *dissolved* species via the electrode, and solution transport of dissolved redox species to and from the electrode and the bulk solution.

Although similar elementary steps are involved, a corroding metal-solution system is a fundamentally different chemical dynamic system from that of a typical electrochemical cell:

- The metal acts not only as an electron-conducting medium (electrode) but also undergoes electron transfer reactions, releasing mass (metal cations) into the solution. That is, the solution is an open rather than a closed chemical system.
- Both the metal oxidation and oxidant reduction half-reactions occur at the same sites, separated only on the molecular or atomic scale. That is, the anode and cathode are not only galvanically coupled, but also essentially in the same location. The diffusion spheres of the metal oxidation product (metal cation) and oxidant reduction product (OH^-) can therefore overlap significantly, and their subsequent reactions can lead to significant changes in the redox and transport conditions in the interfacial region.

These differences can result in a corroding system with chemical dynamics very different from those of a conventional electrochemical system:

- The corroding metal-solution interface is not a Nernstian system and hence the interfacial electron transfer will not adhere to Butler-Volmer kinetics. Consequently, analysis of the relationship between current and potential during polarization by applying relationships such as the Wagner-Traud equation may result in an erroneous determination of the corrosion rate.
- Under certain conditions, the initial or secondary corrosion products can accumulate. The number of elementary steps, and hence the nature of the rate-determining steps, can change with time. The probability of systemic feedback between different steps under these conditions is high. It is normally assumed that the overall corrosion dynamics follow linear dynamics, which permits the application of electrical equivalent circuit analysis. However, when feedback is present, such an approach will not be able to accurately describe the corrosion rate as a function of solution parameters such as pH and oxidant concentration.

This presentation compares the kinetics of the elementary steps occurring in corrosion to those of typical electrochemical systems, and discusses the validities of some widely accepted corrosion mechanisms and the underlying reasons for the inadequacy of existing corrosion rate theories. Various experimental observations that clearly demonstrate the inadequacies of the Wagner-Traud equation and a linear dynamic approach will be presented.

Modeling preferential dissolution in corrosion of multi-principal element alloys using non-equilibrium thermodynamics

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Aqueous corrosion consists of intertwined processes of electrochemical/chemical reactions at anode and cathode, mass/charge transport in aqueous solution and migration of metal/electrolyte interface. Previous modeling efforts focus on the overall corrosion rate and morphological evolution of the metal/electrolyte interface, while the role of individual alloy elements leading to preferential dissolution of multi-component alloys is rarely considered.

Here, we apply the principles of non-equilibrium thermodynamics to model the thermodynamics and kinetics at the metal/electrolyte interface and incorporate the multiple internal dissipation processes of alloy elements by thermodynamic variation of entropy functional. Coupled with CALPHAD-type thermodynamic and kinetic databases, the current work is applied to Ni₃₈Fe₂₀Cr₂₂Mn₁₀Co₁₀ alloy to analyze the preferential dissolution and the corresponding predominant reaction mechanisms. With enhanced capability for multi-component alloys, the current work brings corrosion theories primarily for simple metals (e.g., pure metals and binary alloys) closer to real-life applications for compositionally complex alloys in aqueous environments.

Morphological stability of electrostrictive thin films

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The formation of a passive oxide film provides corrosion resistance of most industrially important metals and alloys. Passive films generally are very thin (few nanometers thick) with an electric field observed to be on the order of 10^8 - 10^9 V/m. The effect of electrostriction induced by such a large electric field is therefore expected to be important on the growth of the passive film¹.

Theoretical modeling of thin-film oxidation with electromechanical coupling is important in understanding the breakdown mechanism of thin oxide films. Stresses associated with the breakdown of oxide films include the stress due to lattice misfit between the substrate and the film and the stress induced by the electrical field, including the Maxwell stress and the electrostrictive stress.

Many models that describe the growth of oxide films are based on the thermodynamics and kinetics of point defects². However, the effect of stress is often neglected. Sato³ studied the effect of Maxwell stress on the growth of passive film. Tang and Ballarini⁴ performed morphological stability analysis with electrostriction. However, in this case the perturbation of electric field within the film is decoupled from the mechanical equations and the interaction between the film and substrate is neglected. Stanton and Golovin⁵ considered the instability with electrostriction but neglect the misfit strain and do not utilize the full electromechanical coupling.

Here, a continuum model that incorporates the lattice misfit and electric field induced stresses is developed. We perform a linear stability analysis of the fully coupled model and show that the electrostrictive effect can dominate the stability behavior of thin films, especially under a large electric field. We show that our model reduces to simpler models in certain limits. The effect of materials and geometrical parameters on instability is studied.

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Exposure Aging of Oxides on Multi-Principal Element Alloys and Ramifications Towards Local Corrosion Resistance

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This talk builds on the previous Scully Group talk and extends the discussion towards Multi-Principal Element Alloys MPEAs. Both highly engineered legacy and emerging alloys lack information on the precise attributes of protective passive films especially after long-time exposures which is when it really matters. Relevant field exposure periods are nearly infinite in time.

The focus of the current work extends from the solid solution Ni-22Cr, Ni-22Cr-6Mo, and Ni-22Cr-6Mo-3W family to a variety of emerging MPEAs. Potential step passivation studies in 0.1 NaCl pH 4 and in other solutions in the passive range were investigated over 10s to 10 days and at select potentials.

Improvements in passive films protectiveness was correlated to enrichment of certain elements and depletion of others. Mn oxides were found to be detrimental when formed over the long term in the outer layer of oxides on MPEAs containing Mn. The most corrosion resistant alloys possess passivating films that are efficacious not only just after formation, but that self-heal as well as improve over long exposure times as evident from impedance spectroscopy. Such alloys were observed to be the most resistant when interrogated for local corrosion compared to other alloys whose impedance response degraded over time. The latter alloys eventually arrived at conditions for breakdown. Oxide exposure aging time, potential, and oxide “transformation” diagrams are utilized herein and provide valuable insights. Factors affecting and limiting Cr enrichment are also discussed.

Flexoelectricity and Morphological Stability in Nickel-based Alloys

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Passivation is a critical phenomenon for protecting metallic systems. Although some metals naturally form protective thin films of oxides on their surfaces, others require alloying with more reactive metals to form passivating layers. Furthermore, the spontaneous formation of oxides at the surface is not a sufficient condition for robust passivation; these passivating layers must also be morphologically stable. Understanding the conditions that lead to morphological instabilities will lead to a better understanding of how to engineer alloys with robust passivation properties.

The energy density of a passive oxide on the surface of a metal consists of mechanical terms related to lattice mismatch between the metal and oxide, an electrical term based on the polarization density of the oxide and various electromechanical terms including electrostriction, piezoelectricity, and flexoelectricity. Electrostriction has been previously studied as a destabilizing driver [1] while piezoelectricity can be ignored in centrosymmetric oxides. In contrast, flexoelectricity, the electromechanical coupling between strain gradient and polarization, has been shown to affect significant local electric fields in locally deformed oxide films [2]. Because such deformations are common in corrosion processes, flexoelectric effects should be accounted for in passivation models.

Here, we present a first-principles study on the flexoelectric coupling of antiferromagnetic NiO, a prevalent oxide in Ni-Cr alloys [3]. We employ density functional theory to probe its bulk flexoelectric effect [4,5] and utilize a recently developed technique to examine the mean-inner-potential contribution to flexoelectricity[6]. We report on magnetic contributions to the flexoelectric response in NiO and the possibility of a spin-polarized flexoelectric tensor. We also discuss possible strategies for including flexoelectric effects in phase-field models of corrosion.

Acknowledgements: The authors were sponsored by the Department of Navy, Office of Naval Research, under ONR Award number N00014-16-1-2280. The US Government has a royalty-free license throughout the world in all copyrightable material contained herein.

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