Surface Science Division
Room 319 - Session SS1+HC-WeM

Alloy Surface Reactivity

Moderator: Zdenek Dohnalek, Pacific Northwest National Laboratory

8:00am **SS1+HC-WeM-1 Development of a Predictive Model for Nb₃Sn Thin Film Growth: Elucidating the Substrate-Mediated Diffusion Pathways Guiding Alloy Formation in Accelerator Infrastructure**, *Sarah Willson,* University of Chicago*; R. Farber,* University of Kansas*; S. Sibener,* University of Chicago

Niobium is the current standard elemental material for superconducting radiofrequency (SRF) cavities, but the required operating temperatures (< 4 K) impose a significant monetary burden. To achieve improved accelerating gradients at increased operating temperatures, efforts are underway to vapor deposit Sn on preexisting Nb SRF cavities to form Nb₃Sn thin films. However, these Nb₃Sn coatings contain high surface defect densities and stoichiometric inhomogeneities; the accelerating performance of Nb₃Sn coated cavities is directly associated with the Nb₃Sn surface morphology. Current Nb₃Sn SRF cavities, therefore, are impractical for implementation in particle accelerator facilities. The implementation of Nb₃Sn SRF cavities necessitates a comprehensive and mechanistic understanding of how to form smooth and homogenous Nb₃Sn films.

To develop a predictive growth model for Nb₃Sn grown *via* Sn vapor deposition, we aim to understand the interplay between the underlying Nb oxide morphology, Sn coverage, and Nb substrate heating conditions on Sn wettability, intermediate surface phases, and Nb₃Sn grain growth dynamics. In this work, Nb-Sn intermetallic species are grown on a single crystal Nb(100) in an ultra-high vacuum chamber equipped with *in situ* surface characterization techniques including Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy/spectroscopy (STM/STS).

Sn adsorbate behavior on oxidized Nb was examined by depositing Sn with sub-monolayer precision at varying Nb sample temperatures (T_S). STM data of Sn deposited on a highly ordered NbO surface reconstruction reveal that the Nb T_S during deposition strongly dictates the competition between Sn incorporation and desorption during subsequent annealing. By tailoring Sn deposition parameters to suppress Sn desorption, AES and XPS data of annealed intermetallic adlayers provide supporting evidence of how Nb substrate oxidization and sample temperature impact Nb-Sn coordination. Ongoing experimental studies aim to demonstrate the impact of altering numerous vapor and substrate conditions on the growth mechanisms and alloying dynamics that ultimately enable optimal Nb₃Sn growth.

8:20am **SS1+HC-WeM-2 Surface Chemical Reactions in the Oxidation of NiCr and NiCrW Alloys**, *Petra Reinke, C. Volders,* University of Virginia, USA*; V. Avincola Angelici ,* University of Virginia*; I. Waluyo, A. Hunt,* Brookhaven National Laboratory*; L. Arnadottir,* University of Oregon

The oxidation of alloys including several reactive elements is controlled by complex reaction pathways where surface chemistry, reactant transport, alloy microstructure, oxide-alloy epitaxy and other factors compete. Our work focusses on the oxidation of Ni-based superalloys frequently used in technologies subjected to a wide range of environmental stressors from chemically aggressive solutions in sea water, batteries and fuel cells to radiation in nuclear waste containers. We address the socalled "third element effect" TEE where a relatively small addition of a specific element has an outsized impact on corrosion and oxidation processes. We specifically address the initial steps in the formation of the protective oxide layer starting with a pristine alloy surface. Significant gaps exist in the mechanistic understanding of the initial reaction steps of their oxidation. Near ambient pressure X-ray photoelectron spectroscopy, XPS and STM were used to study the oxidation with O₂ *in operando* for a sequence of alloy compositions from Ni-5wt%Cr, Ni-15wt%Cr, Ni-30wt%Cr to Ni-15wt%Cr-6wt%W. The experiments were performed at 500 °C, p(O₂)=10⁻⁶ mbar and reflect the initial 25 ms of oxidation at ambient conditions. The formation of Ni and Cr oxides competes under these conditions due to kinetic limitations imposed on the reaction of Cr, which is thermodynamically preferred.

The comparison of oxide evolution for four different alloys with variable Cr and W content quantifies the outsized impact of W as a minor alloying element. For the binary alloys an initial rapid increase in chromia driven by Cr-surface enrichment is followed by NiO nucleation and growth, ultimately seeding a dual-layer structure. The addition of small amounts of W in Ni-15wt%Cr-6wt%W shifts the reaction pathways towards Cr oxidation revealing a high quality chromia layer which is desirable for its protective function. Density functional theory calculations inform that W atoms adjacent to Cr sites embedded in the Ni surface create even more favorable oxygen adsorption sites. In short, a larger Cr content in the surface enhances reaction with oxygen, but the addition of W "supercharges" the reactivity of Cr by funneling the oxygen atoms into Cr sites. The surface chemistry is identified as a decisive contribution to the TEE, and is accompanied by a enhanced grain boundary driven Cr transport in the alloy to sustain chromia growth.

8:40am **SS1+HC-WeM-3 High Throughput Methods for Comprehensive Study of Alloy Segregation and Structure Sensitivity**, *Andrew Gellman, C. Fernandez-Caban, Z. Guo, R. Burnley,* Carnegie Mellon University, USA
INVITED

Comprehensive study of phenomena such as segregation in alloys or structure sensitivity in catalytic surface chemistry is hampered by the fact that the independent variables associated with these phenomena are continuous and multidimensional. In the case of alloy segregation, the relevant independent variable is alloy composition which is continuous and multidimensional in the case of ternary or higher order alloys. In the case of structure sensitivity, the possible orientations of single crystal surfaces span a continuous 2D space. Comprehensive study of these phenomena requires high throughput methods that allow rapid, concurrent measurements of surface composition and chemistry across parameter space.

Composition spread alloy films (CSAFs) have been used as sample libraries for accessing broad and continuous alloy composition spaces. CSAFs are thin alloy films deposited on appropriate substrates such that they have lateral composition gradients. A binary CSAF of components A and B can run from pure A at one end to pure B at the other. A ternary CSAF can be prepared with a triangular region that mimics a ternary composition diagram and literally contains all possible ternary alloy compositions. These alloy sample libraries are ideal for the study of surface segregation. We have used low energy He⁺ ion scattering to map segregation at 100s of alloys spanning the composition spaces of CuPdAu, CuAgAu and NiPdAu ternaries. This work has explored both equilibrium segregation over a range of temperatures and the measurement of surface segregation kinetics.

Surface Structure Spread Single Crystals (S⁴Cs) have been used as sample libraries for accessing broad and continuous ranges of single crystal surface orientations. S⁴Cs are metal single crystal disks fabricated such that one side is a section of a sphere. These usually (but not necessarily) have a low Miller index plane exposed at their center and the rest of the surface exposing all possible surfaces orientations lying within some polar angle (14° in our case) of the low Miller index point. By first adsorbed reactive species on the curved surface and then spatially mapping their coverage versus time, $\vartheta_{hkl}(t)$, at a given temperature we are able to extract reaction rate constants as functions of surface orientations. In this manner, we have studied the enantiospecific decomposition kinetics of D- and L-tartaric acid on all chiral Cu(*hkl*)R&S surfaces vicinal to the three low Miller index planes.

9:20am **SS1+HC-WeM-5 Unveiling the Ability of Rh Single Atoms to Enhance the Dissociation of Molecular Oxygen and Spillover to Cu**, *Volkan Cinar*[1], Tufts University*; D. Guo,* Washington State University, US*; Y. Wang, C. Easton, H. Chen,* Tufts University*; N. Ulumuddin,* Washington State University, US*; R. Hannagan,* Tufts University*; I. Waluyo,* Brookhaven National Laboratory*; J. McEwen,* Washington State University, US*; C. Sykes,* Tufts University

Copper-based catalysts are used in a wide range of heterogeneous catalytic processes such as methanol synthesis, CO oxidation, epoxidation of alkenes, and the water-gas shift reaction. As many of these reactions can take place in oxidizing environments, CuO$_x$ surfaces have been extensively studied to better understand structure-function relationships. Single-atom alloys (SAAs) are a new type of catalyst in which small amounts of reactive dopants (Pd, Pt, Ni, Rh, etc.) are present as isolated atoms in less reactive metals such as Cu. However, literature of the behavior of these materials under oxidizing conditions is limited.

Using surface science experiments we discover that 0.005 monolayers Rh in the surface of Cu(111) enhances the rate of O₂ dissociation by ~20 times. TPD experiments are conducted using the partial oxidation of methanol to formaldehyde to titrate away the adsorbed oxygen and hence quantify the

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[1] **SSD Morton S. Traum Award Finalist**

increased dissociative sticking probability of O_2 on the RhCu SAA vs. Cu(111). CO "poisoning" and annealing experiments were conducted to further investigate the role of the Rh atoms in dissociating molecular oxygen. These TPD experiments reveal that adsorption of ~1% of a monolayer of CO, which block the Rh sites and reduce the O_2 dissociation back to pure Cu(111) providing evidence that Rh is the site for O_2 activation. Furthermore, annealing the surface to 250°C, which induces the subsurface diffusion of Rh, gives the same result. Further quantification of oxygen uptake on the RhCu SAA reveals a spillover effect whereby molecular oxygen dissociates on the Rh atom sites and diffuses to sites on Cu(111). STM experiments are performed to elucidate the atomic-scale detail of this effect. The STM images reveal that on Cu(111) and the RhCu SAA, oxidation occurs at the Cu step edges, consistent with literature reports. However, for the case of the RhCu SAA, we observe features on the terraces, consistent with atomic oxygen spill over from Rh atoms. Our DFT calculations quantify the energetics of the process showing that the molecular oxygen binds to the Rh sites stronger than Cu(111) and that the activation barrier is lower as compared to bare Cu(111). Furthermore, our DFT results support the spillover of oxygen atoms from Rh site to the Cu host. Together, these results begin to shed light on the role of single metal atom dopants in promoting Cu oxidation.

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