

The Surface Kinetics of the Initial Oxidation Stages of Cu and Cu Alloys

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Environmental stability is one of the most important properties for materials exposed to air. As the dimensions of engineered systems approach the nanoscale, fundamental understanding of reactions with oxygen at this length scale becomes critical for environmental stability as well as for processing oxide nanostructures, where surface reactions are commonly used. Because environmental stability is an essential property of most engineered materials, many theories exist to explain oxidation and corrosion mechanisms. However, nearly all classical oxidation theories assume a uniform growing film, where structural changes are not considered because of the previous lack of experimental procedures to visualize non-uniform growth conditions. These macroscopic depictions do not address how initial surface conditions and early stages of oxidation lead to the final oxide scale morphology, though it is well known that surface conditions and secondary elements dramatically impact the oxide structure. These transient stages of oxidation — from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide — represent a scientifically challenging and technologically important *terra incognita*.

These issues can only be understood through detailed structural study of the relevant microscopic processes at the nanoscale *in situ*, combined with comparison to theoretical models. Hence, we are studying the dynamics of the initial and transient oxidation stages of a metal and its alloys with *in situ* methods, including ultra-high vacuum transmission electron microscopy (UHV-TEM) and synchrotron X-ray diffraction. We examined the dynamic responses of Cu and Cu alloy thin films to variations in thermodynamic variables such as temperature, oxygen partial pressure (pO_2), strain, and crystallographic orientation. Our past work demonstrated that the formation of epitaxial Cu_2O islands during the transient oxidation of Cu(100), (110) and (111) films bears a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies [1-4]. We are currently developing multi-scale simulations to directly compare to the Cu oxidation data and provide insight into the mechanisms controlling the initial stages of oxidation [5]. For example, a kinetic Monte Carlo code has been developed to describe three-dimensional island nucleation and growth (www.tfox.org) [6].

The kinetics of early stage oxidation of Cu, Cu-Au and Cu-Ni alloys were visualized using *in situ* ultra-high vacuum transmission electron microscopy (UHV-TEM), where the initial oxidation stages can be observed in real-time under well-controlled surface conditions. These experiments were carried out in a modified JEOL 200CX TEM. This microscope is equipped with an ultra-high vacuum (UHV) chamber with base pressure $\sim 10^{-8}$ Torr. The microscope was operated at 100KeV to minimize the possibility of radiation-induced effects. A controlled leak valve attached to the column permits the introduction of oxygen gas directly into the microscope at a pO_2 between 5×10^{-5} and

$\sim 5 \times 10^{-4}$ Torr. Single crystal Cu, CuAu(100) and CuNi(100) thin films with 400-1000 Å thickness were grown on single crystal NaCl substrates by e-beam evaporation in a Pascal UHV dual e-gun e-beam evaporator system. The metal films were removed from the substrate by flotation in deionized water, washed and mounted on a specially prepared sample holder that allows for resistive heating to a maximum temperature of 1000°C.

Compared with the behavior of Cu films, the oxidation of Cu-Au alloys revealed more complexity. The nucleation barrier for oxide formation decreases with increasing oxide concentration, whereas the addition of Au leads to a self-limiting dendritic growth of the oxide due to the Au build-up around the oxide island [7]. Evolution of the shape and size of the oxide islands can be quantitatively analyzed and provide fundamental insights into the complex kinetics and energetics of oxidation.

We are currently studying the early and transient oxidation stages of Cu-Ni alloys by *in situ* UHV-TEM and synchrotron XRD, where some remarkable differences are observed in comparison to our past studies of Cu and Cu-Au alloys [8]. Firstly, irregular and polycrystalline oxides form on Cu-Ni alloys, in contrast to only single crystal cube-on-cube oxide formations on Cu(100), Cu(110) and Cu(111), as well as all relative concentrations of Cu-Au(001) previously investigated. Secondly, though rapid nucleation followed by growth of oxides is observed, thereby supporting an oxygen surface diffusion model, a second rapid nucleation of compact islands with high number density is also observed, which is due to the formation of NiO initially and then Cu₂O, as elucidated by *in situ* XRD experiments. Further detailed structural studies of the oxides, interfaces, and the effects of small amounts of Ni additions to the surface changes of the Cu-Ni(001) that result in irregular-shaped polycrystalline oxide formation as well as theoretical simulations are necessary to clarify the underlying mechanisms of the early and transient stages of selective oxidation.

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