

The surface kinetics of the initial stages of copper and copper alloy oxidation

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Environmental stability is one of the most important properties for materials exposed to air. As dimensions of engineered systems approach nanoscale, fundamental understanding of reactions with oxygen at this length scale is critical for environmental stability as well as for processing oxide nanostructures, where surface reactions are commonly utilized. The nanoscale 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*. The kinetics of early stage oxidation of Cu and Cu-Au 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. We examined the dynamic responses of thin films to variations in thermodynamic variables such as temperature, oxygen pressure, strain, and crystallographic orientation. The kinetics of the nucleation and growth of three-dimensional oxide islands demonstrate that oxygen surface diffusion is the rate-limiting mechanism for oxide growth during initial oxidation in dry oxygen. Compared with the behavior of Cu films, the oxidation of Cu-Au alloys revealed more complexity. For example, the oxidation of (100)-oriented Cu-Au alloys with low Au content at ~600°C results in the formation of Cu₂O oxide islands with a dendritic morphology and a non-uniform lateral distribution of Au around the islands. 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. Models based on surface orientation, strain development, and diffusion will be discussed to explain the formation of some of the novel oxide nanostructures.