

## The Effects of Au Alloying on Cu-Au Nanoscale Oxidation Reactions

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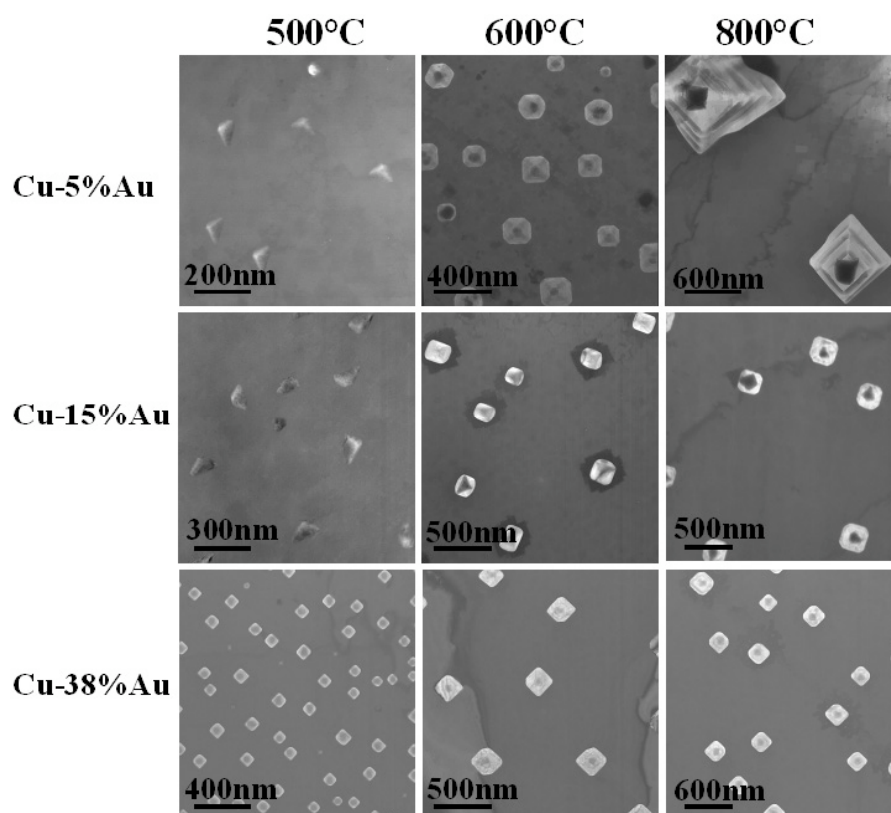
Alloy oxidation has significant technological importance because of the possibility of dramatically improving corrosion resistance through compositional control. The possible effects of alloying elements on behavior also motivate fundamental study of oxidation mechanisms. Surprisingly, the previous lack of tools capable of probing atomic-level and mesoscale behavior have resulted in the initial stages of oxidation being the least well-understood regime of oxidation. Improvements in vacuum technology and nano-characterization have, however, recently led to many novel experiments providing new insights into the details of how oxygen reacts with surfaces. Our focus is on the nucleation and growth of oxides on metal and alloy surfaces, where *in situ* ultra-high vacuum transmission electron microscopy (UHV-TEM) is ideal for providing information of structural changes at this scale where surface conditions are very well controlled. Using primarily *in situ* UHV-TEM experiments of Cu oxidation, we have previously shown that heteroepitaxial concepts describe surprisingly well the nucleation, and growth to coalescence of Cu<sub>2</sub>O islands on Cu(001) [1, 2], where oxygen surface diffusion is the dominant mechanism controlling nucleation and growth. We now focus on Cu-Au oxidation as a model binary alloy system, which is a natural extension of our extensive previous work on Cu [4,5]. Au is a noble element and does not form a stable oxide, and Cu and Au are miscible at the elevated temperatures where oxidation behavior is of interest.

These experiments were carried out in a modified JEOL 200CX TEM [6]. 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 partial pressure ( $p_{O_2}$ ) between  $5 \times 10^{-5}$  and  $\sim 5 \times 10^{-4}$  Torr. CuAu(100) single crystal films with 1000Å thickness were grown on irradiated NaCl(100) by sputter deposition. The alloy 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.

For temperatures ranging from 550 °C to 750 °C and constant oxygen partial pressure of  $5 \times 10^{-4}$  Torr, Cu<sub>2</sub>O islands formed initially with cube-on-cube crystallographic orientation relative to the Cu-Au film. In comparison to Cu(100), the incubation time for Cu<sub>2</sub>O nucleation is longer on the alloy surface. However, once the oxide islands start to appear, the nucleation rate is faster in Cu<sub>0.5</sub>Au<sub>0.5</sub> (001) alloy, i.e. the time from the appearance of the first oxide island to when the island saturation density is reached is significantly shorter for the Cu-Au alloy as compared to Cu. Figure 1 is a bright field TEM image showing how the morphology of a typical Cu<sub>2</sub>O island changes due to composition and temperature. We speculate how the secondary element, Au, alters the oxidation mechanism of Cu<sub>2</sub>O growth from oxygen surface diffusion to an interface limited reaction.

## References

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**Figure 1:** TEM micrographs of  $\text{Cu}_2\text{O}$  formed during *in situ* oxidation on  $\text{Cu}_x\text{Au}_{1-x}$  where morphological changes are noted due to composition and oxidation temperature.