

The Surface Dynamics of the Initial Oxidation Behavior of CuNi Alloys Studied by *in-situ* TEM

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Our extensive research on Cu and Cu-Au oxidation by primarily *in situ* ultra high vacuum transmission electron microscope (UHV-TEM) have demonstrated that oxidation involves nucleation and growth, surface diffusion and solid state reactions, and bears a striking resemblance to heteroepitaxy where strain plays a critical role in the morphological development of the oxide islands [1-3]. As an extension of this work, we are currently visualizing the oxidation of Cu-Ni alloys, where the two components are 100% solid-soluble down to ~300 °C but Cu₂O and NiO show limited miscibility. Nickel oxide, which has the cubic NaCl crystal structure, has a more negative standard free energy of formation than Cu₂O, which is simple cubic, and is expected to form more readily. Depending on the environmental pO₂ and temperature, either one or both components of the alloy will oxidize, thus enabling a systematic determination of the effects of composition on the oxide phase development during oxidation.

Single crystal 80 nm (001) Cu-24%Ni films were produced by co-sputtering Cu (99.999%) and Ni (99.999%) onto irradiated (001) NaCl with an AJA sputtering system, where the base pressure was 10⁻⁸ Torr. The selected deposition rate was 1 Å per second, as monitored by a quartz crystal microbalance (QCM), and the substrate temperature was held at 270~300 °C within an Ar atmosphere of 5 mTorr during deposition. The *in situ* UHV-TEM is a specially modified JEOL 200 CX with a top entry sample holder. The additional pumping on the column of the microscope consists of a combined Thermionics ion/liquid nitrogen cooled sublimation pump and a Balzers turbo molecular pump. Furthermore, a cryoshield surrounds the specimen cartridge which is cooled via conduction through a Cu wire to a cold finger held at liquid nitrogen or liquid helium temperature. The pressure in the sample region was determined by an ion gauge attached above the pole piece. The Cu-Ni film was removed from the NaCl substrate by floatation in de-ionized water, washed and then mounted onto a specially prepared Si mount. The Si mount and the modified specimen holder allow for resistive heating of the specimen up to 1000 °C *in situ*. Scientific grade oxygen gas of 99.999% purity was admitted into the column of the microscope through the leak valve at a partial pressure between 5×10⁻⁵ and 760 Torr.

In remarkable contrast to our previous observations of Cu and Cu-Au oxidation: 1) a second rapid nucleation of compact and dense oxide islands occurred and 2) polycrystalline oxides formed, where only cube-on-cube epitaxial Cu₂O islands nucleated on Cu(001) and CuAu(001) for all temperatures and pressures studied. We speculate that the surface segregation of Cu and Ni towards or away, respectively, from the alloy surface during oxidation could disrupt the surface and cause polycrystalline oxide formation. Furthermore, the formation and evolution of oxide islands and their oxidation dynamics will be studied as a function of increasing Ni concentration in the Cu-Ni alloys both *in situ* and *ex situ* experiments, including XRD.

Reference

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- [2] Zhou, G. W.; Slaughter, W. S.; Yang, J. C., Terraced Hollow Oxide Pyramids. *Physical Review Letters* **2005**, *94*, 246101-4.

[3] Zhou, G. W.; Yang, J. C., The initial stages of Cu(110) oxidation investigated by in situ UHV-TEM. *Surface Science* **2003**, *531*, 359-367.

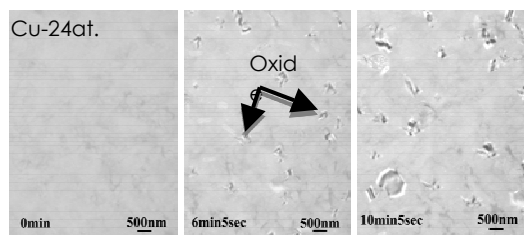


Figure 1. Bright-field images of the *in situ* oxidation of Cu-24at%Ni (001) at $T=500^{\circ}\text{C}$ and $P(\text{O}_2) = 5 \times 10^{-4}$ torr. (a) As-clean, (b) 6 and (c) 10 minutes after oxygen was introduced.

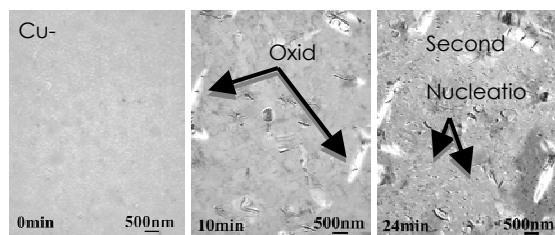


Figure 2. Bright-field images of the *in situ* oxidation of Cu-24at%Ni (001) at $T=600^{\circ}\text{C}$ and $P(\text{O}_2) = 5 \times 10^{-4}$ torr. (a) As-clean, (b) 10 and (c) 24 minutes after oxygen was introduced.

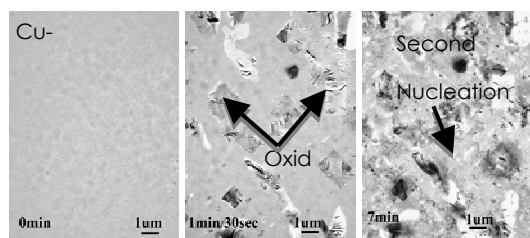


Figure 3. Bright-field images of the *in situ* oxidation of Cu-24at%Ni (001) at $T=700^{\circ}\text{C}$ and $P(\text{O}_2) = 5 \times 10^{-4}$ torr. (a) As-clean, (b) 1.5 and (c) 7 minutes after oxygen was introduced.

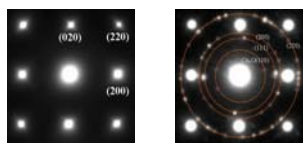


Figure 4. Selected area electron diffraction pattern of Cu-24at%Ni (001) film before and after oxidation at $P(\text{O}_2) = 5 \times 10^{-4}$ torr and $T=600^{\circ}\text{C}$, where the index (111) indicates both $\text{Cu}_2\text{O}(111)$ and $\text{NiO}(111)$, similarly for (200) and (220). Similar polycrystalline diffraction patterns were observed for $T=500^{\circ}\text{C}$ and 700°C .

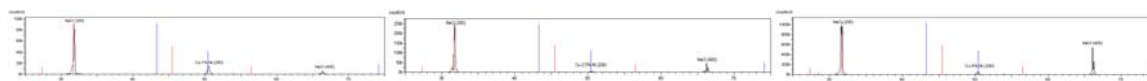


Figure 5. XRD diagram of Cu-1 at% Ni, Cu-2.5at% Ni and Cu-5at% Ni film before *in situ* and *ex situ* oxidation.