

***In situ* TEM investigation of early-stage oxidation of (001)Cu-Au alloys**

G.-W. Zhou, J.A. Eastman, R.C. Birtcher, P.M. Baldo, J.E. Pearson, L.J. Thompson
Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

L. Wang, J.C. Yang
Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, PA 15261

A general strategy for the protection of underlying metals is alloying, which leads to the formation of a protective oxide layer over the alloy surface due to the preferential oxidation of one component of the alloy [1]. Much progress has been made in understanding later-stage oxidation, as formulated by Wagner theory [2]. However, detailed information from early-stage oxidation studies is still very limited, especially in the case of alloys. This is due primarily to the lack of tools capable of probing atomic-level and mesoscale behavior during early stages of oxidation. *In situ* ultrahigh vacuum (UHV) transmission electron microscopy (TEM) is an ideal tool to investigate early stages of metal oxidation [3]. The advantages of *in situ* UHV TEM experiments include visualization of oxidation processes in real time and information on buried interfaces. Furthermore, this technique is capable to provide dynamic information from nucleation to initial growth and coalescence of oxide islands at nanometer scale under controlled surface conditions, which is inaccessible to both surface science methods and traditional bulk oxidation studies, but is essential for fundamental understanding of atomistic oxidation kinetics. Choosing Cu-Au as model system in this work, we perform an in-situ TEM study of the early-stage oxidation kinetics of alloys containing a noble metal and an oxidizable metal, and seek the effects of alloying on nucleation, growth, and morphology of oxide islands. This system is considered since it allows some of the features of alloy oxidation to be examined without the complication of the simultaneous formation of two oxides.

Our *in situ* oxidation experiments were carried out in a modified JEOL 200CX TEM [4]. This microscope is equipped with a UHV chamber. A controlled leak valve attached to the column of the microscope permits introduction of oxygen gas directly into the microscope at a partial pressure (p_{O_2}) between 5×10^{-5} and $\sim 5 \times 10^{-4}$ Torr. Single crystal ~ 1000 Å (001)Cu-Au alloy thin films with different Au mole fraction were grown on irradiated (100)NaCl by sputter deposition. The alloy films were removed from the NaCl substrate by flotation in deionized water, washed and mounted on a specially designed TEM sample holder which allows for resistive heating between room temperature and 1000°C .

Our *in situ* TEM observation indicates that an incubation time is needed for appearance of visible Cu_2O nuclei on the metal surface after admitting oxygen into the microscope. The incubation time depends on oxidation temperature and alloy composition, as shown in Figure 1. After the incubation time, oxide nuclei become visible and their number increases with time until to a saturation density. The quantitative measurements indicate that increasing Au mole fraction in the alloys results in a higher saturated number density of the oxide nuclei, but a slower island growth rate. The alloy composition has an effect on oxide morphology, oxidation of the alloys with Au mole fraction less than 25% results in triangular-shaped oxide islands at $450\sim 550^\circ\text{C}$, and square-shaped islands at $600\sim 800^\circ\text{C}$. Only square-shaped oxide islands are formed at all the oxidation temperatures ($450\sim 800^\circ\text{C}$) in the alloys with larger Au mole fraction. In particular, in-situ TEM observation also revealed that the initially square-shaped Cu_2O islands undergo a remarkable transformation to a dendritic structure as growth proceeds during oxidation of Cu-Au alloys with Au mole fraction less

than 38% at 600°C and above [5]. These results are explained by the effects of Au on oxygen surface adsorption/diffusion, epitaxial strain, and the mechanism of oxide growth.

Reference:

- 1 G. R. Wallwork, Rep. Prog. Phys. **39**, 401 (1976).
- 2 C. Wagner, Z. Phys. Chem. **B21**, 25 (1933).
- 3 J. C. Yang, M. D. Bharadwaj, G.-W. Zhou, and L. Tropa, Microscopy and Microanalysis **7**, 486 (2001).
- 4 M. L. McDonald, J. M. Gibson, and F. C. Unterwald, Rev. Sci. Instrum. **60**, 700 (1989).
- 5 G.-W. Zhou, L. Wang, R. C. Birtcher, P. E. Baldo, J. E. Pearson, J. C. Yang, and J. A. Eastman, submitted (2006).
- 6 Argonne National Laboratory's work was supported by the U.S. Department of Energy, Office of Basic Energy Science under Contract W-31-109-Eng-38. We are thankful to the Materials Research Laboratory, University of Illinois at Urbana-Champaign for use of the *in situ* TEM facility and we thank R. Twesten, M. Marshall, and K. Colravy for their help.

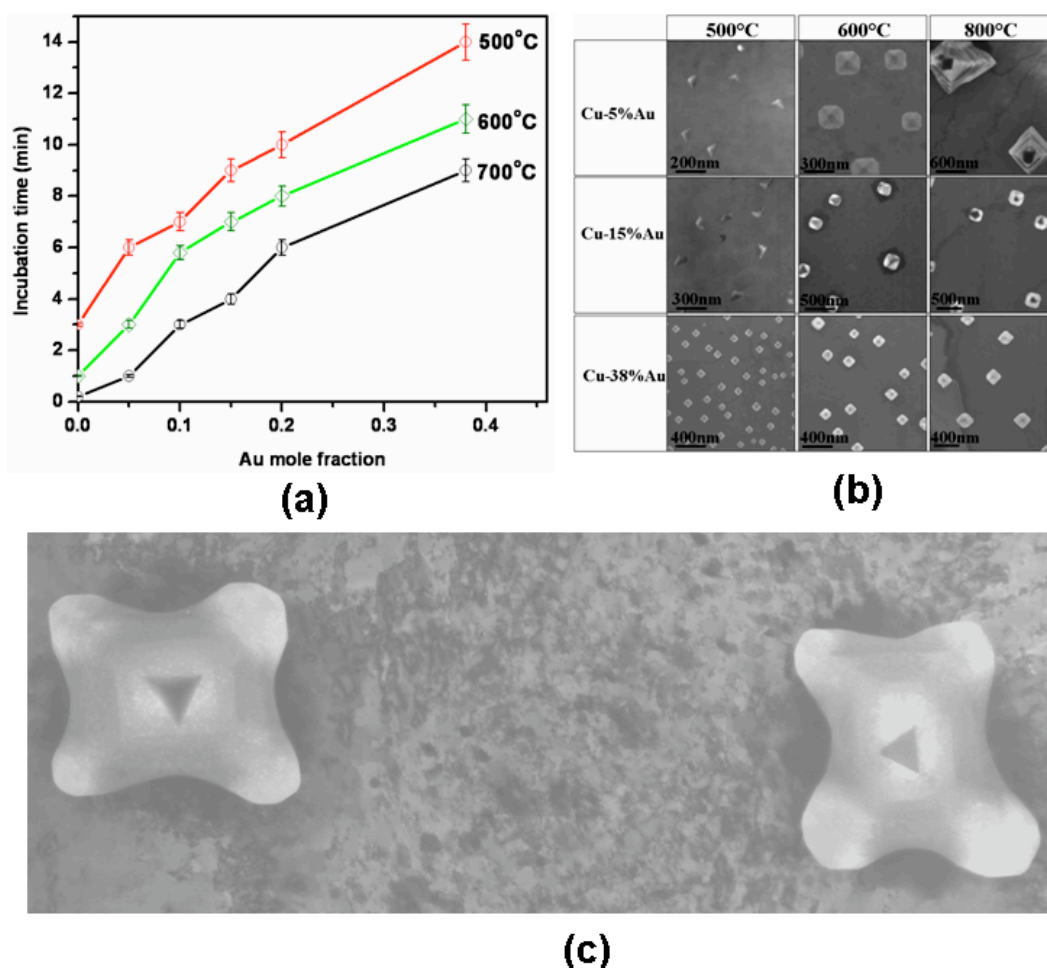


Figure 1: (a) Composition and temperature dependence of the incubation time for the nucleation of Cu_2O islands during oxidation of the Cu-Au alloys; (b) Composition and temperature dependence of the morphology of oxide islands; (c) dendritic transition of initially square-shaped islands as growth progresses.