

***In Situ* Atomic Scale ETEM Observation of Oxide Nucleation and Growth During Initial Oxidation of Cu and Cu-Ni Alloy**

Meng Li, Matthew Curnan, Richard Garza, Michael Gresh-Sill, Stephen House, Wissam Saidi and Judith Yang

University of Pittsburgh, Pittsburgh, Pennsylvania, United States

The initial oxidation processes of metals and alloys are essential to the fundamental understanding of oxidation, as these processes play key roles in corrosion prediction, catalyst design, and oxide control. Despite numerous prior studies in metal and alloy oxidation, the microstructural evolution during initial oxidation processes – namely transition from clean metal/alloy surfaces to oxide scales – is not well understood, especially at the atomic scale. Existing oxidation theories, such as those from Cabrera-Mott and Wagner, did not consider the effects of microstructure on oxidation. Thus, they could not predict how surface orientations, grain boundaries, and surface defects affect the oxidation result. Besides, theories that can predict how alloy elements affect the results of oxidation, especially when there are multiple oxidizing elements, are also lacking. Previous surface science studies on Cu oxidation using Scanning Tunneling Microscope (STM) have revealed formation of multiple surface reconstruction phases on Cu surfaces under O₂, such as the Missing Row Reconstruction (MRR) of Cu(100) surfaces. However, how reconstructed surfaces affect oxide nucleation is still controversial due to a lack of direct experimental proof. Besides, recent computational studies indicate defects, such as surface steps, play a significant role in oxygen diffusion [1]. Nevertheless, the effects of surface steps on surface reconstruction and oxide formation is still unclear. Beyond pure metals, how the addition of alloy elements affects the initial oxidation process is unexplored, largely due to a lack of experimental and computational study.

In this work, using correlated *in situ* Environmental TEM (ETEM) and atomistic simulations, the atomic-scale dynamic processes of oxide nucleation and growth are investigated and compared on pure Cu and Cu-Ni under O₂. Single-crystalline Cu(100) and Cu-Ni(100) thin film samples with a thickness of 60 nm were prepared. Hitachi H-9500 ETEM operating at 300 keV with a home-made gas delivery system was used for the *in situ* ETEM experiment. The films were first reduced inside the ETEM at 600 °C under H₂, in order to reduce native oxides and create holes with (100) and (110) facets. *In situ* oxidation experiments were then carried out on these facets at 350 °C under O₂. Figure 1 shows the atomic resolution initial oxidation process on pure Cu(100) observed by *in situ* ETEM. As shown in Fig. 1(a-b), Missing Row Reconstruction (MRR) is observed to form on the originally clean Cu(100) surface under oxygen. When oxygen pressure increases, a Cu₂O island is observed to nucleate on the Cu(100) surface (Fig. 1c), followed by layer-by-layer island growth (Fig. 1d) [2]. In-depth analysis of the atomic resolution processes of MRR formation, oxide nucleation, and growth processes using home-developed automated ETEM data analysis methods and statistical analysis provides key evidence for initial Cu oxidation. Beyond pure Cu, atomic scale dynamic processes of oxide nucleation and growth on Cu-Ni(100) surfaces were also investigated (Figure 2). In order to better understand the mechanisms behind these experimental observations, a multi-scale simulation framework generalizes density functional theory results via force fields, applying these results to molecular dynamics and kinetic Monte Carlo simulations at larger size and time scales. These atomic scale experimental observations, correlated with multi-scale simulations, will help unveil the initial oxidation mechanisms of metals and alloys [3].

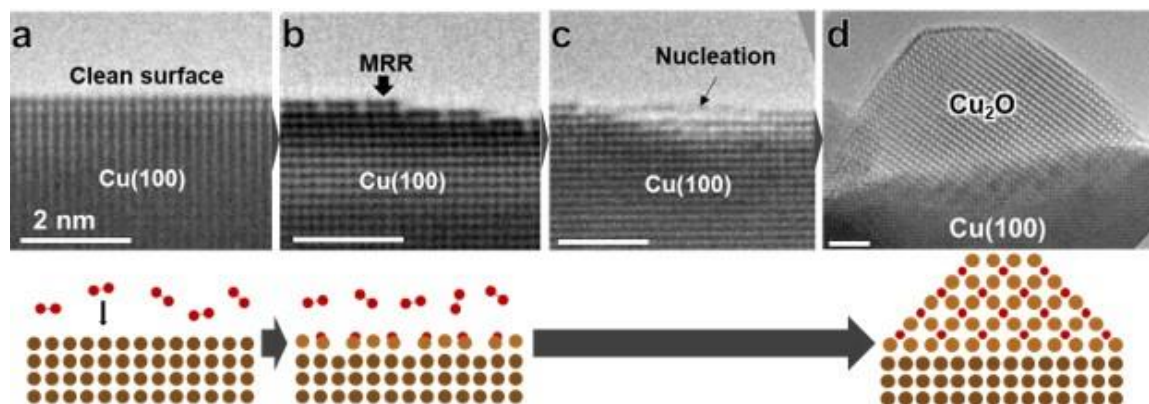


Figure 1. In situ ETEM observation of initial oxidation processes on pure Cu(100) surfaces at 350 °C under O₂. (a) Clean Cu(100) surface in vacuum. (b) Missing Row Reconstruction (MRR) on stepped Cu(100) surface under 0.1 Pa O₂. (c) Cu₂O nucleation on Cu(100) surface under 0.3 Pa O₂. (d) Cu₂O island growth under 0.3 Pa O₂. Scale bars: 2 nm.

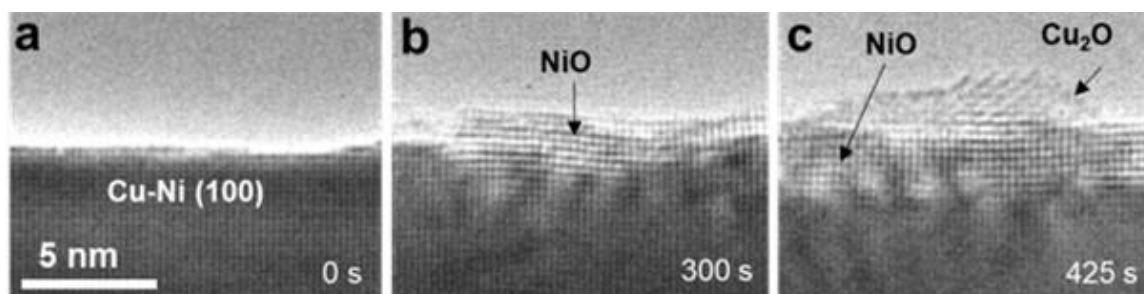


Figure 2. In situ observation of oxide growth on Cu-Ni(100) alloy (10 at.% Ni) at 350 °C under 0.1 Pa O₂. (a) Clean alloy surface in vacuum. (b) Nucleation and growth of epitaxial NiO. (c) Secondary nucleation and growth of Cu₂O.

References

- [1] Curnan, M. T. *et al.* J. Phys. Chem. C 123, 452–463 (2019).
- [2] Li, M., Curnan, M. T. *et al.* Under review.
- [3] The authors acknowledge funding from National Science Foundation (NSF) grants DMR-1410055, DMR-1508417, DMR-1410335, and CMMI-1905647, as well as support from Hitachi-High-Tech and technical assistance from the Nanoscale Fabrication and Characterization Facility (NFCF) in the Petersen Institute of Nano Science and Engineering (PINSE) at the University of Pittsburgh.