Experimental and Theoretical Studies on Oxidation of Cu-Au Alloy Surfaces: Effect of Bulk Au Concentration

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We report results of our experimental and theoretical studies on the oxidation of Cu-Au alloy surfaces, viz., Cu₃Au(111), CuAu(111), and Au₃Cu(111), using hyperthermal O₂ molecular beam (HOMB). We observed strong Au segregation to the top layer of the corresponding clean (111) surfaces. This forms a protective layer that hinders further oxidation into the bulk. The higher the concentration of Au in the protective layer formed, the higher the protective efficacy. As a result, of the three Cu-Au surfaces studied, Au₃Cu(111) is the most stable against dissociative adsorption of O₂, even with HOMB. We also found that this protective property breaks down for oxidations occurring at temperatures above 300 K.

Copper (Cu) and gold (Au) form model binary metallic systems¹–⁶ with stable L₁₀ (CuAu) and L₁₂ (Cu₃Au and Au₃Cu) structures. Experimental studies report surface segregation of Au in Cu-Au alloys⁷–²¹. More recently, extensive studies⁴,¹⁰–¹⁹,²²,²³ on the oxidation of Cu₃Au surfaces found Au-rich top-most layers of Cu₃Au(100), (110), and (111) surfaces. Oxidation, which is one of the more important corrosion process, induces changes in segregation¹⁰–¹⁸,²²–²⁶. Studies have been done to induce Cu segregation to the surface by dissociatively adsorbing energetic O₂¹⁰–¹³,²²,²³. However, even after prolonged doses of 2.3 eV hyperthermal O₂ molecular beam (HOMB), there were no obvious Cu₂O growth observed on (100) and (111). These results suggest that alloying of Cu-based materials with Au works as an efficient protection against oxidation into the bulk¹⁰,¹¹,²³. On the other hand, on the more open (110), additional oxidation processes induced by the enhanced diffusion of constituent atoms from and/or into the bulk contributes to Cu₂O formation. Although Cu segregation on the surface occurs in a similar way¹²,²².

Au segregation depends on the bulk chemical potentials of Au and Cu, i.e., bulk stoichiometry. Thus, we expect to be able to control Au surface segregation, i.e., the Au layer profile on the surface region, by changing the bulk Au concentration¹³,²³. Herein, we report the results of our detailed studies on the Au layer distribution of Cu₃Au(111), CuAu(111) and Au₃Cu(111). We also demonstrate the protective function/nature of such surfaces against oxidation processes induced by energetic O₂. Increasing Au bulk concentration hinders oxidation. Clean Au₃Cu(111) contains ca. 100% Au atoms in the first and second layers. Thus, as expected, Au₃Cu(111) is inert to oxidation. Theoretical studies also support the same conclusion with regard to the protective nature of the surface. However, even on such initially inert surfaces, protection against oxidation fails for processes occurring at higher temperatures.

Experimental & Theoretical Methodology

To characterize the corresponding surfaces, we use X-ray photoemission spectroscopy (XPS) measurements in conjunction with synchrotron radiation (SR). All experiments were performed using the surface reaction analysis

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apparatus (SUREAC 2000), constructed in BL23SU at SPring-8. Briefly, the surface reaction chamber is equipped with an electron energy analyzer (OMICRON EA125) and a Mg/Al \( \alpha \) twin-anode X-ray source (OMICRON DAR-400). A quadrupole mass spectrometer, which was used to analyze the molecular species in the HOMBO, is located opposite to the HOMBO source. The base pressure of the surface reaction chamber was below 2 \( \times 10^{-8} \) Pa. The Cu\(_2\)Au(111) (Surface Preparation Laboratory, SPL), CuAu(111) (MaTeck), and Au\(_3\)Cu(111) (SPL) samples were cleaned by repeatedly sputtering with 1.0~1.5 keV Ar\(^+\) and annealing at 720 K for 30 min, until impurities can no longer be detected by SR-XPS, and corresponding sharp (1 \( \times 1 \)) LEED pattern observed except for the CuAu(111). The clean CuAu(111) revealed a dim (1 \( \times 1 \)) LEED pattern, suggesting a low bulk crystallinity.

We control the kinetic energy of the incident HOMBO by changing the O\(_2\), He, and/or Ar gas mixing ratios. The corresponding nozzle pressures used to produce 0.5 and 2.3 eV HOMBO are 300 and 1400 K, respectively. A typical flux density at the sample position in the present experiments would be ca.10\(^{14}\) to 10\(^{15}\) molecules \( \cdot \) cm\(^{-2}\) \( \cdot \) s\(^{-1}\), at HOMBO kinetic energies of 0.5 and 2.3 eV. After irradiating the Cu\(_2\)Au(111) with the desired amount of HOMB normal to the surface, we measured the corresponding high-resolution SR-XPS spectra at 0°, 35°, and 70° from the surface normal, using a monochromatic SR beam with a photon energy of 1090.5 eV.

We also performed density functional theory based total energy calculations\(^{29,30}\), within the Generalized Gradient Approximation (GGA)\(^{31}\), using plane waves (600 eV cutoff energy) and pseudopotentials\(^{32}\). We model CuAu(111) and Au\(_3\)Cu(111) using periodic slabs. Each slab has seven fcc (111) layers, separated by ca. 1.50 nm of vacuum, repeated in a supercell geometry, with dipole correction applied. Each layer in the slab contains four atoms, so that the composition (of Au) can be varied in steps of 25%. We have chosen sufficiently large supercells so as to avoid interaction between the O(O\(_2\)) in neighboring supercells.

### Results and Discussion

**Au Segregation and Concentration Profile.** In Fig. 1, we show the Au-4f SR-XPS spectra of clean CuAu(111) and Au\(_3\)Cu(111), measured at 0°, 35°, and 70° from the surface normal. (For the Cu\(_2\)Au(111) results, cf., ref. 13). The Au-4f XPS spectra were fitted with the Voigt function, defined as the convolution of a Lorentzian with a Gaussian line shape. The background was subtracted by the Shirley method\(^{34}\). Similar to Cu\(_3\)Au(111)\(^{10,11,35}\), the CuAu(111) and Au\(_3\)Cu(111) were fitted with the Voigt function, defined as the convolution of a Lorentzian with a Gaussian line shape. The background was subtracted by the Shirley method\(^{34}\). The Au-4f XPS spectra were fitted with the Voigt function, defined as the convolution of a Lorentzian with a Gaussian line shape. The background was subtracted by the Shirley method\(^{34}\).

In Fig. 1, we show the Au-4f SR-XPS spectra of clean Cu\(_2\)Au(111) and Au\(_3\)Cu(111), measured at 0°, 35°, and 70° from the surface normal. (For the Cu\(_2\)Au(111) results, cf., ref. 13). The Au-4f XPS spectra were fitted with the Voigt function, defined as the convolution of a Lorentzian with a Gaussian line shape. The background was subtracted by the Shirley method\(^{34}\). Similar to Cu\(_3\)Au(111)\(^{10,11,35}\), the Cu\(_2\)Au(111) and Au\(_3\)Cu(111) can be separated into the corresponding B components. The B components peak at binding energies \( E_b \) = 84.48 eV, 84.39 eV, 84.14 eV (Au-4f\(_{7/2}\)) and 88.50 eV, 88.94 eV, 87.79 eV (Au-4f\(_{5/2}\)) for Cu\(_3\)Au(111), Cu\(_2\)Au(111) and Au\(_3\)Cu(111), respectively. The S components peak at relatively lower \( E_b \) than that of the corresponding B components. We see that, consistent with previous reports\(^{35,36}\), the \( E_b \) peak positions of the B components increase with increasing bulk Au concentrations. Also, consistent with Au-rich termination, we can observe clear Au-4f surface core-level shift (SCLS) in Fig. 1. The corresponding SCLS values are Cu\(_2\)Au(111): −340 meV; Cu\(_3\)Au(111): −420 meV; and Au\(_3\)Cu(111): −370 meV. For comparison, the SCLS for pure Au(111) is −350 meV\(^{37}\). The difference in surface coordination of the Au atoms (vide ante) accounts for the bulk Au concentration dependence of SCLS. Reduced coordination leads to narrower valence bandwidth. Narrowing of the bandwidth, in turn, increases the density of states. To maintain a common Fermi level, charge must flow between the surface atoms and the bulk. If more than half of the valence band is filled, the surface narrowed band center is lower than the bulk Fermi level and the binding energy decreases. In contrast, if less than half of the valence band is filled, the surface narrowed band center is higher than the bulk Fermi level and the binding energy increases. This explains the trends observed experimentally, as corroborated by the measured valence band spectra and the corresponding calculated density of states (cf., Figs 2 and 3).

We determined the layer Au concentration profile from the detection angle dependence of the Au-4f XPS peak intensity, which has B, S, and I (interface layer) components. We can approximate the peak intensity ratio of S to B (\( A_S/A_B \)) for a clean Cu\(_3\)Au surface by the following simple equation,

\[
\frac{A_S}{A_B} = \frac{\sum_{n=0}^{\infty} x_1 \sum_{n=0}^{\infty} x_1 e^{-2d\lambda \lambda \cos \theta}}{\sum_{n=0}^{\infty} x_1 \sum_{n=0}^{\infty} x_1 e^{-2d\lambda \lambda \cos \theta}}
\]

\[x_i\] gives the Au fraction of the \( n \)-th layer from the surface. \( d \) gives the interlayer distance. The corresponding Au-4f photoelectron mean free path \( \lambda \) in each Cu-Au alloy can be obtained following previous studies\(^{38}\). For Cu\(_2\)Au, CuAu, and Au\(_3\)Cu, we get \( \lambda = 1.48, 1.56, 1.63 \) nm, respectively (cf., Supplementary Information). \( \theta \) is the photoelectron detection angle from the surface normal. From \( A_S/A_B \) measured at \( \theta = 0°, 35°, \) and 70°, we obtain \( x_1 \) and \( x_2 \) for the clean surface, assuming \( d \) to be the bulk interlayer distance, ignoring layer relaxation, and taking \( x_{i,3} \) to be the bulk value.

For Cu\(_2\)Au(111): \( d = 0.217 \) nm, \( x_{1,3} = 0.25 \); thus giving us \( x_1 = 0.51 \) and \( x_2 = 0.32 \).

For CuAu(111): \( d = 0.225 \) nm, \( x_{1,3} = 0.50 \); which gives us \( x_1 = 0.94 \) and \( x_2 = 0.72 \).

For Au\(_3\)Cu(111): \( d = 0.230 \) nm, \( x_{1,3} = 0.75 \); and \( x_1 = 1.00 \) and \( x_2 = 1.00 \).
These values agree well with our theoretical predictions, as shown in Table 1. Surprisingly, the first and the second layers of Au₃Cu(111) contain almost 100%-Au atoms. This indicates that Au₃Cu(111) would be inert (to oxidation).

In Figs 2 and 3, we show the measured valence band spectra and calculated sum of the projected density of states (PDOS) of atoms on the top layer of the clean Cu(111), Cu₃Au(111), CuAu(111) and Au₃Cu(111), respectively. The evolution of Au-related features correspond to the Au-segregated layer profile in Table 1. The d-band of surface atoms and d-band centers are shifted to lower energy levels (corresponding to increasing binding energies) with increasing Au concentration on the surface, with a maximum for CuAu(111), consistent with the SCLS results from Fig. 1.

Initial Stages of Oxidation by HOMB & The Protective Layer. In Fig. 4 we show O-uptake curves obtained by integrating a series of O-1s spectra measurements taken after exposing Cu₃Au(111), CuAu(111), and Au₃Cu(111) to HOMB. The HOMB energies used, viz., E_{HOMB} = 2.3 eV and E_{HOMB} = 0.5 eV, correspond to 27000 K and 5900 K, respectively. On Cu₃Au(111), the initial dissociative adsorption of O₂ (O-coverage: ca. Θ ≤ 0.3 ML) does not depend on the incident energy. This indicates that an incident energy of 0.5 eV is enough to overcome the activation barrier for surface Cu-O formation. A previous study reported that a 0.6 eV HOMB would be more efficient to induce initial oxidation, as compared to a 2.3 eV HOMB, at the same nozzle temperature of ca. 1400 K. In the present study (0.5 eV HOMB), we used a nozzle temperature of ca. 300 K. Thus, the difference with previous results may be ascribed to vibrational excitations. At a nozzle temperature of 1400 K, O2 vibrational states ν = 1 and ν = 2 have populations of ca. 16% and 3%, respectively.

The difference in the O-uptake curves of 2.3 and 0.5 eV HOMB for ca. Θ ≥ 0.3 ML can be attributed to the repulsive interactions between pre-adsorbed O and the incoming O₂, increasing the activation barrier to dissociative adsorption. Moreover, oxide formation on the Cu-rich sites via collision induced absorption (CIA)
by energetic HOMB may also contribute to the difference. More importantly, oxidation proceeds accompanied by Cu segregation to the topmost layer. The oxidation induced by the 2.3 eV HOMB occurs less effectively on Cu₃Au(111) than on Cu(111). This result suggests that Au atoms increase the activation barrier to dissociative adsorption.

As we would expect from the Au layer profile shown in Table 1, we find CuAu(111) and Au₃Cu(111) less susceptible to oxidation as compared to Cu₃Au(111) and Cu(111). On the Au₃Cu(111), almost no oxidation occurs even for 2.3 eV HOMB. Thus, two (stable) layers of Au is enough to protect against oxidation. From the slopes, we estimate the initial O sticking probabilities to be as follows: \( S_0 = 1.59 \times 10^{-2} \) at \( E_{\text{HOMB}} = 2.3 \text{ eV} \) on...
Cu(111); $S_0 = 6.35 \times 10^{-3}(6.20 \times 10^{-3})$ at $E_{\text{HOMB}} = 2.3 \text{eV}(0.5 \text{eV})$ on Cu(111); $S_0 = 1.87 \times 10^{-3}(3.82 \times 10^{-4})$ at $E_{\text{HOMB}} = 2.3 \text{eV}(0.5 \text{eV})$ on Cu(111); and $S_0 = 6.13 \times 10^{-5}$ at $E_{\text{HOMB}} = 2.3 \text{eV}$ on Au(111). At low $\Theta$, we expect that the reaction rate would be determined by the atomic density of Cu (Au) on surface. Our experimental results (cf., Table 1) show 49%-Cu (51%-Au) on Cu3Au(111), 6%-Cu (94%-Au) on CuAu(111), and 0%-Cu (100%-Au) on Au3Cu(111). Therefore, we estimate the Cu atomic density ratio of Cu3Au(111), CuAu(111), and Au3Cu(111) to Cu(111) to be 0.47, 0.05, 0, respectively. The sticking probability ratio of Cu3Au(111), CuAu(111), and Au3Cu(111) to Cu(111) are $4.0 \times 10^{-1}$, $1.2 \times 10^{-1}$, and $3.8 \times 10^{-3}$, respectively, at 2.3 eV HOMB. The sticking probability ratio of CuAu(111) to Cu3Au(111) is $6.2 \times 10^{-2}$, at 0.5 eV HOMB. These sticking probability ratios agree well with the surface Cu atomic density ratio, so that the initial stage of oxidation, i.e., O2 dissociative adsorption, depends on the top-layer Cu (Au) concentrations. We can also associate the difference in initial O sticking probability ratio to the location of the corresponding $d$-band center with respect to the Fermi level $E_F$. The shallower the $d$-band center, the more accessible the electrons, and the stronger the binding with O. In the case of Cu-Au alloys, the $d$-band center of Cu3Au(111) is shallower than that of Au3Cu(111) and CuAu(111) (cf., Figs 2 and 3).

Figure 4: Oxygen (O) uptake curves for 2.3 eV hyperthermal O2 molecular beam (HOMB) incident at surface temperature $T_S = 300 \text{K}$ on Cu(111) (red filled), Cu3Au(111) (black filled), Cu0.5Au0.5(111) (blue filled), and Au3Cu(111) (green filled); 0.5 eV HOMB incidence on Cu3Au(111) (orange) and Cu0.5Au0.5(111) (blue). O uptake curves for 2.3 eV HOMB incident at surface temperature $T_S = 500 \text{K}$ on Au3Cu(111) (green), also shown. HOMB incident along the surface normal.

Cu(111); $S_0 = 6.35 \times 10^{-3}(6.20 \times 10^{-3})$ at $E_{\text{HOMB}} = 2.3 \text{eV}(0.5 \text{eV})$ on Cu(111); $S_0 = 1.87 \times 10^{-3}(3.82 \times 10^{-4})$ at $E_{\text{HOMB}} = 2.3 \text{eV}(0.5 \text{eV})$ on Cu(111); and $S_0 = 6.13 \times 10^{-5}$ at $E_{\text{HOMB}} = 2.3 \text{eV}$ on Au(111). At low $\Theta$, we expect that the reaction rate would be determined by the atomic density of Cu (Au) on surface. Our experimental results (cf., Table 1) show 49%-Cu (51%-Au) on Cu3Au(111), 6%-Cu (94%-Au) on CuAu(111), and 0%-Cu (100%-Au) on Au3Cu(111). Therefore, we estimate the Cu atomic density ratio of Cu3Au(111), CuAu(111), and Au3Cu(111) to Cu(111) to be 0.47, 0.05, 0, respectively. The sticking probability ratio of Cu3Au(111), CuAu(111), and Au3Cu(111) to Cu(111) are $4.0 \times 10^{-1}$, $1.2 \times 10^{-1}$, and $3.8 \times 10^{-3}$, respectively, at 2.3 eV HOMB. The sticking probability ratio of CuAu(111) to Cu3Au(111) is $6.2 \times 10^{-2}$, at 0.5 eV HOMB. These sticking probability ratios agree well with the surface Cu atomic density ratio, so that the initial stage of oxidation, i.e., O2 dissociative adsorption, depends on the top-layer Cu (Au) concentrations. We can also associate the difference in initial O sticking probability ratio to the location of the corresponding $d$-band center with respect to the Fermi level $E_F$. The shallower the $d$-band center, the more accessible the electrons, and the stronger the binding with O. In the case of Cu-Au alloys, the $d$-band center of Cu3Au(111) is shallower than that of Au3Cu(111) and CuAu(111) (cf., Figs 2 and 3).

The CIA process is less effective in the oxidation of Cu3Au(111) than of Cu(111). The Au layer profile of Cu3Au(111) after the oxidation is estimated to be as follows: $x_1 = 0$, $x_2 = 47$, and $x_3 = 0.45^{13}$. The oxidation proceeds accompanied by Cu segregation to the topmost layer. The Au-rich second and third layers prevent the bulk from further oxidation. Similar analysis is performed for CuAu(111) (ca. $\Theta = 0.6 \text{ML}$) oxidized by 2.3 eV HOMB (cf., Supplementary Information). The obtained Au layer profile is as follows: $x_1 = 0$, $x_2 = 1$, and $x_3 = 0.56$. The Au-rich second and third layers work as a protective layer against bulk oxidation.

**Breaking the Protective Layer.** Here, we show how such a protective layer is broken. As mentioned above, Au3Cu(111), with a concentration profile of 100%-Au for the surface and subsurface layers, is impervious to oxidation by 2.3 eV HOMB. However, when we increase the surface temperature to 500 K, oxidation proceeds and we obtain an O coverage of $\Theta = 0.2 \text{ML}$. Cu atoms segregate on the surface and the obtained Au layer profile is

| (111) surface | %-Au@ 1st layer | %-Au@ 2nd layer | %-Au@ 3rd layer | Ref. |
|---------------|----------------|----------------|----------------|-----|
| Cu3Au         | 51             | 32             | bulk (25)      | 13a |
| CuAu          | 94             | 72             | bulk (50)      | **  |
| Au3Cu         | 100            | 75             | 50             | a5  |
| Cu0.5Au0.5    | 100            | 100            | bulk (75)      | a5  |

**Table 1.** The layer profile of Au atomic fraction (%) for Cu3Au, CuAu, and Au3Cu (111) surfaces.

*Experimental measurements. **Theoretical calculations. *Present work.
x_1 = 0.31, x_2 = 0.43, x_3 = 0.51 (cf., Supplementary Information). In Fig. 5, we show the calculated surface energy of Au_3Cu (111), under Au-rich and Cu-rich conditions, as a function of the oxygen chemical potential $\Delta \mu_O$ (which is in turn related to the oxygen partial pressures at 300 K and 500 K)\textsuperscript{13,23}. Each line corresponds to one of the tested surface configurations. The lowest surface energy is the most stable and realized surface. The condition for perfect Au_3Cu bulk is close to the Au-rich condition.

Figure 5. Surface free energy of Au_3Cu(111) in equilibrium with Au-rich (upper panel) and Cu-rich (lower panel) Au_3Cu bulk reservoir, as a function of the oxygen chemical potential $\Delta \mu_O$ (which is also related to the oxygen partial pressures at 300 K and 500 K)\textsuperscript{13,23}. Each line corresponds to one of the tested surface configurations. The lowest surface energy is the most stable and realized surface. The condition for perfect Au_3Cu bulk is close to the Au-rich condition.

Figure 6. Optimized structure for O_{0.25ML}/Au_3Cu(111), with O adsorbed at the fcc-hollow site (cf., upper panel, Fig. 5, 500 K, $10^{-8}$ Pa). Au: yellow ball. Cu: blue ball. O: red ball. Structure drawn using the VESTA package\textsuperscript{39}.
Au concentration profile of Cu-Au alloys (viz., Cu₃Au, CuAu, and Au₃Cu) in vacuum. We also studied the initial conditions of the Cu-Au alloys. After exposing the corresponding surfaces to HOMB, we found that surfaces with higher concentrations of Au showed lower susceptibility to oxidation, as determined by the low O sticking probability. At 500 K, Cu segregates on the surface, breaking the protective layer, and oxidation proceeds on the surface, albeit rather slowly as there is still the subsurface. This gives further insight into how we can control the reactivity and robustness of a material, i.e., via the bulk component and the segregation profile.

Conclusion
We determined, both experimentally (HOMB + SR-XPS) and theoretically (DFT-based calculations), the surface Au concentration profile of Cu-Au alloys (viz., Cu₃Au, CuAu, and Au₃Cu) in vacuum. We also studied the initial stages of oxidation of the corresponding surfaces. We observed Au segregation to the surface and subsurface of these Cu-Au alloys. The degree of segregation strongly depends on the bulk Au components. The richer the Au bulk components, the richer the Au surface segregation. The Au-rich layers form a protective layer against oxidation of the Cu-Au alloys. After exposing the corresponding surfaces to HOMB, we found that surfaces with higher concentrations of Au showed lower susceptibility to oxidation, as determined by the low O sticking probability.

At 500 K, Cu segregates on the surface, breaking the protective layer, and oxidation proceeds on the surface, albeit rather slowly as there is still the subsurface. This gives further insight into how we can control the reactivity and robustness of a material, i.e., via the bulk component and the segregation profile.

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Author Contributions
M.O. conceived the experiment(s). M.O., Y.T. and A.Y. conducted the experiments. K.O., K.K., W.A.D. and H.K. conceived the model and performed the calculation. M.O. and W.A.D. drafted the manuscript. All authors contributed to the calculation, analyses of results, and review of the manuscript.

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