

INITIAL DEALLOYING OF $\text{Cu}_3\text{Au}(111)$: AN IN-SITU X-RAY STUDY

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For the understanding of corrosion or catalytic processes, knowledge about the detailed structure of metal surfaces is required. Binary metal alloys are in general of special interest because their properties can be tailored by their composition. However, in our natural environment, all materials are exposed to wet conditions, leading to the formation of thin layers of aqueous electrolyte, and contact potentials, e.g. between different metals, lead to electrochemical corrosion. Despite of keen interest, there is very little understanding of electrochemical processes on alloy surfaces on the atomic scale. This is mainly due to the lack of techniques that can resolve atomic structures in the presence of the electrolyte. We are reporting about an x-ray investigation of the corrosion of $\text{Cu}_3\text{Au}(111)$ as a model system, because of its electrochemical and physical properties. The ordered L1_2 -structure allows us to follow changes in composition and structure during the dealloying by recording Crystal Truncation Rods (CTR) associated with fundamental as well as order induced Bragg peaks. We studied Cu_3Au single crystal surfaces in 0.1M H_2SO_4 electrolyte as a function of electrode potential in-situ by x-ray scattering at the insertion beamline ID32 at the ESRF. During the initial electrochemical corrosion, Cu atoms are dissolved and a passivating layer is formed. Our results identify it as epitaxial $\text{Au}(111)$, which forms on the surface at a potential where Cu dissolution starts. Initially, the in-plane lattice constant of the precipitated Au islands is larger than expected for bulk Au, however, approaching this value with further increasing electrode potential (Fig.1). The thickness of the formed islands is also changing from a few monolayers to several tens of nanometers. With an initial, thin Au overlayer Crystal Truncation Rods (CTR) of the Au overlayer (Fig.2) and the Cu_3Au substrate were recorded, allowing us to determine the changes in composition and order of the interface as well as the evolution of roughness of the Au layer and the interface. We used single crystals, which were free of stacking faults, and thus could observe that the first or second layer of the gold islands violates the stacking sequence of the underlying Cu_3Au substrate. Subsequent Au layers are free of stacking faults. This can be understood, considering the strong attractive interaction between Au and Cu atoms, obviously influencing even the second neighbor shell. Finally, we compare the structure of UHV prepared, clean surfaces with surfaces under dealloying conditions in-situ, employing crystal truncation rod scattering.

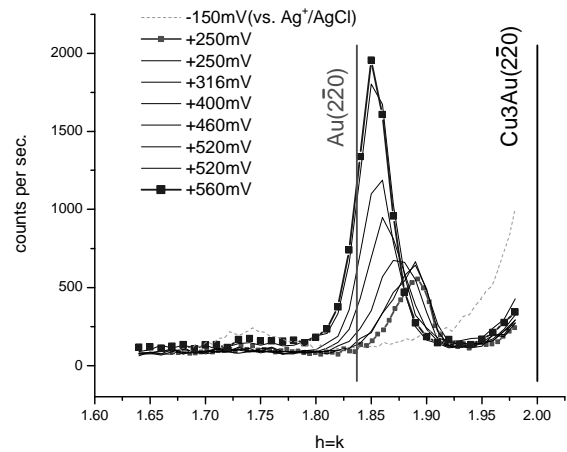


Figure 1. The lattice constant of the initially formed Au layer is shifting with higher potential towards the Au bulk lattice constant. Also the FWHM decreases, indicating an increasing lateral size of the Au islands on top the Cu_3Au .

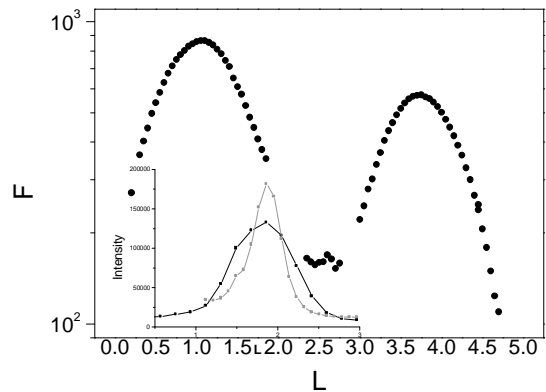


Figure 2. In the initial stage of dealloying (here at +270mV vs. Ag/AgCl) a very thin layer of Au is formed, resulting in very broad features of the shown 20L Au rod. An L-scan on along the 02L Rod is shown in the inset.

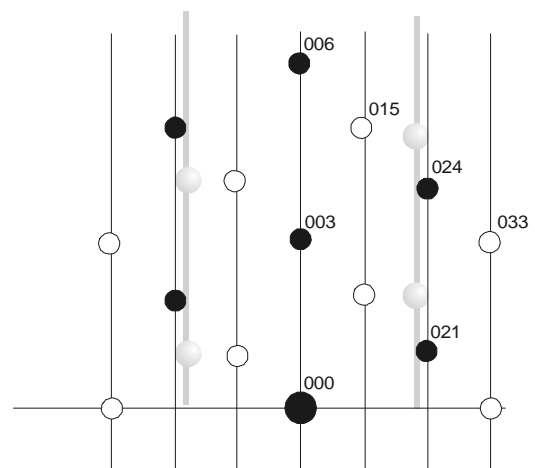


Figure 3. The Au layer produced by dealloying Cu_3Au is growing with a different stacking sequence. Thus the Bragg points show up at different positions on the CTR space. The first or second layer of the gold islands violates the stacking sequence of the underlying Cu_3Au .