


**Experiment title:**

Cu<sub>3</sub>Pd(001) and Cu<sub>3</sub>Au(111) surface structures during their initial corrosion studied in a new electrochemical UHV compatible *in-situ* X-ray cell.

**Experiment number:**  
SI-1281

**Beamline:**
**Date of experiment:**

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**Date of report:**

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**Local contact(s):**

Isabelle Joumard

*Received at ESRF:*

**Names and affiliations of applicants (\* indicates experimentalists):**

Dr. RENNER\* Frank Uwe, ESRF

Dr. KAISER Hermann / Korrosion und Oberflächentechnik, Lehrstuhl für Werkstoffwissenschaften, Martenstrasse 7, D-91058 Erlangen, Germany,

Dipl.Phys. GRUENDER\* Yvonne, ESRF, and Dr. ZEGENHAGEN Jörg, ESRF

**Report:**

We studied the surface structure of Cu<sub>0.83</sub>Pd<sub>0.17</sub> (001) and Cu<sub>3</sub>Au(111) during electrochemical selective Cu dissolution below the critical potential *in-situ* in 0.1M H<sub>2</sub>SO<sub>4</sub> (pH=1) electrolyte. In both cases we observe the formation of an epitaxial layer of nanoscale islands of the noble component of the original alloy (Au or Pd). These islands form a metallic passivation layer suppressing massive dissolution of Cu. By redeposition of Cu ions from the electrolyte solution onto Pd islands, an epitaxial Cu layer is formed. In a continuation of previous studies [SI-861, SI-913, 1] we studied the passivation regime of the Cu<sub>3</sub>Au(111) surface at higher overpotentials, just below the critical potential. We observed that, after an initial formation of nano-scale twin Au islands, the growth of the porous Au layer proceeds by forming legaments with the substrate stacking sequence.

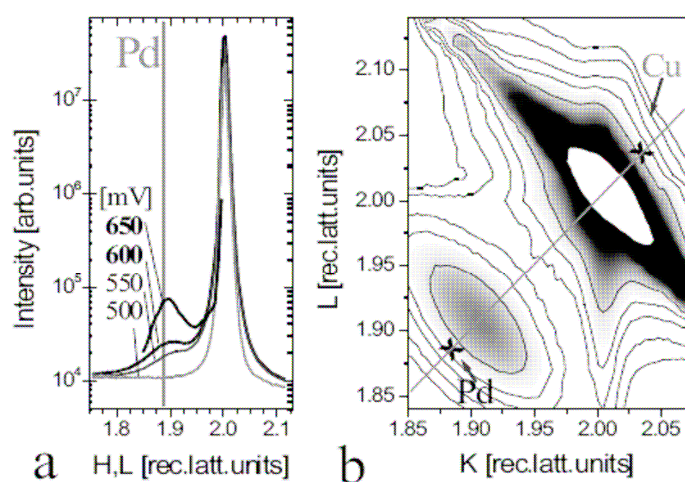


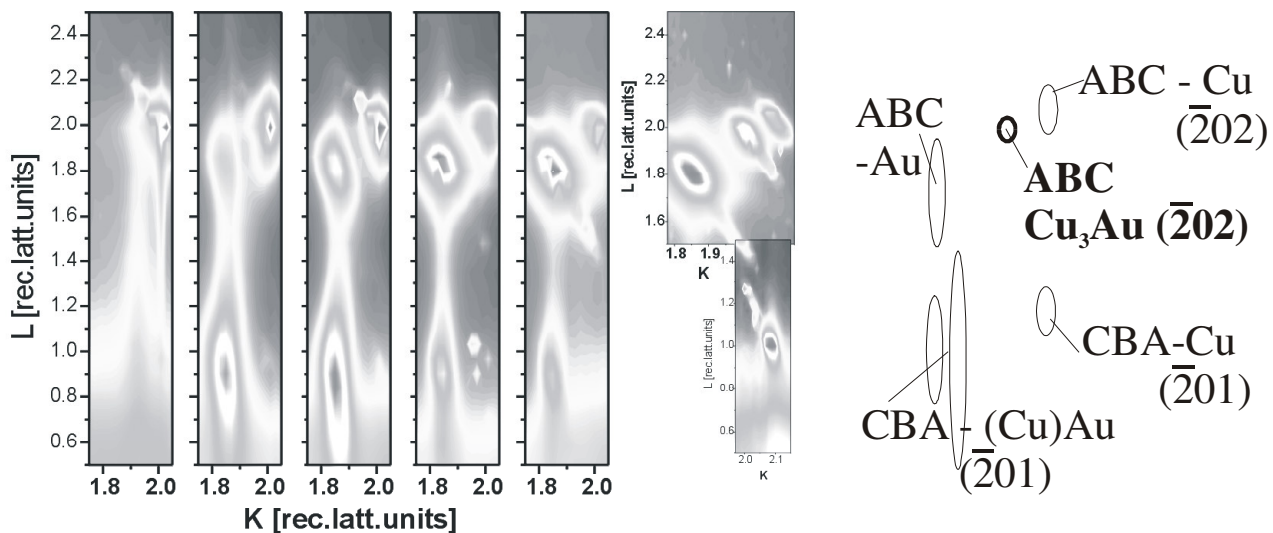
Fig.1. Development of Pd islands on Cu-Pd with increasing potential. (a) Radial scans at 500-650 mV. (b) KL-map at 650mV.

We used a new electrochemical cell setup [2] for *in-situ* xray diffraction mounted on top of a portable UHV chamber. Samples could be transferred without exposure to ambient air from the large UHV system of the ID32 SCL, where atomically clean and ordered surfaces with large terrace sizes had been produced, into the new portable chamber. The samples were then and studied with X-ray diffraction successively in UHV, in controlled gas atmosphere, and in contact with the electrolyte solution, while controlling the electrochemical

potential by a potentiostat. The electrochemical setup employs a droplet geometry, which is guaranteeing good electrochemical conditions for insitu xray measurements and for performing voltammetry.

Compared to the CuAu alloy, Cu-Pd is a more reactive binary alloy system and use of the new setup (Ultra high vacuum transfer electrochemical X-ray chamber for in-situ diffraction, TRECXi), avoiding contact to ambient air after the sample surface preparation in UHV and during the X-ray measurements, was beneficial. Like in the case of Cu<sub>3</sub>Au, the initially applied potential for the Cu<sub>0.83</sub>Pd<sub>0.17</sub> crystal was -100 mV (vs. Ag/AgCl), i.e. cathodic of the dissolution potential of Cu. Again we raised the potential in steps of 50 mV and characterized the surface by Xray diffraction between each potential step. Up to potentials as high as +500 mV, which is close to  $E_c$  of Cu<sub>0.83</sub>Pd<sub>0.17</sub>, we only found Bragg reflections from the original Cu<sub>0.83</sub>Pd<sub>0.17</sub> [2].

In both cases we observed at higher potetials the formation of an epitaxial layer of the noble component of the original alloy (Au or Pd) with the epitaxial relation {001} layer || {001} substrate and [001] layer || [001] substrate . This clear epitaxial relation suggests that well-defined atomic processes are involved in the dealloying process. The layers consist of nm-sized islands. We also tried re-deposition of Cu onto nanoscale Pd islands, which lead to the formation of an epitaxial layer, interestingly with even more welldefined orientational order. In Fig.1 radial in-plane scans (a) and a HL-map (b) of Pd islands on Cu<sub>0.83</sub>Pd<sub>0.17</sub> are shown.



**Fig.2** After an initial formation of Au nano-islands with (CBA) twin stacking sequence [1] (metallic passivation layer) further dissolution leads to the growth of ABC Au "clusters". Most likely we observed the growth of a porous ABC Au layer below the initial passivating CBA Au islands. Cu re-deposition onto nano Au island leads to epitaxial ABC and CBA Cu clusters. (Potentials from left to right: -100 mV, 450, 450, 600, 600, and -50 after 600mV vs Ag/AgCl)

Recent *in-situ* studies of the selective dissolution of Cu from a Cu<sub>3</sub>Au(111) model binary alloy (ABC stacking) showed that the substrate is covered by nano-scale 2-3 nm thick Au islands with a reversed stacking compared to the substrate (twin, CBA) at lower potentials in the passivation regime, which points directly to surface diffusion as a predominant process at these potentials. The experiments performed during SI-1281 showed that the corrosion proceeds at higher potentials by forming Au clusters (10-20nm), which grow now maintaining the substrate stacking (after the formation of the initial twin Au islands). Cu re-deposition onto the formed nano-scale Au islands leads to epitaxial growth of Cu(111) clusters, now with equal ratio of ABC and CBA stacking. Fig.2 shows KL-maps and a sketch indicating the origin of the visible diffraction peaks.

## References

- [1] F.U.Renner et al., Nature **439** (2006),707. [2] F.U.Renner et al., submitted to Thin Solid Films
- [3] F.U.Renner et al., to be submitted to Rev.Sci.Inst.