REPORT ON EXPERIMENT 28-01-1002 - 3^{rd}-9^{th} JULY 2013

Summary

Our objectives for this beam time were to investigate XEOL-XANES and XEOL images from the surface of silver and weathered silver, and to monitor the real time behaviour of silver exposed to ppb levels of O_3 and H_2S using time-lapse XRD. A total of 13 experiments was carried out during this allocation resulting in the collection of 7.5 Gb of data.

Experimental

The interleaving of XEOM 1 with SPEC proved to be straightforward as usual, but using the Mar CCD 165 for the XRD proved to be surprisingly problematic because, at first, *.mccd files were not available. Instead, the images arrived by default in *.edf format. This format, although a good idea in principle with its text header and binary data has been devised by an inexperienced programmer and was useless to us, even though we wrote the code to read the files. Almost all the camera metadata were missing from the header which meant that we had to add a GUI to our software so that missing camera parameters could be added manually. Fortunately, although it was “impossible” to give us the *.mccd files, the impossible was done.

The weathering of silver in-situ in the beam line and the acquisition of time-lapse XRD data using the Mar CCD 165 was totally successful. The exposure of silver to gas flows of hydrogen sulfide and ozone diluted to ppb levels with synthetic air in a controlled relative humidity was accomplished without incident in our electrochemical/environmental cell (eCell)

XEOL-XANES Spectra and Mapping

First attempts to obtain chemical maps from corroded silver surfaces using XEOL microscopy in our XEOM 1 microscope met with mixed success. Whilst the total XEOL signal from a photomultiplier system acting in parallel with XEOM 1 showed high quality XANES data, the images collected by the camera were extremely noisy, and often showed no sign of an edge. A possible malfunction in the camera is being investigated. Nevertheless it was confirmed that the XEOL was modulated in the same way as the fluorescent X-rays at the Ag LIII-edge. These data are summarized in Figure 1 which shows the XEOL-XANES (a) and conventional XANES (b). The higher pre-edge signal from the XEOL-XANES is typical of such data and is due to the excitation of radiative end sates through any de-excitation channels available to ionised levels less tightly bound than Ag LIII. The XANES spectra from weathered samples are all similar and characteristic of the underlying silver. The XEOL-XANES exhibits improved surface specificity and the differences between spectra reflect the chemistry of differently weathered surfaces.

In-Situ Weathering of Silver

Time lapse XRD measurements were taken from silver surfaces exposed to 500 ppb O_3 at 50% RH, 500 ppb O_3 at 90% RH and 500 ppb H_2S at 50% RH. These were compared with surface powder diffraction patterns of reference powders and surfaces. The latter were

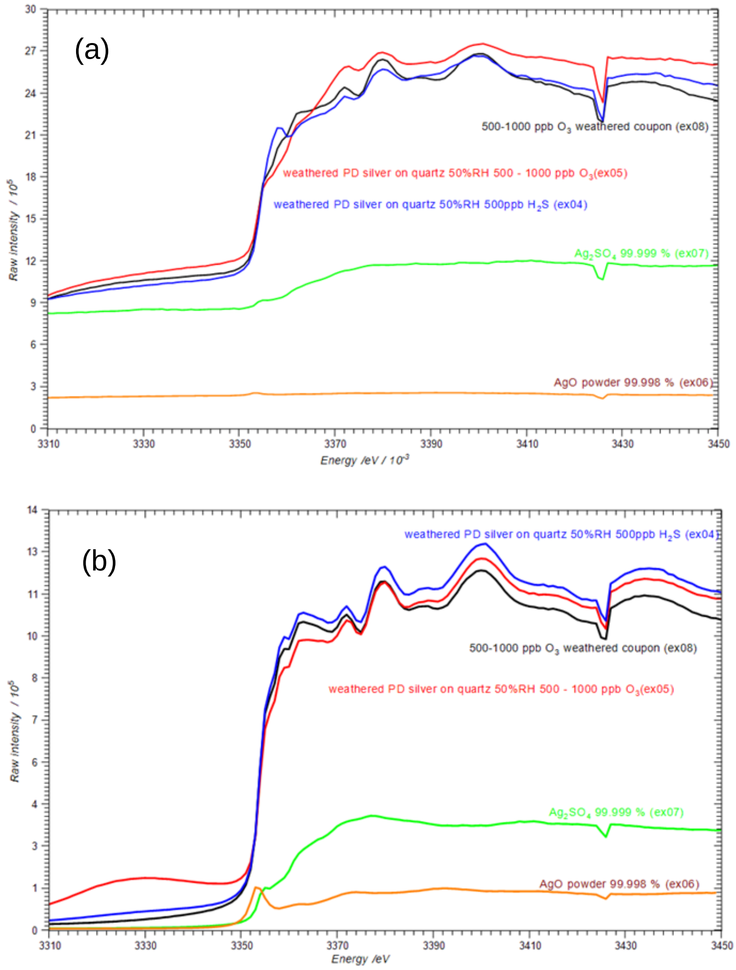

Figure 1: (a) Total XEOL-XAS from the photomultiplier-based detector in parallel with the CCD camera on XEOM 1. (b) XANES measured simultaneously to (a) using fluorescent X-rays and a Vortex detector.

already partly characterized with laboratory XRD and the use of a quartz crystal monitor during weathering to establish growth rates.

Figure 2 shows the before and after diffractograms from pure silver exposed to O_3 at 50% RH. Shown are image numbers 0 and 140 from a set of 140 images acquired for 5 sec per image with an interval of 595 sec between (total elapsed time 23h 20 min). The growth of silver oxides on the surface is clearly visible. Analysis of the time lapse data will establish growth rate and the type of growth (passivating or non-passivating).

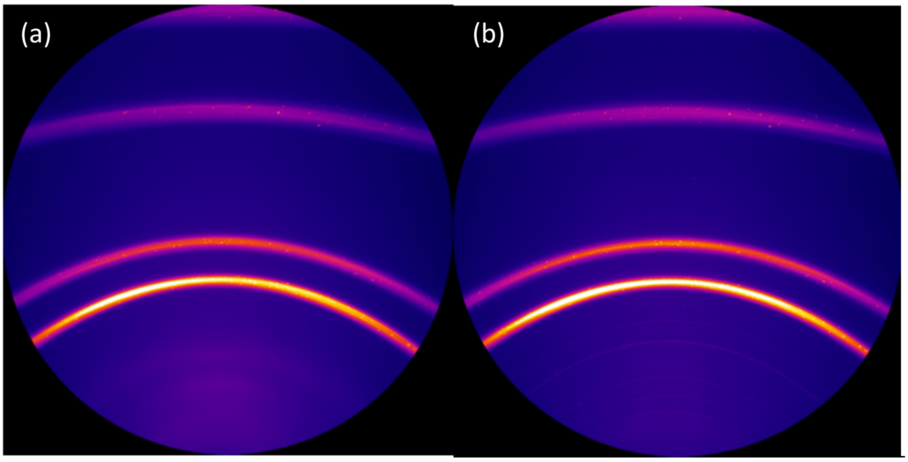

Figure 2: Before (a) and after (b) Mar images from a pure silver surface weathered in-situ in ozone at 50% RH. The elapsed time between the images is 23h 20 min. The bright rings are Silver 111, 200, 113, 220. The fine rings below silver 111 in (b) show formation of the oxide

Conclusions

Overall the beam time was a success and the outcome should be one or more papers on the weathering of silver and the use of synchrotron techniques to monitor this. The weathering equipment and containment worked very well and satisfied the requirements of the safety group for a yellow experiment (was initially designated as red).

The possible failure of the camera on XEOM 1 was a disappointment, but we have written new software tools so that image stacks can be inspected in real time and the spectra they contain viewed as they evolve. Offset against this was the observation that XEOL at the Ag LIII-edge carries the same general modulation as XANES collected using X-ray fluorescence, but the XEOL-XANES is distinctly more surface specific.