Abstract

This work is a contribution to the study of the Cs-U-O system. It deals with the way in which cesium, through its effect on oxygen, modifies the uranium environment and in consequence the valence state of the uranium atom itself. In short, two main points have been addressed to achieve this goal:

1. The crystallographic structure and local uranium environment of several cesium uranates has been determined by Rietveld refinement of neutron and X-ray diffraction data. The uranates were also investigated with X-ray Photoelectron Spectroscopy (XPS) to determine the uranium valences present and with X-ray Absorption Spectroscopy (XAS) to study the local uranium environment directly. The uranium valence information was then coupled to the crystallographic uranium environments using the Bond Valence Sum (BVS) method.

The most interesting compound is Cs$_2$U$_4$O$_{12}$, which distinguishes itself from the previous because of its formal uranium valence of 5.5. The mixed valence character is reflected in its crystal structure that shows four crystallographically different uranium atoms, two with a BVS of around 6 and two around 5. The combined interpretation of crystal structure data from the diffraction experiments, valence data from XPS and XANES/EXAFS local environment information has allowed a founded assessment of the uranium valence attribution problem.

2. Thin layers of stoichiometric uranium dioxide were prepared using sputter deposition techniques and used to model interactions on the grain boundaries in UO$_2$. They were covered with cesium and exposed to controlled amounts of oxygen, while the uranium valence state was followed with Ultraviolet Photoelectron Spectroscopy (UPS) and XPS. In addition, codeposited layers of cesium and uranium (deposition of uranium in an oxygen atmosphere in the presence of cesium vapour) were studied with the same techniques.

The codeposition of cesium and uranium in an oxygen environment was shown to lead to formation of U$^{IV}$, while this oxidation state of uranium could not be obtained in UHV without cesium. To elucidate the mechanism, layered structures of UO$_2$ covered with cesium were exposed to oxygen and studied with XPS and UPS. It was found that the rate of oxidation of uranium is enhanced markedly by the presence of cesium. The controlled exposure of a pure UO$_2$ surface did not lead to any changes in the spectra, while for a cesiated surface, a clearly observable reduction of the U$^V$ signal occurs at increasing exposure. It is thought that the enhanced oxygen dissociation probability in combination with the polyatomic oxygen ions formed by cesium are responsible for this effect, as they are assumed to preferentially react with the UO$_2$. 
