

A photoemission study of UO/UC and UO/UN ternaries, prepared as thin films

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Thin films can be used to address a series of technological and scientific questions in actinide research. Pure elements, compounds, heterogeneous mixtures, etc. are prepared using modern deposition techniques. The properties of these films can be modified continuously and even off-stoichiometric or doped homogeneous compounds, both of great interest in nuclear research can be prepared. Physical properties (electronic structure, magnetism) and chemical reactivity (surface reactions) are investigated on such films.

We present here a study of U-N-O and U-C-O systems, prepared as thin films using elemental (U, C) or simple molecular (N₂, O₂) sources. The elements are mixed together in a plasma and deposited onto Si substrates. Photoelectron spectroscopy (XPS and UPS) is used to identify the chemical species formed and the electronic structure of the compounds.

Special attention was given to the oxynitride (UO_xN_{1-x}) and the oxycarbide (UO_xC_{1-x}), which are solid solutions of UO and UN, and of UO and UC. Pure UO is not stable, and the U-O phase diagram shows that even in presence of U metal UO₂ forms (there are no intermediate phases). However in presence of a third element (S, C), UO may be stabilized as solid solution.

The U-N-O systems were prepared using U/UN, UN and U₂N₃ starting compounds (deposited in absence of oxygen), and gradually introducing oxygen during the deposition. Fig. 1 compares the U-4*f* spectra of U, UN, UN_{0.6}O_{0.3} and UO₂. The U-4*f* core-levels of UN and U have similar binding energies (388.0 eV for the

U-4*f*_{5/2} of U), which is consistent with the low oxidation state of U in UN [1]. The U-4*f* spectrum of UO₂ lies at higher binding energy (391.0 eV for U-4*f*_{5/2}), in agreement with the higher oxidation state (IV) of U in UO₂. The spectrum of UN_{0.6}O_{0.3} cannot be interpreted as a simple superposition of the UN/U and UO₂ spectra. Its binding energy (389.5 eV) is intermediate to those of UO₂ and UN. This indicates that uranium has an intermediate oxidation state. In addition the line is broader compared to those of U, UN or UO₂: several non-equivalent U species are formed. The compound was obtained at pO₂=2×10⁻⁶ mbar and pN₂=5×10⁻⁶ mbar. Under these conditions O₂ and N₂ compete for U metal. Oxygen, however, is the more reactive gas. At high

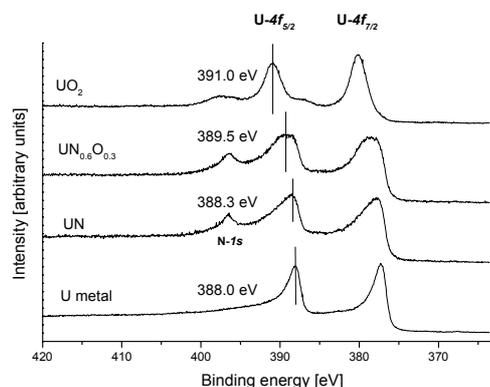


Fig. 1: U-4*f* core level spectra of U, UN, UNO and UO₂.

pressures, O₂ displaces N₂, and eventually the pure oxide is obtained: the N-1*s* line at 396.4 eV disappears. N stabilized UO is only observed at very low oxygen contents.

U-C-O systems were produced using U/UC, UC and UC₂ starting systems. In these systems carbon and oxygen are

competing for U. Fig. 2 shows the evolution of the C-1s lines in UC (starting system), as oxygen is introduced. Initially the C-1s line lies at 282 eV BE, which is

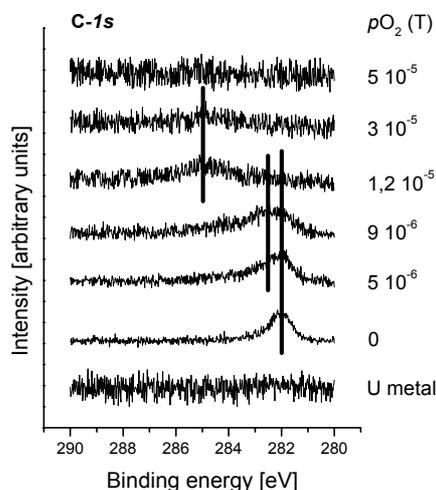


Fig. 2 : C-1s core level spectra evolution (UC starting system) with increasing oxygen pressure.

typical for stoichiometric UC [2]. With increasing oxygen pressure a C-1s component grows at 282.8 eV, typical for UC₂ [3]: as oxygen reacts with part of the uranium, carbon is confined to the remaining uranium, forming a higher carbide. At even higher oxygen pressure graphitic carbon is observed (C-1s at 284.5 eV), together with the U-4f spectrum typical for UO₂. At this stage, carbon forms small inclusions of graphite in UO₂. At highest oxygen pressures, the C-1s signal disappears as carbon reacts with oxygen to form CO and CO₂. These gases do not adsorb on UO₂. Again it is in the initial phase, at low oxygen pressures, that UO has been observed.

Fig. 3 compares UPS valence band spectra of various U systems. Both UCO and UNO have narrow and symmetrical O-2p bands, which are very different from the broad, asymmetrical O-2p band observed for UO₂ (In UNO the O-2p signal is superimposed to the N-2p signal). In addition the U-5f² emission from the localized 5f states of UO₂ are missing in UCO and UNO. This indicates that in these compounds, an oxide different from UO₂ is formed. The 5f states of this oxide are at

the Fermi-level or close to it. Therefore we conclude that this is a metallic oxide with itinerant (or weakly localized) f-electrons. This is consistent with band structure calculations of the (hypothetical) UO, which also show the 5f states to be itinerant, forming a band pinned at the Fermi-level [4].

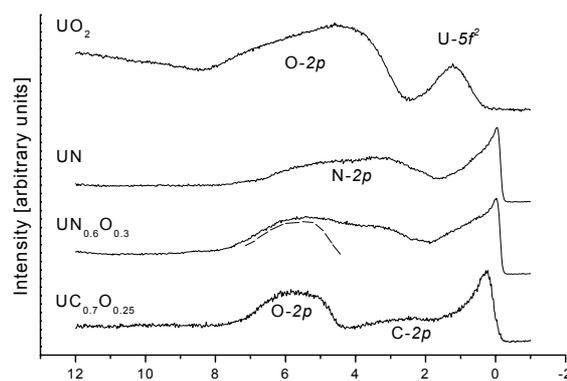


Fig. 3: He II valence band spectra of UCO, UNO, UN and UO₂.

Formation of UO is more pronounced in the case of UC than of UN. UPS spectra of U-C-O systems preserve the symmetrical shape of the O-2p band at much higher oxygen contents than those of U-N-O systems. This is consistent with the fact that oxycarbides have been prepared by classical chemical synthesis [5] and their phase diagram and region of stability are well established. There are no such reports on the synthesis of UNO. XRD studies are planned to confirm the presence of such UO/UN and UO/UC solid solutions.

References

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