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Photoelectron Spectroscopy (UPS/XPS) Study of Np_2O_3 Formation on the Surface of Neptunium Metal*

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Summary. High resolution ultraviolet (UPS) and X-ray induced (XPS) photoelectron spectroscopy of the valence band and the 4f core levels, respectively, have been used to study high purity Np metal and the formation of oxides on its surface. The UPS valence band spectra show a strong emission at E_F attributed to itinerant Np 5f electrons. The narrow and asymmetric 4f core level spectra confirm this description. In the early oxidation stage two distinct satellites appear on the high binding energy side of the 5f and 4f emission lines. The energy separations are similar to those found for UO_2 and Pu_2O_3 and indicate therefore the formation of Np_2O_3 on the surface of the metal, whereas Np_2O_3 does not exist as bulk material. Upon further oxidation the 5f and 4f emission lines for Np metal and Np_2O_3 disappear completely leaving only the NpO_2 line. Thus it is concluded that Np_2O_3 is only stable as a thin layer (~10 Å) on the surface of Np metal.

Introduction

Photoelectron spectroscopy (UPS/XPS) has proved to be a very powerful tool for electronic structure and chemical state studies [1]. The pronounced surface sensitivity of a few monolayers enables in addition the examination of surface properties. As part of the investigation to study the electronic structure and surface properties of actinide metals and their compounds we present here photoemission data for clean Np metal and its surface oxidation behaviour. Recent phase diagram studies for the system Np–O [2] exclude the existence of bulk NpO and Np_2O_3. On the other hand, the deviation of the electronic structure of the surface from that of the bulk may stabilize surface phases that are not formed as bulk materials. A recent analysis of UPS conduction band spectra of Am metal [3] indicates a contribution of divalent Am atoms on the surface of bulk trivalent Am metal.

Experimental

The photoemission spectra were taken with a Leybold–Heraeus LHS-10 spectrometer modified for work with highly radioactive materials as described in detail elsewhere [4]. The Np 4f core level and valence band spectra were recorded using Mg Kα ($h\nu = 1253.6$ eV, resolution $\Delta E = 1.0$ eV) and He II ($h\nu = 40.8$ eV, $\Delta E = 0.07$ eV) radiation, respectively. The pressure in the spectrometer was 1×10^{-8} Pa.

A high purity Np plate was cut from double electro-refined material produced in the Los Alamos National Laboratory. After transfer into the spectrometer the sample was cleaned *in situ* by Ar ion sputtering at 400 K, and just before the measurement it was cooled down to 80 K. The oxidation of the surface was caused by a slow segregation of residual bulk oxygen impurities to the surface.

Results and Discussion

Figures 1 and 2 show the 4f core level and valence band spectra, respectively, for clean metal (curves a) and different oxidation stages (curves b, c, d).

Clean Metal Surface

The XPS 4f core lines (Fig. 1a) are very narrow ($\Delta E = 1.3$ eV) and exhibit an asymmetric line shape that is typical for actinide systems with itinerant 5f electrons, *i.e.* the 5f electrons take part in the metallic bond. Along with the 4f photoelectron excitation, 5f conduction electrons with a high density of states are excited from just below to just beyond the Fermi level E_F generating a large number of low-energy electron-hole pairs. The energy losses from this process cause the asymmetric tail on the high binding energy side of the 4f lines. The UPS valence band spectrum (Fig. 2a) shows directly the high density of 5f states extending to E_F, thus confirming the itinerant character of the 5f electrons. Very similar results have been found for U and Pu metals [5–8] that also have itinerant 5f electrons in contrast to localized 5f electrons in Am metal [8].

Oxidized Metal Surface

The XPS core lines for intermediate and complete oxidation of the metal surface are shown in Fig. 1b, c and d, respectively. In addition to the metal line, two main distinct emission signals appear at about 1.9 and

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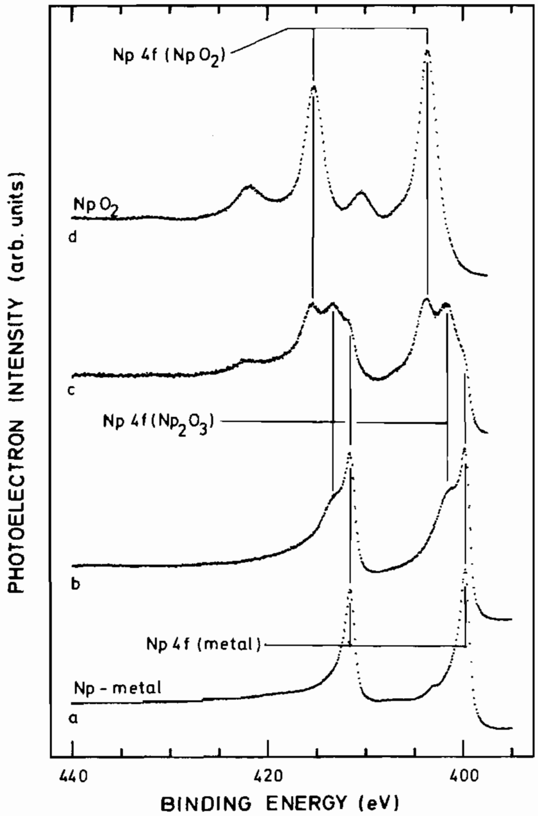

Fig. 1. X-ray induced 4f core level photoemission spectra (XPS, $h\nu = 1253.6$ eV) for increasing surface oxidation of Np metal: (a) clean metal, (b), (c) intermediate oxidation, (d) complete oxidation.

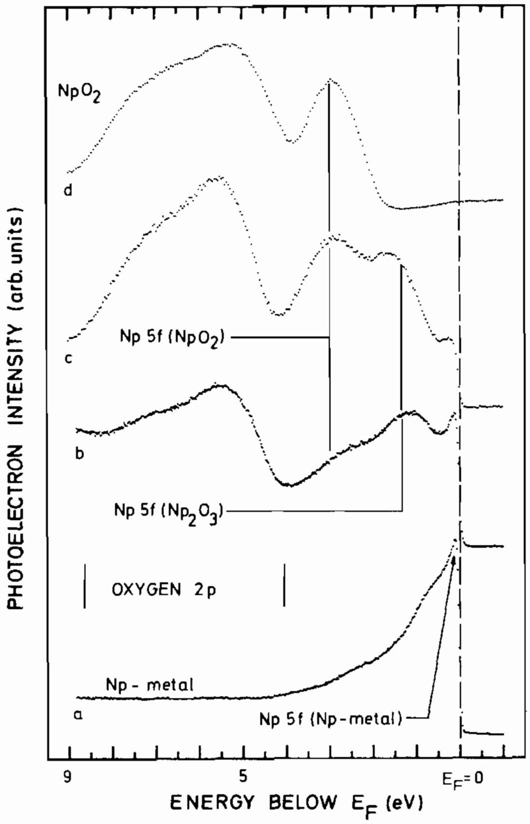

Fig. 2. UV-light induced valence band photoemission spectra (UPS, $h\nu = 40.8$ eV) for increasing surface oxidation of Np metal: (a) clean metal, (b), (c) intermediate oxidation, (d) complete oxidation.

3.9 eV higher binding energies. The line shifted with 3.9 eV is clearly due to the formation of NpO_2 because of the characteristic actinide dioxide signal with a satellite at 6.8 eV higher binding energy (Fig. 1d), as also found for bulk UO_2, NpO_2 and PuO_2 [9–11]. Thus for intermediate oxidation, a lower Np oxide that does not exist in the bulk phase must be formed on the surface in the presence of metal.

This is confirmed by the UPS valence band spectra for the same stages of surface oxidation (Fig. 2b, c and d). With the increase of the oxygen 2p signal around 6 eV, two distinct 5f electron derived satellites appear at about 1.5 and 3 eV[*] as long as the metal signal at E_F is observable; the spectrum for complete surface oxidation (curve d) is again characteristic of NpO_2 [10, 11]. The only difference between the XPS and UPS data is seen for curves b. Whereas in XPS the NpO_2 signal is not clearly seen, the related UPS spectrum shows this signal clearly. This is explained by the much higher surface sensitivity in UPS in which even very small amounts of surface NpO_2 can be detected, in contrast to XPS.

To determine the oxidation degree of Np for the lower oxide surface phase one can use the linear relationship between the oxidation state and the binding energy shift, ΔE, (chemical shift) measured for the XPS 4f core lines. With $\Delta E = 0$ and the oxidation state 0 for clean metal and $\Delta E = 3.9$ eV and the oxidation state 4 for NpO_2, formally an oxidation state close to 2 is found, *i.e.* the lower oxide would be a monoxide. But taking into consideration that the linear relationship is only valid for fully ionic compounds [1] for which the screening of the core hole does not vary for different compounds, the lower oxide is attributed to the hypo-stoichiometric Np_2O_{3-x}. In addition, NpO should be metallic because of a $5f^4\,(6d7s)^1$ electron configuration which results in a small chemical shift due to screening by conduction electrons. A comparison with the surface oxidation of Pu metal [7, 11, 12] also shows a considerably lower formal oxidation state of 2.4 instead

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[*] The energy positions of the oxide signals can only be given roughly because of shifts with oxide coverage. Particularly towards complete surface oxidation the NpO_2 5f signal at 3 eV shifts remarkably towards E_F; in this figure all spectra have been normalized in energy to the maximum O2p emission.

of 3, as expected for Pu_2O_3, which is clearly identified on the surface of Pu metal.

Conclusion

In contrast to oxide formation on U and Pu metal surfaces, where surface and bulk oxides are the same (U: UO_2; Pu: Pu_2O_3, PuO_2) Np forms in addition to NpO_2 a lower oxide. This oxide is attributed to Np_2O_3 and is only stable as a thin surface layer in the presence of Np metal.

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