Surface Oxidation of Uranium Metal as Studied by *X*-Ray Photoelectron Spectroscopy

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X-Ray photoelectron spectroscopy has been used to study the oxidation of uranium metal. The results indicate that even at 1073 K in a residual oxygen partial pressure of less than 1×10^{-8} N m^{-2} the interdiffusion of pure uranium and the surface oxide film is not sufficiently rapid to produce a completely pure uranium surface. Evidence is presented which suggests that under spectrometer conditions the surface layer is composed of a mixture of pure uranium, UO_2 and ' UO ' stabilised by the presence of uranium carbide. It is shown that values previously reported for the binding energies of uranium are in error and they must have been obtained from an oxidised surface. Accordingly values believed to be representative of pure uranium are presented.

THE extreme affinity of pure uranium for oxygen is well known[1] and as a result the study of its surface dependent properties becomes very difficult. This has been borne out by recent work[2] in which the Auger electron emission from a uranium surface was studied. It has been shown that even at high temperature (1073 K) and low oxygen partial pressures ($<1 \times 10^{-8}$ N m^{-2}) the interdiffusion of pure uranium from a bulk sample with only several molecular layers of surface oxide is not rapid enough to maintain a completely pure surface. However, the experimental data indicated that *ca.* 90% of the surface was maintained free of oxygen and other trace contaminants under these conditions and the resulting Auger spectrum was considered to be essentially that of the metal. In principle, *X*-ray photoelectron (*X*-p.e.) spectroscopy should augment considerably these studies. In this technique[3] the sample is exposed to monoenergetic *X*-rays and the photoelectrons expelled are energy-analysed in the spectrometer. The peaks in the resulting kinetic energy spectrum correspond to electrons of specific binding energies in the sample. In the experiments reported here sufficient data were collected to place in doubt the accuracy of previously reported binding energies,[4] and to substantiate previous evidence which indicated that uranium monoxide, UO, can exist in the presence of uranium carbide.[5]

EXPERIMENTAL

The study was carried out using a Vacuum Generators ESCA2 *X*-ray photoelectron spectrometer with Al-K_α radiation (1486·6 eV).

The uranium samples were cut from a bar of commercial purity uranium to a size of *ca.* 8 × 10 × 2 mm. These samples were rapidly oxidised in air to give a black surface. Electropolishing in a solution of 1 part each of H_2O, H_2SO_4, and H_3PO_4 gave samples with a smooth, bright appearance and polishing continued until the samples were thinned by *ca.* 30%, when they were stored, after washing with deionised water, under dry methanol. Following electropolishing a sample was removed from the methanol and placed on a platinum foil mount designed to fulfil two functions. First, it served as a protection for the spectrometer probe to prevent contamination and secondly, it was used as a calibration reference. Although it is well known that platinum physically adsorbs oxygen, recent evidence suggests that thin layers of chemisorbed oxygen are also produced.[6] These films, however, are no more than a few monolayers and the well referenced peaks characteristic of the pure metal are easily observed under vacuum thus providing a convenient calibrant. Here we used the $4f_{\frac{5}{2}}$ platinum line at 74·3 eV as our reference. Normally, a gold calibrant is used, but it was thought to be ill suited to this experiment because of the mutual solubility of gold and uranium at 1073 K and moreover at these temperatures gold would have diffused into the stainless steel probe.

Several experiments were performed and typically the sample and platinum mount were clamped onto the end of a stainless steel variable temperature probe which was subsequently placed into the spectrometer under an argon flow. At all times the cleaned platinum mount, sample, and probe were handled with nylon gloves and clean tweezers to prevent the introduction of contamination from fingerprints.

Following insertion of the sample, the spectrometer was evacuated and baked out to attain the lowest base pressure possible (5×10^{-7} N m^{-2}) and the sample heated to 473 K for 10 min to drive off volatile surface contamination. At this stage the surface was largely composed of uranium dioxide (see below).

The spectra of this surface were recorded for reference and then the series was repeated whilst the sample was heated over a period of several hours to 1073 K, thereby obtaining spectra at several temperatures. By this means the gradual diffusion of pure uranium at the surface could be observed and the changes in chemical composition of the surface layers could be monitored. Following the recording of spectra at 1073 K, which represented the purest surface attainable with the present equipment, the sample was cooled to ambient temperatures and maintained in the spectrometer for 15 h at a residual pressure of 1×10^{-6} N m^{-2}. This residual gas was largely composed of argon, oxygen, carbon monoxide, and water vapour, and under these conditions surface reactions took place largely removing the pure uranium surface, thus generating a film

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[1] J. J. Katz and E. Rabinowitch, ' The Chemistry of Uranium, the Element, its Binary and Related Compounds,' McGraw-Hill, New York, 1951.

[2] G. C. Allen and R. K. Wild, *Chem. Phys. Letters*, 1972, **15**, 279.

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[5] P. Chiotti, W. C. Robinson, and M. Kanno, *J. Less Common Metals*, 1966, **10**, 273.

[6] K. S. Kim, N. Winograd, and R. E. Davis, *J. Amer. Chem. Soc.*, 1971, **93**, 6296.

of uranium dioxide which could easily be observed by recording a series of spectra. Subsequent reheating of the sample to 1073 K followed by the rerecording of spectra at this temperature demonstrated that the clean uranium surface could be routinely regenerated.

RESULTS AND DISCUSSION

The results for several of the peaks in the p.e. spectrum are depicted in Figures 1—3 which show the effect of heating. Details of the peak positions are given in the Table. The peaks due to the surface impurities of oxygen and carbon ($1s_{\frac{1}{2}}$ level in each case) are shown, together with the doublet from the uranium $4f$ level. Count rates are indicated in each case for the spectra recorded at 1073 K. The same scale appertains to all spectra on each Figure; the vertical displacement is made to show the peak shifts.

Binding energies for selected peaks in uranium dioxide and uranium metal (eV) [a]

	$U4f_{\frac{7}{2}}$	$U4f_{\frac{5}{2}}$	$U5d_{\frac{5}{2}}$	$U5d_{\frac{3}{2}}$	$U4d_{\frac{5}{2}}$	$U4d_{\frac{3}{2}}$	$O1s_{\frac{1}{2}}$
UO_2 [b]	380·3 ± 0·3	391·1 ± 0·2	96·7 ± 0·2	104·6 ± 0·2	738·6 ± 0·5	780·9 ± 0·4	530·7 ± 0·3
U [c]	377·0 ± 0·3	387·7 ± 0·3	93·6 ± 0·2	101·8 ± 0·2	736·7 ± 0·5	778·8 ± 0·4	

[a] Peaks calibrated relative to $Pt4f_{\frac{5}{2}}$ peak at 74·3 eV. [b] Sample preparation produced surface layers of UO_2. Recorded at 300 K. [c] Recorded at 1073 K to maintain surface as clean as possible.

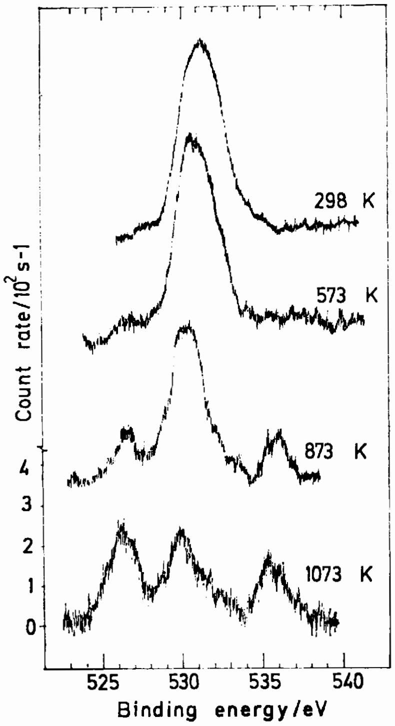

FIGURE 1 Oxygen $1s_{\frac{1}{2}}$ peaks recorded from uranium surface at denoted temperatures

As can be seen from the Figures there is a marked change in count rate and signal to noise ratios in each of the sets of spectra as the temperature is varied. Since the relative intensity of peaks resulting from particular electron energy levels in different elements is not quantitative in X-p.e. spectroscopy too much stress should not be laid on it, but it is pertinent to note the relative changes in the intensity of any one particular peak as the temperature is altered. Thus, whereas the oxygen and carbon intensity dropped somewhat on heating, the uranium $4f$ intensity showed a simultaneous rise which was to be expected if the surface was becoming cleaner. However whilst the relative intensities of the peaks in the spectra are not quantitative, the shifts in binding energy are of significance. These could readily be determined despite the increase in noise levels as the temperature was increased. Furthermore the noise levels on any particular spectrum are somewhat arbitrarily determined, being easily changed by altering ratemeter time constants and scan speeds.

As can be seen in Figure 1 the oxygen peak initially exhibits a broad profile which becomes narrower at higher temperature when it also splits into three components. The carbon data presented in Figure 2 lend support to the view that at high temperatures there are two distinct carbon species present on the uranium surface, the species to lower binding energy appearing at high temperatures.

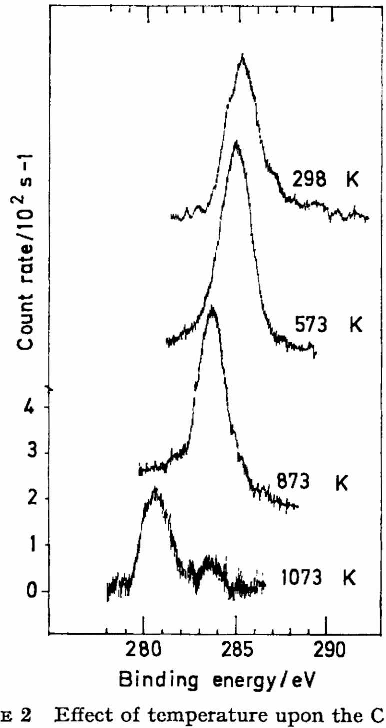

FIGURE 2 Effect of temperature upon the $C1s_{\frac{1}{2}}$ peak recorded from the uranium surface

The results for the uranium spectra are similar. The peaks observed at 300 K show a gradual decrease in intensity whilst a concomitant increase in intensity is observed to the low binding-energy side of each component of the doublet. It may be further observed that at high temperature (1073 K) a residual fraction of the original peak remains in each case, which broadens the prominent peak to the high binding-energy side.

These observations may be explained as follows. The initial electropolishing, overnight bake, and preheating of the sample in the spectrometer produced a surface film of uranium dioxide, slightly contaminated by adsorbed residual gases, including H_2O and small traces of carbon-containing materials (perhaps traces of methanol or pump oil). The uranium dioxide film was gradually removed as the sample was heated and diffusion of the oxide into the bulk and/or diffusion of pure uranium to the surface occurred. However, a totally pure surface was never produced, and at 1073 K although largely composed of pure uranium it remained contaminated by a small quantity of a surface layer. This was mainly composed of a uranium monoxide–uranium carbide mixture, but traces of uranium dioxide remained and carbon monoxide was observed in equilibrium at the surface. The reasons for this interpretation are now presented.

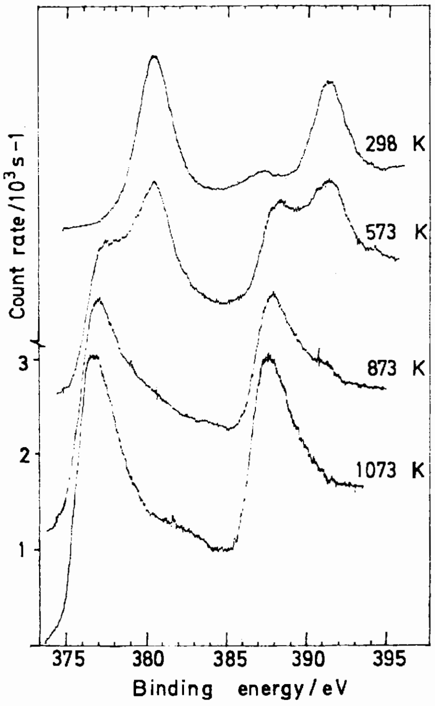

FIGURE 3 Effect of temperature upon the $U4f_{\frac{7}{2}}$ and $U4f_{\frac{5}{2}}$ peaks recorded from the uranium surface

The Uranium Oxide–Oxycarbide System.—Low temperature. The uranium oxide in equilibrium at low temperature (<973 K) with oxygen is UO_3 [7] but its formation is limited by a kinetic barrier, and the oxidation of uranium metal by air at room temperature leads to the formation of UO_2.[1]

In this work one would therefore expect the sample preparation involving methanol storage and air exposure to produce a surface film of uranium dioxide. Furthermore, if any UO_3 or U_3O_8 had formed on the surface it would decompose into UO_2 and oxygen under the temperature and pressures of the pretreatment.[1] Also since the free energy of formation of UO_2 (−509 kJ per mol oxygen) is more negative than that of water (−238 kJ per mol oxygen), uranium is thermodynamically capable of reducing the residual water within the system to form UO_2. According to Cordfunke [8] UO_2 does not become superstoicheiometric in equilibrium with uranium and at these moderate temperatures the UO_2 phase does not extend below the composition $UO_{2\cdot00}$, but several chemisorbed oxygen layers can be formed. It is therefore to be expected that, although the uranium sample surface appeared clean and bright, it is composed of uranium dioxide at least to a depth of several atomic layers. This is borne out by the spectra which were recorded at 298 K following the sample preparation, which show identical relative chemical shift values to those recorded from a sample of UO_2.

The uranium 4*f* and 5*d* doublets (Figure 3 shows the spectra obtained from the 4*f* orbitals) showed clean profiles with no broadening to the low-energy side which would be expected if uranium metal extended to within 5×10^{-10} m of the sample surface. This is the escape depth of electrons having kinetic energy characteristic of the binding energy of electrons in these orbitals. As can be seen from the series of spectra, peaks characteristic of pure uranium are observed only at temperatures in excess of 573 K, at which point diffusion processes begin to bring a sufficient quantity of the metal near enough to the surface for it to be observed. The oxygen peak recorded at 298 K can therefore be basically assigned to UO_2. However the peak is a little broad and as can be observed in Figure 1 upon heating tends to collapse somewhat on the high energy side before splitting into three distinct components. This broadening may be due to the adsorption of residual water vapour, which in the main is removed at 573 K. Water peaks have been observed at similar binding energies on the surfaces of other oxide systems.[9]

The carbon peak observed at 298 K is due to a small amount of adsorbed carbon-containing material. Allen and Wild [2] noted that the presence of carbon on the uranium surface was always observed, even in an ion-pumped system, and since the spectrometer is highly sensitive in this region, small quantities of surface contamination are readily detected. The presence of carbon here is hardly surprising in view of the methanol storage and the presence of oils within the spectrometer pumping system.

High temperature. When the sample was heated the composition of the surface layer of UO_2 (and adsorbed impurities) began to change. The gradual appearance of pure uranium at the surface was marked by a substantial shift (up to 3 eV) in the positions of the uranium

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[7] L. E. J. Roberts, *Quart. Rev.*, 1961, **15**, 442.

[8] E. H. P. Cordfunke, ' The Chemistry of Uranium,' Elsevier, Amsterdam, 1969.

[9] G. C. Allen and P. M. Tucker, unpublished results.

4f, *4d*, and *5d* doublets (see Table and Figure 3), but the surface never became entirely pure. Even after 5 h heating at 1073 K there was still a broadening of the uranium peaks to the high binding-energy side indicating the presence of residual quantities of oxidised uranium. This is borne out also by the presence of carbon and oxygen, albeit in much reduced quantities. It is of interest here to note the appearance at 1073 K of a carbon species with a binding energy of 280·6 eV. This value is 3·1 eV lower than the $1s_{\frac{1}{2}}$ binding energy of 283·7 eV at 1073 K observed for the residual hydrocarbon and is thought to arise from the generation of surface carbides at this temperature. The shift of 3·1 eV from the hydrocarbon line is well within the range determined by Ramqvist *et al.*[10,11] in their studies of the carbides of vanadium, niobium, tantalum, and titanium. This formation of surface carbide species is compatible with the simultaneous presence of lower oxide phases of uranium, *vide infra*. While the carbon line becomes thus resolved the oxygen $1s_{\frac{1}{2}}$ peak is observed to split into three components, of similar intensity, by the growth of peaks on both sides of that resulting (at 529·9 eV) from the residual small quantity of UO_2. These peaks are thought to arise from the presence of UO and CO which, it is surmised, are now present in equilibrium at the uranium surface with UO_2, U, and UC.

The preparation of the lower oxide phase, UO, has been reported but its existence as a discrete phase has not been substantiated. Bessonov [12] has claimed that it can be prepared at temperatures in excess of 1073 K as a result of the reaction and its formation on the

$$U + UO_2 \longrightarrow 2UO$$

surface of uranium at low oxygen partial pressures (10^{-5} N m^{-2}) and temperatures in excess of 1073 K has also been reported.[1] The presence of UO on the surface was recognised by characteristic cubic lattice parameters in the *X*-ray diffraction pattern, in contradistinction to those obtained from UO_2. There are, however, strong indications that the UO phase only exists because of the presence of such impurities as carbon or nitrogen.[13,14] If UO could be formed from uranium and uranium dioxide the heat of formation ($-\Delta H_{UO}$) would be greater than 539 kJ per mol (one half the heat of formation of UO_2). But since magnesium reduces the higher uranium oxides to metal (and not to UO), $-\Delta H_{UO}$ must be less than 593 kJ mol^{-1}. The most probable value is therefore 564 ± 20 kJ mol^{-1}. Chiotti *et al.*[5] in a study of the thermodynamic properties of uranium oxycarbides determined values within this range in a series of experiments which yielded very consistent data, and they concluded that the data indicate that at high temperatures (1023 K) the monoxide is the stable phase in contact with uranium metal and not uranium dioxide. This conclusion appears to be contrary to experience since no pure sample of UO has been prepared and it is to be noted that the thermodynamic calculations employed in their consideration treated oxycarbide phases as binary mixtures of UO and UC which is probably not strictly valid. However, the work lends support to the notion that UO can exist, if only in the presence of carbides. A similar conclusion is drawn from the work of Bazin and Accary,[15] which concerned the determination of the equilibrium overpressures of carbon monoxide above uranium oxycarbide–uranium dioxide mixtures at various temperatures, in which the equation

$$UC + 2UO_2 \rightleftharpoons 3UO_{(\mathrm{dissolved})} + CO$$

was considered as the theoretical basis for the experimental programme. From their work the variation of CO pressure P_{CO} (in atm) as a function of temperature was found to follow the relationship

$$\log P_{CO} = \frac{-39{,}600}{T} + 21{\cdot}42$$

and it is thus to be expected that at temperatures of 1073 K the UO–UC phase could exist in equilibrium with a low partial pressure of carbon monoxide (*ca.* 10^{-9} N m^{-2}).

The evidence from the present series of experiments, particularly data collected at 1073 K, lends some support to these previously published findings. At this temperature many of the conditions thought to favour the formation of UO are extant, namely low partial pressures of oxygen, the presence of an excess of uranium, the presence of carbides, low partial pressure of CO, and the requisite temperature. The appearance of pure uranium is noted by a shift in the uranium peaks in the p.e. spectrum; however, as mentioned above, a residual broadening to the high binding-energy side of the *4f* doublet was observed. This is undoubtedly due to a small quantity of oxidised uranium species remaining at the surface, perhaps in the form of UC and UO together with UO_2. Certainly the central O1*s* peak of the three observed at 1073 K can be reasonably assigned to this residual UO_2 since the peak had been present throughout the series of experiments and the results showed that despite its diminution in intensity at this temperature it never disappeared. It is noteworthy that the three peaks developed under these conditions always had roughly equivalent intensities which lends support to the notion that a complex phase is produced. We therefore tentatively assign the two new O1*s* peaks at 526·2 and 535·7 eV to the oxygen in UO and CO respectively, since if UO does exist in the presence of UC it is to be

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[10] L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman, and C. Nordling, *J. Phys. Chem. Solids*, 1969, **30**, 1835.

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[13] R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, *J. Amer. Chem. Soc.*, 1948, **70**, 99.

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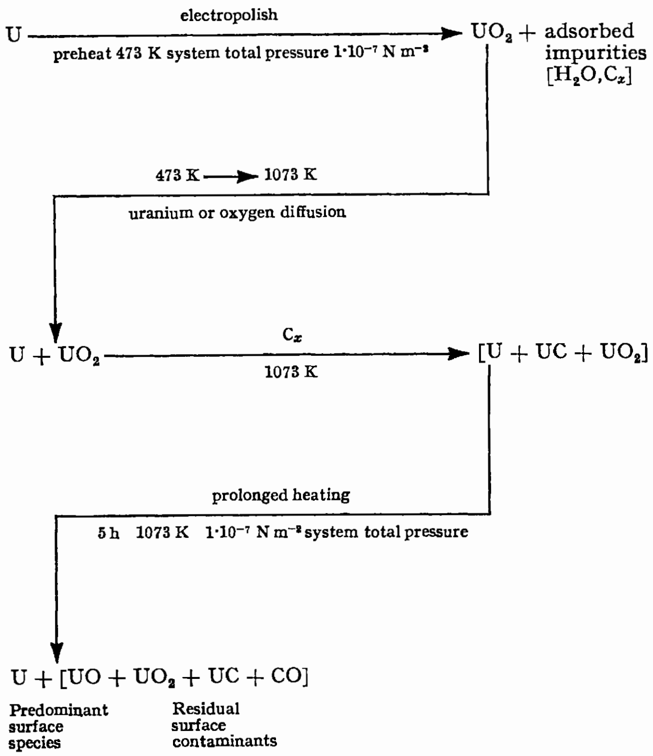

expected[5,15] that an equilibrium level of CO will also be present at the surface. These data indicate that the uranium–oxygen bond in UO must be considerably more ionic than that in UO_2.

The scheme given here is thought to summarise the conditions at the sample surface during the experiment. It is to be emphasised that the spectroscopic evidence indicates the bulk of the sample surface to be composed of pure uranium under these conditions, and the residual levels of the uranium oxide–oxycarbide phases are low. Thus the uranium spectra recorded at these temperatures are considered sufficiently well resolved to be taken as essentially representative of the pure material. The previously reported values for the binding energies of uranium[4] are in good agreement with the values found in this work for uranium dioxide and it is quite likely that the samples used for their determination would have been oxidised since no mention was made of specific treatments to the sample prior to measurements being made. It is thus concluded that the values determined here are more accurate.

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