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X-ray photoelectron spectra of SIMFUEL

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Abstract

An X-ray photoelectron spectroscopy (XPS) study of SIMFUEL, an unirradiated analogue of high-burnup UO_2 fuel, was conducted. This paper reports a revised composition for SIMFUEL with 6 at.% burnup. XPS spectra indicate that the uranium atoms are mainly in the U^{4+} state, with the U^{6+}-to-U^{4+} ratio being less than 0.005. The oxidation state of the dopant elements is discussed: Ru, Rh, Mo and Pd are present in the metallic state, whereas Sr, Ba, Y, La, Zr and Ce are present as oxides. Because of low signal intensity, the oxidation state of Nd could not be determined.

1. Introduction

SIMFUEL, simulated high-burnup UO_2 fuel, has been prepared to replicate the composition, chemical state and many of the microstructural features of used nuclear fuel [1]. We are studying SIMFUEL samples to establish the effects of fission products and actinides (formed during irradiation) on the corrosion behaviour of used UO_2 fuel [2]. This paper presents X-ray photoelectron spectroscopy (XPS) results for a 6 at.% burnup SIMFUEL sample.

2. Experimental procedures

The fission-product composition of SIMFUEL was calculated using the ORIGEN code based on the starting enrichment and irradiation history of the UO_2 fuel. The 13 elements used in this SIMFUEL preparation are listed in Table 1. (Note the difference between Table 1 and the composition given in ref. 1 for Sr.) They represent all the major fission products, except the gases and volatiles, and comprise about 99 wt.% of all expected solid fission products. Elements with similar chemical behaviour are represented by a single dopant, for example La represents itself and the actinide elements Am and Cm, while Nd represents all the rare earths except La and Ce. To replicate the complex microstructure of high-burnup fuel, the SIMFUEL constituents must be mixed intimately on a submicrometre scale and sintered under reducing conditions, at a sufficiently high temperature to achieve diffusion rates that ensure homogeneity and phase equilibrium on an atomic level [1].

The XPS studies were carried out using a PHI-5300 ESCA system, which allowed us to transfer the samples from an inert-atmosphere chamber to the evacuated sample compartment of the XPS spectrometer without exposure to atmospheric oxygen [3]. Sample discs, approximately 12 mm in diameter and 2–4 mm thick, were polished using 600 grit SiC sandpaper, in the inert-atmosphere chamber, to expose a fresh surface for analysis. The XPS spectra were excited using Mg Kα radiation filtered through an Al window [4]. The measured full width at half-maximum peak height (FWHM) for the Ag $3d_{5/2}$ band on our spectrometer is 0.79 eV and is mainly limited by the width of the exciting line [5]. The energy scale of the spectrometer was calibrated using the following line positions in the noble metals: Au $4f_{7/2}$ 84.00 eV, Ag $3d_{5/2}$ 368.29 eV, and Cu $2p_{3/2}$ 932.56 eV (see ref. 3 and references therein). The charge correction was obtained using a value of 529.9 eV for the O 1s peak of O^{2-}.

3. Results and discussion

Low-resolution survey spectra were recorded over the 0–1100 eV range, and high-resolution spectra were recorded for the U 4f, C 1s, O 1s, Zr 3d, Mo 3d, Sr 3d, Ba 3d, Ru 3d and valence-band regions. The binding energies (BEs) of the main peaks of the elements observed in the XPS spectra of the 6 at.% burnup SIMFUEL are listed in Table 1. Figure 1 shows high-

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TABLE 1. Composition and X-ray photoelectron spectra of SIMFUEL[a]

Element[b]	Composition (wt.%)		XPS spectra		
	Measured[c]	Calculated[d]	Binding energy (eV)	Spectrum type[e]	Assignment
U (Pu)	–	94.886	379.9	H	U $4f_{7/2}$
			391.1	H	U $4f_{5/2}$
Zr	0.590	0.593	182.5	H	Zr $3d_{5/2}$
			184.8	H	Zr $3d_{3/2}$
Mo	0.701	0.720	227.5	H	Mo $3d_{5/2}$
			230.7	H	Mo $3d_{3/2}$
Pd	0.408	0.434	335.0	L	Pd $3d_{5/2}$
Ba	0.321	0.307	796.0	H	Ba $3d_{3/2}$
Y	0.069	0.060	157.5	L*	Y 3d
Sr (Cs)	0.419	0.406	133.7	H	Sr 3d
Rh	0.035	0.034	307.5	L*	Rh $3d_{5/2}$
Ru (Tc)	0.712	0.754	279.5	H	Ru $3d_{5/2}$
La (Am, Cm)	0.227	0.254	835.0	L*	La $3d_{5/2}$
Ce (Np)	0.553	0.545	882.0	L*	Ce $3d_{5/2}$
Nd (Gd, Eu, Pm, Pr, Sm)	1.004	1.027	–	–	–
O	–	–	529.9	H	O 1s

[a] 6 at.% burnup.
[b] Elements in parentheses are represented by the first element.
[c] Measured using ICPAES, new data.
[d] Calculated using ORIGEN code.
[e] H high-resolution spectra, L low-resolution spectra, * very weak.

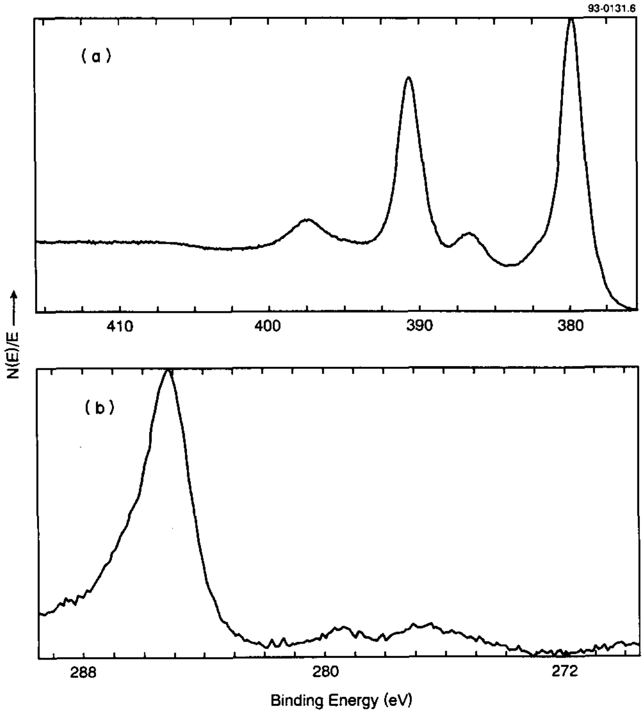

Fig. 1. High-resolution XPS spectra of (a) U 4f and (b) C 1s and Ru 3d regions in (6 at.% burnup) SIMFUEL.

resolution spectra for the U 4f, C 1s and Ru 3d regions, and Fig. 2 shows high-resolution spectra for the Mo 3d, Zr 3d and Sr 3d regions.

The spectrum of the U 4f region is typical of $UO_{2.00}$ [3, 7–9]. An analysis of the U $4f_{7/2}$ band into U^{6+} and U^{4+} components, following our previously published procedure [3], gave a U^{6+}-to-U^{4+} ratio of 0.005. This result is supported both by the peak position of the U $4f_{7/2}$ band (379.9±0.2 eV) and by its FWHM (1.75±0.1 eV).

The shake-up satellite band intensities and positions also indicate that the surface oxidation of uranium in this sample of SIMFUEL is very close to that in $UO_{2.00}$: the separation between the U $4f_{5/2}$ peak and its satellite (on the high-binding energy side) is approximately 6.8 ev, Fig. 1(a), equivalent to that reported by Allen *et al.* for pure UO_2 [8]. A comparatively high intensity for the U 5f band at approximately 1 eV relative to that of the O 2p band at about 5 eV [3, 6–9] is consistent with UO_2 as well. The peak-height ratio of the U 5f band to that of the O 2p band was about 3.6±0.2. The XPS evidence presented above supports the conclusion that the lower lattice parameter obtained for SIMFUEL from X-ray diffraction analysis is not due to the oxidation of uranium beyond $UO_{2.00}$ [1].

Binding energies measured for the Ru $3d_{5/2}$, Mo $3d_{5/2}$ and $3d_{3/2}$, Rh $3d_{5/2}$ and Pd $3d_{5/2}$ peaks indicate that these elements are present in the metallic state. The peak maximum observed here for the Ru $3d_{5/2}$ band is about 0.5 eV lower than the literature value for metallic Ru [4]. The binding energies of the transition

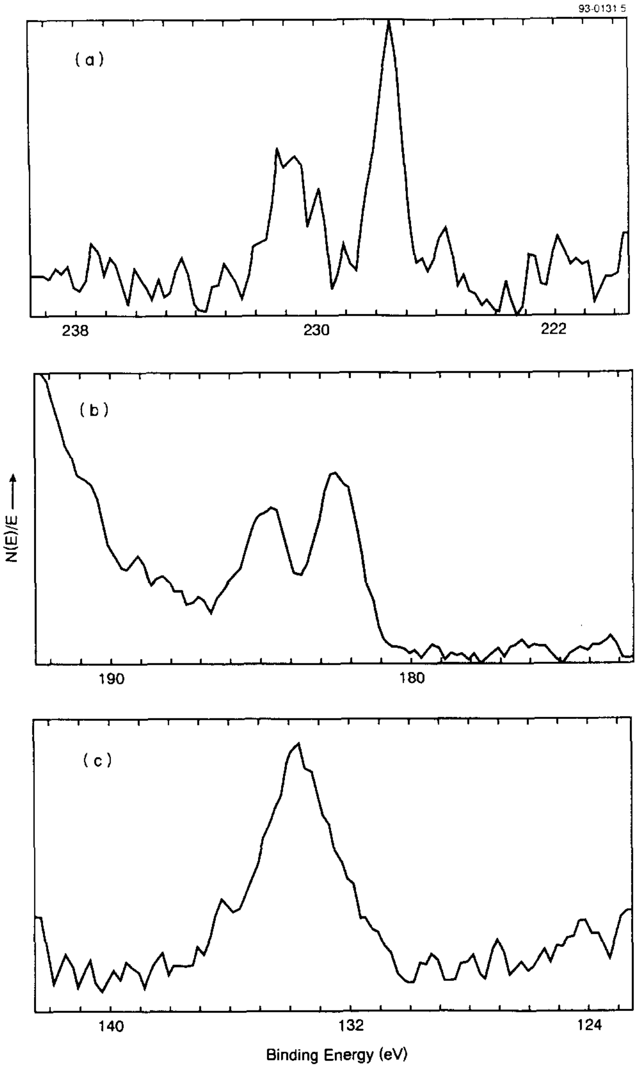

Fig. 2. High-resolution XPS spectra of (a) Mo 3d, (b) Zr 3d and (c) Sr 3d regions in (6 at.% burnup) SIMFUEL.

metals can be lower in alloys than in pure metals (see ref. 5 and references therein). Sr 3d and Ba $3d_{3/2}$ BEs indicate that these elements are present in the +2 state, most probably as complex oxides (the BE of Ba $3d_{5/2}$, the main peak of Ba, is not given in Table 1 because of interference from the U $4d_{3/2}$ band), while Y 3d and La $3d_{5/2}$ BEs are consistent with the +3 oxidation state [4]. The Zr 3d doublet matches that of ZrO_2 well and thus indicates the +4 oxidation state. A very weak feature at 882 eV in the survey spectrum is close to the reported BE of the Ce $3d_{5/2}$ band for CeO_2 [4]. It may be noted here that the BE for the Ce $3d_{5/2}$ band, as reported in the literature [4], does not follow the usual relationship between oxidation state and BE, *i.e.* higher BE for more positive oxidation state. Therefore, any conclusion about the chemical state of Ce in SIMFUEL from the weak feature seen at 882 eV should be considered tentative. The positions of the Nd 3d peaks (the main bands of Nd) are not given in Table 1 as a result of the uncertainties caused by the rather high background in this region (around 981 eV) of the XPS spectrum.

It is true that the XPS signal from a sample is limited to the top few nanometres of the sample surface, *i.e.* 95% of the intensity of the photoelectrons observed in the spectrum is derived from within a distance of 3λ of the sampling path [5]. Here λ is the inelastic mean free path of the emerging electrons. However, the sample surface analysed in this work was freshly exposed (see above) and the spectra were obtained from a rather large sample surface, *i.e.* over 1 cm^2. Therefore, we believe that the XPS results reported here represent the average chemistry of the bulk of the SIMFUEL sample.

We have also studied the spectra of SIMFUEL samples with 3 at.% and 1.5 at.% burnup and they support the conclusions presented above about the chemical state of the elements in SIMFUEL.

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