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# XPS and XRD studies of corrosion of uranium nitride by water

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## Abstract

Corrosion of UN in water was investigated as a function of pH and temperature using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and by measuring the amount of ammonia formed due to its corrosion. The XPS results indicate that a freshly fractured surface of UN is quickly converted to $UO_2$ on exposure to liquid water or water vapours at ambient temperatures. These results show that UN is unstable in contact with water. The corrosion rate of UN is estimated to be $\geq 40$ μmol $m^{-2}$ $h^{-1}$ in deaerated water at approx. 92°C. There was no significant difference in corrosion rates measured in water at initial pHs of approx. 6 and 10.3. These results contradict the literature reports stating that UN is stable in contact with boiling water.

*Keywords:* Uranium nitride; UN; Nuclear fuel; XPS; XRD; Corrosion

## 1. Introduction

Uranium mononitride, UN, has a high melting point (~2850°C), high density (14.32 g $cm^{-3}$) and high thermal conductivity and has been considered as a potential fuel for advanced nuclear reactors [1,2]. Although UN has excellent nuclear properties, there are some uncertainties about its stability in contact with water. For example, several reports suggest that solid UN is stable in contact with liquid water, including boiling water [3], water at 300°C [4], and water containing HCl, $H_2SO_4$ or NaOH [5]. On the other hand, several reports show that UN undergoes hydrolysis by superheated steam [2,6–9]. It is essential to resolve this uncertainty about the stability of UN in aqueous environments if UN is to be considered as a fuel in a water-cooled reactor such as CANDU. We have investigated the corrosion of UN in water using XPS and XRD – in addition to monitoring the changes in the chemistry of water in contact with the UN samples. Results of these studies are reported here.

## 2. Experimental

### 2.1. Materials

Uranium mononitride pellets were prepared at the Transuranium Institute, Karlsruhe, Germany. The pellets had a diameter of ~0.64 cm and a thickness of ~0.56 cm, and weighed about 2 g each. The pellets were black in colour, and polishing did not alter the colour. However, the colour of a freshly fractured surface was silver grey.

The pellets used for XPS and XRD analysis and corrosion experiments were polished, using a 600 grit SiC paper, on all sides including the rim, to expose a fresh surface. The polishing was performed in an anaerobic chamber, to avoid surface oxidation by atmospheric oxygen, using deoxygenated water as a lubricant and dust collector.

The $UO_2$ disks used in the control experiments were obtained by cutting fuel pellets from an unused CANDU bundle.

### 2.2. Corrosion experiments

Hydrolysis of UN by heated water vapour results in the formation of ammonia [4], i.e.,

$$2UN + 4H_2O \rightarrow 2UO_2 + 2NH_3 + H_2 \qquad (1)$$

As ammonia is known to react with many metals to form complexes, we used glass vessels to conduct the corrosion tests so that we could monitor the formation of ammonia if the above reaction occurred in our experiments.

Room-temperature experiments were conducted in an anaerobic chamber. Water (20 ml) was added to the reaction vessel containing a weighed pellet, and the vessel was sealed. At the end of the experiment (~1 or 2 weeks, Table 1), the pellet was removed from the flask, dried and weighed. The pH of the solution was measured, and the

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Table 1
Un corrosion in water: summary of experimental results

| Experiment Number | Sample[a] | Temperature (°C) | Time (h) | pH | | Final Volume (ml) | (U) ($\mu g\, l^{-1}$) | ($NH_3$) ($\mu g\, l^{-1}$) | Corrosion Rate ($\mu mol\ m^{-2}\ h^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | initial | final | | | | |
| A1 | UN(1) | 23 | 168 | 5.48 | 4.99 | 20.0 | 2160 | 125 | 5 |
| A2 | UN(2) | 23 | 168 | 5.48 | 5.30 | 20.0 | 2030 | 65 | 2 |
| A3 | ≠ | 23 | 168 | 5.48 | 4.88 | 20.0 | 6 | 50 | |
| A4 | ≠ | 23 | 168 | 5.48 | 5.36 | 20.0 | 12 | 40 | |
| A5 | ≠ | 23 | 168 | 5.48 | 5.04 | 20.0 | 18 | 40 | |
| A6 | ≠ | 23 | 168 | 5.48 | 4.94 | 20.0 | 9 | 50 | |
| A7 | $UO_2$(1) | 23 | 168 | 5.48 | 5.11 | 20.0 | 341 | 35 | |
| A8 | $UO_2$(2) | 23 | 168 | 5.48 | 5.13 | 20.0 | 764 | 35 | |
| B1 | UN(1) | 92 | 164 | 5.65 | 5.37 | 16.0 | 361 | 180 | 6 |
| B2 | UN(2) | 92 | 164 | 5.53 | 5.32 | 17.6 | 2470 | 400 | 14 |
| C1 | UN(1) | 92 | 334 | 5.84 | 8.02 | 17.4 | 1180 | 2530 | 44 |
| C2 | UN(2) | 92 | 334 | 5.84 | 5.76 | 13.7 | 2550 | 3410 | 46 |
| D1 | UN(1) | 90 | 141 | 10.28 | 8.46 | 19.0 | 510 | 1180 | 53 |
| D2 | UN(2) | 90 | 141 | 10.28 | 8.40 | 17.0 | 1110 | 1140 | 46 |

[a] Number in parentheses denotes the pellet number. All pellets were freshly polished, except in experiments B1, B2, C1 and C2 which were reused after preceding experiments.

≠ - No sample, just water.

solution was analyzed for $NH_3$ and U. Control experiments were conducted using $UO_2$ pellets in place of UN pellets, and without any pellets (Table 1).

For higher temperature (92°C) experiments the sealed glass vessel was placed in a heated sand bath in an oven at 92°C. High-temperature experiments were conducted in ‘pure water’ and in water with the initial pH adjusted to 10.3, a value close to that for CANDU reactor primary coolant, using dilute LiOH solution.

For ammonia analysis, an aliquot (10 ml) of solution was transferred from the reaction vessel into a sample vial at the end of the experiment. The aliquot was acidified, by adding a small amount (0.0689 ml) of dilute (0.35 M) sulfuric acid, to retain ammonia in the solution. The concentration of ammonia was determined using a colorimetric method known as the ‘phenate method’ [10]. After the sample for ammonia analysis was removed, the solution remaining in the vessel was used for uranium analysis. The concentration of uranium in the aqueous phase was determined by the standard addition method, using FLURAN and the Scintrex Fluorescence Uranium Analyzer, Model UA-3.

### 2.3. XPS and XRD

The XPS spectra were obtained using a PHI-5300 ESCA system. A sample was mounted on an XPS specimen holder in the inert atmosphere chamber, then transferred to the evacuated sample compartment of the spectrometer without exposure to air, using a PHI vacuum transfer vessel [11]. The XPS spectra were excited using Mg Kα radiation filtered through an aluminum window.

XRD patterns of the UN pellets were obtained using a Rigaku Rotaflex X-ray diffractometer, equipped with a 12 kW rotating-anode Cu Kα X-ray source and a diffracted-beam graphite monochromator.

## 3. Results and discussion

### 3.1. X-ray photoelectron spectroscopy

Low-resolution survey spectra were recorded for the 0 to 1100 eV region and high-resolution spectra were recorded for the U 4f, N 1s, O 1s and C 1s bands and the valence band region (0 to 20 eV). The XPS spectra of the as-received UN pellets showed strong peaks for C and O, but U peaks were very weak. The pellets were polished (using 600 grit SiC) to remove the ‘impurity’ layer, which may have been masking the U signal from UN; however, this increased only slightly the intensity of the U peaks. Therefore, one face of a UN pellet was subjected to aggressive polishing, using 1 μm $Al_2O_3$ powder, that slightly increased the intensity of the U peaks. A significant increase in the U signal was achieved by recording the spectrum of a ‘fresh surface’ obtained by fracturing a UN pellet in the anaerobic chamber.

Fig. 1 compares the XPS spectra for the region between 370 and 410 eV (U 4f region) of a freshly fractured UN pellet and a freshly polished UN pellet with that of a freshly polished $UO_2$ pellet. The peak maxima of the U 4f bands, shown in Fig. 1, are listed in Table 2. This table also contains the literature values for the binding energies (BE) of these bands in UN and $UO_2$ [12–14]. The binding energies observed for the UN pellets (Fig. 1, Table 2) suggest that these pellets (polished or freshly fractured) are covered with a layer of $UO_2$. This suggests that UN reacts with liquid water (used in polishing) and water vapour (present in the anaerobic chamber atmosphere), at ambient temperatures, to form a $UO_2$ layer detectable by XPS. Note that fracturing of the pellet should produce a fresh UN surface. The $UO_2$ seen on the fractured surface most probably arises from a reaction of UN with water vapour. The reaction with $O_2$ is expected to be less important as

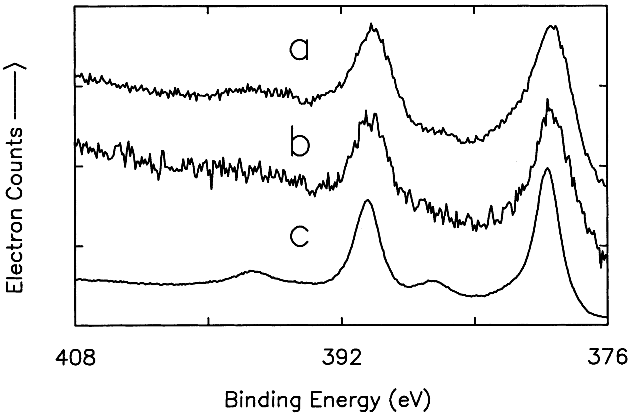

Fig. 1. XPS spectra for the U 4f region of (a) a freshly fractured UN pellet; (b) a freshly polished UN pellet; and (c) a freshly polished $UO_2$ pellet.

the concentration of $O_2$ in the anaerobic chamber atmosphere is much less (~1 ppm) than that of $H_2O$.

The bandwidths observed for the U 4f bands in the spectra of the UN pellet, Fig. 1a and b, are larger than those observed for the corresponding $UO_2$ bands (Fig. 1c). This indicates that the bands in the spectrum of the freshly fractured (or polished) UN pellet probably contain contributions from two or more uranium species. We believe that the larger bandwidths seen for the UN pellets are due to contributions not only from the $UO_2$ film (formed by the reaction of UN with water) but also from the underlying UN.

The resolution of the U $4f_{7/2}$ band in the spectrum of the fractured UN pellet into $UO_2$ and UN components indicates that ~30% of its intensity arises from UN, and the remainder from $UO_2$, Fig. 2. (The parameters used for UN bands were obtained from its literature spectra [13,14].) The presence of the UN signal suggests that the $UO_2$ layer, formed on the surface of the freshly fractured UN pellet by its reaction with water vapour, is thin, i.e., $<3$ nm. This assumes a homogeneous surface layer of $UO_2$, instead of islands of $UO_2$, on the UN surface [9]. Note that there is no indication of the presence of any U(VI) species in the XPS spectra (for the U 4f region) of either the freshly polished or fractured UN pellets.

Table 2
Binding energies for the U 4f bands in the XPS spectra of UN and $UO_2$

| Sample | U $4f_{7/2}$ (eV) | U $4f_{5/2}$ (eV) | Note |
|---|---|---|---|
| UN | 378.4 | 389.2 | [a] |
| UN | 377.3 | 388.0 | [b] |
| $UO_2$ | 379.6 | 390.4 | [c] |
| $UO_2$ | 380.2 | 390.8 | [b] |
| Polished UN Pellet | 379.4 | 390.3 | [d] |
| Fractured UN Pellet | 379.4 | 390.2 | [d] |
| Polished $UO_2$ Pellet | 379.8 | 390.6 | [e] |

[a] Calculated from the results given by Thibaut et al. [12] and Verbist et al. [13].

[b] Measured from Fig. 3 of Norton et al. [14].

[c] From Verbist et al. [13].

[d] UN sample covered with $UO_2$ film.

[e] $UO_2$ sample from an unused CANDU fuel pellet.

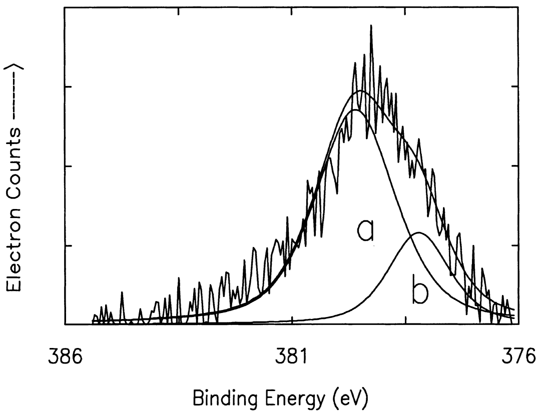

Fig. 2. Resolution of the U $4f_{7/2}$ band seen in the XPS spectrum of a freshly fractured UN pellet into (a) $UO_2$, and (b) UN components.

The O 1s band seen in the spectrum of the freshly fractured UN pellet is most probably from the $UO_2$ formed by the reaction of UN with water vapour. This band was resolved into $H_2O$, $OH^-$ and $O^{2-}$ components, according to the procedure discussed elsewhere [11]. This analysis showed that the intensity of this band arose mainly from the $O^{2-}$ and $OH^-$ moieties.

The strongest band of nitrogen in the XPS spectrum (N 1s) occurs at around 398 eV [15]. The N 1s band is quite weak; its relative atomic sensitivity is lower than that of the U $4f_{7/2}$ band by a factor of about 15 and it occurs in the spectral region where both UN [12] and $UO_2$ [13] have satellite peaks. Therefore, it is difficult to locate the N 1s band unambiguously in the spectra of UN pellets. One can see a hint of the N 1s band in the spectrum of the fractured pellet of UN (a in Fig. 1).

Fig. 3 compares the spectrum for the valence band region (0–20 eV) of a freshly fractured UN pellet with that of a freshly polished $UO_2$ pellet. $UO_2$ shows a sharp band at ~1.2 eV that is assigned to the presence of the valence electrons in the U 5f level [14,16]. On the other hand the

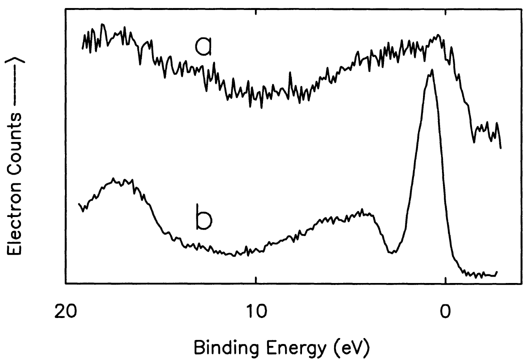

Fig. 3. Valence band region in the XPS spectra of (a) a freshly fractured UN pellet (top), and (b) a freshly polished $UO_2$ pellet (bottom).

valence electrons in UN give rise to a band near the Fermi level (i.e., B.E. close to zero) in its spectrum [14,17]. The valence-electron band of UN is less distinct, at room temperature, than that of $UO_2$. (The valence electrons in UN are considered to have less localized and more itinerant character than those in $UO_2$.) The valence band spectrum of the fractured UN pellet shown in Fig. 3 is closer to the published spectra of UN than those of $UO_2$. This suggests that the $UO_2$ film on UN, indicated by the U 4f bands (see above), is very thin. Note, the XPS signal in this region would arise from a 'thicker layer' of the sample than that in the U 4f region due to the higher kinetic energy (KE) of the photoelectrons in the valence region than that in the U 4f region, i.e., ~1250 eV vs. ~860 eV. The mean free-path of electrons, with a KE of 1250 eV, is higher than those with a KE of 860 eV. Therefore, the contribution of UN, under the $UO_2$ film, is probably greater in the spectrum of the valence band region than that of the U 4f region.

### 3.2. X-ray diffraction

The XRD patterns, for the $2\theta$ range between 10° and 120°, were recorded for freshly polished UN pellets and for corroded UN pellets. Comparison of the observed X-ray diffraction pattern of the freshly polished UN pellets with the literature patterns for UN [18] showed that all major observed XRD peaks can be accounted for by the pattern reported for UN. Computer analyses of the observed patterns also showed that the UN is the main phase in the polished pellets. $UO_2$ was seen only as a trace impurity in the XRD patterns of the freshly polished UN pellets. Therefore, the $UO_2$ film on the surface of the freshly polished UN pellet, as observed using XPS, most likely arose from a surface reaction with water. Note that the thickness of the sample analyzed by XPS is ~3 nm compared to ~3 μm in XRD. The XRD analysis of pellets corroded at room temperature did not show any significant increase in the thickness of the $UO_2$ layer. The XRD pattern for a UN pellet corroded at 90°C for about a week showed formation of trace amounts of $U_3O_7$, and $U_2N_3$, in addition to a slight increase in the $UO_2$ signal. There was also an indication of a very small trace of $UO_3$ and $UN_2$ in the XRD patterns of the pellets corroded at ~90°C. Formation of these phases (except that of $U_3O_7$) has been reported previously in studies investigating the reactions of UN with super-heated steam or $O_2$ [4,9].

### 3.3. Weight changes and uranium concentrations

A small decrease in the pellet weight (less than 0.5 mg) was observed in all corrosion experiments, except one. A slight increase in weight should occur when UN is converted to $UO_2$ (reaction (1)). The decrease in the pellet weights indicates that some of the uranium oxide formed during the corrosion reactions is lost to the solution. This conclusion is supported by the increase in the uranium concentration in the aqueous phase, Table 1.

### 3.4. Ammonia concentrations and corrosion rates

Table 1 also lists the concentration of ammonia in the aqueous phase at the end of each experiment. These results show that detectable amounts of ammonia are formed, even at room temperature, during the corrosion of UN pellets in water. The uncertainty in ammonia measurements is estimated to be 40 $\mu g\ L^{-1}$, the concentration of ammonia seen in the control experiments carried out without a UN pellet (A3 to A8, Table 1).

Based on reaction 1 and using the geometric area of the pellets, we calculated the corrosion rate of the UN from the concentration of ammonia seen in the aqueous phase, Table 1. We estimate the corrosion rate to be approximately 3 $\mu mol\ m^{-2}\ h^{-1}$ for UN in de-aerated water at ambient temperature, and $\geq 40$ $\mu mol\ m^{-2}\ h^{-1}$ at 92°C[1]. These results are in conflict with the literature reports [3,4] that claim that UN is stable in water under the conditions of the present experiments. Our results show that UN reacts with water, even at ambient temperatures, to form a layer of $UO_2$. One possible explanation for the discrepancy between the results presented here and these literature reports is that the samples used in their experiments may have had coatings of $UO_2$. The XPS results, discussed above, show that UN pellets are covered by $UO_2$ upon exposure to water vapour even at ambient temperature. Exposure to $O_2$ also results in the oxidation of a fresh surface of UN [19]. It is well known that $UO_2$ has very low solubility in water. Therefore, a UN sample covered with a $UO_2$ layer may appear unreactive in water. Also, the earlier workers did not have the benefits of the modern instruments used in the present work.

In order to evaluate the potential of UN as a nuclear fuel, the corrosion rate of UN may be compared with that of U metal or other uranium compounds that are of interest as nuclear fuel. For U metal, we estimate, using Bourns data [20], a corrosion rate of ~0.12 $mol\ m^{-2}\ h^{-1}$ in water at 100°C. For uranium silicide, we estimate a corrosion rate of between ~4 $nmol\ m^{-2}\ h^{-1}$ and ~400 $nmol\ m^{-2}\ h^{-1}$ at 100°C [21]. ($U_3Si$ is used as fuel in research reactors which operate at lower temperatures than conventional power reactors.) Thus the corrosion rate for UN is much lower than that for U metal but higher than that of uranium silicide. The high corrosion rates of UN in water (at ~92°C) indicate that UN is not stable in the hot aqueous environment that a failed fuel bundle would

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[1] The geometric surface area of the pellets used in the rate calculations is 1.76 $cm^2$. We have not used the corrosion rates from experiments B1 and B2 to arrive at this rate. These rates are estimated to be the lower limit of the corrosion rates as some ammonia is lost during the experiments at ~90°C by evaporation, as indicated by a decrease in the final volume of the solution.

encounter in a water-cooled reactor. Also, 'used UN fuel' will be a poor waste-form for permanent disposal in a geological disposal vault, similar to that envisaged in the Canadian Nuclear Waste Management Program [11], because of its reactivity in an aqueous environment. Uranium mononitride may be a good fuel for a reactor that uses a non-aqueous coolant (one unreactive with UN) and is operated with a reprocessing option for the final disposal of its used fuel.

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## References

[1] H. Matzke, Science of Advanced LMFBR Fuels. North Holland, Amsterdam, Holland, 1986.
[2] K. Richter, C. Sari, J. Nucl. Mater. 184 (1991) 167.
[3] S. Sugihara, S. Imoto, J. Nucl. Sci. Technol. 6 (1969) 237.
[4] N.J. Bridger, R.M. Dell, V.J. Wheeler, in: J.W. Mitchell (Ed.), Reactivity in Solids, Proceedings of an International Symposium, Wiley-Interscience, New York, NY, 1969, pp. 389–400.
[5] M.B. Sears, J. Inorg. Nucl. Chem. 32 (1970) 2971.
[6] J.E. Antill, Corros. Sci. 6 (1966) 17.
[7] D.G. Cragg, R.J. Dicker, J.D.L. Harrison, J.W. Isaacs, J.R. McLaren, W.G. Roberts, Bull. Soc. Franç. Ceram. 77 (1967) 35.
[8] R.M. Dell, V.J. Wheeler, N.J. Bridger, Trans. Farad. Soc. 63(5) (1967) 1286.
[9] G.A. Rama Rao, S.K. Mukerjee, V.N. Vaidya, V. Venugopal, D.D. Sood, J. Nucl. Mater. 185 (1991) 231.
[10] L.S. Clesceri, A.E. Greenberg, R.R. Trussell, in: Standard Methods for the Examination of Water and Wastewater, 17th Edition, American Public Health Association, Washington, 1989, p. 4-120, p. 4-121.
[11] S. Sunder, J.J. Cramer, N.H. Miller, Mater. Res. Soc. Symp. Proc. 257 (1992) 449.
[12] E. Thibaut, J. Verbist, R. Troc, J. Phys. 40 (1979) C4–77.
[13] J.J. Verbist, J. Riga, C. Tenret-Noel, J.J. Pireaux, G. d'Ursel, R. Caudano, E.G. Derouane, in: H. Blank, R. Lindner (Eds.), Plutonium and Other Actinides, North-Holland, Amsterdam, 1976, pp. 409–419.
[14] P.R. Norton, R.L. Tapping, D.K. Creber, W.J.L. Buyers, Phys. Rev. B. 21 (1980) 2572.
[15] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: J. Chastain (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin–Elmer Corporation, Physical Electronics Division, Eden Prairie, MN, U.S.A, 1992.
[16] N.S. McIntyre, S. Sunder, D.W. Shoesmith, F.W. Stanchell, J. Vac. Sci. Tech. 18 (1981) 714.
[17] B. Rehl, G. Hollinger, F.H. Himpsel, J. Magn. Magn. Mater. 29 (1982) 303.
[18] ICDD. Powder diffraction files. International Center for Diffraction Data, Newton Square, PA, U.S.A., 1994.
[19] K. Ikawa, K. Taketani, Room temperature oxidation of uranium nitride powder, J. Nucl. Sci. Tech. 7(9) (1970) 433.
[20] W.T. Bourns, Corrosion testing of uranium silicide fuel specimens. Atomic Energy of Canada Limited Report, AECL-2718, 1968.
[21] W.T. Bourns, A literature survey of $U_3Si$ corrosion. Atomic Energy of Canada Limited Report, AECL-2609, 1967.