Oxidation States of U and Nb in U–Nb–O Ternary Oxides by means of Magnetic Susceptibility, XPS and ESR*

C. MIYAKE[†], S. OHANA, S. IMOTO

Faculty of Engineering, Osaka University, Suita, Osaka-565, Japan

and K. TANIGUCHI

Osaka Electro-Communication University, Neyagawa, Osaka-572, Japan

In order to have a good understanding of the behavior of fission products in nuclear fuel, as well as that of so-called 'soft fuel' which reduces corrosion by pellet-clad interaction (PCI), the U–Nb–O ternary oxides are one of the most important ternary systems containing uranium and oxygen. The ternary phase diagram of U–Nb–O at 1100 ℃ and a few ternary mixed oxides have been reported previously [1–3]. However, among these systems only UNb_3O_{10} is stable below 1100 ℃.

In the present report UNb_2O_7, UNb_4O_{12} and UNb_3O_{10} were prepared together with non-stoichiometric $UNb_3O_{10.17}$ and $UNb_3O_{10.34}$. The mutual dependence of the oxidation states of uranium and niobium in these ternary oxides was studied by magnetic susceptibility, XPS and ESR measurements.

Experimental

Materials

For sample preparation U_3O_8, Nb_2O_5 and NbO_2 were used as starting materials. U_3O_8 was prepared by oxidizing UO_2 at 700 ℃ under an atmosphere of an O_2 gas flow. Purchased Nb_2O_5 was pretreated under a stream of O_2 gas flowing at 400 ℃, and NbO_2 was prepared by reducing Nb_2O_5 at 1000 ℃ under a flow of H_2 gas. The mixture of starting materials with the required mol ratio was well ground, pressed under 5 t/cm^2 for 15 min, and finally sealed in a quartz tube under vacuum. The reactions were as follows.

$$U_3O_8 + Nb_2O_5 + 4NbO_2 \xrightarrow{1100\ ℃,\ 40\ h} 3UNb_2O_7$$

$$U_3O_8 + 4Nb_2O_5 + 4NbO_2 \xrightarrow{1200\ ℃,\ 60\ h} 3UNb_4O_{12}$$

$$U_3O_8 + 4Nb_2O_5 + NbO_2 \xrightarrow{1100\ ℃,\ 40\ h} 3UNb_3O_{10}$$

In addition to the stoichiometric $UNb_3O_{10.00}$, two kinds of hyperstoichiometric compounds, such as $UNb_3O_{10.17}$ and $UNb_3O_{10.34}$, were prepared, controlling the ratio of the starting materials as follows.

$$2U_3O_8 + 9Nb_2O_5 \xrightarrow{1100\ ℃,\ 40\ h} 6UNb_3O_{10.17}$$

$$8U_3O_8 + 26UO_3 + 75Nb_2O_5 \xrightarrow{1100\ ℃,\ 40\ h} 50UNb_3O_{10.34}$$

The products obtained were identified by X-ray diffraction patterns, as reported previously [1–3]. The color of the samples of $UNb_3O_{10.00} \sim UNb_3O_{10.34}$ is brown and becomes lighter with increasing oxygen content. These products are insoluble in nitric acid solution.

Measurements

The magnetic susceptibility was measured from room temperature down to 1.7 K at 0.5 T using a Faraday-type torsion magnetometer. The field dependence of magnetic susceptibility was measured at room temperature, liquid nitrogen temperature and liquid helium temperature.

XPS spectra were recorded on an ESCA-750 from Shimadzu Co. Ltd., with a Mg target excited by 8 kV with a 30 mA emission current under an atmosphere below 5×10^{-5} Pa. The binding energies were determined with respect to the value of 83.8 eV of Au $4f_{7/2}$ of gold, which was evaporated on the sample surface to correct the effect of charging up.

Results and Discussion

UNb_2O_7 and UNb_4O_{12}

The temperature dependence of magnetic susceptibility is shown in Fig. 1. The magnetic susceptibility

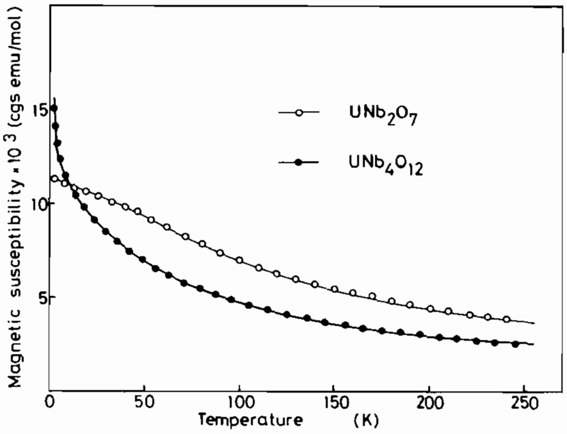

Fig. 1. The dependence of magnetic susceptibility on temperature.

---

[*] Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

[†] Author to whom correspondence should be addressed.

0020-1693/87/$3.50

of UNb_4O_{12} increases monotonically with decreasing temperature and obeys the Curie–Weiss law. On the other hand, the magnetic susceptibility of UNb_2O_7 has a tendency to saturate in a temperature range below 50 K. The magnetic susceptibility is almost independent of magnetic field intensity, suggesting no ferromagnetic impurity.

The effective Bohr magneton numbers estimated from reciprocal magnetic susceptibility–temperature curves, after corrections for diamagnetic susceptibility and temperature -independent paramagnetic susceptibility, are 3.2 and 2.4 for UNb_2O_7 and UNb_4O_{12}, respectively. U^{4+} generally has values of 2–3.5 of the effective Bohr magneton number, depending on the ligands around it in the molecules or crystals. The effective paramagnetic moment of the compounds investigated, therefore, is probably attributed to U^{4+}. If this is the case, the oxidation state of niobium ion is expected to be diamagnetic pentavalent.

Figure 2 shows XPS spectra of these compounds. The signal of U 4f is split into two peaks, U $4f_{7/2}$ and U $4f_{5/2}$, due to spin–orbit coupling. In addition, satellite peaks appear at 7–8 eV higher binding energy than the main peaks. There are several theories dealing with the origin of satellite peaks. In the present case the satellite of the U 4f peaks always accompanies a U 5f signal: the satellite of the U 4f peaks appears only in paramagnetic uranium ions, as described elsewhere [4]. Table I shows the binding energies of U $4f_{7/2}$ and Nb $3d_{5/2}$ for UNb_2O_7 and UNb_4O_{12}, together with those of U $4f_{7/2}$ for UO_2 and UO_3, and those of Nb $3d_{5/2}$ for NbO_2 and Nb_2O_5 [5, 6]. The observed values of U $4f_{7/2}$ for UNb_2O_7 and UNb_4O_{12} are close to that of UO_2, *i.e.*, that of U^{4+}; the values of Nb $3d_{5/2}$ are close to that of Nb_2O_5, *i.e.*, that of Nb^{5+}. Therefore, these results support the oxidation states of the uranium and niobium ions as found from the magnetic susceptibility measurement.

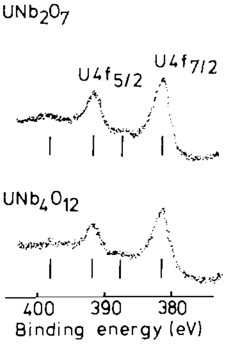

Fig. 2. XPS spectra of U $4f_{7/2}$ and U $4f_{5/2}$.

TABLE I. Binding Energies (eV) of U $4f_{7/2}$ and Nb $3d_{5/2}$

Compound	U 4f $_{7/2}$	Nb $3d_{5/2}$
UNb_2O_7	380.5	207.2
UNb_4O_{12}	380.0	206.8
UO_2	380.5[a]	
UO_3	381.7[a]	
NbO_2		205.0[b]
Nb_2O_5		207.0[b]

[a]Ref. 5. [b]Ref. 6.

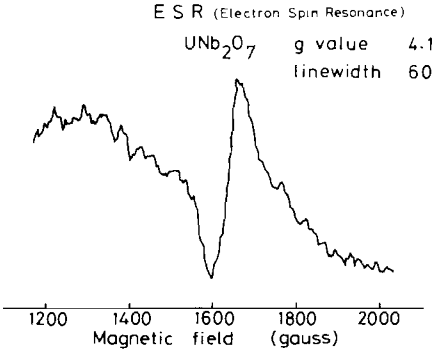

Fig. 3. ESR spectrum of UNb_2O_7 at room temperature.

The ESR signal of UNb_2O_7 at room temperature is shown in Fig. 3, suggesting this signal to be correlated with the *g* value of 4.1 and the linewidth of about 60 gauss, as expected for U^{4+} [7].

The plateau below about 50 K in the magnetic susceptibility–temperature curve of UNb_2O_7 should probably be ascribed to a slightly distorted octahedral crystalline field around U^{4+} [8].

UNb_3O_{10}

UNb_3O_{10} has a wide homogeneous region in the phase diagram as compared with UNb_2O_7 and UNb_4O_{12}. We have prepared three kinds of samples containing different amounts of oxygen, such as $UNb_3O_{10.00}$, $UNb_3O_{10.17}$ and $UNb_3O_{10.34}$.

Figure 4 shows the temperature dependence of the magnetic susceptibility per mol. All the samples

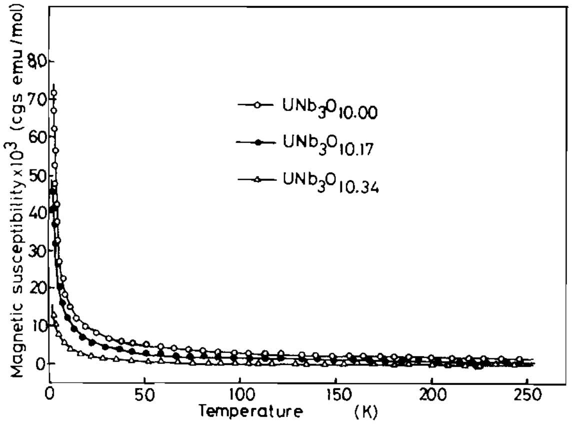

Fig. 4. The dependence of magnetic susceptibility on temperature.

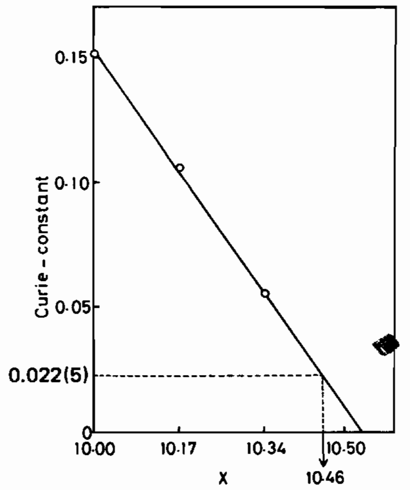

Fig. 5. Curie constant *vs.* oxygen content, *x*, of UNb_3O_x.

indicate that the paramagnetic susceptibility increases monotonically with decreasing temperature, and the magnetic susceptibility decreases with increasing oxygen content. The effective Bohr magneton number obtained from the curve of $UNb_3O_{10.00}$ is 1.1, leading to U^{5+} in this compound. Niobium is also pentavalent in this compound. As the amount of oxygen increases, the oxidation state of uranium becomes higher, *i.e.*, from pentavalent to diamagnetic hexavalent. Assuming that the excess amounts of oxygen in $UNb_3O_{10.17}$ and $UNb_3O_{10.34}$ are compensated by hexavalent uranium, we have the effective Bohr magneton number of 1.1 per net pentavalent uranium in $UNb_3O_{10.17}$ and $UNb_3O_{10.34}$, showing good agreement with that of $UNb_3O_{10.00}$.

Figure 5 shows a linearity between the obtained Curie constant and oxygen contents. The Curie constant of the samples prepared in an oxygen flow or air was 0.022(5), leading to $UNb_3O_{10.46}$ as seen from the Figure. Therefore, it was found that the hyperstoichiometric oxide of UNb_3O_{10} is limited to $UNb_3O_{10.46}$ under these conditions, not to $UNb_3O_{10.50}$ in which all uranium ions are oxidized to hexavalent.

The binding energies of U $4f_{7/2}$ and Nb $3d_{5/2}$ are presented in Table II. The value of U $4f_{7/2}$ of $UNb_3O_{10.00}$ is slightly smaller than that of U^{5+}. This value increases with increasing amount of oxygen, while the value of Nb $3d_{5/2}$ remains constant at 206.6–206.7 eV irrespective of the amount of oxygen. It was found that in UNb_3O_{10} niobium is stable as pentavalent and uranium is progressively oxidized from pentavelent to hexavalent with increasing amount of oxygen. The signals of U 4f for $UNb_3O_{10.17}$ and $UNb_3O_{10.34}$ become slightly broader with increasing amounts of oxygen, indicating that U^{6+} contributes to the signal of U^{5+}, as seen from Fig. 6.

TABLE II. Binding Energies (eV) of U $4f_{7/2}$ and Nb $3d_{5/2}$

Compound	U $4f_{7/2}$	Nb $3d_{5/2}$
$UNb_3O_{10.00}$	380.0	206.7
$UNb_3O_{10.17}$	380.2	206.6
$UNb_3O_{10.34}$	381.2	206.6

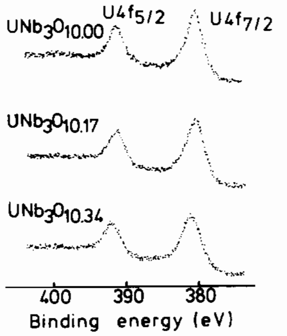

Fig. 6. XPS spectra of U $4f_{7/2}$ and U $4f_{5/2}$.

Conclusion

The oxidation states of uranium and niobium are tetravalent and pentavalent, respectively, in UNb_2O_7 and UNb_4O_{12}, but are both pentavalent in UNb_3O_{10}.

References

1 C. F. Miller, U. Merten and J. T. Porter, 'GA-1896 Final Report,' U.S. Atomic Energy Commission, Office of Technical Information, 1961.
2 C. Keller, *J. Inorg. Nucl. Chem.*, *27*, 1233 (1965).
3 P. W. Mirwald and H. Schrocke, *Neues Jahrb. Miner. Abh.*, *125*, 201 (1975).
4 C. Miyake, H. Sakurai and S. Imoto, *Chem. Phys. Lett.*, *36*, 158 (1975).
5 D. Chadwick and J. Graham, *Nature, Phys. Sci.*, *237*, 127 (1972).
6 D. Simon, C. Perrin and P. Baillif, *C. R. Acad. Sci. Paris, Ser. C*, *241*, 283 (1976).
7 T. Yoshimura, C. Miyake and S. Imoto, *J. Inorg. Nucl. Chem.*, *37*, 739 (1975).
8 B. C. Lande and L. M. Venanzi, *Inorg. Chim. Acta.*, *3*, 239 (1969).