

Phase relations of the uranium–neptunium–oxygen system

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Abstract

Phase equilibria of the uranium–neptunium–oxygen system were studied by high temperature X-ray diffractometry and thermogravimetry at temperatures between room temperature and 1300 K in atmospheres of He–8% H_2 , CO_2 –1% CO , N_2 –100ppm O_2 , N_2 –1% O_2 and air. The ternary UO_2 – U_3O_8 – NpO_2 phase diagram at 1273 K was drawn from the result of this investigation. The solid solution with fluorite-type structure, $(Np,U)O_{2+x}$, occurs in the composition range bounded by $UO_{2.25}$, UO_2 , NpO_2 and $Np_{0.6}U_{0.4}O_{2.27}$.

1. Introduction

During the burn-up of nuclear fuels, long-lived lighter actinides are accumulated in the fuel; neptunium is one element produced in high yield. In this work, phase relations and thermodynamic properties of the Np–U–O system will be presented.

Little is known of the basic properties of the Np–U–O system compared with the U–Pu–O and U–Th–O systems. Paul [1] studied the quasi-binary UO_{2+x} – NpO_2 phase diagram in 1 atm of O_2 between 1373 and 1823 K, and reported that there were three phase regions in the system: a narrow U_3O_8 phase at the uranium-rich side; a two-phase region of U_3O_8 and a fluorite solid solution (MO_{2+x}); a wide MO_{2+x} phase at the neptunium-rich side. Alain [2] reported that a linear relationship was observed between the lattice parameter of MO_{2+x} phase and compositions at 1273 K in vacuum.

In this paper we will describe the phase relations of the UO_2 – U_3O_8 – NpO_2 ternary system from the results of high temperature X-ray diffractometry and thermogravimetry under atmospheres of He–8% H_2 , CO_2 –1% CO , N_2 –100ppm O_2 , N_2 –1% O_2 and air.

2. Experimental details

Neptunium dioxide, which was provided from Fontenay auch Roses, France, was heated at 1273 K before use. The main impurities were Na (50 ppm), Si (50 ppm) and Fe (200 ppm). The isotopic purity of the ^{237}Np was higher than 99.99% by mass spectroscopic

analysis. U_3O_8 was prepared by oxidizing high purity uranium metal blocks with total metallic impurities of less than 20 ppm [3] in air at about 1000 K and then was reduced to UO_2 in a stream of purified hydrogen at 1273 K for 10 h.

Weighed amounts of NpO_2 and UO_2 powders were intimately mixed and the mixtures (50 mg) were heat treated at 1573 K for 6 h in air. The products were then crushed, mixed and heat treated again.

The X-ray diffraction patterns were taken using a diffractometer with a high temperature attachment. Powder specimens were loaded on a small dent (5 mm \times 5 mm) of a platinum sample holder without binder and mounted in the high temperature attachment. Specimens were heated at a rate of 5 K min^{-1} to 1273 K and then held at this temperature for 6 h. Measurements were carried out with the samples maintained in atmospheres of He–8% H_2 , CO_2 –1% CO , N_2 –100ppm O_2 , N_2 –1% O_2 or air. Specimens were cooled to room temperature at a rate of 0.5 K min^{-1} .

The thermogravimetric analysis was made with a Sartorius MP8 electric balance (sensitivity, 0.01 mg). The powder specimen (about 40 mg) in a fused quartz crucible was suspended from the balance and heated at a rate of 2 K min^{-1} to 1273 K and then held at this temperature for 10 h.

3. Results and discussion

The lattice parameters a_0 of a fluorite-type solid solution, MO_{2+x} ($M=U+Np$), obtained at room tem-

perature was expressed as a linear function of oxygen non-stoichiometry x and neptunium fraction y ($= [\text{Np}]/[\text{M}]$):

$$a_0 \text{ (pm)} = 547.04 - 7.5x - 3.66y$$

This equation shows that the lattice parameter diminishes with increasing x and y .

Lattice parameters of MO_{2+x} and the phases present in specimens heated at 1273 K in various atmospheres are summarized in Table 1. The intensity ratio of the reflection of the (111) plane of MO_{2+x} to that of the (130) plane of the U_3O_8 phase was used to estimate the U_3O_8 fraction in the two-phase mixtures; this ratio is given as a percentage in the fifth column of the table. The average O:M ratio was calculated from weight increase of the specimen when it was heated in oxidizing atmospheres, assuming that the O:M ratio of the specimen was 2.00 when heated in He-8% H_2 .

As seen in the table, the specimen is either a two-phase mixture of MO_{2+x} and U_3O_8 or an MO_{2+x} single phase. For samples heated in air, a two-phase mixture

of U_3O_8 and MO_{2+x} was identified for specimens with $y \leq 0.5$, whereas only an MO_{2+x} phase was observed when $y \geq 0.6$. After heating in atmospheres of CO_2 -1% CO and He-8% H_2 , the products contained only an MO_{2+x} phase. Since the lattice parameter of NpO_2 heated in He-8% H_2 at 1273 K is in good agreement with that heated in air, NpO_2 is considered to be practically a line compound, which is consistent with the result of Richter and Sari [4].

The ternary UO_2 - U_3O_8 - NpO_2 phase diagram at 1273 K, as deduced from this investigation, is shown in Fig. 1. Open symbols indicate single-phase regions and filled symbols two-phase mixtures. Double circles indicate the limiting composition of MO_{2+x} phases in the two-phase mixtures; these were calculated from the lever rule [5], under the assumption that Np was not dissolved in the U_3O_8 phase. This assumption might not give a significant error, since the solubility of NpO_2 in the U_3O_8 phase has been reported to be less than 3.5 mol.% [1]. At 1273 K, the limiting compositions for the MO_{2+x} phases are (1) UO_2 to NpO_2 at the lowest

TABLE 1. Lattice parameters for MO_{2+x} , average O:M ratios and phases at 1273 K

Atmosphere	Np content	Lattice parameter (pm)	Average O:M ratio	Phases at 1273 K
air	0.2	548.60	2.54	$\text{MO}_{2+x} + \text{U}_3\text{O}_8$ (68%)
	0.4	548.85	2.36	$\text{MO}_{2+x} + \text{U}_3\text{O}_8$ (24%)
	0.5	548.84	na	$\text{MO}_{2+x} + \text{U}_3\text{O}_8$ (11%)
	0.6	549.14	2.26	MO_{2+x}
	0.7	548.96	2.20	MO_{2+x}
	0.8	548.76	2.15	MO_{2+x}
	0.9	548.58	na	MO_{2+x}
	1.0	548.57	2.00	MO_{2+x}
$\text{N}_2/1\%\text{O}_2$	0.4	548.97	2.34	$\text{MO}_{2+x} + \text{U}_3\text{O}_8$ (23%)
	0.5	549.09	na	$\text{MO}_{2+x} + \text{U}_3\text{O}_8$ (tr)
	0.6	549.23	2.23	MO_{2+x}
	0.7	549.09	2.16	MO_{2+x}
	0.8	548.69	2.14	MO_{2+x}
$\text{N}_2/100 \text{ ppmO}_2$	0.4	549.30	2.30	$\text{MO}_{2+x} + \text{U}_3\text{O}_8$ (8%)
	0.5	549.18	na	MO_{2+x}
	0.6	549.37	2.17	MO_{2+x}
	0.7	549.14	2.14	MO_{2+x}
	0.8	548.74	2.10	MO_{2+x}
$\text{CO}_2/1\%\text{CO}$	0.4	550.31	2.04	MO_{2+x}
	0.5	549.97	na	MO_{2+x}
	0.6	549.94	2.03	MO_{2+x}
	0.7	549.48	2.02	MO_{2+x}
	0.8	549.04	2.01	MO_{2+x}
He/8% H_2	0.4	550.59	2.00	MO_{2+x}
	0.5	550.36	2.00	MO_{2+x}
	0.6	550.07	2.00	MO_{2+x}
	0.7	549.68	2.00	MO_{2+x}
	0.8	549.20	2.00	MO_{2+x}
	1.0	548.69	2.00	MO_{2+x}

MO_{2+x} is a fluorite-type solid solution. The U_3O_8 content is indicated in parentheses. na, not available; tr, trace.

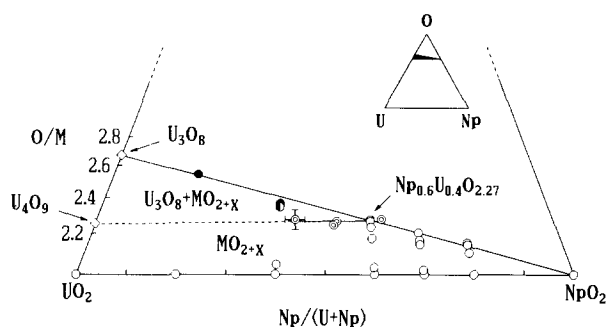


Fig. 1. The ternary U-Np-O phase diagram for 1273 K: \circ , \diamond , single phases; \bullet , two-phase mixtures; \odot , limiting composition of MO_{2+x} phases in the two-phase mixtures; the broken line is tentative.

O:M ratio, (2) $\text{UO}_{2.25}$ to $\text{Np}_{0.6}\text{U}_{0.4}\text{O}_{2.27}$ at the highest O:M ratio, and (3) $\text{Np}_{0.6}\text{U}_{0.4}\text{O}_{2.27}$ to NpO_2 on the U_3O_8 - NpO_2 line.

Paul [1] reported that the phase boundary of MO_{2+x} was $y=0.55$ at 1373 K in 1 atm of O_2 , which is in fair agreement with the present value, $y=0.6$, at 1273 K

obtained in air, taking into account the difference in experimental conditions.

The limiting compositions of the MO_{2+x} phase on the U_3O_8 - ThO_2 and the U_3O_8 - PuO_2 lines have been reported to be $\text{Th}:(\text{Th}+\text{U})\approx 0.45$ [6] and $\text{Pu}:(\text{Pu}+\text{U})=1$ [7] respectively. The limiting $\text{An}:(\text{An}+\text{U})$ ($\text{An}=\text{Th}, \text{Np}, \text{Pu}$) ratios increase with increasing atomic number of the An and, therefore, with decreasing An^{4+} radius.

References

- 1 R. Paul, *KFK-1297*, 1970.
- 2 T. Alain, *FRNC-TH-1146*, 1981.
- 3 H. Hashitani, A. Hoshino and T. Adachi, *JAERI-M-5343*, 1973.
- 4 K. Richter and C. Sari, *J. Nucl. Mater.*, 148 (1987) 266.
- 5 W.J. Moore, *Physical Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1962, p. 127.
- 6 R. Paul and C. Keller, *J. Nucl. Mater.*, 41 (1971) 133.
- 7 *The Plutonium-Oxygen and Uranium-Plutonium-Oxygen systems: A Thermochemical Assessment*, Technical Report Series No. 79, IAEA, Vienna, 1967, p. 58.