Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 421 (2004) 69–71
thermochimica acta
www.elsevier.com/locate/tca

Thermal expansion of ThO_2-2, 4 and 6 wt.% UO_2 by HT-XRD

A.K. Tyagi [a,*], M.D. Mathews [a], B.R. Ambekar [a], R. Ramachandran [b]

[a] *Applied Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*
[b] *Radiometallurgy Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*

Received 6 October 2003; accepted 24 February 2004
Available online 19 May 2004

Abstract

The lattice thermal expansion (quasi-isotropic) behaviour of polycrystalline sample of ThO_2-2, 4 and 6 wt.% UO_2 has been investigated from room temperature to 1623 K in vacuum using high-temperature X-ray diffraction (XRD). The incorporation of UO_2 systematically influences the thermal expansion behaviour of ThO_2. The coefficients of quasi-isotropic average lattice thermal expansion of ThO_2, ThO_2-2, 4 and 6 wt.% UO_2, over a temperature range of 293 and 1623 K, are found to be as 9.67×10^{-6}, 9.82×10^{-6}, 10.09×10^{-6} and 10.37×10^{-6} K^{-1}, respectively. This study will be useful in designing the nuclear reactor fuel assembly based on ThO_2.

Keywords: Lattice thermal expansion; ThO_2; X-ray diffraction

1. Introduction

Both ThO_2 and UO_2 are known to form a continuous solid solution over the entire composition range [1,2]. Thorium is envisaged to play an important role in the third stage of the Indian nuclear power generation programme [3]. Since Th itself is not a fissile material in the thermal region of neutrons, it is proposed to use about 2–6 wt.% of fissile uranium and plutonium dioxides in the ThO_2 matrix. Thermal expansion is an important thermo-physical property, which governs the design of a nuclear fuel pin. The bulk thermal expansion data of sintered UO_2, ThO_2 and several mixed oxides of Th and U containing higher amounts of UO_2, i.e., ≥10% are well reported in the literature [4–6]. Recently, we reported [7] the quasi-isotropic lattice thermal expansion of ThO_2 containing 2 wt.% UO_2 (natural uranium) from room temperature to 1473 K. In continuation of these investigations, herein we report the lattice thermal expansion of ThO_2 containing 4 and 6 wt.% of UO_2, proposed fuel compositions in futuristic nuclear reactors, from 293 to 1623 K. ThO_2 and ThO_2-2 wt.% UO_2 were also reinvestigated from 293 to 1623 K for a better comparison and over a wider temperature range than used in the earlier study.

2. Experimental

Various MOX samples were prepared by a ceramic route, as reported earlier [7]. X-ray diffraction (XRD) patterns were recorded on polycrystalline samples for the phase identification using monochromatic Cu Kα radiation using a Philips X-ray diffractometer, Model PW 1729. High temperature X-ray powder diffraction studies were carried out using a Philips Xpert Pro unit, having an Anton Paar High temperature attachment. A small amount of the sample was finely ground and mounted on a Pt stage-heating element. A Pt/Pt-13%Rh thermocouple spot-welded to the bottom of the stage was used for temperature measurement. The XRD patterns were recorded in the range $10 < 2\theta < 90^{\circ}$ from room temperature to 1623 K. The silicon powder and platinum stage were used to calibrate the instrument. In order to avoid the oxidation of U^{4+}, all the experiments were performed in vacuum of the order of 2×10^{-5} Torr. The unit cell parameters were determined using a least squares refinement program. The coefficient of quasi-isotropic average lattice thermal expansion was also evaluated in each case.

3. Results and discussion

The ambient temperature XRD patterns of all the four samples are given in Fig. 1. The observed cubic lattice

* Corresponding author. Tel.: +91-22-559-5330; fax: +91-22-550-5151.
E-mail address: aktyagi@magnum.barc.ernet.in (A.K. Tyagi).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.02.025

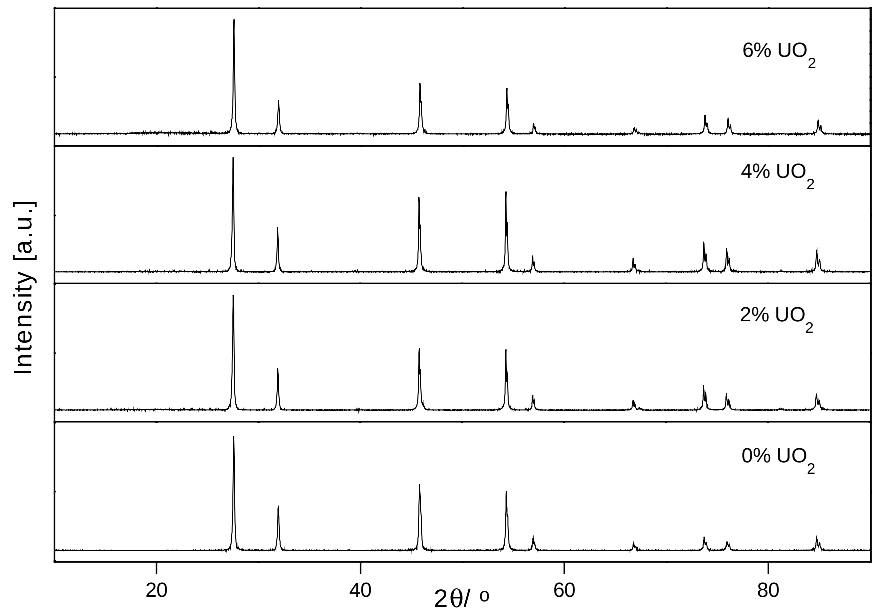

Fig. 1. XRD patterns of various samples in ThO_2–UO_2 system, at 293 K.

parameters for ThO_2, ThO_2-2, 4 and 6 wt.% UO_2 were 5.599(1), 5.591(1), 5.589(1) and 5.585(1) Å, respectively. The systematic decrease in lattice parameter, which can be explained based on ionic size considerations, indicates the homogeneous incorporation of U^{4+} into the lattice of ThO_2. Typical XRD patterns of one of the samples, i.e., ThO_2-4 wt.% UO_2, at different temperatures are given in Fig. 2. In order to study the thermal expansion behaviour, the unit cell parameters were determined, as a function of temperature, using a least squares refinement program. The lattice parameter of each sample at different temperatures is given in Table 1. The percentage lattice expansion from

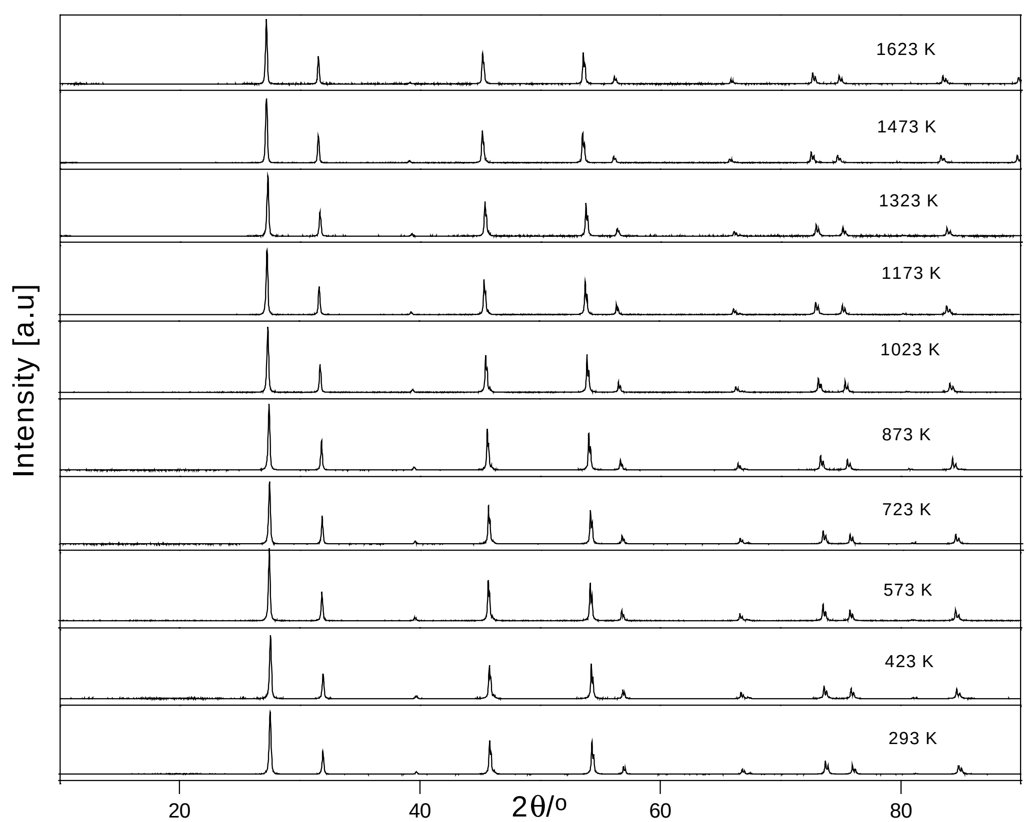

Fig. 2. Typical XRD patterns of ThO_2-4 wt.% UO_2, at different temperatures.

293 to 1623 K of these samples was also computed and the polynomial fits are given below (T in K).

For ThO_2

$$100 \cdot \Delta a/a_o = -0.23235 + (7.77504 \times 10^{-4})T + (1.38240 \times 10^{-8})T^2 + (1.24972 \times 10^{-10})T^3 - (4.53325 \times 10^{-14})T^4 \quad (1)$$

For ThO_2-2 wt.% UO_2

$$100 \cdot \Delta a/a_o = -0.31363 + (0.00121)T - (6.83202 \times 10^{-7})T^2 + (5.73693 \times 10^{-10})T^3 - (1.44256 \times 10^{-13})T^4 \quad (2)$$

For ThO_2-4 wt.% UO_2

$$100 \cdot \Delta a/a_o = -0.25737 + (8.50794 \times 10^{-4})T - (8.93762 \times 10^{-8})T^2 - (8.9702 \times 10^{-11})T^3 - (5.21547 \times 10^{-14})T^4 \quad (3)$$

For ThO_2-6 wt.% UO_2

$$100 \cdot \Delta a/a_o = -0.442786 + (0.00198)T - (1.98649 \times 10^{-6})T^2 + (1.48007 \times 10^{-9})T^3 - (3.59568 \times 10^{-13})T^4 \quad (4)$$

The quasi-isotropic coefficients of average lattice thermal expansion (α_a) in the temperature range 293–1623 K are included in Table 1. The α_a of ThO_2, ThO_2-2, 4 and 6 wt.% of UO_2 are 9.67×10^{-6}, 9.82×10^{-6}, 10.09×10^{-6} and 10.37×10^{-6} K^{-1}, respectively. The average thermal expansion coefficients for these compositions, in the temperature range 293–1173 K are also given in Table 1. It can be seen that there is a systematic increase in the average thermal expansion coefficient after incorporating UO_2 into ThO_2. This trend can be correlated to the higher melting point of ThO_2 as compared to that of UO_2. Earlier, we had reported the α_a value for ThO_2 and ThO_2-2 wt.% UO_2 as 9.58×10^{-6} and 9.74×10^{-6} K^{-1}, respectively, in the temperature range 293–1473 K. Springer [4] had reported the average linear thermal expansion coefficient (α_a) for ThO_2 with 10 and 20 mol% of UO_2 in the temperature range 293–1173 K ($\alpha_a \times 10^6 = 10.10$ and 10.05 K^{-1}, respectively). These values show almost similar thermal expansion coefficient for the two compositions. A comparison of the these values with that of ThO_2, ThO_2-2, 4, and 6 wt.% of UO_2, in the temperature range 293–1173 K (Table 1), shows a systematic increase in α_a up to 10 mol% of UO_2.

Table 1
Lattice parameter at different temperatures and variation of thermal expansion coefficient in ThO_2–UO_2 system

Temperature (K)	ThO_2	ThO_2-2% UO_2	ThO_2-4% UO_2	ThO_2-6% UO_2
293	5.599	5.591	5.589	5.585
423	5.605	5.597	5.595	5.593
573	5.612	5.605	5.603	5.601
723	5.620	5.613	5.611	5.608
873	5.628	5.620	5.618	5.615
1023	5.636	5.628	5.626	5.624
1173	5.644	5.637	5.635	5.634
1323	5.654	5.646	5.644	5.642
1473	5.662	5.655	5.653	5.652
1623	5.671	5.664	5.664	5.662
$\alpha_a \times 10^{6*}$ (293–1173 K)	9.13	9.35	9.35	9.97
$\alpha_a \times 10^{6*}$ (293–1623 K)	9.67	9.82	10.09	10.37

$\alpha_a = \Delta a/a_o$ (T-293).
* Unit: K^{-1}.

4. Conclusion

The lattice thermal expansion behaviour of two new compositions of Thoria doped with low concentration of UO_2 has been investigated. Comparison of the present data with those of Springer [4] shows that the thermal expansion coefficient increases with UO_2 content in ThO_2 up to 10 mol%. These data will supplement the data on ThO_2–UO_2 solid solutions having higher contents (≥10 mol%) of UO_2. To best of our knowledge, this is the first thermal expansion study on ThO_2-4,6 wt.% UO_2.

Acknowledgements

We thank Dr. N.M. Gupta, Head, Applied Chemistry Division for his keen interest and encouragement to this work.

References

[1] W.A. Lambberston, M.H. Mueller, F.H. Gunzel, J. Am. Ceram. Soc. 36 (1953) 397.
[2] J. Belle, Uranium Dioxide: Properties and Nuclear Applications (USAEC, 1961) p. 291.
[3] R. Chidambaram, in: M. Srinivasan, I. Kimura (Eds.), Proceeding of Indo-Japan Seminar of Thorium Utilization, Bombay, India, 10–13 December 1990, p. 7.
[4] J.R. Springer, Report No. BMI-X-10210, 1968.
[5] J.B. Conway, R.M. Fincel, R.A. Hein, III UN Conference at Geneva, CONF-39–50, 1963.
[6] M.D. Burdick, H.S. Parkar, J. Am. Cream. Soc. 39 (1956) 181.
[7] A.K. Tyagi, M.D. Mathews, J. Nucl. Mat. 278 (2000) 123.