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Letter to the Editors

Thermal expansion of ThO_2–2 wt% UO_2 by HT-XRD

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Abstract

The linear thermal expansion of polycrystalline ThO_2–2 wt% UO_2 has been investigated from room temperature to 1473 K in flowing helium atmosphere using high temperature X-ray diffractometry. ThO_2–2 wt% UO_2 shows a marginally higher linear thermal expansion as compared to pure ThO_2. The average linear and volume thermal expansion coefficients of ThO_2–2 wt% UO_2 are found to be $\bar{\alpha}_a = 9.74 \times 10^{-6}\ K^{-1}$ and $\bar{\alpha}_v = 29.52 \times 10^{-6}\ K^{-1}$ (298–1473 K). This study will be useful in designing the nuclear reactor fuel assembly based on ThO_2.

1. Introduction

Both ThO_2 and UO_2 have a face centered cubic (fcc) lattice with CaF_2-type structure which is retained up to their melting points. They are known to form a continuous solid solution over the entire composition range [1,2]. It was found that, within the experimental accuracy, Vegard's law is obeyed in this system, indicating the existence of an ideal solid solution. However, there are a few reports [3,4] where slight deviation from the ideality has been observed. Thorium has attracted considerable attention in the recent past as it is expected to play an important role in the third stage of the Indian nuclear power generation program [5]. Since Th itself is not a fissile material in the thermal region of neutrons, it is proposed to use about 2–6% of fissile uranium and plutonium dioxides in the ThO_2 matrix. Thermal expansion and thermal conductivity are two of the most important thermo-physical properties which directly affect the performance of a fuel. The bulk thermal expansion data of sintered UO_2, ThO_2 and several mixed oxides of Th and U are well reported in the literature [6–9]. It was found that all reports are on the thermal expansion of ThO_2 containing higher amounts of UO_2, i.e., $\geqslant 10\%$. It is observed that the thermal expansion of UO_2 is higher than that of ThO_2 in a given temperature range. The addition of UO_2 to ThO_2 increases its thermal expansion and the resulting increase is more or less proportional to the amount of UO_2 added. There were no reports of ThO_2 containing 2 wt% UO_2 (natural uranium) which is one component of the proposed fuel for nuclear reactors envisaged in the third stage of the Indian nuclear power generation program. Hence, it is necessary to study the thermal expansion behavior of ThO_2 containing 2 wt% of UO_2.

2. Experimental

ThO_2 and 2 wt% UO_2 were mechanically mixed for about 4 h, pressed into pellets and heated at 1923 K for 4 h in a flowing N_2–8% H_2 atmosphere. X-ray diffraction (XRD) patterns were recorded on polycrystalline samples for the phase identification using monochromatic Cu-Kα radiation in a Philips X-ray diffractometer, Model PW 1729. High temperature X-ray powder diffraction studies were carried out using an MRC Model X-86 N3 high temperature diffractometer attachment. A small amount of the sample was ground to ca. 100 μm particle size and mounted on a Pt–40% Rh stage-heating element. A Pt/Pt–13% Rh thermocouple spot-welded to the bottom of the stage was used for temperature measurement. The temperature was controlled by an MRC

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Model X-8600-5000-2 proportional temperature controller. The XRD patterns were recorded in the range $20° < 2\theta < 85°$ from room temperature to 1473 K. The silicon and platinum stage were used to calibrate the instrument. In order to avoid the oxidation of U^{4+}, all the experiments were performed in flowing helium atmosphere. The unit cell parameters were accurately determined using a least squares refinement program. The unit-cell volumes were calculated from the cell parameters, and the coefficients of average linear and volume thermal expansion were also evaluated. Thermal expansion of ThO_2 was reinvestigated along with the ThO_2–2 wt% UO_2 sample for comparison under identical conditions.

3. Results and discussion

In order to ascertain the incorporation of U^{4+} into the lattice of ThO_2, the room temperature XRD patterns of ThO_2 and ThO_2–2 wt% UO_2 were refined. The observed cubic lattice parameters for ThO_2 and ThO_2–2% UO_2 were 0.5599(1) nm and 0.5590(3) nm, respectively. The small decrease in lattice parameter, which can be explained by ionic size considerations, indicates the uniform incorporation of U^{4+} into the lattice of ThO_2. The homogeneity of this product was also confirmed by EPMA [10]. Each XRD pattern recorded at different temperatures was indexed to get lattice parameters (Table 1). The lattice parameter and unit cell volume of ThO_2 increases from 0.5599(1) nm to 0.5662(1) nm and 0.17552 nm^3 to 0.18151 nm^3, respectively, whereas that of ThO_2–2 wt% UO_2 increases from 0.5590(3) nm to 0.5654(4) nm and 0.17468 nm^3 to 0.18074 nm^3 on going from 298 to 1473 K. The percent lattice and volume thermal expansion for both the samples were also computed from the lattice parameter and cell volume at each temperature of measurement, and their polynomial fits are given below.

(i) For ThO_2:

$$\frac{\Delta a}{a}\times 100 = -0.28843 + (9.56431\times 10^{-4})T + (9.75144\times 10^{-8})T^2 - (1.80224\times 10^{-10})T^3 + (7.82203\times 10^{-14})T^4,$$

$$\frac{\Delta V}{V}\times 100 = -0.88967 + (0.00302)T - (6.54992\times 10^{-9})T^2 - (2.71076\times 10^{-10})T^3 + (1.56339\times 10^{-13})T^4.$$

(ii) For ThO_2–2 wt% UO_2:

$$\frac{\Delta a}{a}\times 100 = -0.52878 + (0.00262)T - (3.60021\times 10^{-6})T^2 + (3.06898\times 10^{-9})T^3 - (8.90284\times 10^{-13})T^4,$$

$$\frac{\Delta V}{V}\times 100 = -1.58844 + (0.00805)T - (1.15524\times 10^{-5})T^2 + (1.0089\times 10^{-8})T^3 - (2.97048\times 10^{-12})T^4.$$

The coefficients of average linear and volume thermal expansion ($\bar{\alpha}_a$ and $\bar{\alpha}_v$) in the temperature range 298–1473 K are also included in Table 1. It is found that after incorporating 2 wt% of UO_2 into ThO_2, the coefficient of quasi-isotropic (as studies were performed on polycrystalline samples) average linear thermal expansion, $\bar{\alpha}_a$, increases from 9.58×10^{-6} K^{-1} to 9.74×10^{-6} K^{-1}. The coefficient of average volume thermal expansion, $\bar{\alpha}_v$, increases from 29.04×10^{-6} to 29.52×10^{-6} K^{-1}. Thus there is an increase in the average thermal expansion by about 1.7% in the temperature range 298–1473 K after incorporating 2 wt% of UO_2 into ThO_2.

Table 1
Lattice parameter, cell volume and coefficients of average linear and volume thermal expansion for ThO_2 and ThO_2–2 wt% UO_2

Temperature (K)	ThO_2		ThO_2–2 wt% UO_2	
	a (nm)	Volume (nm^3)	a (nm)	Volume (nm^3)
298	0.5599(1)	0.17552	0.5590(3)	0.17468
423	0.5606(2)	0.17618	0.5599(4)	0.17552
573	0.5614(2)	0.17694	0.5605(3)	0.17609
723	0.5621(2)	0.17760	0.5611(3)	0.17665
873	0.5631(2)	0.17855	0.5622(4)	0.17769
1023	0.5636(2)	0.17902	0.5629(4)	0.17836
1173	0.5646(2)	0.17999	0.5638(4)	0.17922
1323	0.5653(3)	0.18065	0.5647(5)	0.18007
1473	0.5662(1)	0.18151	0.5654(4)	0.18074
$\bar{\alpha}_a, \bar{\alpha}_v$ $(K)^{-1}$ [a]	$\bar{\alpha}_a = 9.58\times 10^{-6}$	$\bar{\alpha}_v = 29.04\times 10^{-6}$	$\bar{\alpha}_a = 9.74\times 10^{-6}$	$\bar{\alpha}_v = 29.52\times 10^{-6}$

[a] Coefficients of average linear and volume thermal expansion from 298 to 1473 K.

4. Conclusion

The 2 wt% UO_2 doping in ThO_2 does not change its thermal expansion behavior drastically. This observation is attributed based on the individual thermal expansion behavior of UO_2 and ThO_2. It may be noted here that doping of 2 wt% of UO_2 has got a relatively more pronounced effect on thermal conductivity of ThO_2 in different temperature segments [11].

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