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Ceramics International 32 (2006) 609–612

CERAMICS
INTERNATIONAL

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Lattice thermal expansion studies of $Th_{1-x}Nd_xO_{2-x/2}$ solid solutions

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Received 7 December 2004; received in revised form 14 March 2005; accepted 24 April 2005
Available online 5 July 2005

Abstract

The synthesis, characterization and lattice thermal expansion studies of the ThO_2–Nd_2O_3 phase with general compositions $Th_{1-x}Nd_xO_{2-x/2}$ are reported. Based on XRD data the composition corresponding to solid solubility limit of $NdO_{1.5}$ in ThO_2 lattice under conditions of slow cooling from 1673 K was previously reported as $Th_{0.50}Nd_{0.50}O_{1.75}$. The lattice thermal expansion (293–1473 K) behavior of the solid solutions has been investigated by high temperature XRD and found to show a gradual increase with increasing content of $NdO_{1.5}$ in $Th_{1-x}Nd_xO_{2-x/2}$ series.

Keywords: C. Thermal expansion; Phase relation; Thoria; Solid solubility

1. Introduction

In nuclear reactors involving UO_2 and (U, Th)O_2 fuels, two types of solid fission products are found, viz. metallic and non-metallic inclusions [1–3]. Among the non-metallic solid fission product compounds, the rare-earth oxides Ln_2O_3 (Ln = La, Ce, Y, Nd, Sm, Eu and Gd), ZrO_2 and alkaline earth oxides MO (M = Sr and Ba) are the major components. These fission products are known to form solid solutions with UO_2, while rare-earth oxides are known to be soluble in ThO_2 and (U, Th)O_2 [4–6].

Thorium is envisaged to play an important role in the third stage of the Indian nuclear power generation program [7]. A research program on investigation of various aspects of thorium-based mixed oxide systems has been initiated in our laboratory. One of the major activities is on the bulk and lattice thermal expansion behavior of different thoria-based phases having relevance to the proposed thorium oxide-based nuclear reactors. Unlike the urania-based systems, phase relations, thermodynamic and thermophysical data on thoria-based systems are sparse. As a part of this program, the thermal expansion behavior of ThO_2 containing 2, 4, 6 wt.% UO_2 has been investigated [8] by high temperature X-ray diffractometry. The preparation and bulk thermal expansion studies of $BaThO_3$ and $SrThO_3$ were also reported [9]. The preparation of nano-crystalline thoria powder was carried out by a gel combustion route using glycine as a fuel [10].

Doped thoria is an important material also in view of its potential applications as a solid electrolyte for its use in oxygen concentration cells. There are few reports on the solubility of Nd_2O_3 in ThO_2 under long annealed, in situ and quenched conditions. Phase relations in the ThO_2–$NdO_{1.5}$ system were reported in 1954 by Brauer and Gradinger [11]. They found a solubility of about 50 mol% $NdO_{1.5}$ at 1673 K in ThO_2. However, according to Sibieude and Foex [12] only 35 mol% $NdO_{1.5}$ is soluble in ThO_2 at 1673 K and they reported that the solubility increases to 40 mol% at 2473 K. However, there are little data on phase relations in the ThO_2–$NdO_{1.5}$ system under slow cooled conditions and on the thermal expansion behavior of the solid solutions. In view of this, we have recently investigated the phase relations and bulk thermal expansion behavior of ThO_2–$NdO_{1.5}$ system by thermo-dilatometry [13]. Nd_2O_3 was chosen as a guest ion because it is a major fission product in nuclear fuels. Therefore, it is desired to know its chemical state in the nuclear fuel. The results showed that under conditions of slow cooling from 1673 K, up to 50 mol% of $NdO_{1.5}$ is

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doi:10.1016/j.ceramint.2005.04.020

Table 1
Lattice parameters at different temperatures of the fluorite-type $Th_{1-x}Nd_xO_{2-x/2}$ solid solutions

Solid solution	Lattice parameters (Å)						
	293 K	473 K	673 K	873 K	1123 K	1273 K	1473 K
$Th_{0.90}Nd_{0.10}O_{1.95}$	5.594	5.608	5.612	5.624	5.639	5.644	5.664
$Th_{0.80}Nd_{0.20}O_{1.90}$	5.594	5.601	5.610	5.624	5.640	5.650	5.665
$Th_{0.70}Nd_{0.30}O_{1.85}$	5.595	5.605	5.614	5.625	5.644	5.653	5.667
$Th_{0.60}Nd_{0.40}O_{1.80}$	5.594	5.604	5.615	5.626	5.644	5.652	5.667
$Th_{0.50}Nd_{0.50}O_{1.75}$	5.592	5.602	5.614	5.625	5.643	5.652	5.665

Standard deviation of lattice parameters is from ±0.001 Å (at lower temperatures) to ±0.003 Å (at higher temperatures).

soluble in ThO_2 while retaining the fluorite structure and that the coefficients of average linear thermal expansion of the monophasic solid solutions increased with increasing $NdO_{1.5}$ contents. It may be noted that the bulk thermal expansion data, as investigated by a thermo-dilatometry, suffers from several drawbacks such as porosity factor and the influence of microcracks, etc. The lattice thermal expansion behavior by high temperature-XRD gives a better definition of intrinsic thermal expansion behavior. The present investigation is a continuation of these studies. We report on the lattice thermal expansion behavior of the solid solutions, as well as of Nd_2O_3, in the temperature range of 293–1473 K in the $Th_{1-x}Nd_xO_{2-x/2}$ series, as investigated by HT-XRD. Since thermal expansion is an important property, which governs the performance of the nuclear fuel pin assembly, these investigations were undertaken.

2. Experimental

Nd_2O_3 (AR grade) and ThO_2 (99.9% obtained from Indian rare-earths) were first dried by heating at 1173 K overnight. Appropriate mixtures to give the nominal compositions $Th_{1-x}Nd_xO_{2-x/2}$ were prepared by an intimate mixing of the starting materials and pressed into 8 mm pellets and heated at 1573 K for 36 h in static air. Each product was once again thoroughly ground, pelletized and heated at 1673 K for 48 h followed by slow cooling to the room temperature at 2 K/min. The heating was performed in a resistance furnace, with a temperature accuracy of ±1 °C. The XRD patterns were recorded on a Philips X-ray diffractometer (Model PW 1710) with monochromatized Cu Kα radiation: silicon was used as an external standard. The XRD patterns were analyzed by comparing with reported patterns taken from JCPDS (PC-PDF). In order to determine the solubility limits, the lattice parameters were refined by a least squares method.

The lattice thermal expansion studies were carried out on $NdO_{1.5}$ and selected single-phase compositions in the $Th_{1-x}Nd_xO_{2-x/2}$ series by high temperature X-ray powder diffractometer using a Philips Xpert Pro Unit with an Anton Paar high temperature attachment. The XRD patterns were recorded in the range $2\theta = 10–90^\circ$, using Cu Kα radiation, in the range 293–1473 K at an interval of 200 K at a reduced pressure of approximately 2×10^{-5} Torr. The diffracted beam was monochromatized using a curved graphite monochromator. The sample was heated to a desired temperature at the rate of 20 °C/min and held for 10 min for equilibration and then XRD data were collected. The temperature was controlled with a Eurotherm temperature programmer, with an accuracy of ±1 °C. The unit cell parameters were determined using a least squares refinement program. Nine reflections were observed in from $2\theta = 10–$

Table 2
Lattice parameters of Nd_2O_3 at different temperatures

Temperature (K)	Nd_2O_3 (hexagonal)	
	$a = b$ (Å)	c (Å)
293	3.826	5.996
473	3.832	6.03
673	3.838	6.04
873	3.846	6.06
1123	3.852	6.08
1273	3.870	6.09
1473	3.881	6.10

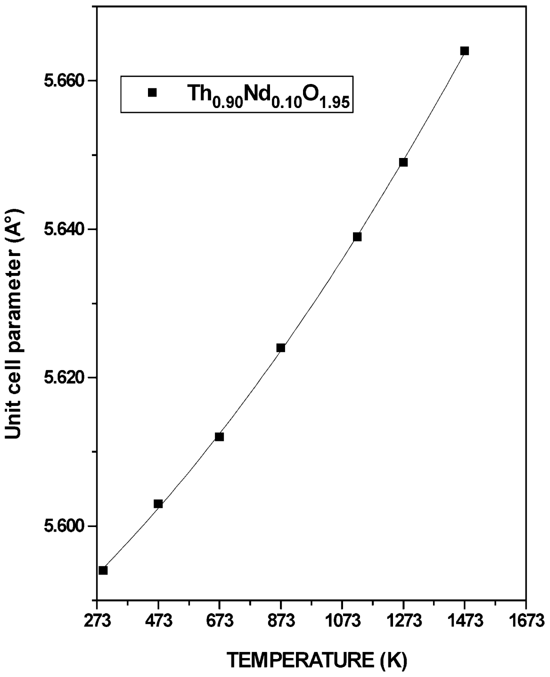

Fig. 1. A typical variation of unit cell parameter (Å) as a function of temperature (K).

Table 3
Coefficients of average linear bulk thermal expansion (α_l) and of lattice thermal expansion (α_a) of $Th_{1-x}Nd_xO_{2-x/2}$ solid solutions

Nominal composition	$\alpha_l \times 10^6$ (K^{-1}) (293–1123 K)[a] from dilatometry	$\alpha_a \times 10^6$ (K^{-1}) (293–1123 K) from HT-XRD	$\alpha_a \times 10^6$ (K^{-1}) (293–1473 K) from HT-XRD
ThO_2	9.04	9.13	9.55
$Th_{0.90}Nd_{0.10}O_{1.95}$	9.48	9.70	10.60
$Th_{0.80}Nd_{0.20}O_{1.90}$	9.69	9.90	10.76
$Th_{0.70}Nd_{0.30}O_{1.85}$	9.91	10.55	10.91
$Th_{0.60}Nd_{0.40}O_{1.80}$	10.34	10.76	11.06
$Th_{0.50}Nd_{0.50}O_{1.75}$	10.77	10.99	11.06
Nd_2O_3 (hexagonal)		$\alpha_a = \alpha_b = 8.82$, $\alpha_c = 16.88$	$\alpha_a = \alpha_b = 12.18$, $\alpha_c = 14.70$

[a] Investigated by thermo-dilatometry as reported earlier [13].

90°, all were considered for refinement. The coefficients of average lattice thermal expansion were also evaluated in each case.

3. Results and discussion

Based on powder XRD studies it was previously reported by us [13] that about 50 mol% of $NdO_{1.5}$ can be retained in the lattice of ThO_2, under the experimental conditions used in the present study, while retaining the fluorite-type structure. The lattice parameter did not show much variation in $Th_{1-x}Nd_xO_{2-x/2}$ series as a function of x, which was explained by the very close ionic radii of host and guest ions (ionic radii of Th^{4+}, Nd^{3+}, are 1.05 Å, 1.02 Å, respectively, in eight-fold coordination). The absence of peaks due to any other phase up to $Th_{0.5}Nd_{0.50}O_{1.75}$ indicated that 50 mol% $NdO_{1.5}$ can be incorporated into the ThO_2 lattice. The present results reveal that the solubility limits of Nd^{3+} into ThO_2 lattice under annealed and quenched conditions as reported by Brauer and Gradinger [11] and under short annealed and slow cooled conditions [13] do not differ much. At and beyond the compositions of $Th_{0.5}Nd_{0.50}O_{1.75}$, phase separation of excess Nd_2O_3 was observed.

The lattice parameters of the solid solutions and of Nd_2O_3 at different temperatures are given in Tables 1 and 2, respectively. A typical plot of the variation of cell parameter of $Th_{0.90}Nd_{0.10}O_{1.95}$ as a function of temperature is shown in Fig. 1. The cell parameters of the solid solutions showed a nearly linear increase with increase in temperature.

The lattice thermal expansion coefficients (α_a) of the solid solutions as evaluated from the cell parameters in the temperature range of 293–1123 K and 293–1473 K are given in Table 3. The lattice thermal expansion coefficients of Nd_2O_3 along each crystallographic axis (α_a, α_b and α_c) in the ranges of 293–1123 K and 293–1473 K were also evaluated from the high temperature XRD data and are included in Table 3. As can be seen from this table, the coefficient of thermal expansion along the c-axis (α_c) of Nd_2O_3 is higher than along its 'a' and 'b' axes. It appears from the higher value of coefficient of thermal expansion along the c-axis (α_c) of Nd_2O_3 that the inter-atomic bonding along the c-axis of Nd_2O_3 is weaker than along the other two axes. However, this is an indirect inference which needs to be supported by other methods.

The thermal expansion behavior of the Nd_2O_3 seems to contribute significantly to the thermal expansion behavior of the solid solutions they form with thoria. The lattice thermal expansion coefficients in $Th_{1-x}Nd_xO_{2-x/2}$ series increase progressively on increasing the content of Nd^{3+}. The much higher values of the thermal expansion coefficients of Nd_2O_3 i.e. α_a and α_c (293–1473 K) = 12.18×10^{-6} and $14.70 \times 10^{-6}\ K^{-1}$, seem to dominate the defect (anion vacancy) concentration effect, which usually reduce the thermal expansion to some extent. Hence, α_a values of solid solutions increase progressively on increasing the Nd^{3+} content of the solid solutions. The linear bulk thermal expansion (α_l) of the solid solutions and of Nd_2O_3 in the range 293–1123 K, which were reported earlier [13], are also included in Table 3 to compare with the corresponding lattice thermal expansion coefficient (α_a) in the same range. The values of α_1 and α_1 in the temperature range 293–1123 K also showed a similar trend as a function of composition in this series. The slightly lower value of α_l of the solid solutions compared to their corresponding α_a value is attributed to the effect of bulk density (about 80% of theoretical density in the present investigation) on the dilatometric measurements. The porosity tends to mask thermal expansion behavior to some extent, which is responsible for a lower thermal expansion coefficients obtained from dilatometry compared to those obtained from HT-XRD data.

4. Conclusion

The detailed high temperature XRD analysis of the phases was used to determine the lattice thermal expansion of $NdO_{1.5}$ doped single phasic solid solutions. The values of coefficients of lattice thermal expansion of the solid solutions were found to increase with increasing content of $NdO_{1.5}$ in ThO_2. These observations would be useful to determine the chemical state of Nd in ThO_2-based nuclear fuels at different burn-ups and their influence on thermal expansion.

Acknowledgements

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

References

[1] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.

[2] E.H.P. Cordfunke, R.J.M. Kinings, J. Nucl. Mater. 152 (1988) 301.

[3] C.E. Johnson, I. Johnson, P.E. Blackburn, C.E. Crouthamel, Reactor Technol. 15 (1972–1973) 303.

[4] M. Ugajin, T. Shiratori, K. Shiba, J. Nucl. Mater. 84 (1979) 26.

[5] A.M. Diness, B. Rustam, J. Mater. Sci. 4 (1969) 613.

[6] P.S. Murti, C.K. Mathews, High Temp. High Press. 22 (1990) 379.

[7] R. Chidambaram, in: M. Srinivasan, I. Kimura (Eds.), Proceedings of the Indo-Japan Seminar on Thoria Utilization, Indian Nuclear Society and Atomic Energy Society of Japan, Bombay, India, December 1990, p. 7.

[8] A.K. Tyagi, M.D. Mathews, B.R. Ambekar, R. Ramachandran, Thermochim. Acta 421 (2004) 69.

[9] R.D. Purohit, A.K. Tyagi, M.D. Mathews, S. Saha, J. Nucl. Mater. 280 (2000) 51.

[10] R.D. Purohit, S. Saha, A.K. Tyagi, J. Nucl. Mater. 288 (2001) 7.

[11] G. Brauer, H. Gradinger, Z. Anorg. Allg. Chem 276 (1954) 209.

[12] F. Sibieude, M. Foex, J. Nucl. Mater. 56 (1975) 229.

[13] M.D. Mathews, B.R. Ambekar, A.K. Tyagi, J. Alloys Compd. 386 (2005) 234.