



Solubility studies and thermophysical properties of uranium–neodymium mixed oxides system

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Received 22 April 2013; received in revised form 27 August 2013; accepted 27 August 2013

Available online 12 September 2013

Abstract

Uranium–neodymium mixed oxides ($(U_{1-y}Nd_y)O_{2\pm x}$ ($y=0.2-0.85$)) were prepared by citrate gel-combustion and characterized by XRD. Single phase fluorite structure was observed up to $y=0.80$. For solid solutions with $y > 0.80$ additional lines pertaining to hexagonal neodymium oxide were observed. Lattice thermal expansion of these samples was investigated by using high temperature X-ray diffraction (HTXRD). The coefficients of thermal expansion for $(U_{1-y}Nd_y)O_{2\pm x}$ for $y=0.2, 0.4, 0.6,$ and 0.8 in the temperature range 298–1973 K were found to be 16.46, 16.64, 16.79, and $16.89 \times 10^{-6} K^{-1}$, respectively. Heat capacity and enthalpy increment measurements were carried out by using DSC and drop calorimetry in the temperature range 298–800 K and 800–1800 K respectively. The $C_{p,m}$ values at 298 K for $(U_{1-y}La_y)O_{2\pm x}$ ($y=0.2, 0.4, 0.6,$ and 0.8) are 63.4, 64.3, 61.8, and $58.9 J K^{-1} mol^{-1}$ respectively.

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Keywords: C. Thermal expansion; Uranium; Neodymium; Solid solution; Heat capacity

1. Introduction

Solid solutions of uranium–plutonium mixed oxides are used as fuels in fast reactors. During irradiation, a number of fission products are introduced into the fuel matrix which significantly alter the composition and physicochemical properties of the latter [1–3]. Further, the thermal gradient results in chemical potential gradients of fuel constituents (viz., U, Pu and fission products) leading to the transport of these materials radially and axially across the fissile column. Thus the composition of the fuel changes as a function of time and the radial position due to the thermally induced transport phenomena and the chemical interactions among the fuel constituents (including fission products). Therefore, knowledge of the chemical states of these fission products is quite relevant and useful for they significantly influence many physicochemical properties of the fuel. The extreme chemical environment can affect the mechanical as well

as chemical properties of cladding and could lead to clad wastage and clad failure. All the above interactions in turn decide the fuel performance and limit the life of the fuel in the reactor. It is useful to have a good understanding of the physicochemical processes involving the formation of various compounds and their thermo-physical and thermochemical properties. Among the fission products the rare earths form a sizable fraction (fission yield 50 at%) [4]. One of the major rare earth fission product elements is Nd (fission yield 20 at%) [4]. The heat capacity, enthalpy increment and thermal expansion characteristics of uranium–neodymium mixed oxides are therefore important in understanding the in-pile behavior of the fuel. In the present work, the solid solutions $(U_{1-y}Nd_y)O_{2\pm x}$ with different compositions ($y=0.2-0.85$) were prepared by the citrate gel-combustion route. These specimens were investigated for the extent of solid solubility of the constituent members by using X-ray diffraction (XRD). Measurements on their heat capacity were carried out by using differential scanning calorimeter (DSC) in the temperature range 298–800 K while, enthalpy increment measurements were carried out by using a high temperature drop calorimeter in the temperature range 800–1800 K. Thermal expansion characteristics

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were studied by using HTXRD in the temperature range 298–1973 K for all the single phase mixed oxides ($y=0.2-0.8$). The results are discussed in the paper.

2. Experimental

2.1. Sample preparation

Neodymium oxide of 99.9% purity supplied by M/s. Indian Rare Earths and nuclear grade uranium oxide supplied by NFC, Hyderabad were used for preparing the samples. These solid solutions ($U_{1-y}Nd_y$) $O_{2\pm x}$ ($y=0.2-0.85$) were prepared by citrate gel combustion syntheses. UO_2 was converted into U_3O_8 by heating in air at 873 K for 6 h. Nd_2O_3 was heated in air at 673 K in order to remove the adsorbed gases. Stoichiometric amounts of U_3O_8 and Nd_2O_3 were dissolved in concentrated nitric acid by heating at 353 K. The excess nitrate was removed by heating the mixture until near dryness. The nitrate salts obtained was dissolved in distilled water. The concentration of nitrate present in the solution was determined by titrimetry. Citric acid was then added to this nitrate solution and clear solution was obtained. The relative amounts of the metal nitrate and citric acid were so chosen as to maintain the ratio of citric acid to nitrate ion as unity. The solution was then heated in a hot plate. Combustion of the mixture took place with a flame. The resultant fine powder was calcined at 1073 K in air for 4 h in order to remove the carbonaceous material from the sample. This powder was designated as the calcined powder. The calcined powder was compacted into pellets using a double acting hydraulic press. These sample pellets were reduced by heating in a stream of Ar+8% H_2 gas mixture at 873 K. Subsequently these pellets were sintered by at 1873 K for 6 h. The heating/cooling rate maintained was 250 K min^{-1} . Before heating the samples, the furnace was evacuated (10^{-3} mbar) and filled with ultra high pure Ar+8% H_2 gas mixture three times. The sintered pellets were stored in an argon atmosphere glove box containing less than 20 ppm of moisture and oxygen in order to prevent oxidation of these samples.

2.2. Sample characterization

The concentrations of U and Nd in the sample pellet were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), the concentrations of other metallic impurities were determined by using an inductively coupled plasma-mass spectrometer (ICP-MS) (model number ELAN 250 of M/s. Perkin Helmer, Canada) and oxygen to metal ratio (O/M) by the spectrophotometric method. The procedures for the analyses using ICP-AES, ICP-MS and spectrophotometric methods were described in our previous publications [5–7]. Structural characterization was carried out by using XRD. The XRD patterns were recorded in the range, $10^\circ < 2\theta < 80^\circ$. Peak positions and their relative intensities were computed by using a peak-fit program of the Philips X'pert Plus[®] software. The calibration of the diffractometer was carried out by using single crystal silicon and α -alumina standards. The lattice parameter pertaining to the solid solution samples was estimated by considering the eight major reflections of the CaF_2 structure. Finally an effective high angle

corrected lattice parameter at each temperature was obtained by the standard Nelson Riley extrapolation procedure.

2.3. Thermal expansion studies

These HTXRD studies were performed in a Philips-X'pert MPD[®] system, equipped with the Buehler[®] high vacuum heating stage. The thermal expansion characteristics of these samples were studied by using HTXRD in the temperature range 298–1973 K. Typical instrument related parameters were: operating voltage of 40 kV; current of 45 mA for the X-ray tube; scan speed 0.02 deg s^{-1} with a counting time of 6 s per step in the range $20 < 2\theta < 80^\circ$. The heating stage consisted of a thin ($\sim 80 \mu m$), resistance heated tantalum foil, on top of which the sample was placed. The temperature was measured by using a W–Re thermocouple, which was spot-welded to the bottom of the tantalum heater and controlled to an accuracy of about ± 1 K. The diffraction patterns of the sample holder (Ta) were co-recorded along with the sample for internal temperature calibration. Calibration of the diffractometer was carried out by using single crystal silicon and α - Al_2O_3 standards obtained from the National Institute of Standards and Technology (NIST), USA. These diffraction studies were performed using CuK_α radiation in the Bragg–Brentano geometry, in steps of 100 K up to 1973 K. A heating rate of 1 K min^{-1} and a holding time of 60 min at each temperature of measurement were adopted. The specimen stage was purged with high purity helium three times before the start of every experimental run and a vacuum level of about 10^{-5} mbar was maintained throughout the experiment. Acquisition and preliminary analysis of the data were performed by the Philips X'pert Plus[®] software; although independent processing of the raw data was carried out for a precise determination of the peak positions. Room temperature XRD pattern was again taken after the completion of thermal expansion measurements in order to confirm that no oxidation of the sample had taken place during the measurement.

2.4. Calorimetric measurements

A heat flux type differential scanning calorimeter, model number DSC821e/700 supplied by M/s. Mettler Toledo GmbH, Switzerland was used in this study. Temperature, heat flow, heat flow rate and τ -lag calibrations were carried out, as explained in our previous publications [8,9]. The uncertainty in the heat capacity data measured by the DSC was estimated to be in the range of 2–3% based on our previous measurements on standard ThO_2 samples [10]. In order to remove the gases adsorbed on to the sample, the latter was heated to 573 K before the start of the experiment. In a typical measurement about 100–150 mg of the sample in the form of a pellet was weighed accurately and hermetically sealed into a 40 μl Al-pan. The flow rate of the purge gas (ultra high pure argon) was 50 mL min^{-1} . The procedures for the measurement of heat capacity by using DSC was similar to that explained in our previous publications [8,9]. The enthalpy increments of these samples in the temperature range 800–1800 K were determined by using drop a high temperature calorimeter equipped

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