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Oxidation and thermo physical studies of non-stoichiometric thorium uranium oxides prepared by gel combustion method

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ABSTRACT

Thorium uranium oxide powder with uranium concentrations 10, 20, 30, 40, 50 and 70 mol% was prepared by gel combustion method. The sintering behaviour of the powders studied by dilatometry indicated that samples containing uranium up to 30 mol% had similar shrinkage behaviour with single step sintering. However, samples containing 40, 50 and 70% uranium followed two step sintering process. Though the air calcined powder shows two phase system beyond 30% uranium containing samples, sintering results into single phase system for samples containing up to 50% of uranium. The temperature programmed reduction-oxidation experiments showed that compositions containing up to 50-mol% of uranium show single reducible species throughout the temperature range. X-ray photoelectron spectroscopic studies of these sintered pellets showed presence of uranium in 6^+ and 4^+ oxidation states in these oxides. The experimentally determined heat capacities of solid solutions were found to have higher values than that of computed using Neumann–Kopp's molar additivity rule.

1. Introduction

$(Th,U)O_2$ and $(Th,Pu)O_2$ solid solutions are being considered as potential fuels for advanced thermal reactors [1–3]. Investigations on the oxidation behaviour of these materials are not only useful in understanding the nature of oxidation process to establish its mechanism but also of relevance in their industrial applications as nuclear fuels. Considerable studies have been carried out on oxidation behaviour and the limits of oxygen solubility in the ThO_2–UO_2 system [4–6]. But a good agreement of literature with regard to the nature and stability of uranium oxides is lacking. The oxidation of uranium dioxide proceeds both in air and oxygen atmospheres through two distinct stages under the regime of linearly increasing temperature [7]. In the first stage, uranium dioxide oxidizes to tetragonal U_3O_7 phase in a reaction, which is controlled by oxygen diffusion either through the UO_{2+x} lattice or the product layer. The U_3O_7 so formed is oxidized to orthorhombic U_3O_8 phase in the second reaction, which is controlled by a process of nucleation and growth. It is of great interest to investigate how the above oxidation bahaviour varies with atomic ratio of thorium to uranium when a stable solid solution of thorium and uranium oxide is oxidized. Many workers studied the oxidation behaviour of ThO_2–UO_2 solid solutions [5,8–13]. However, none of these studies have tried to identify the different uranium species present in the air sintered UO_2–ThO_2 system. The reported oxygen content of thoria–urania solid solution sintered in air is in excess of the stoichiometric amount. The complexity of the uranium–oxygen system is mainly due to the fact that uranium may exist in three different valency states, namely 4, 5, and 6. The valency or combination of valencies uranium assumes in a system depends on the temperature, pressure and the nature of gaseous species surrounding the sample. The oxygen content of urania is affected by thorium ion, which is in solid solution with it, occupying the neighboring lattice sites around it. In a ThO_2–UO_2 solid solution the net effect of Th^{4+} substitution would be to inhibit any increase in the oxygen-uranium ratio above 2.0 and in doing this to restrict any changes in the original cubic fluorite lattice.

Information on the binding energies of U $4f_{7/2}$ and Th $4f_{7/2}$ electrons of $(U_xTh_{1-x})O_2$ solid solutions is important to understand the chemical bonding in the solid solutions, which has a bearing on various physico-chemical properties of the solid solutions. Anthonysamy et al. [14] studied the oxidation states of uranium in the urania-thoria solid solutions prepared in Ar- 8% H_2 gas mixture. But there is not much data available urania-thoria solid solutions prepared by heating in air atmosphere.

In the present work the oxidation behaviour of uranium in thoria

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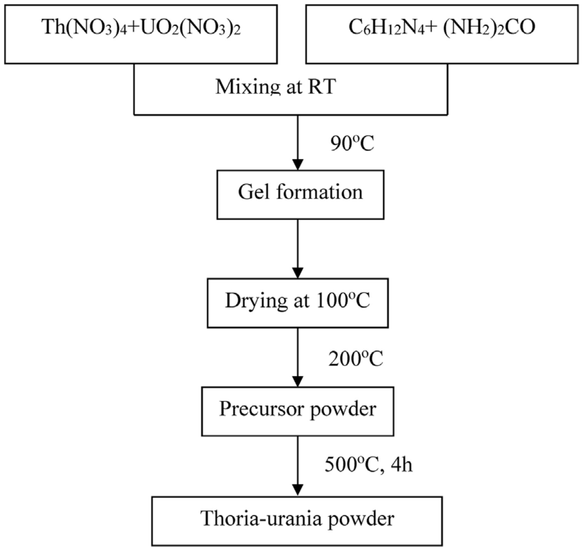

Fig. 1. Flow-sheet for preparation of (Th,U)O_2 powder from gel combustion method.

matrix heated in air atmosphere was attempted. For this study, thoria urania powder with uranium content of 10, 20, 30, 40, 50 and 70 mol% was prepared by gel combustion method [15]. Since, both the components (U and Th) are mixed in solution stage; the homogeneity of the powder is better compared to solid state route. Pellets made from these powders were sintered at 1400 °C in air atmosphere for 2 h. Thermo-physical properties of these non-stoichiometric oxides were evaluated by Temperature programmed reduction- oxidation (TPR-TPO), dilatometry and heat flux DSC. XPS studies were carried out to determine different oxidation states possessed by the system.

2. Experimental

2.1. *Preparation of thoria, urania and thoria-urania powders by gel combustion method and characterization*

ThO_2, UO_2 and thorium uranium oxide containing 10 (ThU1), 20 (ThU2), 30 (ThU3), 40 (ThU4), 50 (ThU5) and 70 (ThU7) mole% of uranium was prepared by a self propagated ignition reaction known as gel combustion method”. The flow sheet used for the preparation is given in Fig. 1. “The process of preparation of powders used is a soft chemical route which involves mixing of thorium nitrate and uranyl nitrate in a required molar ratio, to produce the transparent mixed metal nitrate solution. The sample table for all the chemicals used in the various steps of preparation is given in Table 1. All the samples were prepared using natural uranium [16] and thorium [17]. 3 M hexamethylenetetramine-urea solution was added to it gradually at room temperature which is capable of binding the metal ions and acting as a fuel in combustion reaction. The solution was kept in an air oven preheated to 90 °C. The precursor is subjected to an external temperature of about 200 °C, which triggers the combustion reaction. At this stage, exothermic decomposition of the fuel-oxidant precursor associated with evolution of large volume of gases results in the voluminous powder. The precursor powder thus obtained was calcined in air at 500 °C for 4h.

For phase identification, XRD patterns of the calcined powders were recorded on a DIANO X-ray powder diffractometer using Cu K_α radiation (λ = 1.5406 Å) with a graphite monochromator. The applied voltage was 45 kV and the current was 30 mA.

2.2. *Pelletisation and sintering studies*

The powders calcined at 500 °C in air were pelletized in a single acting manual press at 250–300 MPa pressure, using 4% stearic acid in acetone as die lubricant. The obtained green pellets were 1.0 cm in diameter and about 0.3 cm thick. The sintering behaviour of the pellets in air was studied using a thermomechanical analyser, TMA-24, Setaram, France up to 1400 °C at a heating rate of 6 °C/min. Alternatively, another set of pellets were sintered at 1400 °C for 2 h in an air furnace. The density of the sintered pellets was determined by both geometrical method as well as liquid displacement method. “For density measurement by geometrical method, the pellets were weighed using an analytical balance. The diameter and height of each pellet were determined using a micrometer screw gauge from which the volume of these pellets was measured. From mass (m) and volume (v) of these pellets, the geometrical density was calculated. The densities of sintered samples were also determined using liquid displacement method for which water was used as the wetting liquid. A pycnometer glass vessel (glass density bottle) was used for measuring the volume of the pellets. The density of the samples were determined from the known density of the water, the weight of the pycnometer filled only with water, the weight of the pycnometer containing both sample and water, and the weight of the sample. For the preparation of UO_2 powder, the pellet derived from calcined uranium oxide powder was sintered in Ar + 8% H_2 atmosphere at 1400 °C for 2 h.”

2.3. *“ O/U by chemical analysis*

The O/U of all samples heated in air was determined using chemical analysis. For this, known quantities of the oxide was dissolved in concentrated phosphoric acid and total uranium as well as U(IV) in these solutions were analyzed by potentiometric titration using mod-

Table 1
Sample table of various chemicals being used in the preparation of Thorium uranium oxide.

Chemical Name	Source	Initial Mole Fraction Purity	Final mole Fraction Purity	Analysis Method
Thorium nitrate	REDS[a], BARC[b]	0.9995		AES[c]
Uranium(V,VI) oxide, U_3O_8(s)	Nuclear Fuel Complex, Hyderabad, India	0.9995		AES[c]
Hexamethylene tetramine	M/s Sigma Aldrich	0.9900		Titration
Urea	M/s Sigma Aldrich	0.9900		Titration
Carbon tetrachloride	M/s Merck Ltd, Germany	0.9990		AES[c]
Supra pure HNO_3	M/s Merck Ltd, Germany	0.9999		Titration
NH_3 solution	M/s Chemco fine chemicals, Mumbai	0.95		Titration
Thorium uranium oxides[d]			0.997	ICPAES[e]
ThO_2	Gel combustion synthesis		0.997	AES[c]
$UO_{2.01}$	Gel combustion synthesis		0.997	AES[c]

[a] Rare Earth Development Section.
[b] Bhabha Atomic Research Centre.
[c] Atomic Emission Sepctroscopy.
[d] Thorium and uranium content in all the samples.
[e] Inductively Coupled Plasma Atomic Emission Spectroscopy.