



Preparation of UO_2 , ThO_2 and $(\text{Th,U})\text{O}_2$ pellets from photochemically-prepared nano-powders



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HIGHLIGHTS

- Photochemically prepared UO_2/ThO_2 nano-powders were pelletized.
- The nano-powders of crystalline oxides were pelletized without any binder.
- Pellets were sintered at 1300 °C (UO_2 and $(\text{Th,U})\text{O}_2$) or 1600 °C (ThO_2 pellets).
- The theoretical density of the sintered pellets varies from 91 to 97%.

GRAPHICAL ABSTRACT



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ABSTRACT

Photochemically-induced preparation of nano-powders of crystalline uranium and/or thorium oxides and their subsequent pelletizing has been investigated. The preparative method was based on the photochemically induced formation of amorphous solid precursors in aqueous solution containing uranyl and/or thorium nitrate and ammonium formate. The EXAFS analyses of the precursors shown that photon irradiation of thorium containing solutions yields a compound with little long-range order but likely “ ThO_2 like” and the irradiation of uranium containing solutions yields the mixture of U(IV) and U(VI) compounds. The U-containing precursors were carbon free, thus allowing direct heat treatment in reducing atmosphere without pre-treatment in the air. Subsequent heat treatment of amorphous solid precursors at 300–550 °C yielded nano-crystalline UO_2 , ThO_2 or solid $(\text{Th,U})\text{O}_2$ solutions with high purity, well-developed crystals with linear crystallite size <15 nm. The prepared nano-powders of crystalline oxides were pelletized without any binder (pressure 500 MPa), the green pellets were subsequently sintered at 1300 °C under an Ar:H_2 (20:1) mixture (UO_2 and $(\text{Th,U})\text{O}_2$ pellets) or at 1600 °C in ambient air (ThO_2 pellets). The theoretical density of the sintered pellets varied from 91 to 97%.

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1. Introduction

Uranium (IV) oxide (UO_2) has been widely utilized as nuclear fuel in various types of reactors, while thorium (IV) oxide (ThO_2)

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and mixed ((Th,U)O₂) oxides have been tested regarding their feasibility [1–3]. Prepared oxide powders are typically mixed with binders and lubricants and then compacted into the pellets by a powder metallurgy method. UO₂ and ThO₂ powders are typically compacted at 150–500 and 40–300 MPa [4,5], respectively. The density of the green (i.e. non-sintered) pellets usually reaches 50–60% of theoretical density (TD) [4]. Green pellets are subsequently sintered where the first step is dewaxing (removal of volatile additives at approximately 600–800 °C) [4]. UO₂ pellets are then sintered at temperatures of 1600–1800 °C under controlled (reducing) atmosphere for 3–10 h [4], whereas ThO₂ pellets are sintered at temperatures of 1600–1700 °C and the sintering can be performed under both oxidizing and reducing conditions [5,6]. Generally, sintered pellets feature high mechanical strength and density [4]. The density achieved in laboratory conditions is usually higher than 80% of TD [7]; pellets with 95% of TD or higher are denoted as high density pellets [8].

UO₂ and ThO₂ powders are usually prepared via precipitation or sol–gel routes [5]. Novel preparations of various oxides via the photochemical method have recently also been reported [9] (the mechanisms of water photolysis and oxides formation are summarized therein). The biggest advantage of this method is formation of nanoparticles with uniform particle size. The material preparation is based on the irradiation of aqueous solutions of metal salts and OH radical scavengers, resulting in the formation of finely dispersed solid phases.

Preparation of nano-particles of UO₂, ThO₂ and (Th,U)O₂ by photochemical method using mercury UV lamps as the radiation source has been reported recently [10]. Amorphous solid precursors formed under the irradiation were subsequently heat treated at 300–550 °C to convert them to nano-crystalline oxides. Photochemical methods typically produce nano-sized powder with high specific surface area. Such kind of materials can be usually sintered at lower temperature [11–13] when compared to materials with larger crystallite size. The method produces solid precursors that are nitrogen and carbon free, thus allowing direct heat treatment in reducing atmosphere without pre-treatment in air [10].

This paper is focused on the pelletizing of photochemically prepared UO₂, ThO₂ and (Th,U)O₂ powders. Characterization and properties of the powders, green pellets and sintered pellets, are discussed in detail.

2. Experimental

Nano-crystalline UO₂/ThO₂ powders were prepared following the previously described procedure [10]. All solutions contained 0.1 mol dm⁻³ ammonium formate (≥99.995% trace metals basis, Sigma Aldrich). They consisted of either 0.01 mol dm⁻³ uranyl nitrate (GR, Lachema Chemapol) or 0.01 mol dm⁻³ thorium nitrate (p.a., Merck) or both 0.005 mol dm⁻³ uranyl nitrate and 0.005 mol dm⁻³ thorium nitrate. Solutions were prepared without any further purification of the chemicals. Deionized water was used in all experiments. The solutions were irradiated for 60–180 min by low pressure mercury lamps TUV 25 W 4P SE (Speziallampen GmbH).

The amorphous solid precursors formed under irradiation were separated from the solutions by filtration (Millipore HAWP 0.45 μm), washed and dried at room temperature and structurally characterized by extended X-ray absorption fine structure (EXAFS) spectroscopy.

EXAFS measurements of the thorium and uranium precursors, contained in 1.5 mm thick aluminum frames with Kapton windows, were performed at the Th and U L₃ X-ray absorption edges, respectively. The data were collected at the wiggler beam line I811 at MAX-lab, Lund University, which operated at 1.5 GeV and a

maximum current of 220 mA. The synchrotron beam was monochromatized using a Si[111] double crystal monochromator, with higher order harmonics reduced by detuning the second monochromator crystal to reflect 80% of maximum intensity at the energy at the end of the EXAFS range scanned. Measurements were performed simultaneously in transmission and fluorescence mode using ion chambers with stationary gas mixtures of krypton and helium and a Passivated Implanted Planar Silicon (PIPS, <http://www.canberra.com/products/438239.asp>; accessed May 17, 2015) detector, respectively. The spectrum of a Zr foil (defined as 17.998 keV [14]) was recorded simultaneously in transmission mode as reference. Spectra were recorded as continuous scans and averaged for the data analysis for all samples.

The EXAFS calculations were performed using the EXAFSPAK program package [15], incorporating the FEFF code [16]. The energy scale of each X-ray absorption spectrum was calibrated by assigning the first inflection point of the K edge of metallic zirconium foil to 17998 eV. The pre-edge was subtracted by fitting with a linear function. The background was removed with a 4th polynomial spline fit using a Victoreen function for data collected in the fluorescence mode. The EXAFS function was *k*³-weighted to enhance the contribution at higher *k*-values. Theoretical EXAFS spectra were computed with the FEFF code for single scattering (SS) paths, as well as multiple scattering (MS) ones. The fitting procedure was performed in *k*-space. During the fitting procedure, the energy shift, Δ*E*, and the amplitude reduction factor, *S*₀², were allowed to vary, but kept the same for all the paths in one sample. In the FEFF calculations eight-coordinated thorium(IV) solid thorium(IV) oxide and the hydrated thorium(IV) in aqueous solution have been used as models; for eight-coordinated uranium(IV) solid uranium(IV) oxide and for two + five coordinate uranyl(VI) solid uranyl(V) nitrate and hydrated uranyl(VI) ion in aqueous solution were used.

Elemental (C, H, N) analysis of the precursors was performed using a PERKIN ELMER 2400 Series II CHNS/O Analyser. Subsequently, amorphous solid precursors were heat treated at 300–550 °C in ambient air or under Ar:H₂ (10:1) atmosphere. The yields of crystalline uranium and/or thorium oxides formed were determined as described in our previous study [10].

X-ray diffraction (XRD) was used to identify and characterize the solid powder oxides and pellets, using Rigaku MiniFlex 600 diffractometer with Cu–K_{α1,2} radiation (λ_{av} = 0.15418 nm) and a scintillation detector; the ICDD PDF-2 database was used for the identification of prepared crystalline materials [17]. Linear crystallite size (*l*) was calculated using Scherrer equation: $l = (0.89 \cdot \lambda) / (B \cdot \cos \theta)$, where λ is the wavelength of used radiation (0.15418 nm), *B* is FWHM of selected peak obtained at higher θ after subtraction of instrumental broadening and θ is Bragg diffraction angle. The instrumental broadening was determined by measurement of SRM 640d standard. The values of interplanar distances were calculated from Bragg condition (where *d* is the interplanar distance, *k* positive integer and other symbols have the same meaning as above: $2 \cdot d \cdot \sin \theta = k \cdot \lambda$). The lattice parameters (*a*) were calculated using the equation for cubic crystals (where *h*, *k* and *l* denote the Miller indices): $a = d \cdot (h^2 + k^2 + l^2)^{0.5}$. Specific surface area (SSA) of oxides was measured by selective adsorption of nitrogen from the mixture of hydrogen and nitrogen at the temperature of liquid nitrogen [18], using the Quantachrome Monosorb MS-22.

Powder UO₂ and/or ThO₂ nanoparticles were pressed into pellets without addition of any lubricant or additives to the oxide powder. The powders have been pressed by a manual laboratory press (BSL – 2, BRIO Hranice s. r. o.), using stearic acid as die-wall lubricant (i.e. by pressing the stearic acid powder into pellets). The powders were compacted at the pressure of 500 MPa for 30 min into a pellet of 10 mm in diameter and 1 mm in theoretical height.

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