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CeO_2 pellet fabrication as spent fuel matrix analogue

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ABSTRACT

The near field performance assessment of the final high level waste disposal requires information about the spent fuel matrix dissolution because it constitutes the largest source of radionuclides under repository conditions. A possible way to single out the effects of matrix corrosion behaviour of irradiated fuel is to study CeO_2 as an inactive analogue of the irradiated UO_2 matrix. The aim of this work was the production and characterization of CeO_2 pellets with the same microstructure as that obtained for irradiated matrix for further simulation studies. Radial pellets with two zones were fabricated by a two-step process in which the inner ring was obtained by axial pressing and the outer ring by slip casting using well-dispersed, concentrated aqueous suspensions. Porous samples were also obtained by colloidal routes using fructose as pore former. Green samples were sintered at 1600 °C in air and characterised by XRD and SEM.

1. Introduction

Today's nuclear fuels are achieving moderate to high burn-up (BU) in the reactor. In order to reduce the amount of fresh fuel required and the mass of spent fuel inventories (radioactive waste) it is desirable for the fuel to reach higher BUs. Nuclear fuels are subjected to high levels of radiation, which results in substantial modifications of the initial fuel microstructure [1] such as damage in the material, local defects like interstitials, loops and vacancies. Furthermore, accumulation of solid fission products in the lattice and formation of gas bubbles result in a reduction of thermal conductivity of the pellet. Fuel cracks appear from the beginning of the irradiation due to thermal stresses, the fuel pellets swell owing to the accumulation of fission gas bubbles in the matrix and the segregation of low-density fission-products phases (metallic and ceramic precipitates). Finally in the central sections of the fuel pellet (at higher temperature) grain growth, porosity build-up and larger gas release will occur. On the contrary at the periphery the original microstructure transforms into a nano-porous matrix high burn-up structure (known as rim effect) [2–4] through restructuring of the accumulated irradiation defects [5]. The final result is a fuel microstructure which may show extensive differences across the fuel pellet [6]. Therefore, during interim storage and during transport to the final disposal facility, the spent fuel will have a completely different structure to non-irradiated fuel. Since no direct measurement of stored fuel and/or packages can cover the full time extension of interest, complementary studies aimed at targeting specific aspects and processes expected to affect properties and behaviour of spent fuel during many decades of storage are necessary. Tests conducted under simulated conditions can thus contribute to the safe implementation of extended storage concepts.

Surface stability of the irradiated fuel and the possible radiotoxicity release from the storage has been largely studied with fuel but this will not represent the spent fuel. Therefore, it is necessary to investigate the microstructure and surface properties of spent fuel prior to and during disposal. Recent research [7] has demonstrated the suitability of using CeO_2 as analogue for UO_2 in dissolution kinetics tests and its lower uncertainty in the long term performance of spent fuel in a geological disposal facility. The use of spent nuclear fuel and its matrix as main component UO_2, is problematic due to issues surrounding radiotoxicity.

It is, therefore, necessary to produce suitable non-radioactive analogues that closely resemble nuclear fuel in terms of crystallography and microstructure so that we can gain a better understanding of how changes in the sample surface affect [8]. Such an analogue should have the same fluorite crystal structure as UO_2 (face centred cubic, space group Fm-3m). This is common in other f-block oxides, notably the rare-earth element cerium, CeO_2 [9–11]. The analogue must also have a microstructure similar to that of a typical UO_2 spent fuel; the grains should be randomly oriented [12]

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and have a specific size and porosity (95%TD (theoretical density) in the main part of the fuel pellet and 75%TD in the rim, outer part of the pellet) [13]. This is determined by the burn-up conditions of the fuel, e.g. porosity increases with increasing burn-up [14].

The ideal composition and resulting microstructures of an analogue material can be achieved by varying the sintering temperatures of the starting material. Stennett et al. [11] showed that particle size of starting powder is one of the most relevant factors in pressing process since the reactivity of a powder is influenced by its surface area that is directly determined by its particle size, and very low particle sizes display poor flow characteristics resulting in poor powder packing and a lower measured density when compacted. Zhang et al. [15] reported that CeO_2 powder is difficult to densify below 1500 °C, so that it is common to dope it with sintering promoters, such as Fe_2O_3 or Bi_2O_3. Although these promoters could preserve the crystal structure, these addition retard or limit the grain growth [16,17] or could change the grain boundary structure [18]. In previous work [19] the production and characterisation of CeO_2 pellets by axial pressing and further sintering to obtain compacts with controlled porosity was reported. However, the production of pressed compacts with several layers maintaining a radial symmetry is complex and high pressures are required, thus leading to high rejection. In addition, this procedure does not allow meeting the critical porosity requirements. The objective of the present work is to establish a simple procedure for the production of such radial structures by combining two fabrication pathways: on one hand axial pressing and on the other hand slip casting in order to reproduce the porosity gradient of the final structure of the spent fuel [20]. Due to that the colloidal and rheological properties of aqueous suspensions were optimised for the preparation of the composite by slip casting the outer ring around the green inner disc obtained by pressing. Sintering conditions, phase and microstructural characterisation are also reported.

2. Experimental

A commercial cerium oxide powder was employed as starting material (Cerium IV oxide, REacton®, 99.99% REO, Alfa Aesar, Karlsruhe, Germany). This powder has an average particle size of 14 μm according to the supplier.

The starting powder was previously characterised by measuring the particle size distribution, the morphology of the particles and agglomerates, the specific surface area, the density, and the crystalline phases. Particle sizes were determined using a laser diffraction analyser Mastersizer S (Malvern, United Kingdom) by dispersing in deionised water, without dispersant, in order to evaluate the agglomeration state of the as-received powders. The powder microstructure was analysed by Scanning Electron Microscope (SEM; HITACHI S2500, Japan). Its specific surface area was determined by one-point BET adsorption (Micromeritics ASAP 2020, USA) and crystalline phases by X-ray diffraction (Philips PANalytical X'Pert-MPD, USA) with a CuKα source (λ = 1.5405 Å). Diffraction patterns were collected between $2 < 2q < 80°$ at $2° \text{ min}^{-1}$ using a step size of 0.04°.

The as-received powder was used to produce pellets consisting of two rings with different microstructure and a radial symmetry in order to reproduce the spent fuel materials. Inner rings were prepared by uniaxial pressing in a press of 100 tons C256C (Power team, Johannesburg, South Africa) with an applied pressure of 700 MPa. The starting powder was mixed with 0.5 wt% ethylene-bis-stearamide (EBS, $C_{38}H_{76}N_2O_2$, Tokyo chemical industry. Japan) which was used as both binder and lubricant for the punch and die [21].

For the outer ring, the slip casting technique was used. The inner green cylinders obtained by pressing were placed in the centre of a flat plaster mould surrounded by a plastic ring at the distance needed to obtain the desired thickness. The slurry can then filtrate by the bottom plaster surface, but can also filter through the inner green disc walls, thus improving adhesion between both layers. For the preparation of the outer cast rings the suspensions were optimised by studying the zeta potential and rheological behaviour at different preparation conditions. Zeta potential values were evaluated in order to characterise the colloidal stability and to determine the isoelectric point (IEP) through the laser Doppler velocimetry technique using a Zetasizer NanoZS instrument (Malvern, United Kingdom). Firstly, suspensions of 10^{-1} g l^{-1} of CeO_2 powder in 10^{-2} M KCl as inert electrolyte were prepared to different pHs and zeta potentials were measured to obtain the isoelectric point (IEP). Suspensions were prepared by mechanically mixing the powders in deionised water and subsequent application of 1 min sonication (Dr. Hielscher U400S, Germany).

To improve the dispersion an ammonium salt of a polyacrylic acid PAA (Duramax D3005, Rohm & Hass, PA, USA) with low molecular weight (3200 Da) was used as a polyelectrolyte to provide electrosteric stabilisation at moderate pH values as we could observe in previous work [22]. Deflocculant concentrations of 0.1, 0.5, 0.7, 1.0, 1.5 and 2.0 wt% with respect to the powder total mass were studied. Once the optimum content of polyelectrolyte was established the zeta potential as a function of pH was measured for suspensions containing that content of deflocculant in order to confirm that adsorption occurred.

Commercial D-fructose (Panreac, Spain) was used as a pore former, whose efficiency for such purpose was demonstrated in previous work [23]. In order to control the colloid chemistry of the process after the incorporation of fructose, its interaction with the particles in the suspension has to be studied. Thus, the effect of fructose addition on the zeta potential as a function of pH and the IEP was studied in order to elucidate whether specific adsorption on the particles surfaces occurs or not. Accordingly, two different suspensions were prepared changing the additives and their order of addition. The first one was prepared adding 5 wt% fructose followed by the CeO_2 powder and finally the deflocculant. The second was prepared by adding first the deflocculant (1 wt% PAA), later the CeO_2 powder and finally 5 wt% fructose; in this case it is intended to allow the adsorption of the deflocculant on CeO_2 surface prior to the addition of fructose. In both cases KCl 10^{-2} M was used as inert electrolyte.

When the stability conditions were established, concentrated cerium oxide suspensions were prepared to a solids loading of 30 vol.% to evaluate their rheological behaviour. The rheological characterization was carried out with a rotational rheometer RS50 (Haake, Thermo Electron Co., Germany). The measurement system was a double-cone and plate system (DC 60/2°) operating under controlled rate (CR) conditions. The measuring programme consisted of an increasing shear rate ramp from 0 to 1000 s^{-1} in 5 min, a dwell time at 1000 s^{-1} of 1 min and, a comeback ramp from the maximum shear rate to rest conditions in 5 min, maintaining temperature constant at 25 °C. The effect that sonication has on the dispersion of the particles was studied in order to obtain a well-dispersed suspension avoiding agglomerates. Sonication was applied with an ultrasounds probe UP400S (Dr. Hielscher GmbH, Germany) in an ice-water bath to avoid heating the suspension with 80% of amplitude in continuous mode, for periods of 1 min followed by 10 min of mechanical stirring.

Once the optimum dispersing conditions were established samples of CeO_2 with and without fructose were slip cast on porous moulds to obtain green samples. Since the material fabricated in this work has to simulate the spent fuel to be disposed in a final repository the cladding of the real fresh fuel, Zircaloy rods 10 mm [24], were used as the moulds. After casting, the green samples were dried at room conditions for 48 h to assure there is no water