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Mechanical behaviour of porous lanthanide oxide microspheres: Experimental investigation and numerical simulations

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ABSTRACT

Actinide oxide microspheres are considered as promising substituents to powder precursors for the production of ceramic pellets of nuclear fuel or targets. Porous microspheres of sub-millimetric size are synthesised using the Weak Acid Resin process. Controlling their microstructure and their mechanical properties is essential to predict the microstructure of green compacts and sintered pellets. Here, cerium and gadolinium are used to mimic actinides as metal cation. Single microspheres are crushed experimentally using a micropress in a Scanning Electron Microscope (SEM) to investigate their mechanical properties and visualise their fracture behaviour. The results are compared to numerical simulations based on the Discrete Element Method (DEM). In DEM, a microsphere is modelled as an assembly of bonded spheres representing aggregates. Bonds may fracture in tension or shear. A limited number of material parameters (aggregate elastic modulus, bond strength) are sufficient for the accurate simulation of the fracture behaviour of a microsphere.

1. Introduction

One of the main concerns of high level nuclear waste management is the reduction of long-term radiotoxicity and heat source of ultimate waste in order to optimise the use of available space in disposal sites. Spent nuclear fuel, after irradiation in a reactor, is composed of 95% of uranium, 4% of fission products, 1% of plutonium and 0.1% of minor actinides (neptunium, americium and curium). In the case of a fuel cycle comprising the plutonium mono-recycling option [1], minor actinides and especially americium are the main contributors of long term radiotoxicity and long term heat power of high level nuclear wastes [2]. A potential solution envisioned for their management is the heterogeneous transmutation of minor actinides, and more specifically americium, into short-lived fission products in sodium fast reactor [3,4]. In this transmutation mode, americium is diluted in ceramic pellets of mixed uranium-americium oxide called Americium Bearing Blanket (AmBB), which are located at the periphery of the reactor core. Those dense ceramic pellets must meet strict specifications because they are submitted to strong irradiation flux and high temperature during operation [5]. Currently, those ceramic pellets are produced by powder metallurgy processes involving numerous grinding and milling steps [6,7]. Granular media preparation generates very fine, highly contaminating and irradiating particles. In this context, a viable option for reducing the amount of those fine particles would be to develop a dustless process by working on much coarser particles. Sub-millimetric-sized oxide sphere precursors seem to be an interesting alternative to produce ceramic pellets without dust manipulation. The first pellet fabrication process to use oxide microsphere precursors was the Sphere-Cal process and was developed in the late sixties [8–10]; it was based on the sol-gel process and aimed at fabricating coarse oxide particles. Another interesting route to produce sub-millimetre-sized spheres was the Weak Acid Resin process [11–14] developed in the early seventies. Oxide microspheres were obtained by the fixation of metal cations into beads of ion exchange resin followed by a thermal treatment to remove the poly-acrylic skeleton and produce porous and brittle oxide microspheres [15]. Microspheres need to be strong enough to be handled safely and poured into the matrix and yet brittle enough to ensure their complete fracture during the compaction process. Comprehensive characterizations of the microstructure and mechanical properties of oxide microspheres are thus essential to better understand their behaviour into the matrix when producing pellets. In this work, cerium and gadolinium have been considered as surrogates of actinide compounds

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to facilitate laboratory tests. Experimental data on material microstructure and mechanical properties of cerium and gadolinium oxide microspheres have been collected on different batches of precursor. These data have been used to model microsphere crushing using numerical simulations, which provided qualitative and quantitative information on the link between the microstructure and the mechanical properties [16].

The discrete element method (DEM) is a natural tool to represent porous microstructures in which aggregates or grains hold together through bonds created by a thermal treatment or a partial sintering process. DEM is especially powerful when fracture and post-fracture behaviours must be simulated. This is because fracture involves local topological modifications that are difficult to capture with standard methods such as Finite Element Method. In earlier works, we have shown that DEM may successfully model compaction [17] and green strength [18] in powder metallurgy. More generally, DEM is now recognised as an important tool in the area of particulate systems (see Zhu et al. [19] for a review). In our discrete element simulations, each aggregate is represented as a dense and unbreakable sphere that interacts with its contacting neighbours through bonds. A single oxide microsphere is represented as a spherical assembly of tens of thousands of aggregates. As in the experiments, it is subjected to a crushing test. Its strength is investigated in relation with the important microstructural parameters that describe the aggregates and their packing arrangement in the microsphere.

2. Materials and methods

2.1. Microsphere synthesis

Microsphere synthesis is carried out from metal loaded ion exchange resin beads [13,15,20] that are mineralised by thermal treatment under air to obtain regular-shaped oxide microspheres. The ion exchange resin used for the fixation was a gel-type IMAC HP333 carboxylic resin supplied by Dow Chemicals Company (Dow Chemical Company, Chauny, France). Concentrated ammonia solution (Merck, 25 %, Pro Analysis) and nitric acid solution (Fisher Chemical, 70%, Certified ACS Plus) were used to prepare molar solutions for resin preparation. Salts of hexahydrate cerium (III) nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) (Alfa Aesar, 99.5 % purity) and hexahydrate gadolinium (III) nitrate ($Gd(NO_3)_3{\cdot}6H_2O$) (Acros, 99.9% purity) were used for the preparation of 0.25 M Ce(III) and Gd(III) solutions.

The wet resin was previously sieved and washed according to a method described by Remy et al. [21]. A size distribution between 630 and 800 µm was selected for this study. The 0.25 M cerium (III) or gadolinium (III) nitrate stock solutions were recirculated through a column of resin in its ammonium form during approximately 5 h at room temperature in order to complete the exchange of ammonium counter-ions for cerium or gadolinium trivalent cations. Once equilibrium was achieved, the full metal-loaded resin was washed with deionised water, drained under vacuum, recovered in a crystalliser dish and dried at 110 °C during 12 h.

The thermal conversion of the metal-loaded resin was first studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis at a heating rate of 2 °C/min from room temperature to 1000 °C in synthetic air (Air Liquide, Alphagaz 1) with an STA 449C Netzsch equipment. Thermal conversion was then applied to the full metal-loaded resin spread in an alumina crucible at a temperature between 800 and 1400 °C into a tubular furnace (Nabertherm, HTRH 100–300) swept by synthetic air (Air Liquide, Alphagaz) to obtain cerium or gadolinium oxide microspheres. The heating scheme for the thermal conversion was as follows: 20–200 °C at 5 °C/min; 200–600 °C at 1 °C/min; 600 °C to the final temperature at 3 °C/min followed by a dwell time of 4 h at the final temperature.

2.2. Experimental characterisation

Morphology characterizations of oxide microspheres were performed by Scanning Electron Microscope (Zeiss, SEM FEG Supra 55). Their internal microstructure was observed on several microspheres cold mounted with epoxy resin (Struers, EpoFix) within a ring mould and progressively polished. Crystallographic structures of oxide microspheres were acquired by powder X-Ray diffraction (XRD) using a D8 advance Brucker diffractometer. Lattice parameter was determined using the Diffrac.suite Topas software and refined with the Le Bail method [22].

Effective density and open porosity of oxide microspheres were measured by helium pycnometry (Micrometrics, Accupyc 1330), based on the true density of oxide materials (7.216 g/cm^3 and 7.407 g/cm^3 for CeO_2 and Gd_2O_3 respectively [23]). Bulk density and closed porosity were determined from weight measurement and optical microscopy observations on a hundred beads. Sample volume was estimated from microsphere perimeter measurements using the Ellix pattern recognition software. Mesoporosity and macroporosity were also measured using a mercury porosimeter (Micromeritics, AutoPore IV 9500). Specific surface area was obtained using Tristar II Micromeritics equipment by N_2 adsorption and desorption at −196 °C using the Brunauer-Emmet-Teller method [24] (BET).

Microsphere mechanical properties were characterized by recording crushing tests of a single microsphere using a micro press (DEBEN, Mini tensile tester 200 N) equipped with a 5 or 200 N load cell. This micro press was implemented into a Scanning Electron Microscope (Zeiss, SEM FEG Supra 55) to measure the tensile strength and follow in-situ the deformation and the evolution of local damage and cracks.

2.3. Model description

Simulations of the crushing of oxide microspheres are carried out using the Discrete Element Method (DEM). Discrete simulations are used to represent a porous material as an assembly of discrete spherical particles that interact with each other through their contacts as initially described in [25]. In DEM, Newton's second law is resolved explicitly at each time step to compute the acceleration, the velocity and the new position of all particles. The total force acting on a particle is computed from contact forces of neighbouring particles. Here, contact forces are derived from bond laws and described hereafter. Particles are considered unbreakable. In our simulation of a microsphere, the unbreakable unit particle models an aggregate (diameter: 2 µm) (Fig. 1a). Aggregates are linked with their contacting neighbours by breakable bonds.

A bond between two aggregates mimics the solid bridge (or solid neck) that has formed during the calcination process. The bond is characterized by its radius a_b and the indentation h between the two aggregates (Fig. 1b). Normal (N_b) and tangential (T_b) forces between bonded particles are derived using the Jefferson et al. model [26]. Details on the full model derivation can be found in earlier applications [17,18].

In this model, for two bonded particles of radius R, the normal contact force, N_b, depends linearly on the normal displacement between the two particles, u_N:

$$N_b = \frac{E}{1-\nu^2} f_N\left(\frac{a_b}{R}, \nu\right) a_b u_N \tag{1}$$

where E and ν are the Young's modulus and Poisson's ratio of the aggregates, f_N is a function that depends on a_b, the radius of the bond, and on the Poisson's ratio [25]. Similarly, the tangential contact force, T_b, varies linearly with the accumulated tangential displacement, u_T:

$$T_b = -\frac{4E}{(1+\nu)(2-\nu)} f_T\left(\frac{a_b}{R}, \nu\right) a_b u_T \tag{2}$$

where the function f_T depends on the size of the contact and on the