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Synthesis of dense yttrium-stabilised hafnia pellets for nuclear applications by spark plasma sintering

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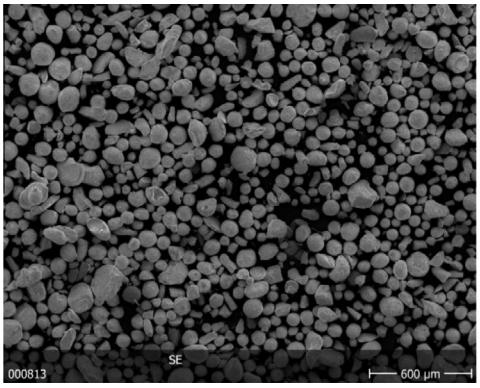
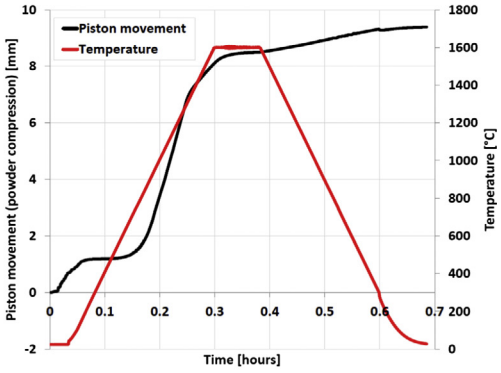
GRAPHICAL ABSTRACT

Densification of HfO_2–Y_2O_3 micro-beads by Spark Plasma Sintering High density pellets with homogenous distribution of Hf and Y serve as neutron absorbers.





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ABSTRACT

Dense yttrium–stabilised hafnia pellets (91.35 wt.% HfO_2 and 8.65 wt.% Y_2O_3) were prepared by spark plasma sintering consolidation of micro-beads synthesised by the "external gelation" sol–gel technique. This technique allows a preparation of HfO_2–Y_2O_3 beads with homogenous yttria–hafnia solid solution. A sintering time of 5 min at 1600 °C was sufficient to produce high density pellets (over 90% of the theoretical density) with significant reproducibility. The pellets have been machined in a lathe to the correct dimensions for use as neutron absorbers in an experimental test irradiation in the High Flux Reactor (HFR) in Petten, Holland, in order to investigate the safety of americium based nuclear fuels.

1. Introduction

Hafnia based ceramic materials, pure or composite, have been given significant scientific attention for decades [1–5]. Hafnium dioxide has interesting refractory and nuclear properties [6]. Hafnium has a similar chemical behaviour as zirconium, but in

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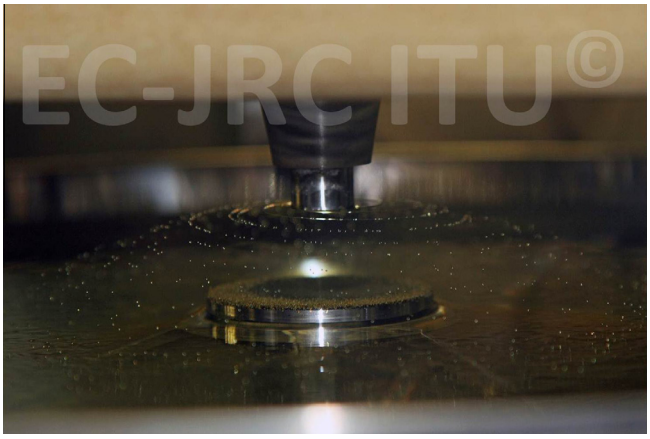
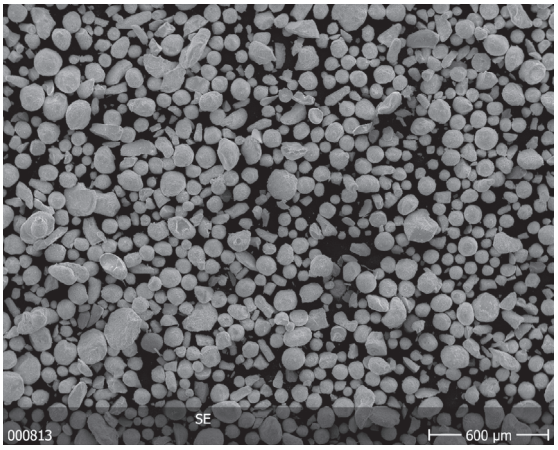


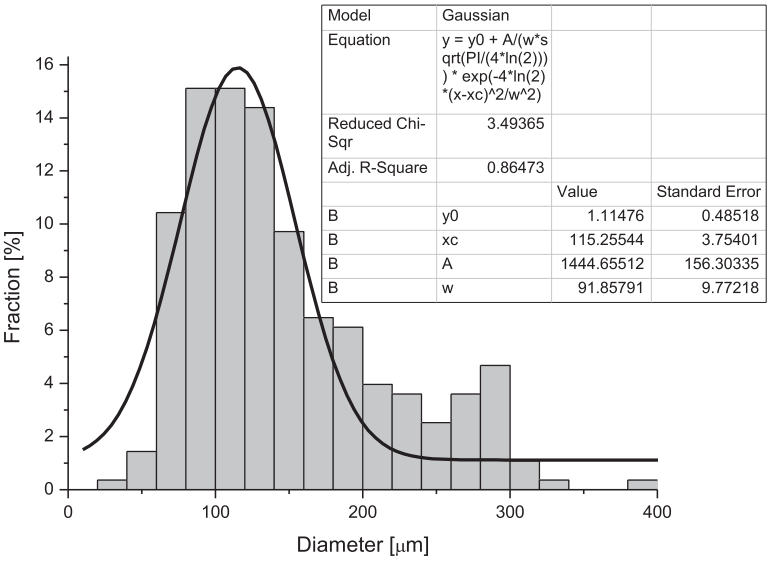
Fig. 1. In house developed rotating cup dispersing gel beads bearing Hf and Y solution. Drops are caught in an ammonia bath at the bottom, where the precipitation occurs.

contrast it has a significant cross-section for thermal neutrons and can therefore act as a neutron absorber. Indeed, hafnium was used as an absorber in the control rods in the first generation of the western light water reactors (LWR) [7] and this concept has also been investigated in a form of HfO_2–TiO_2 and Dy_2O_3–HfO_2 mixtures for eastern LWRs of the third generation [8–10]. Both of these properties (neutron capture and refractoriness) permit hafnia usage in the mitigation of severe accidents as well. Yttria–stabilised hafnia, in the form of porous pellets (compactness from 48% to 95% of the theoretical density), have been prepared by semi-isostatic pressing and sintering of mixtures of powder and styrene butadiene copolymer spheres as a porous agent. These materials were tested under severe accident conditions in the VERDON facility in CEA (France) [11,12]. Comprehensive phase relations at high temperatures in the systems hafnia, zirconia and yttria with rare-earth oxides have been reported in [13].

The sol–gel technique is a well suited method for the preparation of hafnia (and hafnia based composites) [14–17]. The JRC-ITU has established a variant of the sol–gel technique called "external gelation", or more precisely gel supported precipitation, for

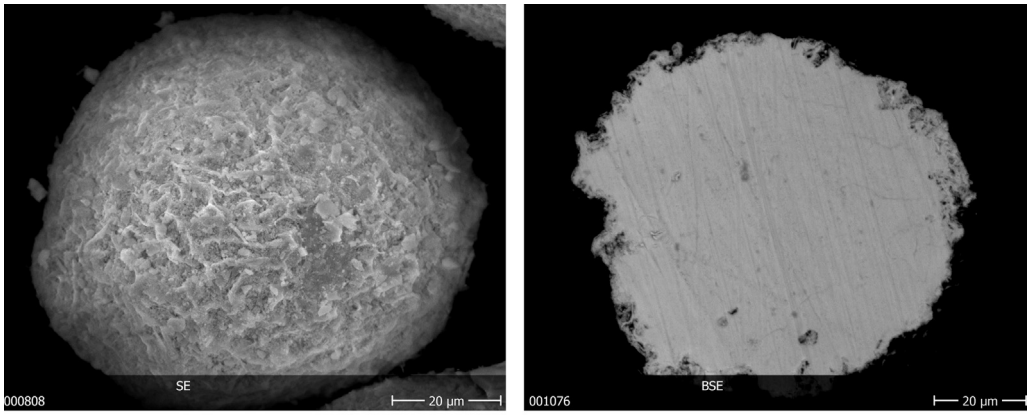


(a)



(b)

Fig. 2. (a) SEM image of the micro-beads calcined to 800 °C in air and (b) size distribution of the particles obtained from the image analysis of OM pictures, based on a statistical set of 278 particles. The size distribution is at the central value of each 20 µm interval.



(a) (b)

Fig. 3. (a) Detailed particle surface morphology by SEM, and (b) bead cross-section by SEM in back-scattered electron mode.