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Development of CAP process for fabrication of ThO_2–UO_2 fuels Part I: Fabrication and densification behaviour

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Abstract

The coated agglomerate pelletization (CAP) process is a novel and innovative technique for the fabrication of (Th, ^{233}U) mixed oxide fuel pellets. This technique is being investigated to fabricate the fuel for the forthcoming Indian Advanced Heavy Water Reactor (AHWR). In the CAP process, ThO_2 is converted to free flowing agglomerate by powder extrusion route. As only ThO_2 is handled to this stage, all the operations are carried out in a normal glove-box facility. Subsequent operations are carried out in a shielded glove-box or hot cell facility using manipulators. In this study, fabrication of ThO_2–4%UO_2 and ThO_2–20%UO_2 (all compositions are in weight percent) pellets was carried out by CAP process. For having these ThO_2–UO_2 pellets, ThO_2 granules and U_3O_8 powders were used as the starting materials. The densification behaviour of the pellets was studied in reducing and oxidizing atmospheres using a high temperature dilatometer. The microstructure was examined by optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

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1. Introduction

ThO_2 and UO_2 are identical in crystal structure (fcc CaF_2 type) with close lattice constants of 0.5592 and 0.54704 nm, respectively [1]. Th^{4+} and U^{4+} have similar electronic configurations and their chemical properties are alike. ThO_2 and UO_2 from continuous solid solutions [2,3], i.e. they produce $(Th,U)O_2$ solid solution of the same crystallographic structure at all Th:U ratios [4,5]. ThO_2 solid solution containing around 4%$^{233}UO_2$ (composition in wt%) is the proposed fuel for the forthcoming Advanced Heavy Water Reactor (AHWR) [6]. ThO_2–20%$^{233}UO_2$ is considered as a probable candidate for the fast reactor fuel. The mixed oxide pellets are generally prepared by the conventional powder metallurgy route. Fabrication of $(Th,^{233}U)O_2$ fuel is difficult because it usually contains daughters of ^{232}U (half-life 73.6 years) namely, ^{212}Bi and ^{208}Tl, which emit strong gamma radiations of 0.7–1.8 MeV and 2.6 MeV, respectively. Therefore the fabrication of the thorium fuel requires operations in the shielded glove-boxes to protect the operators from radiation [7–12]. The coated agglomerate pelletization (CAP) process was developed by Bhabha Atomic Research Centre (BARC) to replace the conventional powder metallurgy process that consists of direct blending of $^{233}UO_2$ and ThO_2 powders [13]. The radiation exposure problems can be minimized by quick processing of ^{233}U into finished fuel, as the first decay of ^{232}U has a comparatively longer half-life compared to the remaining daughter products.

The flow sheet of the CAP technique is made of the segmented processes to be performed in the unshielded

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and shielded facilities on the assumption to use freshly prepared ^{233}U oxide in order to minimize man-rem problem. The main reasons for developing the CAP technique to produce (Th–U)O_2 fuel are [13]:

- to minimize the dusty operations,
- to minimize the number of process steps requiring shielded operation,
- to reduce the man-rem problems since the highly radioactive ^{233}U is confined to only certain steps in the fabrication route.

Thorium fuel cycle is attractive for producing long term nuclear energy with low volume of radiotoxic waste. ^{232}Th is a better fertile material than ^{238}U in thermal reactors since the absorption cross section of ^{232}Th for thermal neutrons is nearly three times that of ^{238}U [14]. In recent years, renewed interest is attached to the thorium cycle because of the following reasons [14]:

(i) the intrinsic and proliferation resistance of thorium fuel cycle due to the presence of ^{232}U,
(ii) better thermo-physical properties and chemical stability of ThO_2, as compared to UO_2,
(iii) lesser long lived minor actinides than those found in the uranium cycle,
(iv) superior plutonium incineration in $(Th, Pu)O_2$ fuel as compared to $(U, Pu)O_2$ and
(v) attractive features of thorium related to accelerated driven system (ADS) and energy amplifier (EA).

Indian nuclear power programme is based on closed nuclear fuel cycle for the efficient utilization of its nuclear resources. India has vast reserves of thorium. The currently known Indian thorium reserves amount to 358 000 GWe-yr of electrical energy, which meet the energy requirements during the next century and beyond that. As mentioned above, the mixed oxide of ThO_2 with around 4%$^{233}UO_2$ (containing about 2–5 ppm of ^{232}U) is proposed fuel for the forthcoming Advanced Heavy Water Reactor (AHWR), which is being developed in India with the specific aim to utilize thorium for power generation. This reactor is of vertical pressure tube type cooled by boiling light water and moderated by heavy water. It incorporates several advanced passive safety features, e.g., heat removal through natural circulation. The reactor has been designed to produce 920 MW(th) at a discharge burn-up of fuel in excess of 24 000 MWd/te [6].

The goal of this work is to develop mixed thorium–uranium dioxide (ThO_2–UO_2) fuel by CAP technique using ThO_2 granules and U_3O_8 powders as the starting material. MOX fuel is generally manufactured under a stringent quality assurance programme. At each step of the fabrication process, quality assurance plans have been established to verify various factors that affect the fuel performance in the reactor. The criteria for adoption of manufacturing process include the acceptable microstructure and the uniform distribution of fissile elements in the pellet matrix [13]. To verify the above points, detailed studies have been carried out on densification and characterization of ThO_2–UO_2 pellets by optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). So far, however, studies have not been reported on the above process. The results presented here are divided into two parts. Part 1 deals with procedures for fabrication of ThO_2, ThO_2–4%UO_2 and ThO_2–20%UO_2 pellets by CAP process and its densification behaviour. Part 2 deals with characterization and evaluation of thermophysical properties of the pellets prepared by CAP process.

2. CAP process

The flow-sheet of fabrication of $(Th, U)O_2$ pellets by CAP process is given in Fig. 1. In this process, a wide option is possible for the ThO_2 starting material. ThO_2 should be in the form of free flowing agglomerate which can be obtained either by pre-compaction and granulation technique or by extrusion of powders. The ThO_2 microspheres obtained by sol–gel technique can also be used in the CAP process. To make free flowing agglomerates in the extrusion route, the ThO_2 powder is mixed with an organic binder and extruded through perforated rollers. The CAP process is schematically shown in Fig. 2. The extruded ThO_2 paste is converted to agglomerates in a spherodiser. The agglomerates are sieved and subsequently dried to remove the organic binder. As only ThO_2 is handled up to this stage, all these operations are carried out in a normal alpha tight glove-box facility. The operations carried out under shielding are [13]:

(a) coating of ThO_2 agglomerates with desired amount of ^{233}U oxide,
(b) compaction in a multi-station rotary press into green pellets,
(c) sintering in air,
(d) pellet loading and encapsulation into fuel rods.

Preliminary investigation was carried out to find out the optimum ThO_2 agglomerate size. For this purpose ThO_2 agglomerates were made by extrusion route. These agglomerates were segregated into various classes depending upon their size. This was done by sieving them through various mesh sieves, i.e. −20, −30 and −40 meshes. The maximum particle size corresponding to −20, −30 and −40 meshes are 840, 630 and 420 μm, respectively. The agglomerates segregated were mixed with 4%U_3O_8 powder in a planetary ball mill. The surface area of U_3O_8 powder used in this study was 2.15 m^2/g. The mixed powder was then compacted into pellets at 300 MPa pressure, which were then sintered in air at 1450 °C for 8 h. The obtained density of the sintered pellet was found to be in a range of 90–95% T.D. The as-polished microstructure of the sintered pellet made by using −20 mesh granules was