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ScienceDirect
Journal of Nuclear Materials 374 (2008) 9–19
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Characterization of $(Th,U)O_2$ fuel pellets made by impregnation technique

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Received 15 December 2006; accepted 9 July 2007

Abstract

Impregnation technique is an attractive alternative for manufacturing highly radiotoxic ^{233}U bearing thoria based mixed oxide fuel pellets, which are remotely treated in hot cell or shielded glove-box facilities. This technique is being investigated to fabricate the fuel for the forthcoming Indian Advanced Heavy Water Reactor (AHWR). In the impregnation process, porous ThO_2 pellets are prepared in an unshielded facility which are then impregnated with 1.5 molar uranyl nitrate solution in a shielded facility. The resulting composites are dried and denitrated at 500 °C and then sintered in reducing/oxidizing atmosphere to obtain high density $(Th,U)O_2$ pellets. In this work, the densification behaviour of ThO_2–2% UO_2 and ThO_2–4% UO_2 pellets was studied in reducing and oxidizing atmospheres using a high temperature dilatometer. Densification was found to be larger in air than in Ar–8% H_2. The characterization of the sintered pellets was made by optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The grain structure of ThO_2–2% UO_2 and ThO_2–4% UO_2 pellets was uniform. The EPMA data confirmed that the uranium concentration was slightly higher at the periphery of the pellet than that at the centre.

PACS: 81.20.Ev; 61.72.−y; 66.30.Fq; 62.20. Fe; 81.70.P

1. Introduction

The technology of fabrication of Pu-bearing uranium fuels like MOX for both LWR's or FBR's has now been mastered industrially by many countries. Generally, the large scale production of MOX fuel pellets is carried out by sintering the green compacts in a reducing atmosphere at high temperatures around 1700 °C [1,2]. However, when the fabrication of fuels containing highly radioactive materials, such as ^{233}U, americium, curium, long-lived fission products or transmutation nuclides is considered, the production of dust and consequent radiation exposure to personnel could restrict the use of the above usual process consisting of co-milling, cold compaction and sintering. Therefore, alternative fabrication routes that are more amenable for remotization and automation procedures are being considered [3–6]. Some of the promising methods other than powder pellet route are (a) sol–gel microsphere pelletization (b) vibro-sol route and (c) impregnation technique [7]. Among them, the impregnation technique is an attractive alternative for manufacturing highly radiotoxic ^{233}U bearing thoria based mixed oxide fuel pellets [8–10]. In this process, low density pellets (⩽75% T.D.) with open porosity are first prepared in an unshielded area. The ThO_2 pellets thus prepared are impregnated in uranyl nitrate (^{233}U) solution followed by sintering to obtain ThO_2-based mixed oxide pellets of high density and good microhomogeneity [7]. That is to say, handling of fine ^{233}U bearing powders in remote facilities can be avoided. Another advantage of this process is that it can be coupled with the reprocessing plant so that the purified feed from

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doi:10.1016/j.jnucmat.2007.07.004

ion exchange columns may be straightway used as the infiltrant [7–10]. The impregnation process can thus simplify the fuel reprocessing operation and eliminate several expensive stages from operations. As no precipitation or washing steps are required within the shielded area, the amount of radioactive wastes produced in the process is small [9,11].

Thorium fuel cycle contributes to produce long term nuclear energy with a small amount of radiotoxic waste. The fuel not only reduces plutonium production but also reduces the formation of highly radioactive isotopes [12–16]. Regarding to waste management, the Th containing fuel creates more ^{129}I and ^{234}U due to higher amount of ^{233}U in it. However, the U fuel forms more ^{99}Tc, ^{237}Np and ^{239}Pu and some heavier actinides [17,18]. The amount of thorium in the earth crust is estimated to be three times that of uranium. India has vast thorium reserves (five times that of uranium) in contrast to modest quantity of uranium. The currently known Indian thorium reserves amount to 358000-GWe year of electrical energy, which can easily meet the energy requirements during the next century and beyond [19]. Accordingly, while formulating the national programme, thorium has been envisaged as the fuel for the third and the largest phase of Indian nuclear power programme. India is currently engaged in the design of a thorium fuelled advanced heavy water reactor (AHWR) for generation of power. The AHWR is being developed in India with the specific aim to utilize thorium for power generation. AHWR is a 300 MWe, vertical, pressure tube type reactor cooled by boiling light water and moderated by heavy water. It incorporates several advanced passive safety features, e.g., heat removal through natural circulation [20,21]. The AHWR fuel comprises a 54 pin composite fuel cluster containing 24 $(Th–Pu)O_2$ pins and 30 $(Th–^{233}U)O_2$ pins. Fabrication of $(Th–^{233}U)O_2$ mixed oxide fuel is, however, not easy 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 above fuel requires operations in shielded glove-boxes to protect the operators from radiation. The aim of this work is to develop the impregnation technique to fabricate ThO_2–2% UO_2 and ThO_2–4% UO_2 fuel pellets. The mixed oxide of ThO_2 containing ~4% $^{233}UO_2$ is the proposed fuel for the AHWR and ThO_2–2% $^{233}UO_2$ is considered as an alternative fuel for thermal reactors. In this study, natural U has been used as a surrogate for ^{233}U.

The objectives of this study are listed below:

1. Fabrication study of high quality $ThO_2–UO_2$ pellets by impregnating ThO_2 with uranyl nitrate solution.
2. Evaluation of shrinkage behaviour of ThO_2–2% UO_2 and ThO_2–4% UO_2 compacts in the atmospheres of Ar–8% H_2 and air.
3. Study of the microstructural features of the pellets of the above compositions.
4. Investigation of uranium distribution in the above pellets after sintering.
5. Search of alternate method to produce the mixed oxide pellets which is more economic with minimum processes of handling of highly toxic or radioactive materials in shielded environment.

2. Impregnation technique

The impregnation technique of Bhabha Atomic Research Centre (BARC) is very similar to infiltration of radioactive materials (INRAM) [22–29] which has recently been applied for Am target fabrication. The process relies on the action of capillary forces to draw the solution into the pores of the host material. The amount of the second material introduced into the pellet can be controlled by adjusting the concentration of the infiltrant solution. The only requirement for the application of this process to the fabrication of fuel pellet is that the pellet should be insoluble in the solution containing the infiltrant and that the infiltrant can be easily convertible into the desired chemical form [9,11]. It is important that many of the porosities are interconnected and distributed uniformly across the pellet otherwise the impregnation will not be effective. Use of microwave during impregnation for local heating of the partially sintered low density pellets has been tested for expulsion of entrapped gas to accelerate impregnation. For uniform distribution of actinide in the sintered pellets, annular pellets are more suitable than the conventional ones. The concentration of the added material can be increased by multiple impregnation or by the use of the solution containing higher concentration of the material.

The flow-sheet of fabrication of ThO_2–4% UO_2 pellets by impregnation process is given in Fig. 1. The procedures for the fabrication of $ThO_2–UO_2$ pellets followed by Bhabha Atomic Research Centre (BARC) involve the following steps [30]:

1. Fabrication of low density (~66% T.D.) ThO_2 pellets by powder route in an unshielded facility.
2. Impregnation of the above pellets by uranyl nitrate solution under vacuum in a shielded facility.
3. Drying and final sintering at 1700 °C in reducing atmosphere.

The U loading in ThO_2 pellet can be varied by controlling the following parameters such as:

(a) Density of the pre-sintered ThO_2 pellets.
(b) Concentration of uranyl nitrate solution.
(c) Duration of impregnation.

3. Experimental

3.1. Preparation of green compacts

The ThO_2–2% UO_2 and ThO_2–4% UO_2 green pellets for this study are prepared as described in Section 3.2 by the impregnation process. The characteristics of the