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Preparation of $(U,Pu)O_2$ pellets through sol–gel microsphere pelletization technique

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Abstract

Mixed uranium–plutonium oxide microspheres were prepared by internal gelation process using feed solution of optimized composition. In the feed, total metal concentration was maintained at 1.5 M and hexamethylenetetramine (HMTA)-urea to metal mole ratio (R) was kept at 1.0. The gel particles obtained from each batch were dried and heated at 250 °C in air and then calcined in O_2 at 800 °C followed by reduction in $8\%H_2/92\%N_2$ at 600 °C for 1 h to obtain soft $(U,Pu)O_2$ microspheres containing 4 mol% Pu. The soft $(U,Pu)O_2$ microspheres were directly taken for the preparation of pellets. The microspheres were characterized with respect to surface area, tap density, crush strength and O/M ratio. X-ray diffraction analysis of the mixed oxide microspheres was carried out to identify the phases. The mixed oxide pellets were characterized for their density and micro-homogeneity. The sintering behaviour was studied by dilatometric investigations. The green pellets were sintered in $8\%H_2/92\%N_2$ at 1600 °C for 2 h. The density of the sintered pellet was found to be 10.40 ± 0.05 g/cm^3 with grains in the size range of 3–6 μm with an excellent micro-homogeneity.

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1. Introduction

As a consequence of the dismantling of many plutonium based nuclear devices, large amounts of plutonium became available for other applications. Uranium–plutonium mixed oxide pellets containing plutonium up to 4 mol% is being considered as fuel for thermal reactors for its effective utilization in power production. Fabrication of the pellets of such fuel is usually made by the well established powder oxide pellet (POP) [1–11] route. However, the problems associated with handling of highly radiotoxic plutonium powders call for the development of a technique which would avoid handling of plutonium powders and the accompanying dose related problems. Sol–gel microsphere pelletization (SGMP) technique combines the advantages of

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sol–gel route, which is free from powder handling with an increased amenability to automation, with the proven technology of powder pellet route, thereby offering an excellent solution to these problems. The SGMP technique is particularly attractive for mixed oxide fuel because it gives a high degree of micro-homogeneity of uranium and plutonium in the solution stage. The prolonged ball-milling of oxide powders for achieving good micro-homogenization in the standard powder pellet route is unnecessary. The disuse of the powder mixing step prevents build-up of radioactive dust in the glove box, minimizing the dose related problems to the operating personnel. Gilissen et al. [12] reported the preference of gel-derived microspheres to powder as feed material for pellet pressing. They employed the external gelation process for the preparation of gel microspheres. But they could not obtain good quality sintered pellets. Zimmer et al. [13] and Ganguly et al. [14,15] have demonstrated the preparation of soft UO_2 and $(U,Pu)O_2$ microspheres suitable for gel pelletization by addition of carbon black as pore former. However, the controlled calcination step with low heating rate, necessary for complete and safe removal of carbon, makes the process time consuming. It has been demonstrated by some investigators that by proper choice of process and heat treatment parameters the soft urania and mixed urania–plutonia microspheres suitable for gel pelletization could be prepared without the addition of pore former [16–20]. Mathews and Hart [16] and Tiegs et al. [17] have demonstrated the feasibility of making good quality UO_2 pellets by gel pelletization from soft UO_2 microspheres prepared by internal gelation process. They suggested the small UO_2 microspheres of 50–400 μm as suited for obtaining good quality pellets. However, their production process involves the use of small size capillaries (<0.5 mm) which tend to be clogged. Also the process needs longer time. Under these circumstances, Suryanarayana et al. [18–20] have studied the role of gelation parameters on the properties of UO_2 microspheres relevant to pelletization and proposed a simplified process flow sheet for gel pelletization without using the step of carbon addition and its subsequent removal. Kumar et al. [21] explored the feasibility of this process for the preparation of soft $(U,Pu)O_2$ microspheres.

The present work deals with the extension of the process established for urania to mixed urania–plutonia. During this study the effect of key parameters such as temperature of gelation and calcination temperature on the crush strength and tap density of the product microspheres was also studied. Both these parameters play an important role in deciding the l/d ratio (l = length; d = diameter of pellet) and final achievable density of the pellet.

2. Experimental

2.1. Preparation of uranyl nitrate solution

Nearly acid free 3 M uranyl nitrate solution was prepared by dissolving the calculated amount of nuclear grade U_3O_8 powder in a deficient amount of concentrated HNO_3 solution. The addition of the powder was controlled in such a manner that the temperature of the solution does not increase beyond 55 °C. The solution was analysed for uranium content by both gravimetry and volumetry. For gravimetric analysis, an aliquot of the sample solution containing 200–300 mg of uranium was taken in a pre-weighed silica crucible. The sample was first heated gradually to 200 °C till dryness and then to 800 °C in air until a constant weight was obtained. The constant weight of the sample was taken as the weight of U_3O_8.

Alternatively, uranium was also analysed volumetrically in which an aliquot of the solution containing around 200 mg of uranium was first reduced to U(IV) by an excess of Fe(II) in concentrated H_3PO_4 medium, followed by selective oxidation of the excess Fe(II) by HNO_3 in presence of Mo(VI) as catalyst and subsequent titration of U(IV) with standard $K_2Cr_2O_7$ solution after dilution with 1 M H_2SO_4.

The concentration of NO_3^- ion in the solution was determined by redox titration. For this, an aliquot containing 40–60 mg of nitrate was taken in a conical flask to which 25 ml of 0.2 M $Fe(NH_4)_2(SO_4)_2$ solution was added followed by the addition of 5 ml of conc. HCl and 15 ml of conc. H_2SO_4. This mixture was boiled for 5 min and cooled to room temperature. After dilution with 1 M H_2SO_4, the excess Fe(II) was titrated with standard $K_2Cr_2O_7$ solution using Ferroin (1,10 phenanthrolene) indicator.

2.2. Preparation of plutonium nitrate solution

$Pu(NO_3)_4$ was prepared by dissolving the required amount of plutonium oxide powder in concentrated HNO_3 solution added with a few