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Journal of Nuclear Materials 298 (2001) 316–320

journal of nuclear materials

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Structural and thermal investigations on cerium oxalate and derived oxide powders for the preparation of $(Th,Ce)O_2$ pellets

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Received 14 May 2001; accepted 22 June 2001

Abstract

$Ce_2(C_2O_4)_3 \cdot nH_2O$ powder was prepared by adding oxalic acid to a cerium nitrate solution. Cerium oxalate was identified by chemical and thermal analysis (DTA/TGA). Cerium oxalate powder was calcined to oxides at different temperatures and the powder properties (specific surface area, particle size distribution, mean particle size, bulk and tap densities) of these oxides were determined. X-ray diffraction (XRD) patterns of cerium dioxide powders obtained at different calcination temperatures were evaluated. The crystallite size was calculated both from XRD data using Sherrer's equation and from specific surface area data for each temperature. $(Th_{0.95}Ce_{0.05})O_2$ powder was prepared by mixing the binary oxides. The compacted pellets were calcined in air at 1050 °C. The XRD patterns of these pellets were evaluated to characterise the formed solid solution.

1. Introduction

Different combinations of fissile and fertile materials can be used in various reactor systems. In self-sustaining equilibrium thorium cycles, no external fissile is required at equilibrium. Such cycles can start with thorium and any suitable externally supplied fissile material (^{235}U, ^{239}Pu) [1,2]. The interest in ThO_2–PuO_2 fuel is a long-term one as starter fuel for a Th–^{233}U fuel cycle. ^{239}Pu–Th exhibits a lower fuel-cycle cost than ^{235}U–Th. This cost difference is basically due to the large cross-section of plutonium which reduces the enrichment requirement necessary for a given fuel exposure [3].

Plutonium, dangerous to work with because of its high radioactivity involves specific precautions and necessitates complex equipment. On the other hand, most of the countries are deprived of plutonium. For these inconveniences, plutonium is simulated by cerium in the maintained studies on the $(Th,Pu)O_2$ fuel production in many laboratories around the world. The thermodynamic and crystallographic properties of cerium dioxide are similar to those of plutonium dioxide. It is well known that ThO_2, UO_2, PuO_2 and CeO_2 have the same crystallographic structure (CaF_2 type, cubic). Therefore, mixed in any ratio, they form solid solutions [4].

In this study, the preparation conditions and powder properties of cerium oxalates and derived oxide powders were investigated to obtain $(Th,Ce)O_2$ mixed-oxide pellets with high homogeneity and density.

2. Experimental

2.1. Preparation of oxalate and oxide powders

Analytical grade $Ce(NO_3)_3 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 5H_2O$ (Merck) were used as initial materials. $Th(C_2O_4)_2 \cdot 6H_2O$ powders were precipitated with oxalic acid from thorium nitrate solution at the conditions determined in our previous work and were decomposed (350 °C, 24 h) and calcined (900 °C, 24 h) to oxide [5].

Two different types of precipitation methods were studied to produce more reactive and easily filterable cerium oxalate powders: (1) precipitation of cerium oxalate from 1 M cerium(III) nitrate solution by rapid addition of an excess solid oxalic acid at ambient temperature, (2) precipitation of cerium oxalate from 1 M cerium(III) nitrate solution by slow addition of an excess

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PII: S0022-3115(01)00655-9

1 M oxalic acid solution at 50 °C. After 1 h digestion time, the precipitates were filtered using a Buchner funnel with Whatman No. 42 filter paper. The oxalates were washed free of excess oxalic acid by distilled water and air dried at room temperature.

Thermal decomposition of the $Ce_2(C_2O_4)_3 \cdot nH_2O$ powder was investigated and the conversion temperature to oxide was determined. The effects of different calcining temperatures on the physical properties (mean particle size, particle size distribution, specific surface area, bulk and tap densities) of the oxide powders were evaluated. For this purpose the cerium oxalate powders were calcined at 300, 350, 400, 500, 700 and 900 °C in air for 24 h.

Thorium dioxide and cerium dioxide (each calcined at 900 °C for 24 h) were mixed in a diagonal rotating drum for 3 h in a ratio of 95% Th and 5% Ce. The mixed oxide powders were compacted into pellets at a pressure of 300 MPa using a hydraulic press with a floating die system and double pressing action. $(Th,Ce)O_2$ pellets were calcined in air at 1050 °C.

2.2. Identification and characterisation

The methods of analysis which are used to determine the chemical composition of cerium oxalate powders are listed as follows; cerium content: potentiometric titration with Fe(II) [6] (Metrohm titroprocessor 686); thorium content: EDTA titration; $C_2O_4^{2-}$: titration with $KMnO_4$; H_2O: thermogravimetry.

Thermal decomposition of these powders were controlled by thermal analysis using a Shimadzu thermal analyser. Cerium oxalate samples were weighed ($\simeq$27 mg) and operated at the following conditions; atmosphere: air; heating rate: 10 °C/min; full scale: 50 mg; range: 4 mV/min. The X-ray diffraction (XRD) patterns of cerium dioxide powders calcined at different temperatures and $(Th_{0.95}Ce_{0.05})O_2$ powders prepared under the previously described conditions, were obtained by a Perkin–Elmer model diffractometer using Cu-Kα radiation ($\lambda = 154.18$ pm). In order to investigate powder properties, the specific surface area was measured by the BET method using a high speed surface area analyser (Micrometrics 2200 model). Before nitrogen adsorption the samples were degassed at 300 °C for 40 min. The particle size distribution and mean particle size were determined by particle sizer (Mastersizer-S Malvern). The bulk and tap densities of these powders were measured.

The crystallite size D of cerium dioxide powders calcined at different temperatures was calculated from the Scherrer equation using the XRD peak of the (1 1 1) reflection [7]

$$D = \frac{K\lambda}{\beta\cos\theta}. \tag{1}$$

Conversion to radian measure, the Scherrer equation is defined as follows:

$$D = \frac{K\lambda}{\beta\cos\theta}\,\frac{360}{2\pi}, \tag{2}$$

where D is the mean crystallite dimension, K is the crystallite shape constant (0.9), θ is the Bragg angle (14.3°), λ is the X-ray wavelength (154.18 pm), and β is the pure diffraction breadth due to crystallite size effect. β was obtained by a graphical method from curves calculated by Alexander [7]. These values are 1.261, 0.774, 0.446, 0.346 for the powders calcined at 400, 500, 700, and 900 °C, respectively.

The crystallite size D of cerium dioxide powders calcined at different temperatures was also calculated from the following equation using the specific surface area values:

$$D = \frac{6}{S\rho F}, \tag{3}$$

where S is the specific surface area (measured as 90, 96.5, 70, 56.5, 46 m^2/g for the powders calcined at 350, 400, 450, 500, and 600 °C, respectively), ρ is the density of the powder (7.132 g/cm^3) and $F = 1$ (packing factor indicative of the surface area not available for nitrogen gas adsorption).

3. Results and discussion

The chemical analysis indicates that the cerium oxalate powders dried in air includes 38.65% cerium and 36.41% oxalate. These results are in perfect agreement with the theoretical values calculated from the chemical formula of $Ce_2(C_2O_4)_3 \cdot 10H_2O$. The thermal analysis results of the cerium oxalate powders confirm also that the chemical composition of oxalate powders is closely dependent on this formula. As clearly seen in Fig. 1 the

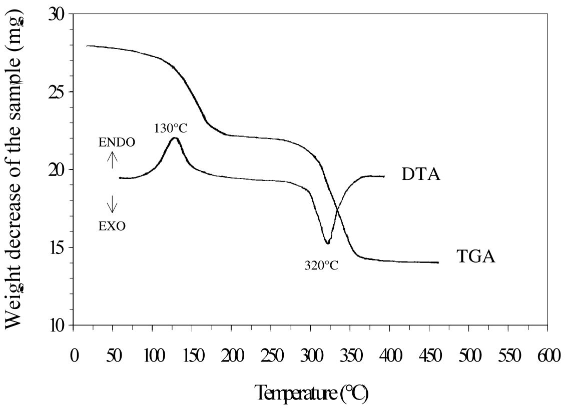


Fig. 1. Thermal decomposition of $Ce_2(C_2O_4)_3 \cdot nH_2O$.

decomposition of the cerium oxalate occurs in two steps. The first endothermic peak at 130 °C indicates the loss of 10 molecules of water. The second exothermic peak at 320 °C indicates that the decomposition of oxalates occurs in a single step. The complete conversion of oxalate to oxide occurs at 360 °C. The thermal decomposition of $Ce_2(C_2O_4)_3 \cdot 10H_2O$ is similar to $Pu_2(C_2O_4)_3 \cdot 10H_2O$ [8].

Cerium oxalate powders prepared by solid oxalic acid addition at ambient temperature have a smaller particle size than those prepared by 1 M oxalic acid addition at 50 °C (Fig. 2). These powders with higher reactivity are also filterable and can provide the desired properties. Variation of bulk and tap densities of CeO_2 powders with calcination temperature is given in Fig. 3. As clearly seen, these values increase considerably with increasing calcination temperatures.

The particle size distribution of cerium oxalate and derived oxides obtained by their calcination at 900 °C is given in Fig. 4. The mean particle size of the cerium oxalate was 39 μm. 99% of the particles were less than 110 μm and no particle less than 0.3 μm in size was observed. Regardless of the calcination temperatures, about 99% of the particles were less than 70 μm and no particles less than 0.3 μm in size were observed. Only a slight reduction in the number of fines was noticed as the temperature was increased and the mean particle size only increased from 24.7 μm at 400 °C to 29.5 μm at 900 °C, see Table 1.

The specific surface area of the cerium oxalate powders calcined at 300, 350, 400, 500, 700 and 900 °C is given in Fig. 5. As clearly seen, the maximum specific surface area was obtained at 400 °C. A sharp decrease of the specific surface area was observed above this temperature. Taking into consideration the thermal analysis results, where 400 °C was the complete conversion value of oxalate to oxide, we can say that these are the most reactive powders. But, a sizable amount of carbon is retained during calcination at this temperature and the presence of the residual carbon in the oxide strongly interferes with the sinterability. For this reason, the oxalate powders were calcined at 900 °C in air for 24 h.

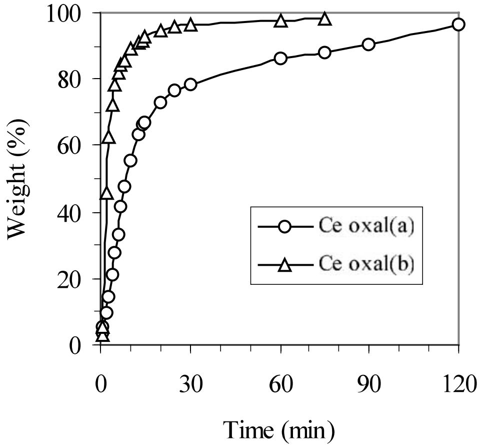


Fig. 2. Sedimentation rate of oxalate powders (○ Ce oxalate (a) precipitated with solid oxalic acid at ambient temperature, △ Ce oxalate (b)) precipitated with 1 M oxalic acid at 50 °C.

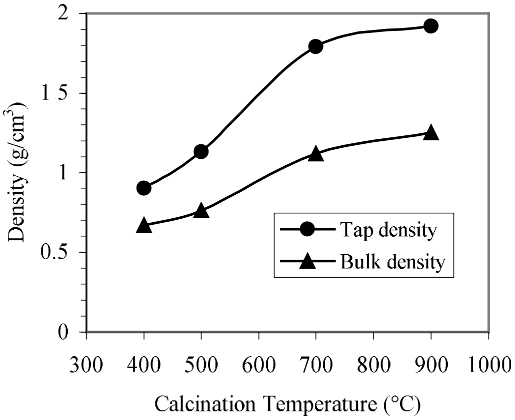
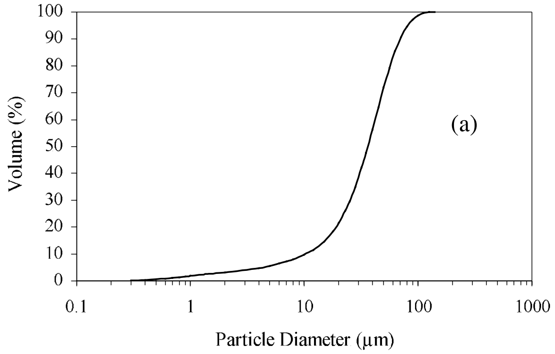


Fig. 3. Variation of bulk and tap densities of CeO_2 powders with calcination temperature.



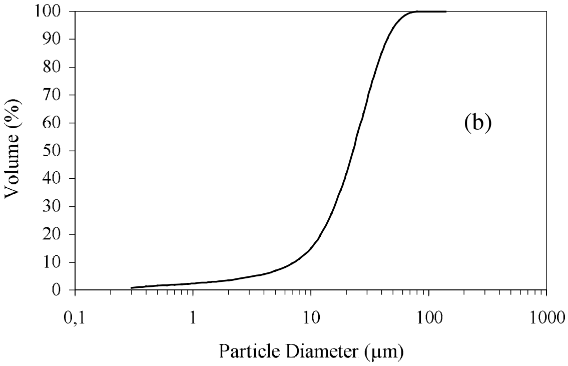


Fig. 4. Particle size distributions of $Ce_2(C_2O_4)_3 \cdot nH_2O$ powder and derived oxide obtained by its calcination at 900 °C: (a) air-dried; (b) 900 °C.

Table 1
The mean diameters of $Ce_2(C_2O_4)_3 \cdot nH_2O$ powder and derived oxides obtained by its calcination at different temperatures

Calcination temperature (°C)	Mean diameters (μm)
Air-dried	38.77
400	24.69
500	23.03
700	23.57
900	29.46

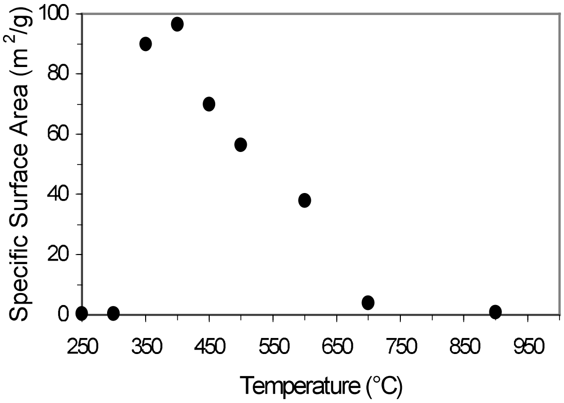


Fig. 5. The variation of specific surface area values of cerium oxalate powder with the calcination temperature.

The crystallite size of the cerium dioxide powders was calculated both from XRD data using Scherrer's equation and from specific surface area data. The results are given in Fig. 6. It was observed that the crystallite size calculated from XRD patterns is smaller than that calculated from SSA data. The difference between the crystallite sizes calculated from the two methods may be explained by certain influences arising from the specific properties of each method. The XRD line breadth is not only dependent on the crystallite size but also on other influences of which the most important are: the instrumental influences arising from the X-ray diffractometer; the deviations arising from crystallographic faults. It is possible to reduce the error rate to 10% by correcting the mentioned effects. Although these corrections were made according to the literature [9], the rate of error $(1 - D_{XRD}/D_{SSA})$ is considerably higher than 10%. In this case the difference between the crystallite sizes may be attributed to the specific surface area measurements. The crystals may form compact agglomerates and this prevents nitrogen adsorption using the BET method. As a result, this causes smaller specific surface area values. In contrast, the XRD method is not affected with such influences. For an approximation to true crystallite size values, it is necessary to correct the SSA values with a factor F. This factor calculated from the comparison of the results was ≈1.4. It is possible to say that the crystallite size values calculated both from XRD and SSA data are found to be in good agreement using an F correction factor. It is clearly seen that the crystallite size increases with increasing temperature.

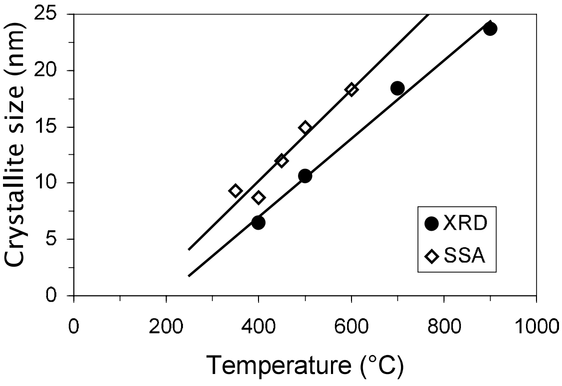


Fig. 6. The variation of crystallite size of cerium oxalate powder with the calcination temperature (● calculated from XRD data; ◇ calculated from SSA data).

The green densities of pellets pressed from $(Th_{0.95}Ce_{0.05})O_2$ powders were 52–55% of theoretical density. The XRD data of $(Th_{0.95}Ce_{0.05})O_2$ pellets are given in Table 2. The lattice parameter is $a = (557.3 \pm 1.1)$ pm. The value of ThO_2 and CeO_2 is given as $a = 560.0$ pm and $a = 541.1$ pm, respectively. (ASTM card No: 4-0556 and 4-0593) [10]. Regarding peak shifts and the lattice constant values we can say that the solid solution formation was reached to a certain degree at this temperature. However, the cerium fraction is too small to give distinct peaks in such a large thorium matrix, it was observed that cerium peaks are not sharp and have a diffuse appearance indicative of incomplete solid solution formation.

As a result, $(Th_{0.95}Ce_{0.05})O_2$ powder obtained in this study satisfies the basic requirements needed to obtain good and dense pellets. The achievement of high sintered pellet densities is only possible by investigations of the

Table 2
XRD data of the $(Th_{0.95}Ce_{0.05})O_2$ powder

d (pm)	I/I_0	hkl	a
321	100	1 1 1	556.0
278	45	2 0 0	556.0
197	70	2 2 0	557.2
168	62	3 1 1	557.2
161	14	2 2 2	557.7
139	10	4 0 0	556.0
128	23	3 3 1	557.9
125	17	4 2 0	559.0
114	18	4 2 2	558.5
			$\bar{a} = (557.3 \pm 1.1)$ pm

sintering behaviour and optimisation of the sintering conditions.

Acknowledgements

We are grateful to the Nuclear Fuel Technology Division of the Çekmece Nuclear Research and Training Center of Turkish Atomic Energy Authority for their helpful discussion and valuable contributions.

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