

INVESTIGATION OF POWDER PROPERTIES OF $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ DERIVED CeO_2 FOR THE PREPARATION OF $(\text{Th,Ce})\text{O}_2$ PELLETS

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ABSTRACT

The preparation conditions and powder properties of cerium oxalates and derived oxide powders were investigated to obtain of high homogeneity and density $(\text{Th,Ce})\text{O}_2$ mixed-oxide pellets. For this purpose, $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ was precipitated from cerium nitrate solutions with an excess of oxalic acid. Thermal decomposition of the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ powder was investigated and the conversion temperature to oxide was determined. The effects of different calcining treatments on the physical properties of the oxide powders were evaluated.

INTRODUCTION

In recent years, there is a special interest of thorium fuel cycle, especially in the countries who have considerable amounts of thorium resources. 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). It is well known that ThO_2 , UO_2 , PuO_2 and CeO_2 have a similar crystallographic structure (CaF_2 type, cubic). Therefore, mixed in any ratio, they can form solid solutions [1]. The experience of high density and high homogeneity mixed oxide preparation by the conventional route of powders mixing, pressing and sintering, shows that the key step is the distribution and homogeneity of the constituents [2].

Plutonium, dangerous to work with because of its high radioactivity, involves to take specific precautions and necessitates complex equipment. On the other hand, most of the countries are deprived from plutonium. For these inconveniences, plutonium is simulated with cerium in many laboratories around the world. The structural, thermodynamic and transportal properties of cerium are similar to those of the plutonium [3].

The aim of this study is to investigate the preparation conditions and powder properties of cerium oxalates and derived oxide powders to obtain of high homogeneity and density $(\text{Th,Ce})\text{O}_2$ mixed-oxide pellets. For this purpose, $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ was precipitated from cerium nitrate solutions with an excess of oxalic acid. Thermal decomposition of the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ powder was investigated and the conversion temperature to oxide was determined. The effects of different calcining treatments on the physical properties of the oxide powders were evaluated; properties measured included particle size distribution, mean particle size, bulk and tap density.

EXPERIMENTAL

The analytical grade $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (Merck) were used as initial materials. $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ powders were precipitated with oxalic acid from thorium nitrate solution at the same conditions determined in our previous work and decomposed (350°C , 24 h.) and calcined (900°C , 24 h.) to oxide [4].

Three different types of precipitation method was studied for the preparation of the cerium oxalate powders in order to have similar powder properties with thorium oxalate.

- 1) *Precipitation of cerium oxalate from cerium(III) nitrate solution by rapid addition of solid oxalic acid at ambient temperature.*
- 2) *Precipitation of cerium oxalate from cerium(III) nitrate solution by slow addition of oxalic acid solution at 50°C .*
- 3) *Precipitation of cerium oxalate from cerium(IV) nitrate solution by slow addition of oxalic acid solution at 50°C .*

** Cerium oxalates obtained from above conditions are nominated as CeI, CeII and CeIII , respectively*

Thermal decomposition of these powders were controlled by thermal analysis using a Shimadzu thermal analyser. In our thermogravimetric analysis, 27.1 mg of cerium oxalate sample was weighed and operated at the following conditions: atmosphere: air; heating rate: $10^\circ\text{C}/\text{min}$.; full-scale: 50 mg; range: 4mV/min.

The particle size distribution and mean particle size of these powders were determined by particle sizer (Mastersizer-S Malvern) and also determined spectrophotometrically by the sedimentation method based on Stoke's Law. For the determination of the particle size distribution, each of the 20 mg of the cerium oxalate and oxide powders is weighed in a 1 cm glass tube of the Shimadzu UV-260 spectrophotometer and 2-octanol is added. The tube is shaken strongly until a uniform suspension occurs. As soon as the sample is placed in the spectrophotometer, the optical density is measured at 432 nm by regular intervals. Pure-2-octanol is used as reference.

The bulk and tap densities of these powders were measured.

Cerium oxalate powders were calcined to oxides at 400, 500, 700 and 900°C in air during 24 hours. The particle size distribution, mean particle size, bulk and tap densities of the cerium oxide powders were determined.

ThO_2 and CeO_2 were mixed in a diagonal rotating drum during 3 hours at a ratio of 95% Th and 5% Ce, compacted into pellets and the pellets were calcined in air at 1000°C . Taking into consideration of solid solution formation difficulties of oxides mechanically mixed, thorium and cerium which are principal constituents were mechanically mixed as theirs oxalates at the same

conditions, calcined to oxide, compacted into pellets and the pellets were calcined in air at 1000°C.

RESULTS AND DISCUSSION

The chemical analyses indicate that the cerium oxalate powder includes 38.61% cerium and 36.40% $\text{C}_2\text{O}_4^{=}$. These results are in perfect agreement with the values theoretically calculated from the chemical formula of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. The thermal analysis results of the oxalate powders also confirm that the chemical composition of oxalates powders is closely dependent on this formula. The decomposition of the cerium oxalates powders occurs in two steps. It loses 10 molecules of water in the first step at 130°C. The oxalates are decomposed in the second step at 320°C. The complete conversion of the oxalates to the cerium dioxide occurs at 360°C. The thermal decomposition of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ is similar to $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ [5].

The cerium oxalate powders obtained from three different types of precipitation were compared with the thorium oxalate powders. As clearly seen in Fig.1, in view of the sedimentation rate, CeI powders are more similar to the thorium oxalate powders.

Bulk and tap densities of the Th, CeI, CeII and CeIII were given in Table.1. The values are very close except CeIII.

In order to obtain a good mixture of thorium and cerium oxalates or oxides, each component must have similar powder properties. Having very close powder properties with thorium oxalate, CeI powders were chosen for the following operations.

CeI powders were calcined at 400, 500, 700 and 900°C. Bulk and tap densities of the cerium dioxide powders as a function of calcining temperatures were given in Table.2. The values for the cerium dioxide increased considerably with the calcining temperature from 400 to 900 °C.

Particle size analysis (Malvern Mastersizer) data of CeO_2 powders calcined at different temperatures were given in Table.3. Regardless of the calcining temperatures, about 99% of the particles were less than 70µm and no particles less than 0.3µm in size were observed. Only slight reduction in the number of fines was noticed as the temperature was increased and the median (50%) particle size only increased from 24.69 µm at 400°C to 29.46 µm at 900 °C.

The particle size distribution curves obtained by the spectrophotometric sedimentation method for the CeO_2 powders calcined at different temperatures are in agreement with the Mastersizer results (Fig.2).

The XRD studies on the $(\text{Th,Ce})\text{O}_2$ pellets prepared by the mixture of individual oxides and by the mixture of individual oxalates is going on. The evaluation of the results to the respect of solid solution formation will take place after investigation of the sintering conditions.

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Table.1. Comparison of densities of oxalate powders

Oxalates	Th	Ce I	Ce II	Ce III
Bulk density (g/cm^3)	0.52	0.53	0.51	0.39
Tap density (g/cm^3)	0.68	0.70	0.69	0.65

Table.2. Comparison of densities of CeO_2 powders calcined at different temperatures

CeO_2	400 °C	500 °C	700 °C	900 °C
Bulk density (TD %)	9.4	10.7	15.7	17.5
Tap density (TD %)	12.6	15.9	25.10	26.9

Table.3. Particle size analyse of CeO_2 powders calcined at different temperatures by Mastersizer

Material	Calcine temp (°C)	Calcine time (hour)	Particle size		Mean diameters (μm)
			D(v.0.5) (μm)	D(v.0.98)/D(v.0.1) (μm)	
CeO_2 from Ce oxalate	400	24	22.89	60.11/7.22	24.69
	500	24	21.06	58.13/6.18	23.03
	700	24	21.25	59.74/7.06	23.57
	900	24	26.83	72.73/8.44	29.46

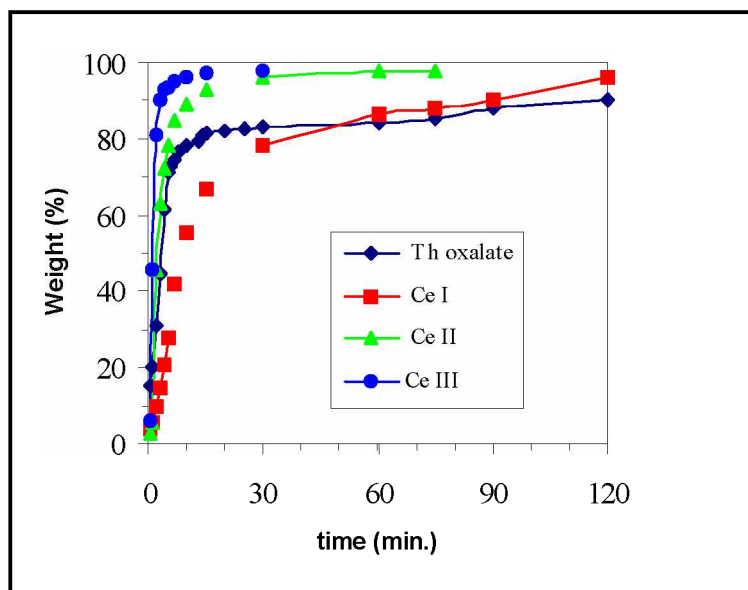


Fig.1. Sedimentation rate of oxalate powders

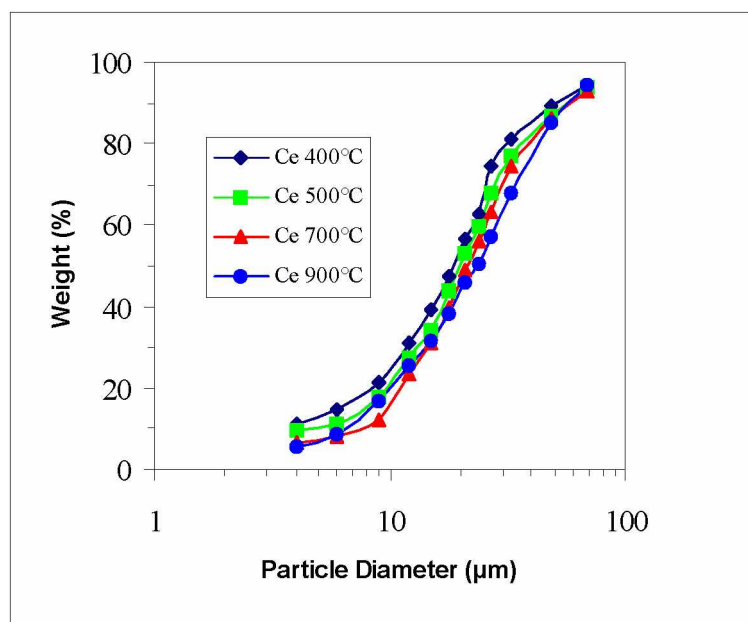


Fig.2. Particle size distribution of CeO₂ powders calcined at different temperatures