Production of ultra-fine ceria particles by hydrothermal synthesis under supercritical conditions

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Ceria (cerium oxide) is widely used as both a polishing compound and a refractory material because of its hardness and stability at high temperatures. Recently, ceria fine particles have been used in fuel battery materials and various sensor materials [1]. The size requirements of the ceria fine particles depend on the particular application, but, in general, it is desirable for the particles to have a narrow size distribution. For polishing applications, particle sizes tend to be of sub-micrometer order whereas for ceramic materials, particle sizes are typically of nanometer order [2].

Ceria fine particles can be produced by thermal decomposition [3–4], flash combustion [5–6], sol–gel [7–8], precipitation [2] and hydrothermal synthesis [9–11] methods. Products formed by thermal decomposition and combustion give large aggregations of nearly 10 μm, making these techniques difficult to adapt to nanometer particle production. For the case of sol–gel and precipitation, calcination of gels or precursors at high temperatures (> 1000 °C) to produce cerium oxide, additional treatment (a grinding and classification) is necessary to obtain ultra-fine particles with narrow size distribution [8]. Hydrothermal synthesis at lower temperatures (< 300 °C) is a well-known method for metal oxide fine particles [9–11]. Hydrothermal synthesis does not require calcination and can produce nanometer-size particles. However, hydrothermal techniques require long heat treatment for several hours because of the slow reaction rate.

We have proposed a rapid and continuous method for production of metal oxide particles using supercritical water as the reaction media [12–13]. The results of those studies suggest that the method has potential to change particle morphology and particle size because of its controllable thermodynamics and transport properties. Through these studies, we also found that ultra-fine particles could be preferentially produced. This letter focuses on the production of ultra-fine ceria particles by the supercritical water (SCW) hydrothermal synthesis method.

Aqueous cerium nitrate solution (0.05 mol/L) was prepared by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ (Kanto Chemicals Inc., Tokyo) into distilled water. Fig. 1 shows the schematic diagram of the experimental apparatus. Cerium nitrate aqueous solution was fed by a high-pressure pump (NP-AX-15, Nihon Seimitsu Kagaku, Tokyo) with a flow rate of 2 cm^3/min. The solution was mixed with pre-heated
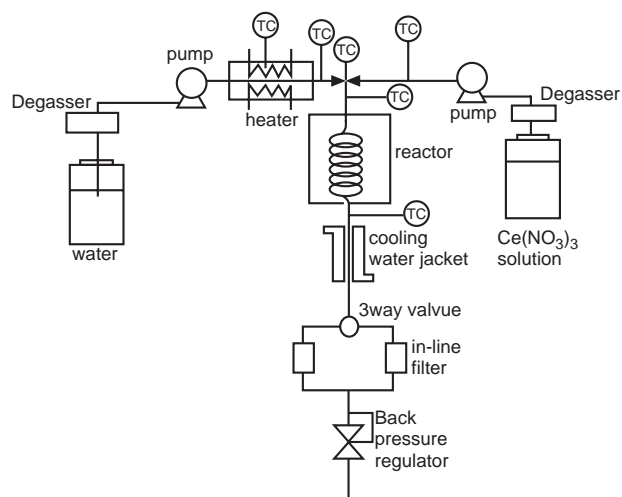

Figure 1 Flow apparatus for producing fine particles in subcritical and supercritical water.

water ($\sim$ 450 °C), which was fed through another line at a flow rate of 6 cm^3/min. The solution was rapidly heated to the desired reaction temperature at the mixing point, and the reaction occurred. The reactor was maintained at the reaction temperature by an external heater. At the outlet of the reactor, the solution was cooled by a water jacket. Pressure in the system was held at 30 MPa with a back pressure regulator (Model 26-1722-24, Tescom Corp., Elk River) at the exit. Residence time of the solution in the reactor was varied by changing reactor volume, which was set to be 0.15 $\sim$ 7.7 cm^3. The residence time was evaluated from the reactor volume, density of pure water at the reaction temperature and pressure and total flow rate, where the density of solution was assumed to be that of pure water density at the given system temperature and pressure.

Particle-water suspensions recovered were filtered with a membrane filter (0.1 μm), and then the powders were oven-dried at 60 °C for 24 h. Observation of particle morphology, and measurement of particle size and particle size distribution, was performed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM)(H-8010, Hitachi, Tokyo). The crystal structure of the powders obtained was analyzed by X-ray diffraction (XRD) using CuKα radiation (Model 2013, Rigaku, Tokyo). XRD analysis was also used to determine

TABLE I Experimental conditions and results

Temperature (°C)	Residence time (sec.)	Conversion (%)	Average particle size, (nm)	Dispersion[a] (nm²)
250	0.8	25.2		
	15.5	79.8		
	27.8	98.5	220[1]	
300	0.7	44.8	120[1]	
	14.1	95.0		
	22.5	99.8	180[1]	
	43.4	99.9	280[1]	
340	0.7	96.7	84[2]	59
380	0.6	99.8	22[2]	18
400	0.4	99.9	20[2]	14
	11.9	99.9	19[3]	
	20.4	99.9	21[3]	

a) $dispersion = (\sum_i^N (d_i - \overline{d})^2)/N$: where N is the number of particles sampled, d_i was particle size and $\overline{d}$ was average particle size.
1) evaluated by SEM photograph, where the number of particles sampled was < 50.
2) evaluated by TEM photograph, where the number particles sampled was > 100.
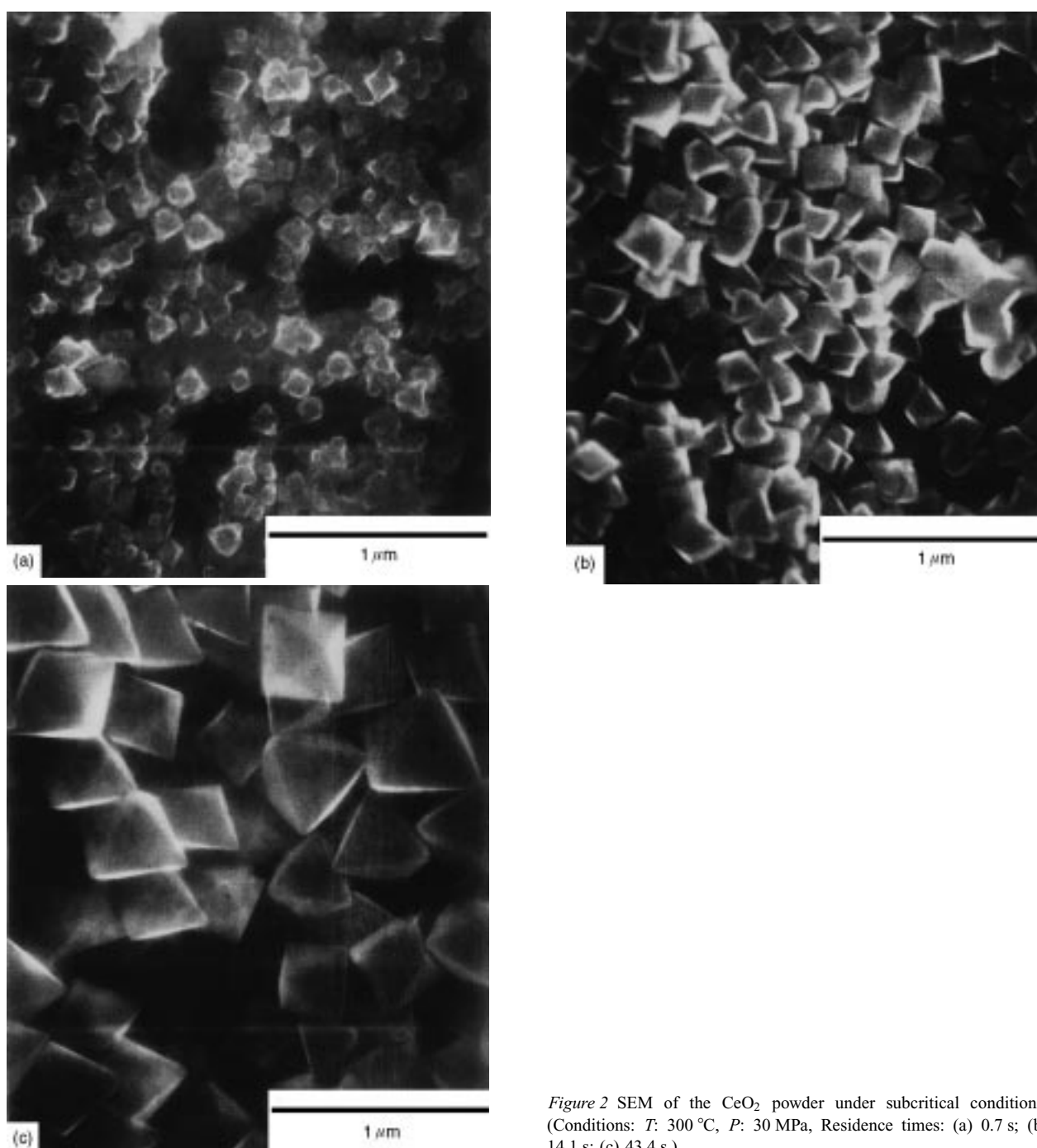3) evaluated by XRD analysis with Sharer's formula.

Figure 2 SEM of the CeO$_2$ powder under subcritical conditions. (Conditions: T: 300 °C, P: 30 MPa, Residence times: (a) 0.7 s; (b) 14.1 s; (c) 43.4 s.)

crystal size by Sharer's formula. Inductively coupled plasma (ICP) analysis (SPS-1200, Seiko, Tokyo) was used to determine the concentration of Ce ion in the solution recovered, from which conversion of cerium nitrate was evaluated.

Table I summarizes the experimental conditions and results. At 200 °C, the outlet solution was clear, but it appeared as a particle-water suspension at higher temperatures ($>$ 250 °C). From the results of XRD analysis, products were CeO_2. Above the critical temperature (374 °C), conversion of cerium nitrate at the shortest reaction time (0.4 $\sim$ 0.6 seconds) was nearly 100%. This implied that the hydrolysis reaction was complete and that a great amount of monomers were produced within an extremely short time.

In comparing results under various reaction temperatures, particle sizes became much smaller at temperatures higher than the critical point of water (374 °C). Regarding particle growth during the observation period, particles became larger with increasing residence time at subcritical conditions, whereas particles grew little under supercritical conditions.

Fig. 2 shows SEM photographs of ceria particles obtained at various residence times at 300 °C. At 300 °C, characteristic octahedron ceria particles were produced. Particles grew with increasing residence time, as shown in Fig. 2 and also Table I. At 400 °C, products formed an aggregation on the membrane filter and had a size of 70 $\sim$ 120 nm, as shown in the SEM photograph in Fig. 3. Fig. 4 shows a TEM photograph of the same products. Ultra-fine particles of about 20 nm with an octahedron shape were observed. From the XRD analysis with Sharer's formula, the crystalline size of these products was about 20 nm and did not vary with increasing
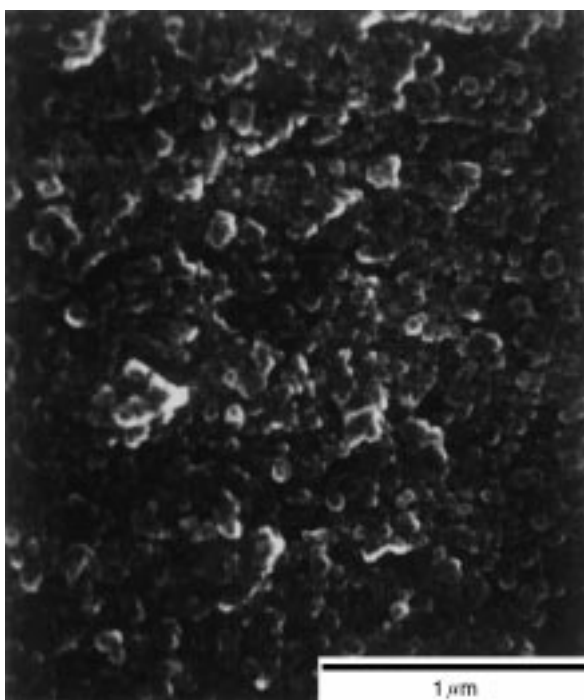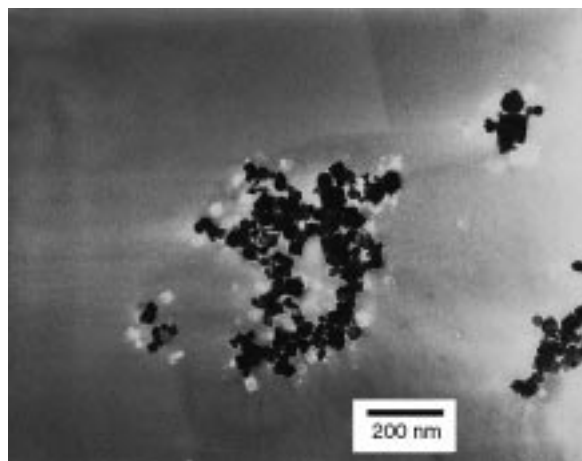

Figure 4 TEM photograph of the CeO_2 powder produced at the same conditions as Figure 3. (Conditions: T: 400 °C, P: 30 MPa. Residence time: 0.4 s.)

residence time in the range of 0.4 to 20.4 s, as shown in Table I.

We found that ultra-fine ceria particles could be produced rapidly ($<$ 1 s) under supercritical conditions. Although a detailed mechanism cannot be clarified at this point, the formation of ultra-fine particles in supercritical water seems to be attributed to the extremely high hydrolysis reaction rate and the low solvent power of supercritical water that most likely leads to a high degree of supersaturation.

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Figure 3 SEM photograph of the CeO_2 powder under supercritical conditions. (Conditions: T: 400 °C, P: 30 MPa. Residence time: 0.4 s.)