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Hot pressing of nanocrystalline TiO_2 (anatase) ceramics with controlled microstructure

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Abstract

The preparation conditions of nanocrystalline phase-pure TiO_2 anatase ceramics by hot pressing are described. Density, surface area, pore size distribution and grain size are determined by various techniques, including gas adsorption, mercury porosimetry, transmission electron microscopy (TEM) and X-ray diffraction (XRD). The evolution of the structural parameters is followed as function of temperature and pressure programme. It is shown that the porosity, grain and pore size of the ceramics can be controlled by a suitable choice of experimental conditions. Ceramics with densities higher than 90% of the theoretical limit with a mean grain size of 30 nm can be obtained at temperatures as low as 490 °C under 0.45 GPa for 2 h. The experimental results are discussed in view of the sintering theory.

Keywords: Sintering; Grain size; Porosity; Oxides

1. Introduction

Materials with ultrafine grain size have attracted much interest by virtue of their unusual physical properties, very often with useful applications. A nanocrystalline ceramic is a dense material (relative density above 90% of theory) with a mean crystallite size below 100 nm. Nanocrystalline ceramics exhibit ductility at low temperature,[1,2] which is critical for the fabrication of ceramic components. In recent years, various studies on nanocrystalline binary oxide ceramics and thin-films have been published, including ceria,[3,4] zirconia[5,6] and titania. A literature overview on sintering of nanocrystalline TiO_2 reveals that dense rutile,[7–9] two-phase anatase-rutile[10–12] or pure anatase nanoceramics[13] were obtained. Various techniques were employed, including classical sintering, hot pressing and sinter-forging.[9] Siegel et al.[14] determined by classical sintering that the densification of nanocrystalline TiO_2 becomes significant at 500 °C and that grain growth starts at 550 °C, but remains slow until 800 °C. To avoid exaggerated grain growth, sintering must be performed at moderate temperature using pressure to accelerate the densification. Furthermore, it has been reported that grain growth becomes important when a relative density of 90% is achieved[8]: grains can grow when the continuous network of pores breaks down on grain boundaries.

Hot pressing appears as a very appropriate technique to densify nanocrystalline ceramics. Hahn et al.[7] reported an improvement of sintering with negligible grain growth by pressure application. However, a phase transition of anatase into rutile can occur at high pressure and temperature, in spite of possible stabilization of the anatase phase at small grain size.[15] Temperature and pressure programmes applied to the ceramics must be optimized to keep the initial grain size and the original anatase phase. The objective of this work is to study the influence of experimental parameters of hot pressing, pressure P and temperature T on the grain and pore size of anatase ceramics. The microstructure of the ceramics is investigated by electron microscopy, the size of crystallites is determined by XRD and the pore size distribution is studied by nitrogen adsorption measurements and mercury porosimetry. Another objective is to interpret the evolution of these data in term of densification mechanism, including diffusion and plastic deformation contributions.

2. Experimental

The anatase powders were prepared by the sulfate route.[16] In this process, the mineral precursor is dissolved in sulfuric

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Table 1
Temperature of calcination and initial powder particle size d, green density ρ_i ($P = 0.2$ GPa, $T = 25\,^\circ$C), final density ρ_f ($P = 0.45$ GPa, $T = 490\,^\circ$C, $t = 2$ h) and experimental conditions for a final density above 90%

$T_{calcination}$ (°C)	d (nm)	ρ_i (%)	ρ_f (%)	Conditions for $\rho_f > 90\%$	$d_{ceramic}$ (nm)	
					Scherrer	TEM
300	12 ± 3	45 ± 5	91 ± 2	490 °C, 2 h	50 ± 20	30 ± 10
600	24 ± 10	51 ± 4	91 ± 2	490 °C, 2 h	–	–
700	35 ± 15	54 ± 4	85 ± 2	680 °C, 0 h	60 ± 20	–
800	70 ± 35	62 ± 3	78 ± 2	585 °C, 2 h or 680 °C, 0 h	–	75 ± 10

The given uncertainties are standard deviations from around 20 experiments.

acid and the titanium sulfate solution subsequently hydrolyzed by heating to 95–110 °C. The hydrolysis product is filtered and the filtrate thoroughly washed until neutral pH is obtained. It is then calcined under air for 1 h at different temperatures ranging between 300 and 800 °C, which allow several powdered samples differing by their particle size distribution to be prepared. The list of samples is given in Table 1. The obtained powders were chemically analyzed by gravimetric techniques and ICP emission analysis[17]: total impurity content is lower than 0.25 mol% for all samples. The mean particle sizes were determined by three experimental methods that are in good agreement for this set of samples[17]: X-ray diffraction (XRD, which gives access to the crystallite size), transmission electron microscopy (TEM) followed by image analysis on more than 100 particles and nitrogen adsorption measurements (a mean particle size is determined from the surface area by assuming spherical shape for the particles).

The hot press is a prototype built in collaboration with Cyberstar, Grenoble.[16] It permits densifying the ceramics under uniaxial load of up to 5000 kg at temperatures up to 1100 °C. The dies are made from pure alumina with internal diameters of 4, 6, and 12.7 mm (SOTIMI, Grez sur Loing). The procedure is to apply first the pressure and then to increase the temperature with a rate of 5 K/min. After reaching the desired temperature, the sample is either directly cooled down or held at this plateau temperature for 2 h before cooling down. The real sample temperature was measured by a Pt-Rh30%/Pt-Rh6% thermocouple. Relative densities were calculated using the geometrical dimensions, the mass of the pellets and the theoretical density of the anatase phase: 3.84 g cm^{-3}.[18]

X-ray diffraction was used to check the phase purity of the ceramic samples and to determine the mean crystallite size d from Scherrer's equation:

$$d = \frac{\lambda}{W \cos\theta} \quad (1)$$

W is the full width at half maximum of the (1 0 1) and (2 0 0) diffraction peaks of the anatase phase and θ is the Bragg angle. Instrumental line broadening is corrected as described previously.[17] These tests were carried out on a Siemens D5000 diffractometer with conventional Bragg–Brentano (θ–2θ) geometry and Cu Kα radiation ($\lambda = 0.15406$ nm). Step size was 0.01° with a counting time of 4 s.

The ceramics microstructure was observed by high resolution Scanning Electron Microscopy with field emission gun (Philips XL305) in secondary electron mode at 10–15 kV acceleration voltage. Furthermore, thin ceramic samples prepared by Focused Ion Beam cutting (Philips FIB 200) were observed by Transmission Electron Microscopy (JEOL 2010 F, operated at 200 kV). Nitrogen adsorption and mercury porosimetry measurements were performed at 77 K and ambient temperature, respectively, using commercial apparatuses (Micromeritics ASAP 2010 and Autopore II 9220).

3. Results and discussion

3.1. Evolution of relative density

Detailed microstructural characterizations of powders, which present an agglomerated state, were described in a previous paper.[17] The average particle sizes and standard deviations, determined by TEM observations, are summarized in Table 1 for powders calcined at 300, 600, 700 and 800 °C for 1 h. The green densities obtained by cold compaction at 0.2 GPa of the powders (Table 1) show a particle size dependence. During cold compaction, a low densification occurs by partial de-agglomeration or by rearrangement due to sliding, which depends on granulometric characteristics of the initial powder. The increased green density may be due to better packing associated with small particles filling the voids between bigger ones, according to ref.[19] This is why the green density increases with the relative width of the particle size distribution, which increases here with the particle size.

The isothermal density evolution as function of pressure (Fig. 1) at 490 °C, for powders with initial particle sizes below 30 nm, shows a plateau above 0.45 GPa with densities around 90%. The similarity of experimental data obtained with different internal die diameters shows that pressure repartition in the die is relatively homogeneous. This result was confirmed by other experiments with pellets of lower thickness. Between 0.1 and 0.4 GPa, the relative density evolution versus pressure can be expressed by a power law with exponent 1/4 (Fig. 1)

$$\rho_f \approx K P^{1/4} + \rho_i \quad (2)$$

where ρ_i is the green density at 25 °C.

The isobaric density evolution as function of temperature was studied at a pressure of 0.45 GPa (Fig. 2) for powders with initial particle sizes below 30 nm. The flattening of the density curve observed beyond 500 °C corresponds to a relative density above 90%, as reported before for the pressure dependence at 490 °C.