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# Densification and grain growth during pressureless sintering of $TiO_2$ nanoceramics

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**Abstract**

Anatase titania nanopowders with mean particle sizes of 7, 15, 26 and 38 nm synthesized by sol–gel method were used to sinter bulk $TiO_2$ nanoceramics. The relative densities and average grain sizes of the $TiO_2$ nanoceramics were studied as a function of the compaction pressure on green sheet, sintering temperature, and mean particle size of the starting $TiO_2$ nanopowders. The relative density of the $TiO_2$ nanoceramics increases rapidly and average grain size increases slowly with increasing sintering temperature below 800 °C. Sintering at higher temperatures above 800 °C enhances the densification of the $TiO_2$ nanoceramics and leads to a increase of the grain size. Bulk $TiO_2$ nanoceramics with an average grain size of less than 60 nm and relative density over 95% was obtained by a phase-transformation-assisted pressureless sintering at a relatively low temperature (800 °C).


*Keywords:* Titania; Nanocrystalline ceramics; Phase-transformation; Pressureless sintering

## 1. Introduction

Nanostructured materials, characterized by an ultrafine grain size, have stimulated much research interest by virtue of their unusual mechanical, electrical, optical, and magnetic properties. Nanostructured ceramics exhibit ductility at low temperature, which is critical to the fabrication of ceramic components [1–4]. Some methods such as hot-pressing, hot-isostatic pressing, spark plasma sintering and so on have been employed to prepare nanoceramics [5–7]. Conventional pressureless sintering is the most common low cost approach to sinter the ceramics in those methods. Unfortunately, in the pressureless sintering, both processes of the densification and grain growth are driven by diffusion. And it is difficult to realize densification without promoting grain growth. For example, Hahn et al. [8] and Siegel et al. [9] obtained dense titania ceramics by pressureless sintering of the green compacts of the rutile $TiO_2$ powders by the gas-condensation method, but the grain size of the as-prepared titania ceramics is over 100 nm. Therefore, it is necessary to study the processes of densification versus grain growth in more detail so as to find some clues to resolve this dilemma.

The anatase-to-rutile phase transformation in the titania system is a metastable-to-stable irreversible transformation [10]. The phase transformation of this type is very important both from grain growth and densification in the titania system. Kumar et al. obtained dense nanostructured titania coatings with near theoretical densities and an average grain size of less than 60 nm by sintering a titanium oxide gel at the anatase-to-rutile phase-transformation temperature [11]. Liao et al. and Kear et al. prepared bulk nanocrystalline $TiO_2$ ceramics by the phase-transformation-assisted high pressure/low temperature sintering method. They found that the grain growth is limited by the low sintering temperature and $TiO_2$ phase transformation depending on the high pressure/low temperature combination [5,12]. However, few systematic works on the preparation of bulk nanostructured $TiO_2$ ceramics by conventional pressureless sintering assisted by the phase transformation have been reported so far.

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In our present work, bulk $TiO_2$ nanoceramics were prepared by a phase-transformation-assisted pressureless sintering method. The effects of the compaction pressure on green sheet, sintering temperature, and mean particle size of the $TiO_2$ nanopowders synthesized by sol–gel method on the microstructure, average grain size, and relative density of the $TiO_2$ nanoceramics were investigated.

## 2. Experimental procedures

### 2.1. Synthesis of the $TiO_2$ nanopowders and green compacts

Anatase titania nanopowders were prepared by sol–gel method, using the mixed solution of $C_{16}H_{36}O_4Ti$ (tetra-*n*-butyl-titanate) and ethanol as the precursor. The precursor was heated to 33 °C in a thermostatic bath for a certain duration. Then the mixed solution of distilled water, ethanol, and hydrochloric acid was slowly added into the heated precursor solution. The mixture was successively stirred until a transparent gel was obtained. The resulting $TiO_2$ gel was dried at 40 °C in air for several days to allow the generation of $TiO_2$ xerogel. The $TiO_2$ powders as the raw materials were obtained by milling the $TiO_2$ xerogel in air and calcinated at predetermined temperatures for 2 h with a heating rate of 10 °C/min.

The green compact pellets (15 mm in diameter and 1–2 mm in thickness) were obtained by uniaxial pressing of the calcinated $TiO_2$ powders at 500, 720 and 920 MPa for 5 min in air at room temperature. The nanoceramics were prepared by heating the green compacts in air at a rate of 10 °C/min upto a predetermined temperature and sintering for 2 h at the temperature.

### 2.2. Characterization

X-ray diffraction analysis of the crystalline phases of the calcinated $TiO_2$ powders and bulk ceramics was performed on a Rigaku D/max-2400 X-ray diffractometer. The mean particle size of the calcinated $TiO_2$ powders and average grain size of bulk ceramics were estimated using the Scherrer equation from the diffraction peak widths with the instrument and wavelength related broadening eliminated [13]. Transmission electron microscopy (JEM-1200EX) was employed to observe the morphology and determine the mean particle sizes of the calcinated $TiO_2$ powders and the average grain sizes of the sintered nanoceramics. A differential thermal analyzer (DTA, CD-4P) and a thermogravimetric analyzer (TG, Du Pont 1090) were used to analyze the thermal effects that occurred in the $TiO_2$ xerogel powders at a heating rate of 10 °C/min in air. The relative densities of the as-sintered ceramics were measured by the Archimedes method. The relative density was calculated with respect to the theoretical density of anatase (3.84 g cm$^{-3}$) and rutile (4.26 g cm$^{-3}$).

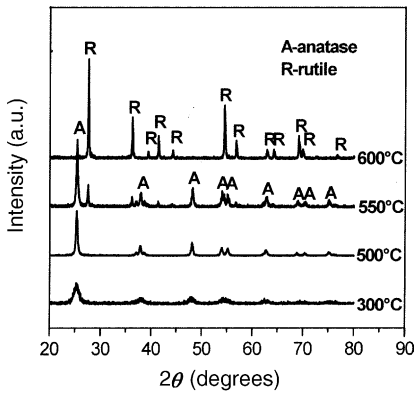


Fig. 1. XRD patterns of the $TiO_2$ xerogel powders calcinated at different temperatures for 2 h.

## 3. Results and discussion

The X-ray diffraction (XRD) patterns of the $TiO_2$ xerogel powders calcinated at different temperatures for 2 h are shown in Fig. 1. It is seen that the anatase phase forms by the crystallization of the xerogel powder during calcination at 300 °C. A small amount of the rutile phase forms along with the anatase phase as the xerogel powder is calcinated at 550 °C, whereas only the rutile phase exists as the $TiO_2$ xerogel powder is calcinated above 600 °C. The rutile phase of the $TiO_2$ powder starts to appear at 550 °C while the temperature of complete transformation from the anatase to rutile phase is about 600 °C. The result is in good agreement with the results of the DTA and TG analysis of the $TiO_2$ xerogel powder in air (Fig. 2). According to the TG analysis, the major part of the weight loss appears to occur below 250 °C, and the reaction is complete above 500 °C. The weak endothermic peak at 100 °C in the DTA curve can be attributed to the desorption of water molecules. The exothermic peaks at approximately 230 and 380 °C can be associated with the crystallization and oxidative elimination of organic residue. The TEM micrograph of the nanopowders calcinated at 400 °C is shown in Fig. 3. The powders of the spherical particles with a mean particle size of 15 nm have a narrow size distribution and weak agglomeration. And the mean particle size determined

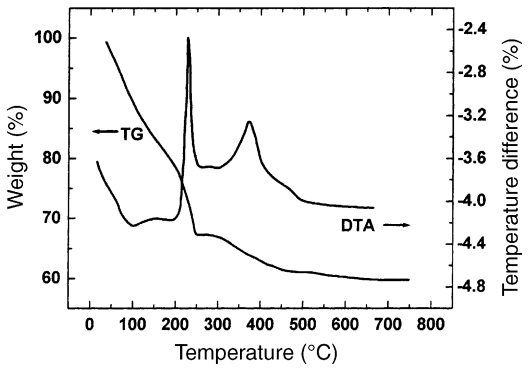


Fig. 2. DTA and TG traces of the $TiO_2$ xerogel powders measured at a heating rate of 10 °C/min in air.