

## Preparation and Microstructural Development of Nanocrystalline Titania and Alumina

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**Abstract.** The preparation of nanocrystalline titania and alumina was investigated by sol-gel methods using titanium isopropoxide, boehmite and aluminum isopropoxide. Various drying control chemical additives like oxalic acid, acetic acid and polyacrylic acid were used for modifying the drying behaviour and shrinkage of the gels. The sintered densities of the ceramics prepared by sol-gel processing and the dried gels were in the 79-99% of theoretical density for rutile. The green and sintered densities of the pellets prepared by uniaxial pressing of powders derived from sols, gels and precipitation techniques for titania were in the 40-52% and 55-83% respectively. The titania ceramics were observed to experience anatase-rutile phase transformation upon heat treatment at 650°C. The grain size of the sintered ceramics at 650°C was determined to be about 26 nm. Grain size of titania increased to 213 nm. at 850°C. The mechanical properties of these nanocrystalline ceramics were investigated by using microhardness testing.

### Introduction

Ceramics with grain sizes below 100 nm are known as nanocrystalline ceramics. Nanocrystalline ceramics can have different chemical physical and mechanical properties compared to coarser grained ceramics. They may have a great potential in application related to sensors, catalyst, coating materials, optical devices, pigments, dielectric ceramics, bonding agents, and miniaturization of devices [1,2]. Nanocrystalline ceramics can also have cost reducing properties such as low temperature sintering and superplasticity. Superplasticity can be loosely defined as the ability of a crystalline material to undergo tremendous elongations prior to failure, on the order of hundreds or thousands of percent [3]. Therefore, manufacturing near-net shaped pieces without machining is possible with nanocrystalline ceramics [4, 5]. These applications depend on the chemical and physical properties which are affected by the powder synthesis methods. There are various techniques for the preparation of nanocrystalline ceramics. Some of the well-known processes are: plasma synthesis, chemical vapor deposition and sol-gel synthesis. Among them, the sol gel synthesis is a powerful method for the design of new materials based on the hydrolysis and condensation reactions of molecular precursors such as metal alkoxides[6].

In this work, we have tried to find new approaches to prepare bulk nanocrystalline titania and alumina ceramics by sol gel synthesis and investigated the influence of synthesis conditions on microstructure.

### Experimental

Titania and alumina ceramics were prepared from titanium (IV) isopropoxide (Aldrich, 97%), aluminium isopropoxide (Aldrich, 98%) and Boehmite precursor (Sasol). The molar ratio of the reactants for the preparation of titania sol was  $\text{Ti}[\text{OC}(\text{CH}_3)_2]_4:\text{HNO}_3:\text{H}_2\text{O}:\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 = 1:0.0537:2:20$ . Predetermined amounts of titanium (IV) isopropoxide were diluted with half of the required amount of 2-propanol. 1.44 M nitric acid solution was mixed with the rest of the total 2-propanol. The acid-alcohol solution was added to the alkoxide-alcohol solution slowly while the mixture was stirred vigorously with a magnetic stirrer. The sol (pH=3.09) gelled in 3-4 days at room temperature. Gels were then dried at 40°C in a vacuum oven. In order to reduce the extent of cracking of the gels, some DCCA's (Oxalic acid, acetic acid, and polyacrylic acid) were introduced into the sols in 1-2 wt-% solids concentrations. Powder A was prepared from titania gels dried at

175°C for about 10 hours and subsequently ground in a mortar followed by ball milling in an alcoholic medium for 12 hours. This suspension was ultrasonically treated for five hours and subsequently dried at 70°C. Powder B was prepared by the precipitation of the sol in a large quantity of water. Precipitation occurred simultaneously and the precipitate was separated by centrifugation, further dried at 70°C and subsequently ground in a mortar. Powder C was prepared by drying the gel at 80°C for ten hours, ball milled for 12 hours in an alcoholic medium and dried at a temperature of 110°C for 15 hours. The calcination of the powders were carried out at 400°C for two hours. Aluminum isopropoxide was hydrolyzed at 80°C for 3 hours peptised with appropriate amounts of acid to form a stable colloidal solution and was kept at about 80°C under vigorous stirring. The molar ratio the reactants was  $\text{Al}[\text{OC}(\text{CH}_3)_2]_4:\text{HNO}_3:\text{H}_2\text{O}=1:0.25:100$ . The sol was dried at room temperature and subsequently ground by ball mill for 2 hours.

Green pellets were prepared by uniaxial dry pressing in a 10 mm. diameter die to a final thickness of about 1 mm. at 304 MPa. Titania gels and pellets were air sintered at 650, 700, 750, 800 and 850°C for two hours (Carbolite 1600 RHF) with 10°C/min. heating rate for two hours. The final density of the sintered samples were determined by using Archimedes' method (Sartorius YD01). The samples were characterized by using TGA-51/51H, Shimadzu Co., by Vickers Micro-Hardness Tester (HVS-1000), X Ray diffractometer Philips 'XPERT Pro and SEM Philips XL 30S FEG.

## Results and Discussion

Significant shrinkage was observed during drying of the titania gels because of low sol solids content (about 6 wt-%). Most gels cracked during the slow solvent removal process. The addition of 1 wt-% polyacrylic acid caused faster gelation and gelation occurred in 1-2 days. Formation of blurry sols and very fast gelation were observed when polyacrylic acid was added at 2 wt-% levels. The use of oxalic acid at 1 wt-% level didn't affect the gelation time but 2 wt-% addition caused gelation in 2 days. Acetic acid additions didn't affect sol clarity and the gelation time at 1-2 wt% levels.

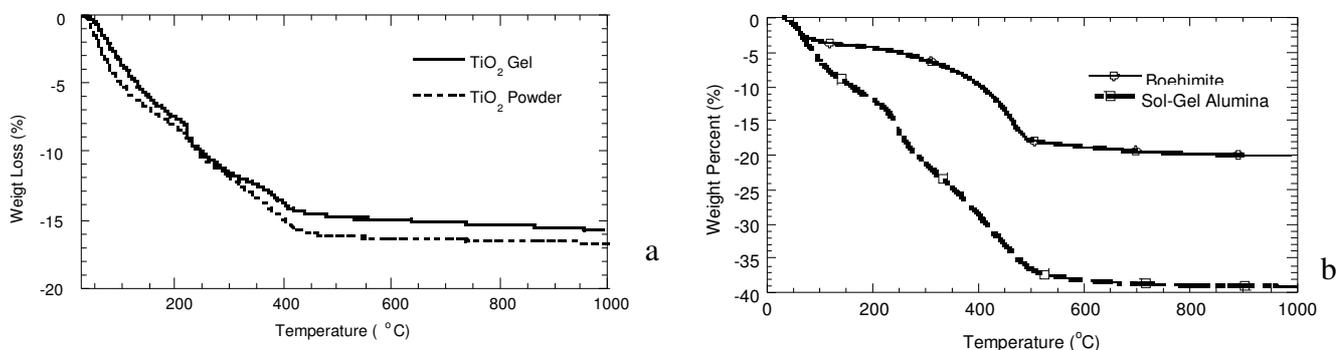


Fig.1. TGA curves of the Titania (a) and Alumina (b) samples.

TGA curves of the titania gel without DCCA's and powder A is shown in Fig.1-a. Total weight loss about 15% was observed at around 400°C. This steady weight loss may be due to the removal residual alcohol and organics from the samples. The powder calcination temperature was chosen as 400°C for titania. The total weight losses of sol-gel derived alumina and boehmite are about 37% and 20% respectively at about 500°C. The calcination temperature was chosen as about 500°C. The densification behavior of dried gels and powder pellets is shown in Fig.2. The green densities of Powder A pellets were in the 49-53% of theoretical density range (theoretical density of rutile was taken as 4.21 g/cm<sup>3</sup>). The sintered density increased to 55% and 72% at 650°C and 850°C with significant levels of open and closed porosity (14.39% and 30.61% at 650°C, 10.11% and 17.39% at 850°C respectively). The green body densities of powders B and C were in the 41-46% and 49-52% ranges respectively. The sintered density of the precipitation derived powder B increased steadily with respect to temperature to 82% of theoretical density at 850°C (13.1% open porosity and 4.9% closed porosity). The use of ultrasonic treatment, the gel drying temperature and sol precipitation all seem to have affects on the sintering behavior of those powders. The sintered densities of dried gel

pieces were above 88% of theoretical density at 650°C. The addition of DCCA's as shown in Fig. 2 generally improved the final sintered densities.

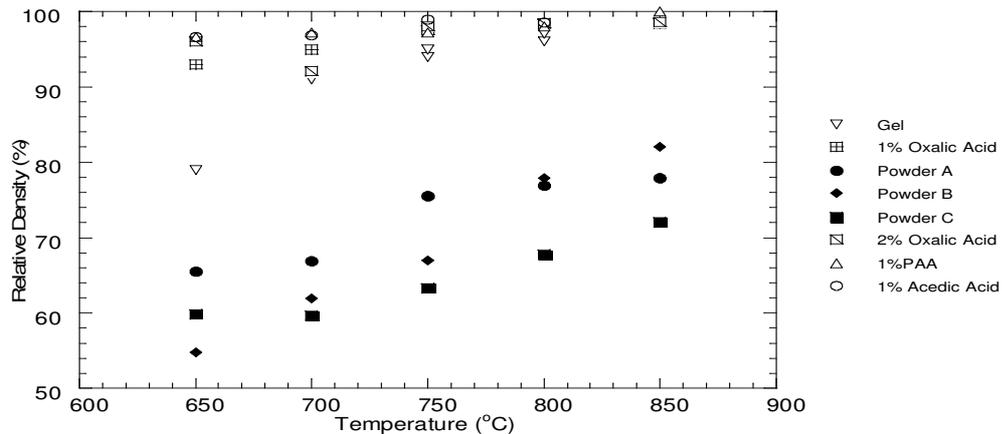


Fig.2. Sintering behavior of Route A, B, C, the gels with and without DCCAs.

According to the XRD data, calcined titania samples were in anatase form, and anatase-rutile transformation occurs at 650°C and was totally rutile at 700°C. Boehmite transformed into  $\gamma$ -Alumina at 500°C and was stable up to 900°C and  $\alpha$ -alumina was the dominant phase at 1200°C.

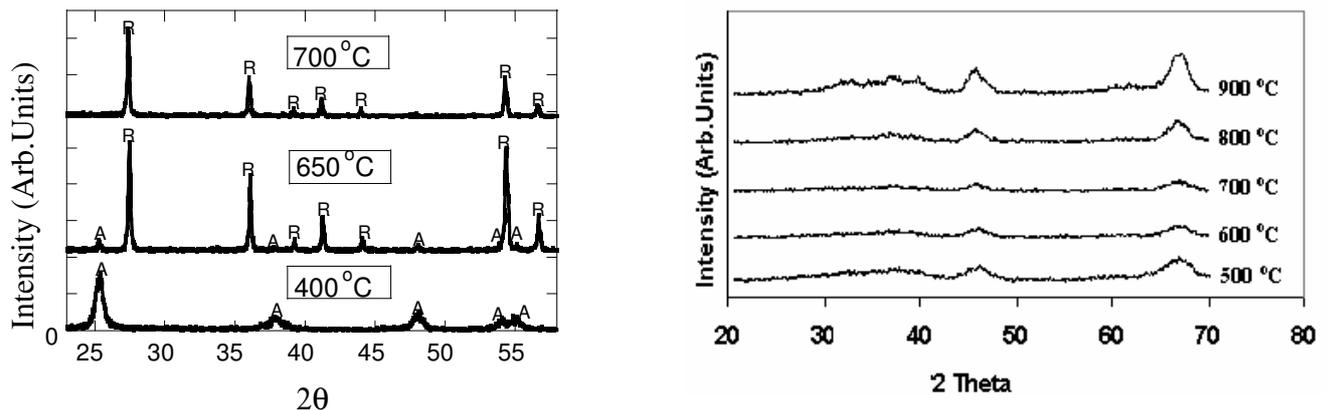


Fig. 3. XRD diffraction pattern of (a) Titania and (b) Alumina sintered at various temperatures.

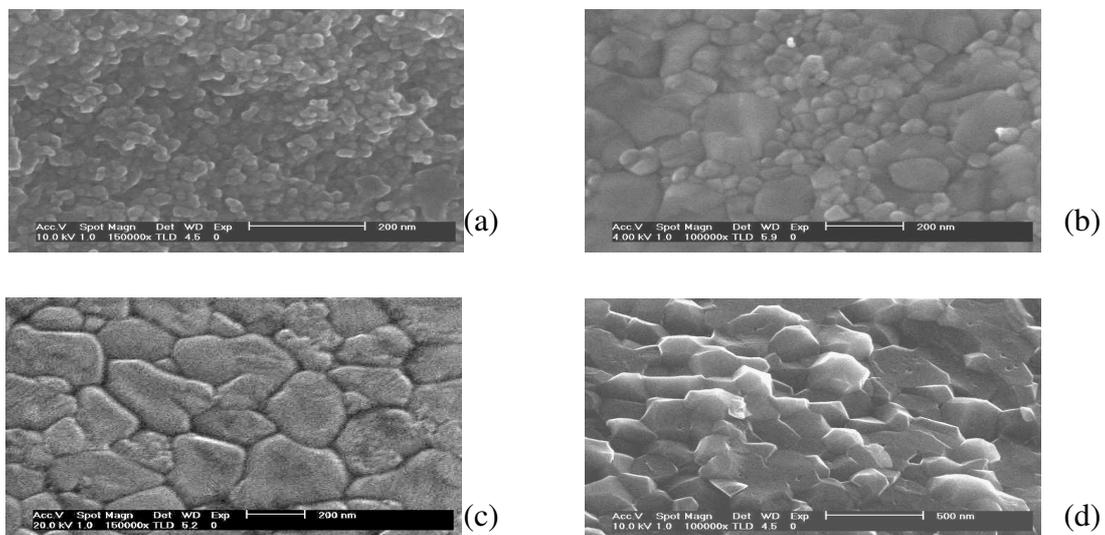


Fig.4. SEM micrographs of Titania Samples sintered at (a)650, (b)700, (c)750, (d)850.

The grain size of the titania samples sintered at 650°C was uniform with a grain size of about 25 nm. as seen in fig. 5. The grain size increased from 51 nm. to 208 nm. (Fig. 6), when the samples sintered at 700 and 850°C. For the titania sintered at 700°C showed non-uniform grain size distribution, most probably due to the anatase-rutile transformation.

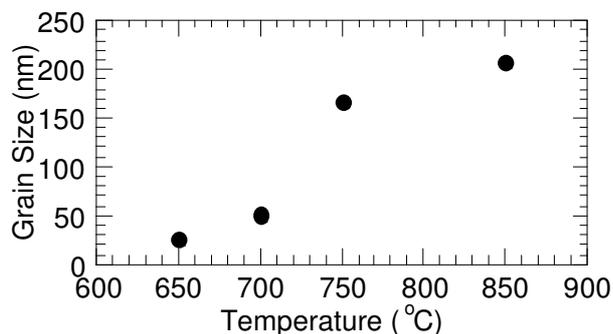


Fig.5. Grain size distribution of titania sintered at 650, 750, 850°C.

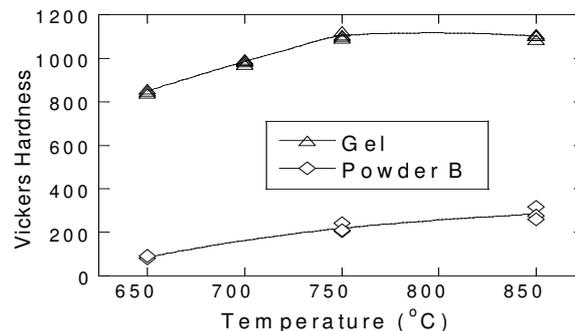


Fig.6. Hardness vs. temperature for titania samples.

The Vickers hardness test results of the sintered gel and powder B pellets are shown as a function of sintering temperature in Fig. 7. The hardness of the sintered gels increased until 750°C remained almost constant between 750-850°C, which is in agreement with the sintering behavior of the gels given in Fig. 2.

### Summary

Nanocrystalline titania ceramics were prepared from sol-gel derived powders the gels in the 650-850°C sintering range. The powder pellets compacted at 300MPa had lower densities than the gels. The gels mostly fractured into several pieces during drying. The extent of gel cracking was reduced with the addition of 1-2% PAA, acetic acid and oxalic acid to the sols. High relative sintered densities for the gels (>90%) were obtained at 650°C. The XRD patterns showed that titania transformed from anatase to rutile at 650°C and alumina transforms from boehmite to  $\gamma$ -Alumina at 500°C. The grain size of the titania samples was 26 nm at 650°C and it increased to 213 nm at 850°C. The vicker's hardness of the gel derived titania ceramics was about 1000 MPa.

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