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PREPARATION AND CHARACTERIZATION OF NANOCRYSTALLINE TITANIA

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ÖZ

Nanokristal seramikler, ileri seramiklerin gelecekteki uygulamalarında önemli etkileri olabilecek özgün kimyasal, fiziksel ve mekanik özelliklere sahiptir. Bu çalışmada, titanyum izopropoksit'ten titan seramikleri hazırlanması ve karakterizasyonu incelendi. Şekillendirilmiş yapılar 650-850^{0}C aralığında hava ortamında sinterlendi. Sol-jel prosesi ve jellerin kontrollü kurutulması ile elde edilen seramiklerin yoğunlukları teorik yoğunluğun %79-99'u olarak bulundu. Sollar, jeller ve çökertme yöntemleriyle hazırlanan tozlardan preslenen peletlerin sinterleme işlemi öncesi ve sonrası yoğunlukları sırasıyla teorik yoğunluğun %40-52 ve %55-83'ü olarak bulundu.

Anahtar Kelimeler: nanokristal seramikler, titan, sinterleme, sol-jel

ABSTRACT

Nanocrystalline ceramics possess unique chemical, physical and mechanical properties which may have a significant impact on the future applications of advanced ceramics. The preparation and characterization of titania ceramics from titanium isopropoxide precursor was investigated in this work. Green bodies were air sintered in the 650-850°C range for the determination of the sintering behaviour.The sintered densities of the ceramics prepared by sol-gel processing and controlled drying of the gels were in the 79-99% of theoretical density. The green and sintered densities of the pellets prepared by uniaxial pressing of powders derived from sols, gels and precipitation were in the 40-52% and 55-83% respectively.

Key Words: nanocrystalline ceramics, titania, sintering, sol-gel

1. INTRODUCTION

Nanocrystalline (grain size <100 nm) ceramics have attracted significant interest due to their unique properties [1, 2] such as superplastic behavior, low sintering temperatures and potentially reduced thermal conductivity. Superplasticity is the ability of the polycrystalline material to experience large elongation to failure at moderate temperatures. Therefore, manufacturing near-net shaped pieces without machining is possible with nanocrystalline ceramics [3, 4]. Nanocrystalline ceramics are sintered at low temperatures in order to avoid extensive grain growth. There are also indications that nanocrystalline ceramics have extremely low thermal conductivity. Thermal conductivity is directly proportional to the mean path length of phonons which is delimited by phonon-phonon scattering events. This is in the order of a few nanometers in nanocrystalline ceramics. The distance between grain boundaries approach to the nanometer scale and hence the grain boundaries can also contribute to the scattering processes. Therefore, nanocrystalline ceramics are a potential thermal barrier. They can also have a potential application of diffusion bonding for gluing larger ceramic parts [5].

These potential applications necessitate the preparation of nanocrystalline ceramics with final densities close to the theoretical density. Non-agglomerated ultrafine powders are required for the production of nanocrystalline ceramics [6].

In this work, the preparation of nanocrystalline ceramics by using sol-gel techniques has been investigated. Clear sols of titania prepared by using titanium alkoxide were gelled by aging at room temperature. These gels containing drying control chemical additives (DCCA's) were further dried to form dense compacts with nanometer sized particles. The sintering behavior of dried gels and pellets prepared by uniaxial pressing of powders derived from sols, gels and precipitation were examined.

2. EXPERIMENTAL PROCEDURE

Titania sols were prepared from titanium (IV) isopropoxide ($Ti[OC(CH_3)_2]_4$) via hydrolysis and condensation reactions[7, 8]. The preparation methods utilized in the sol-gel processing is given in detail in earlier work [5]. The green titania bodies were prepared by using four different processing routes using the same sols with optimized compositions.

For the preparation of the gel derived green bodies, sols were aged at room temperature for 3-4 days until they gelled. Gels were then dried at 40°C in a vacuum oven. Although the drying process was very slow, gels shrinked extensively, therefore, cracked in several pieces after and/or during drying. In order to reduce the extent of cracking of gels, some DCCA's were introduced into the sols in 1-2 wt-% solids concentrations. Oxalic acid, acetic acid, polyacrylic acid and stearic acid were used as DCCA's. Oxalic acid and polyacrylic acid were found to be most effective DCCA's reducing the extent of cracking during drying. Gel formation did not occur after 20 days when stearic acid was used as the DCCA.

Three different powder preparation routes were investigated in this study in order to control agglomeration in the powders which may have significant adverse effects during densification. Powder A was prepared from titania gels. Following gel drying at 175°C for about ten hours, gel pieces were ground in a mortar followed by ball milling of medium size gel pieces in an alcoholic medium for 12 hours. This suspension was ultrasonically treated for five hours and subsequently dried at 70°C. The powder was further calcined at 400°C for two hours.

Powder B was prepared by the precipitation of the sol (which was kept at room temperature for a day for the stabilization of the chemical and physical properties) in a large quantity of water. Under constant stirring, the sol was slowly added to water. Precipitation occurred simultaneously and the precipitate was separated by centrifugation. This precipitate was further dried at 70°C and subsequently ground in a mortar. The calcination of the powder was carried out at 400°C for two hours.

Powder C was prepared by drying the gel at 80°C for ten hours and ball milling for 12 hours in an alcoholic medium. This suspension was dried at a temperature of 110°C for 15 hours. The calcination of the powder was carried out at 400°C for two hours.

Green pellets were prepared from powders A, B and C by uniaxial dry pressing in a 10 mm. diameter die to a final thickness of about 1 mm. at 304 MPa.

Gels and pellets were sintered in a programmable furnace (Carbolite 1600 RHF) at 650, 700, 750, 800 and 850°C. The heating and cooling rates (10 °C/minute) and soaking time (two hours) were kept constant for the all sintering experiments. Higher temperatures were not investigated due to the possibility of extensive grain growth in the sintered ceramics.

The final density of the sintered titania gels and pellets were measured by using Archimedes' method and a Sartorius YD01 density measurement kit. The TGA curves were obtained by Thermogravimetric Analyzer (TGA-51/51H, Shimadzu Co.). The pore size distributions were determined by ASAP 2010. The micro-hardness of the sintered pellets and gels were determined by Vickers Micro-Hardness Tester (HVS-1000).

3. RESULTS AND DISCUSSION

Drying of the gels was very a slow process so that the gels mostly cracked due to the high rate of solvent evaporation. Significant shrinkage of the gel occurred during drying because of the relatively low solids content (about 6 wt-%) of titania sol. Gels mostly didn't stay in one piece by the end of the drying process. In order to prevent excessive crack formation and control of the solvent removal process DCCA's were added during the sol preparation stage. The addition of 1 wt-% polyacrylic acid accelerated the gelation process and gels were formed in 1-2 days. Formation of blurry sols and very fast gelation was observed when polyacrylic aid 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 faster gelation in 2 days. Acetic acid additions didn't affect the gelation time and sol clarity at 1-2 wt% levels. The sols with stearic acid additions didn't gel and precipitation was observed in the sol.

TGA curves of the gel without DCCA's and powder A is shown in Figure 1. Total weight loss of about 15% was achieved at around 400°C. This steady weight loss may be due to the removal of residual alcohol and organics from the samples. The powder calcination temperature was chosen as 400°C based on these TGA curves.

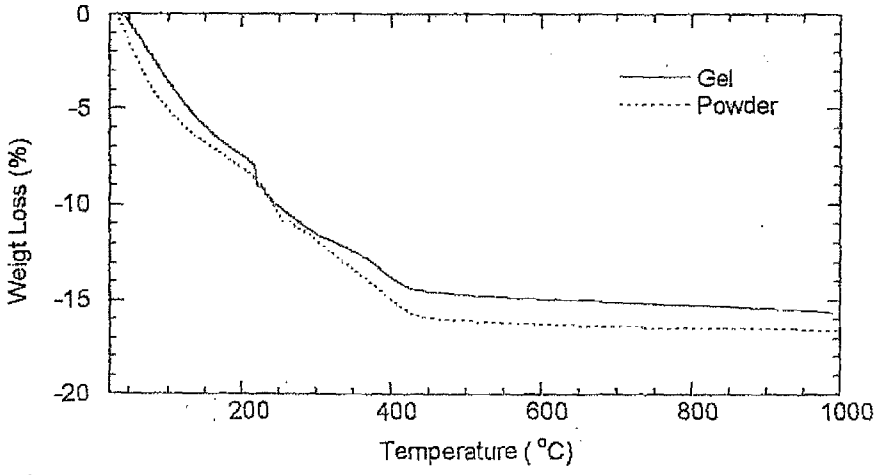

Figure 1. TGA curves of the Powder A and the Gel

The results of the sintering studies on powder pellets are shown in Figure 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^3). 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 the sintering temperature to a final density of 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 these powders.

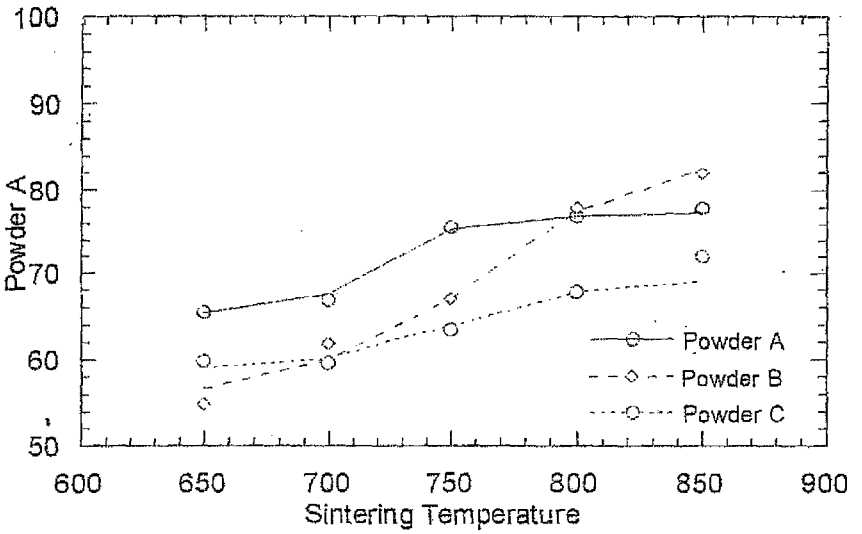

Figure 2. Sintering behavior of Powder A, B and C.

The sintered densities of dried gel pieces were above 88% of theoretical density at 650°C and most of the specimens had sintered densities in the 94-99% range. The addition of DCCA's as shown in Figure 3 generally improved the final sintered densities. Results given in Figure 3 indicate that the preparation of dense TiO_2 ceramics through DCCA controlled gel drying with grain sizes lower than 100 nm may be a reality.

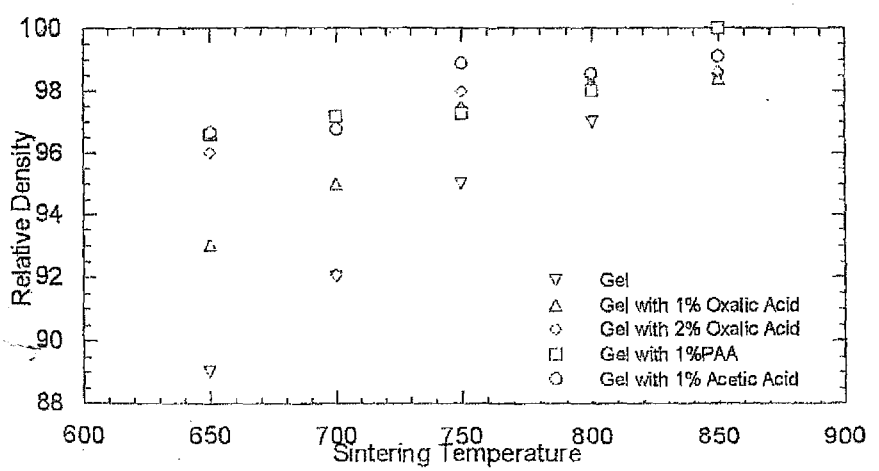

Figure 3. Sintering behavior of the gels with and without DCCA's.

The results of Vicker's hardness measurements on sintered gel and powder B pellets are shown in Figure 4. There was approximately 900Hv difference in hardness between the gels and pellets with gel hardness values above 1000 Hv for 700-750^{0}C sintered samples.

The pore size distribution for DCCA free gel pieces by using desorption data and BJH method is shown in Figure 5. The presence of a sharp peak located at about 4 nm. pore diameter indicates that the unfired structure is very uniform. The BET surface area derived particle size in these calcined gels were about 20 nm. The densities of the gel pieces before sintering was estimated as 70% by using the cumulative pore volumes obtained by the BJH method.

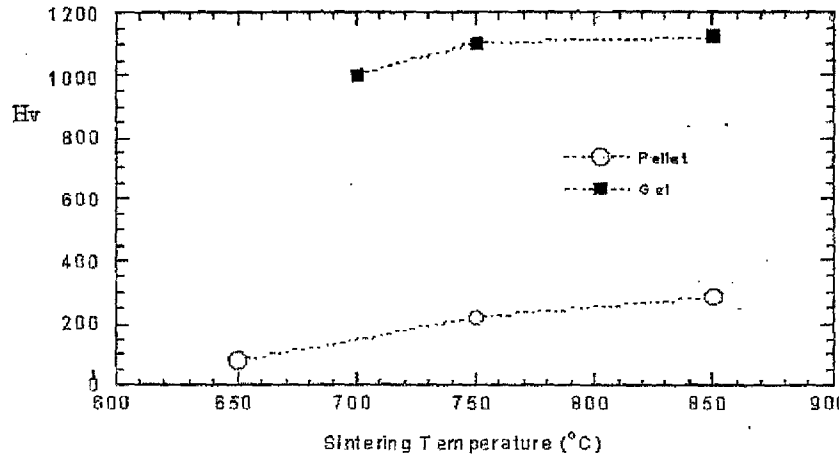

Figure 4. Vicker's Micro-hardness Test Results of the Powder B and the Gel.

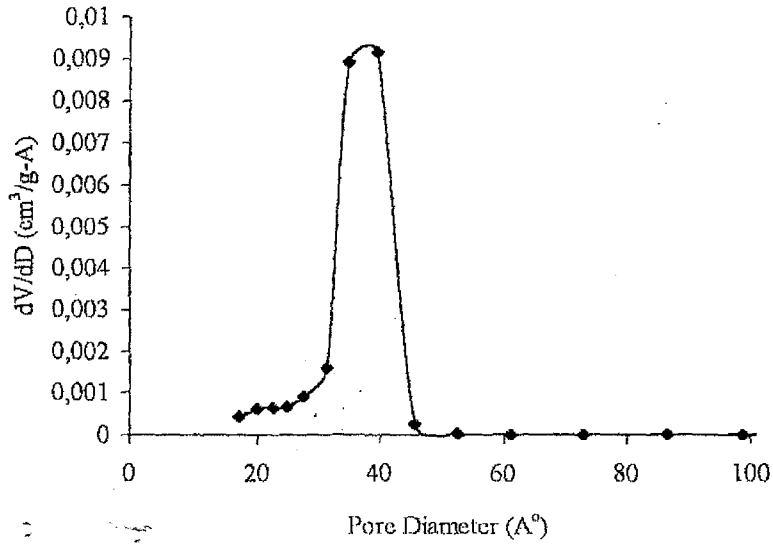

Figure 5. BJH cumulative pore volume plot for dried gel pieces.

4. CONCLUSION

The effect different processing methods on the sintering behavior of TiO_2 green bodies in the 650^0C-850^0C was investigated in this work. The use of DCCA's during controlled gel drying may make the preparation of dense TiO_2 ceramics at 700-750^0C. Ceramics with such nanometer sized grains may have interesting potential applications.

5. REFERENCES

1. Mayo M.J., Processing of nanocrystalline ceramics from ultrafine particles, International Materials Reviews(1996) vol.41, no.3, 85-115
2. Mayo M.J., Synthesis and applications of nanocrystalline ceramics, Materials design (1993), vol. 14, 323-329
3. Mayo M.J., Hague D.C., Using superplastic flow to process nanocrystalline ceramics, The Minerals, Metal and Materials Society (1997), 31-45
4. Mayo M.J., Hague D.C., Chen D.-J., Processing nanocrystalline ceramics for applications in superplaticity, Materials Science and Engineering A166 (1993), 145-159
5. Caglar Ö. The Preparation, Chracterization and Sintering of Nanocrystalline Ceramics, Izmir Institute of Technology, 1999
6. Mayo M.J., Ciftcioglu M., Processing of Nanocrystalline Ceramics, Material Research Society Symposium (1990), vol:196
7. Scherer G.W., Theory of Drying, J. of American Ceramic Society, 73, no:1, pp. 3-14,1990
8. Scherer G.W., Aging and Drying of Gels, J. of Non-Crystalline Solids, 100, pp. 77-92,1988