

Fabrication of ultra-fine TiO₂ Ceramics by a high-frequency induction heated sintering method

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High-frequency induction heated sintering (HFIHS) is utilized to consolidate ultra-fine rutile TiO₂ ceramics. Densification to near theoretical density in a relatively short time can be accomplished using this method. Samples of TiO₂ with a relative density of up to 98% and an average grain size of about 160 nm could be obtained by sintering at 830°C for 5 minutes under a pressure of 100 MPa. The influence of sintering temperature and mechanical pressure on the final density and grain size of the sintered products was investigated. The sintered materials had fracture toughness and hardness values of 12.8 GPa and 3.1 MPa·m^{1/2}, respectively.

Key words: Rapid Sintering, High-Frequency Induction Heated Sintering, TiO₂, hardness, fracture toughness.

Introduction

TiO₂, titania, is a widely employed material due to important technological applications in photocatalytic and photoelectric devices, chemical sensors and optical coatings [1-4]. TiO₂ presents three crystalline structures: brookite, anatase and rutile. The most common are anatase and rutile, since brookite is rather unstable. Submitting TiO₂ to high thermal treatments promotes the transformation of anatase to rutile, which is the thermodynamically stable phase at high temperatures. The different phases can affect several properties of titania, such as the catalytic activity or the gas sensing response [5]. Moreover, the titania grain size increases when anatase transforms to rutile, which as well alters the sensing response. The temperature at which the phase transition occurs depends on the preparation method, the precursors used and the additives introduced in the base TiO₂.

Recently, nanocrystalline TiO₂ has been used as a model system to investigate the size-dependent phase transition behavior of nanoscale oxides in terrestrial environments [6]. Because of the technological and fundamental importance, numerous experimental and computational studies have investigated the phase stability and properties of macrocrystalline TiO₂ polymorphs. Significant progress has been made recently in the identification of various macrocrystalline polymorphs and their properties [7-9].

When conventional sintering processes are used to

sinter nano-sized titania powders, concomitant grain growth leads to the destruction of the nanostructure. This focuses attention on consolidation methods in which grain growth can be eliminated or significantly reduced. To accomplish this, rapid sintering methods have been widely used to sinter nano-sized powders. The most obvious advantage of rapid sintering is that fast heating and cooling rates, and the short dwell time lead to bypassing low-temperature, non-densifying mass transport (e.g., surface diffusion) [10-12]. However, conventional rapid heating can lead to temperature gradients and thus differential densification (non-uniform microstructures), low density, or specimen cracking. To overcome these difficulties, other rapid sintering techniques, such as the spark plasma sintering (SPS) method [13, 14], have been developed.

High-frequency induction heated sintering (HFIHS) is a new rapid sintering method which was developed recently for the fabrication of ceramics and composites [15-18]. This method combines a short time, high-temperature exposure with pressure application. During the HFIHS, a large current will be induced in the sample and in the graphite die. As a result, the sample can be sintered uniformly and rapidly. In this work, we report results on the sintering of rutile titanium oxide by the HFIHS method. The goal of this work is to produce dense, ultra-fine TiO₂ ceramics in relatively short sintering times. In addition we report on the effect of sintering temperature and mechanical pressure on the sintering behavior and on the mechanical properties of the densified TiO₂ materials.

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Experimental Procedure

The anatase titanium oxide powder used in this research was supplied by Nanostructured and Amorphous Materials, Inc. (Houston, TX, USA). The powder had a grain size of 5 nm measured by specific surface area (SSA) and was reported to be 99% pure. The crystalline phase consisted of a tetragonal phase according to the supplier's information and as verified by X-ray analysis.

The TiO_2 powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the high-frequency induction-heated sintering system (Eltek Co., Korea). A schematic diagram of this method is shown in Figure 1. The system was first evacuated and a uniaxial pressure of 80 MPa or 100 MPa was applied. An induced current (frequency of about 50 kHz) was then activated and maintained until the densification rate was negligible, as indicating by the observed shrinkage of the sample. Sample shrinkage was measured in real time by a linear gauge measuring the vertical displacement. Temperatures were measured by a pyrometer focused on the surface of the graphite die. A heating rate of $200^\circ\text{C}/\text{min}$ was used in this study. At the end of the process, the induced current was turned off and the sample was allowed to cool to room temperature. The process was carried out under a vacuum of 5.33 Pa.

The relative densities of the sintered samples were measured by the Archimedes method. Microstructural information was obtained from product samples, which had been polished and fractured. Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with an energy dispersive spectro-

scope (EDS). Vickers hardness was measured by performing indentations at a load of 10 kg_f and a dwell time of 15 s. The oxide grain size, d_{wc} was obtained by the linear intercept method [19, 20].

Results and Discussion

The variations of shrinkage displacement and temperature with heating time during the sintering of TiO_2 ceramics under 100 MPa pressure are shown in Figure 2. As the induced current is applied, the shrinkage displacement increased with temperature up to about 750°C . When the temperature reaches 800°C , the densification rate becomes nearly negligible, and as will be seen later, the samples have densified to 98% of theoretical density in about 5 minutes at 830°C . The XRD patterns of TiO_2 powder before (as-received) compaction and after sintering at 830°C are shown in Figure 3. Here anatase can be observed only in the pristine sample. The transition from anatase to rutile of the sample can be identified easily.

Figure 4 shows the densities of the TiO_2 samples as a function of the sintering temperature for a constant holding time of 5 minutes and a heating rate of $200^\circ\text{C}/\text{min}$ for samples sintered under pressures of 80 and 100 MPa. For the case of 80 MPa, the results show that significant densification is obtained only when the temperature is above 1000°C . If the sintering temperature is higher than 900°C , however, significant grain growth can occur, as shown in Figure 5. So, the sintering temperature should be maintained below 850°C to control the grain growth of the product. Figure 4 also shows the influence of the applied pressure on the density. The higher pressure resulted in a higher density as well as a lower sintering temperature. Using 100 MPa pressure, a nearly fully dense sample can be obtained at

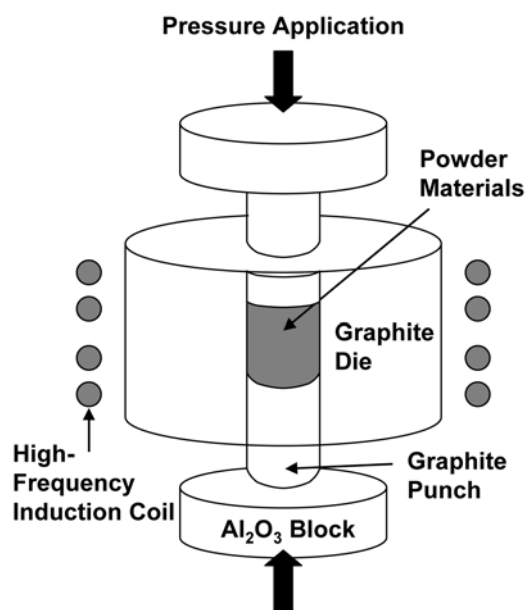


Fig. 1. Schematic diagram of apparatus for high-frequency induction heated sintering.

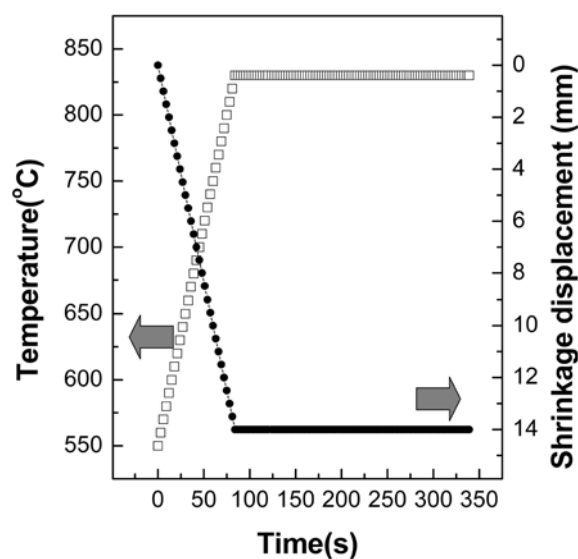


Fig. 2. Variations of temperature and shrinkage displacement with heating time during sintering of TiO_2 ceramics (under 100 MPa pressure, 830°C for 5 minutes).

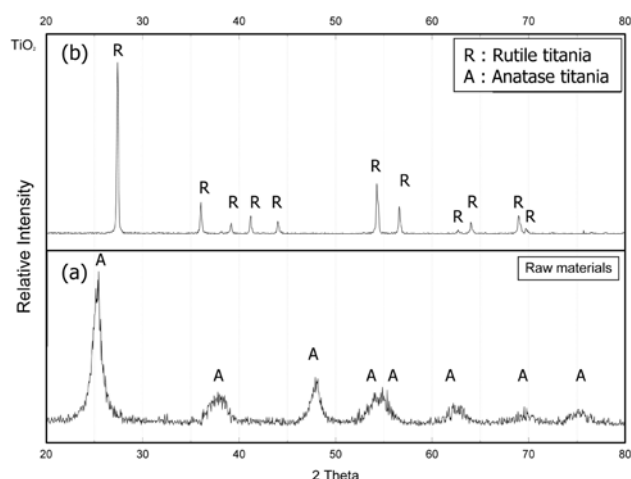


Fig. 3. XRD patterns of TiO_2 ceramics. (a) Raw materials and (b) sintered sample at 830 °C under 100 MPa.

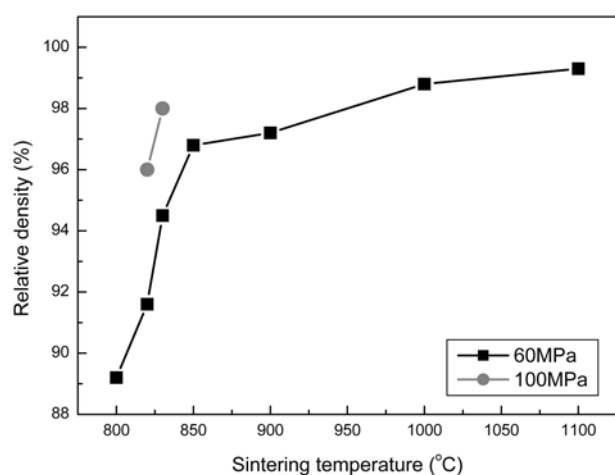


Fig. 4. Relative densities of samples sintered at different temperatures under two levels of applied pressure. The holding time was 5 minutes and heating rate 200 °C/min.

830 °C with a 5 minutes holding time.

As the sintering temperature is increased from 800 to 1100 °C, an increase in grain size was observed. This is seen from the SEM images of fracture surfaces of samples sintered at various temperatures for 5 minutes with a pressure of 80 MPa, as shown in Figure 5. This figure shows that the grain size was noticeably different depending on the sintering temperature. As can be seen from this figure, the TiO_2 grains of the raw material are generally round and exhibit some agglomeration. The initial particle size measured by a linear intercept method and XRD was just below 10 nm. The average sizes of TiO_2 grains determined by the linear intercept method were about 80, 700, 720, 2550 and 3140 nm for samples produced by HFIHS at 800, 850, 900, 1000 and 1100 °C for 5 minutes, respectively. Sintering between 800 and 850 °C, an abrupt grain growth was observed and the fracture surface of specimens changed to faceted grains. To reduce the grain size and increase relative densities, the sintering temperature was carefully

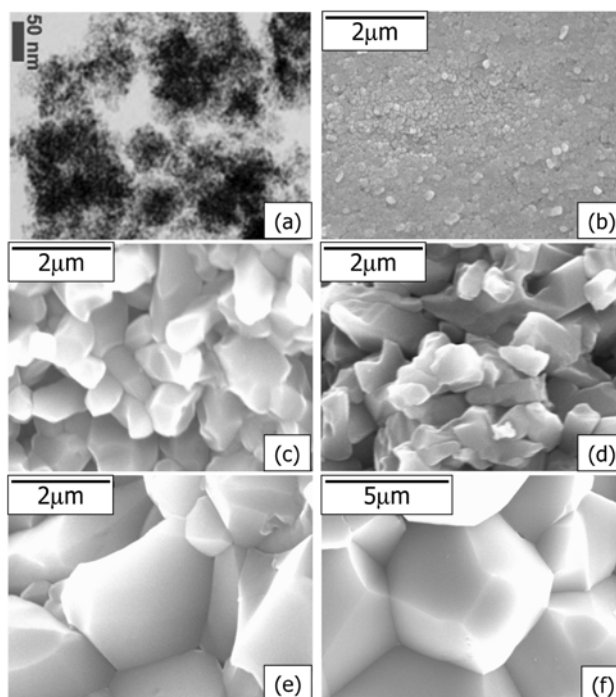


Fig. 5. SEM images of TiO_2 ceramics (a) raw materials, sintered at (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 1000 °C and (f) 1100 °C under 80 MPa.

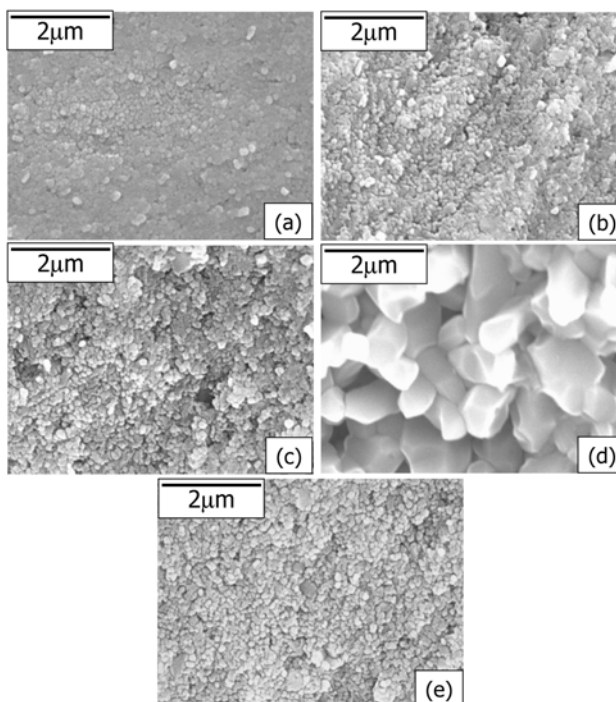


Fig. 6. SEM images of TiO_2 ceramics sintered at (a) 800 °C, (b) 820 °C, (c) 830 °C, (d) 850 °C under 80 MPa and (e) 830 °C under 100 MPa.

controlled and the applied pressure was increased from 80 to 100 MPa. When the sintering temperature was 830 °C for 5 minutes and the applied pressure was 100 MPa, a 160 nm grain sized TiO_2 ceramic with 98% theoretical density was obtained as shown in Figure 6.

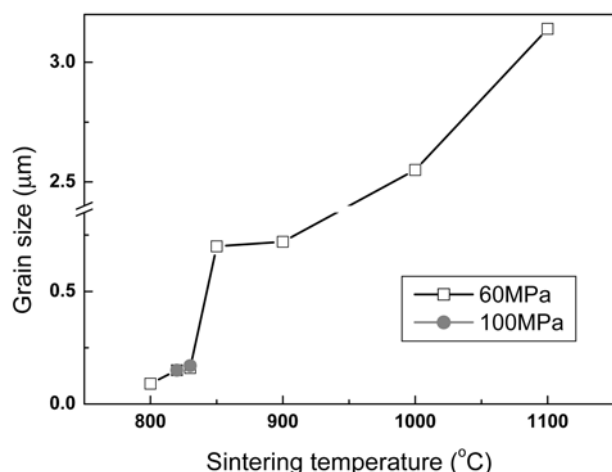


Fig. 7. Dependence of grain size of TiO₂ on sintering temperature and applied pressure.

The dependence of grain size on sintering temperature is shown in Figure 7. A grain size of less than about 250 nm could be obtained only at temperatures below 830 °C. Sintering at higher temperatures resulted in a dramatic increase in grain size, and for the highest temperature, 1100 °C, the size is greater than about 3 μm.

A nanostructured TiO₂ ceramic is of great importance in the low-temperature creep and electrical properties of TiO₂. For example, it has been reported that the specific grain boundary resistivity of TiO₂ significantly decreased with decreasing grain size [21]. To reduce the grain size and to increase the density, a higher mechanical pressure of 100 MPa was used. In the case of 80 MPa pressure, it was not possible to obtain fully dense samples at sintering temperatures below 850 °C. With a pressure of 100 MPa, however, fully dense samples with a grain size of about 160 nm could be obtained, as shown in Figure 6.

That the applied pressure has a significant influence on the densification process is clearly demonstrated by the results shown in Figure 4. At 830 °C, the final relative density of the samples increased from about 94% to about 98% as the applied pressure increased from 80 to 100 MPa. However, Figure 7 also shows that the pressure has apparently no effect on the grain size over the range investigated, between 80 and 100 MPa. The application of pressure during the initial stage sintering adds another term to the surface energy driving force such that the total driving force, F_D , is now [22]:

$$F_D = \gamma + (P_a r / \pi), \quad (1)$$

where γ is the surface energy, P_a is the applied pressure, and r is the radius of the particle. The effect of pressure on the densification of nanometric, undoped zirconia during sinter-forging was investigated by Skandan et

Table 1. Hardness and toughness values of TiO₂ produced by HFIHS at 830 °C for 5 minutes

Applied pressure (MPa)	Hardness (GPa)	Toughness (Niihara et al. [25], MPa·m ^{1/2})	Toughness (Anstis et al. [24], MPa·m ^{1/2})
80	8.2	2.6	2.1
100	12.8	3.9	3.1

al. [23]. A significant increase in the relative density was observed as the pressure was increased from about 35 to 300 MPa for sintering at 950 °C for 180 minutes.

To investigate the mechanical properties, Vickers hardness and fracture toughness measurements were made on polished sections of the TiO₂ ceramics using a 10 kg_f load and 15 s dwell time. The mechanical properties were investigated on samples densified under 80 and 100 MPa with a heating rate of 200 °C/min and a holding time of 5 minutes at 830 °C. The hardness values obtained under two mechanical pressures are 8.2 GPa and 12.8 GPa, respectively, as shown in Table 1. Indentations with large enough loads produced radial cracks emanating from the corners of the indent. Fracture toughness was calculated from cracks produced in indentations under large loads. From the length of these cracks, fracture toughness values can be determined using two expressions. The first expression, proposed by Anstis et al. [24], is :

$$K_{IC} = 0.016 (E/H_v)^{1/2} P/C^{3/2} \quad (2)$$

where E is Young's modulus (TiO₂=280 GPa), H_v the indentation hardness, P the indentation load, and C the trace length of the crack measured from the center of the indentation. The second expression, proposed by Niihara et al. [25, 26], is :

$$K_{IC} = 0.203 (c/a)^{-3/2} H_v a^{1/2} \quad (3)$$

where c is the trace length of the crack measured from the center of the indentation, a half of the average length of two indent diagonals, and H_v the hardness.

Typically, one to three additional cracks were observed to propagate radially from the indentation. As in the case of hardness values, the toughness values were derived from the average of five measurements and investigated on samples densified under 80 and 100 MPa at 830 °C for 5 minutes. The results are also presented in Table 1. Two sets of fracture toughness values are shown in this table, as calculated by the two relationships cited above. The toughness values obtained by the two methods of calculation are 3.1 and 3.9 MPa·m^{1/2}, respectively. The hardness and fracture toughness increased with increasing applied pressure. It is considered that the improvements in properties are due to the higher density of the samples with a similar grain size.

Summary

Using the high-frequency induction heated sintering (HFIHS) method, rapid consolidation of ultra-fine TiO₂ was accomplished. TiO₂ with a relative density up to 98% and a grain size of about 160 nm could be obtained with simultaneous application of 100 MPa pressure and induced current. The influence of sintering temperature and mechanical pressure on the final density and grain size of products were investigated. With an increase in the sintering temperature, the relative density and grain size increased. Increasing the applied pressure resulted in a decrease in the required sintering temperature and an increase in the relative density. However, the pressure had no apparent effect on the grain size. The hardness and fracture toughness of the dense TiO₂ ceramics produced by HFIHS were 12.8 GPa and 3.1 MPa m^{1/2}, respectively for sintering with a pressure of 100 MPa at 830 °C for 5 minutes.

Acknowledgements

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