Ceramic Engineering 111
Sintering

By:

William G. Fahrenholtz

Ceramic Engineering Department
University of Missouri-Rolla
Rolla, MO 65409

January 5, 2004

Signature Here
William Fahrenholtz

The Abstract is a short summary of what you did and what you learned. The abstract should tell readers three things: 1) what you did; 2) how you did it; and 3) your most important conclusion. You should include some quantitative examples from your results in your abstract. Potential readers will scan an abstract to determine if they want to spend the time to read an entire document. Make sure your abstract includes the one fact that you want people to get from your work. Hopefully, this will convince the reader to examine the whole document.

In general, the abstract is written last. For me, the abstract is the most difficult section to write.

For a longer document, you might include a table of contents after the abstract, but that is not necessary for our lab reports.

Abstract

TiO_2 pellets were examined to determine the effect of green density, firing time, and firing temperature on the fired density and average grain size. Pellets were prepared by dry pressing a granulated ceramic powder. Two pressing pressures were used to produce pellets with different green densities. Pellets pressed at 7 MPa (1000 psi) had an average relative density 40% while those pressed at 70 MPa (10,000 psi) had an average green density of 45%. Three different time-temperature combinations were used for the heat treatments, 1250°C for 30 minutes, 1400°C for 30 minutes and 1400°C for 4 hours. The density of fired pellets was determined using Archimedes' technique. It was found that pellets with a higher green density had a higher fired density, compared to pellets with low green density, for the same sintering time and temperature. The relative density of sintered TiO_2 pellets increased from 73% to 91% when the sintering temperature was increased from 1250°C to 1400°C. Finally, an increase in the sintering time from 30 minutes to 4 hours at 1400°C increased in grain size by more than a factor of 2, but increased the relative density by only 5 percent.

The data collected and analyzed in this study can be used to control the microstructure and, therefore, the properties of fired TiO_2. Two different routes were used to sinter pellets to around 90% relative density: 1) firing high green density pellets for 30 minutes at 1400°C or 2) firing low green density pellets for 240 minutes at 1400°C. The grain size of pellets produced at condition 1 had a grain size of 7.9 μm while those prepared at condition 2 had a grain size of 15.3 μm.

Introduction

Heat treatment is one of the final step in the ceramic fabrication process. Ceramic powder compacts undergo several significant changes during heat treatment, including binder burnout, chemical reactions (e.g. decomposition, oxidation), phase transformations, and sintering.[1] Sintering is a diffusional process that proceeds at relatively high temperatures, usually between 1/2 and 3/4 of the melting temperature of the ceramic.[2] During sintering, material is transported to inter-particle necks to build a strong ceramic bond. The goal of the sintering step is to convert a porous powder compact into a useful part. For a few ceramics such as porous insulating refractories, this means vapor phase transport of material that builds strong necks without a significant increase in bulk density.[3] In contrast, many ceramics undergo a significant increase in density during sintering that is crucial for developing desirable properties such as mechanical strength, optical translucency, or dielectric constant.[2] Examples of neck growth during non-densifying and densifying sintering are shown in Figure 1.

$$(a) \qquad\qquad (b) \qquad\qquad (c)$$

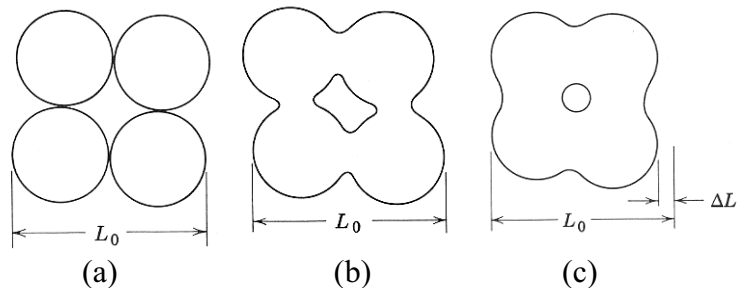Figure 1. Schematic representations of a) a powder compact, b) non-densifying neck growth, and c) densifying neck growth.

Barsoum defines solid-state sintering as the process that converts powder compacts to strong, dense ceramics.[2] During sintering, several material transport mechanisms may be active. These are summarized in Table I. To increase the density of a powder compact, material must be

Table I. Material Transport Mechanisms During Sintering.[3]

Method	Transport	Source	Sink	Densify
1	Surface Diffusion	Surface	Neck	No
2	Lattice Diffusion	Surface	Neck	No
3	Vapor Transport	Surface	Neck	No
4	Boundary diffusion	Grain Boundary	Neck	Yes
5	Lattice Diffusion	Grain Boundary	Neck	Yes
6	Lattice Diffusion	Dislocations	Neck	Yes

transported from between the particle centers to the neck region. Necks form as material deposits near the original point of contact between two powder particles.[1]   Methods 1-3 are coarsening mechanisms that only promote the growth of necks. They do not increase the density of the compact because the source of material is the particle surface. Mechanisms 4-6 increase the density of a compact by removing material from between the particle centers and depositing it at the neck. As the bulk density of the ceramic powder compact increases, individual grains begin to grow. This phenomenon is known as grain growth. Typically, the grain size of a dense ceramic is 10 to 100 times greater than the original particle size of the compact. Large grains tend to grow at the expense of smaller ones.[3]

Many ceramics cannot be sintered to full density. In effect, an ultimate sintered density exists for most materials. Above some threshold, densification proceeds slowly compared to grain growth.[3] To maximize the useful properties of most ceramics, it is desirable to maximize density while keeping grain size to a minimum.[1] This can require a compromise between density and grain size. As such, it is often necessary to characterize the average grain size of fired ceramics. One technique for doing this is the lineal intercept method.[3]   Lineal

analysis assumes that the average grain volume, average cross sectional area, and average lineal intercept length are equivalent, an assumption that requires counting of 500 or more grains for statistical accuracy.[3] The lineal intercept method calculates the grain size of a sample from representative micrographs of polished cross sections.[3] First, horizontal lines are drawn across micrographs at random intervals. Next, the total number of times these lines intercept grain boundaries is counted. Dividing the total line length by the number of intercepts gives the number of intercepts per unit length. It is important that the line length is converted to the magnification of the micrograph. Making the assumption that the grains are uniform (i.e., roughly spherical) in shape, the average grain diameter is 3/2 of the average intercept length. Other assumptions are made for different grain shapes such as rods or platelets.

Accurate density measurements are an important part of characterizing the physical properties of ceramics. In this experiment, the density of as-pressed pellets was calculated from the sample mass and volume. Mass was measured using a digital balance and sample volume was calculated from the external dimensions of the samples, which were right regular cylinders. A liquid displacement method, Archimedes' technique, was used to determine the density of fired pellets. The bulk density of the sample was calculated from precise measurements of the dry, saturated, and suspended weight. Bulk density is the weight of an object divided by the bulk volume, V_b, the volume of solid plus all open and closed pores. According to the Archimedes' theorem, the bulk density of a solid is given by Equation 1:

$$\rho_{bulk} = \frac{w_{dry} \sum \rho_{liq}}{w_{sat} - w_{susp}} \tag{1}$$

Where: ρ_{bulk} is the bulk density of the sample
w_{dry} is the dry weight
ρ_{liq} is the density of the saturating/suspending liquid
w_{sat} is the saturated weight
w_{susp} is the suspended weight.

The volume of open and closed pores can also be calculated using Archimedes' measurements. The volume of open pores, V_O, is given by Equation 2:

$$V_o = \frac{w_{sat} - w_{dry}}{\rho_{liq}} \qquad (2)$$

The volume of closed pores can be calculated only if the theoretical density, TD, of the material is known. 4.26g/cm^3 is the theoretical density of TiO_2 in the rutile form.[4] The dry weight divided by the theoretical density gives the true volume, V_t. True volume is the volume of solid in the pellet. The volume of closed pores, V_{cp}, is then:

$$V_{cp} = V_b - V_o - V_t \qquad (3).$$

Where: $V_b = (w_{sat} - w_{susp})/\rho_{liq}$.

The purpose of this experiment was to determine the effect of green density, firing time, and firing temperature on the sintered density and final grain size of TiO_2 pellets. Understanding the relationship between the process variables and the properties of the fired ceramic is the essence of ceramic science and engineering.

Procedure

Sintering Study

TiO$_2$ pellets were prepared by dry pressing a ceramic powder that was pan-granulated using polyvinyl alcohol (PVA) binder (Elvanol fully hydrolyzed PVA, DuPont, Wilmington, DE). The details of powder preparation are given elsewhere.[5] Pellets were formed by pressing (Model 3853, Carver Laboratory Equipment, Wabash, IN) approximately 1.0 g of powder in a 12.7 mm (1/2 inch) diameter hardened steel die. Two different pressing pressures were used to produce pellets with different green densities. 7 MPa (1000 psi) was selected as the lower pressure because this pressure corresponded to the lowest reproducible load that could be applied with the press. The higher pressure used was 70 MPa (10,000 psi). Above 70 MPa, pellets often fractured during ejection from the die or handling due to pressing defects. The density of each pellet was calculated from its mass[*] and external dimensions.[†] Pellets were fired in air in a furnace equipped with MoSi$_2$ heating elements (Model LZ160, Lindbergh, Inc., Asheville, NC). Zirconia setters were used to hold the pellets. The sintering conditions were 1200°C for 30 minutes, 1400°C for 30 minutes, or 1400°C for 4 hours. The heating rate was 5°C/min while the cooling rate was 20°C/min.

Characterization

The density of fired pellets was determined by Archimedes' technique.[6] Pellets were weighed dry, then saturated with kerosene under vacuum until all bubbling ceased. The suspended weight was measured by hanging a saturated pellet from the balance into a beaker of kerosene. Next, the saturated weight was measured by removing a pellet from the saturating liquid, lightly wiping it to remove excess kerosene

---

[*] BB2440, Mettler Instrument Co., Hightstown, NJ.
[†] Metric Dial Caliper, Scienceware, Pequannock, NJ.

from the surface, then quickly transferring it to the balance. The bulk density was calculated using Archimedes' relations. Kerosene density, measured by liquid pycnometry, was 0.7878 g/cm^3.

The microstructure of fired pellets was examined using a scanning electron microscope (Model T330A SEM, JEOL, Tokyo, Japan). SEM observations were made on the surface of a sintered sample and on a fracture surface. Observations on the sintered surface were used to calculate an average grain size using the lineal intercept method.[3] At least 100 intercepts were counted on each sample. Fracture surfaces were examined to determine the distribution of porosity within the sample and to examine the fracture path.

Results

Table II. Green Density of TiO$_2$ Pellets Pressed at 1000 psi.

Pellet	Mass (g)	Mass of TiO$_2$ (g)	Thickness (mm)	Diameter (mm)	Density (g/cm^3)	Percent Theoretical
L1	1.00	0.95	4.46	12.7	1.68	39.5%
L2	1.00	0.95	4.35	12.7	1.72	40.5%
L3	1.00	0.95	4.37	12.7	1.72	40.3%
L4	1.00	0.95	4.38	12.7	1.71	40.2%
L5	1.00	0.95	4.42	12.7	1.70	39.8%
L6	1.00	0.95	4.36	12.7	1.72	40.4%
L7	1.00	0.95	4.39	12.7	1.71	40.1%
L8	1.00	0.95	4.42	12.7	1.70	39.8%
L9	1.00	0.95	4.38	12.7	1.71	40.2%
L10	1.00	0.95	4.44	12.7	1.69	39.6%
L11	1.00	0.95	4.37	12.7	1.72	40.3%
L12	1.00	0.95	4.41	12.7	1.70	39.9%

Average　40.0%
Standard Deviation　0.31

Table III. Green Density of TiO$_2$ Pellets Pressed at 10,000 psi.

Pellet	Mass (g)	Mass of TiO$_2$ (g)	Thickness (mm)	Diameter (mm)	Density (g/cm^3)	Percent Theoretical
H1	1.00	0.95	4.01	12.7	1.87	44.3%
H2	1.00	0.95	3.90	12.7	1.92	45.0%
H3	1.00	0.95	3.92	12.7	1.91	44.9%
H4	1.00	0.95	3.93	12.7	1.91	44.8%
H5	1.00	0.95	3.97	12.7	1.89	44.3%
H6	1.00	0.95	3.91	12.7	1.92	45.0%
H7	1.00	0.95	3.94	12.7	1.90	44.7%
H8	1.00	0.95	3.97	12.7	1.89	44.3%
H9	1.00	0.95	3.93	12.7	1.91	44.8%
H10	1.00	0.95	3.99	12.7	1.88	44.2%
H11	1.00	0.95	3.92	12.7	1.91	44.8%
H12	1.00	0.95	3.96	12.7	1.89	44.5%

Average　44.6%
Standard Deviation　0.29

Table IV. Density of TiO$_2$ Pellets Sintered at 1250°C for 30 minutes.

Pellet	Dry Weight (g)	Suspended Weight (g)	Saturated Weight (g)	Bulk Density (g/cm^3)	Percent Theoretical
H1	0.95	0.77	1.01	3.11	73.0%
H5	0.95	0.77	1.02	3.07	72.0%
H9	0.95	0.77	1.01	3.15	74.0%
H12	0.95	0.77	1.02	3.07	72.0%
L1	0.95	0.77	1.03	2.94	69.0%
L4	0.95	0.77	1.02	3.02	71.0%
L5	0.95	0.77	1.03	2.90	68.0%
L9	0.95	0.77	1.02	3.02	71.0%

Table V. Density of TiO$_2$ Pellets Sintered at 1400°C for 30 minutes.

Pellet	Dry Weight (g)	Suspended Weight (g)	Saturated Weight (g)	Bulk Density (g/cm^3)	Theoretical Density
H2	0.95	0.77	0.96	3.83	90.0%
H6	0.95	0.77	0.96	3.88	91.0%
H8	0.95	0.76	0.96	3.83	90.0%
H10	0.95	0.76	0.96	3.79	89.0%
L2	0.95	0.76	0.96	3.66	86.0%
L6	0.95	0.76	0.96	3.71	87.0%
L8	0.95	0.76	0.97	3.62	85.0%
L10	0.95	0.76	0.97	3.66	86.0%

Table VI. Density of TiO$_2$ Pellets Sintered at 1450°C for 4 hours.

Pellet	Dry Weight (g)	Suspended Weight (g)	Saturated Weight (g)	Bulk Density (g/cm^3)	Theoretical Density
H3	0.95	0.77	0.95	4.09	96.0%
H4	0.95	0.77	0.95	4.13	97.0%
H7	0.95	0.77	0.95	4.09	96.0%
H11	0.95	0.77	0.95	4.05	95.0%
L3	0.95	0.76	0.95	3.92	92.0%
L7	0.95	0.76	0.95	3.92	92.0%
L11	0.95	0.76	0.95	3.96	93.0%
L12	0.95	0.77	0.95	4.09	96.0%

Table VII. Average Sintered Density of Pellets.

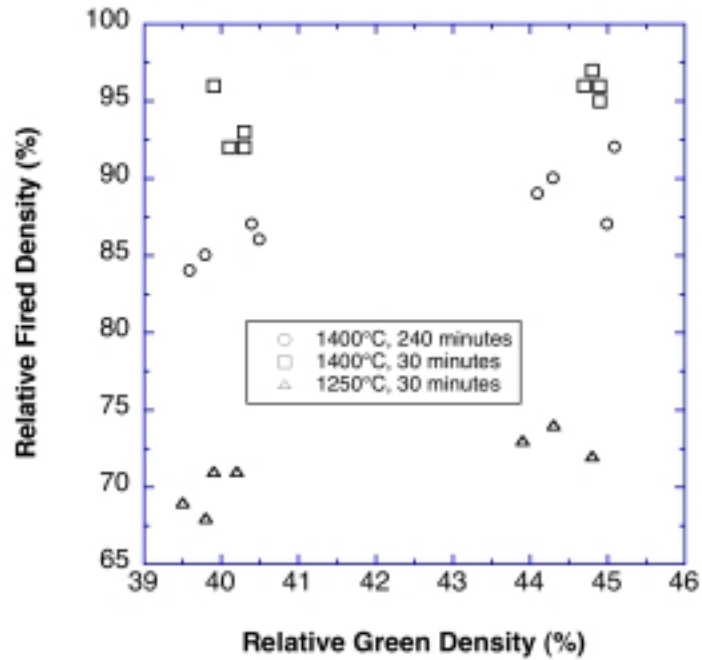| Green Density (g/cm³)	Sintering Temp. (°C)	Sintering Time (min)	Average Relative Density	Standard Deviation
H	1250	30	72.8%	0.96
L	1250	30	69.8%	1.50
H	1400	30	90.7%	0.82
L	1400	30	85.5%	1.29
H	1400	4	96.0%	0.82
L	1400	4	93.3%	1.89

Figure 2.   The fired density as a function of green density for TiO_2 pellets.
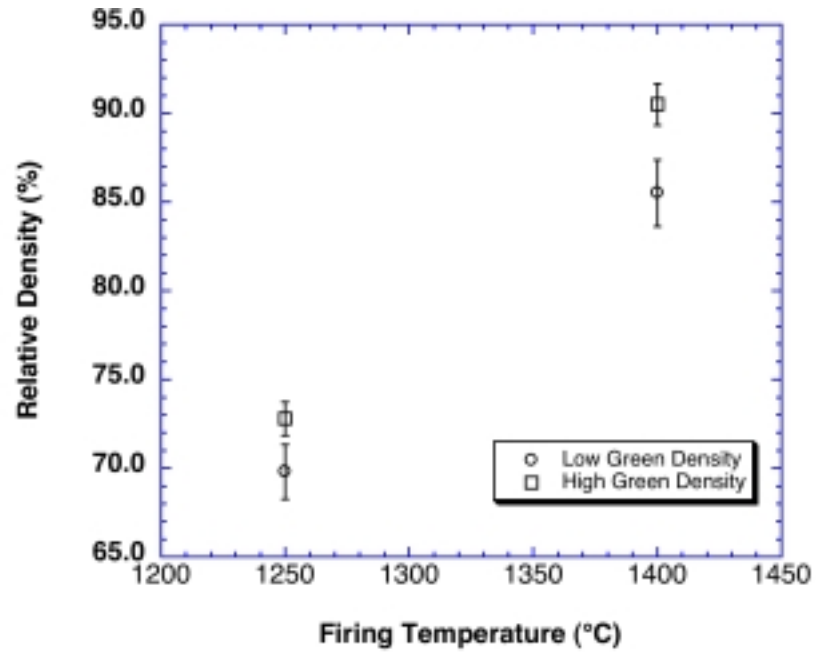
Figure 3. The average bulk density of TiO$_2$ pellets sintered for 30 minutes at 1250°C or 1400°C.
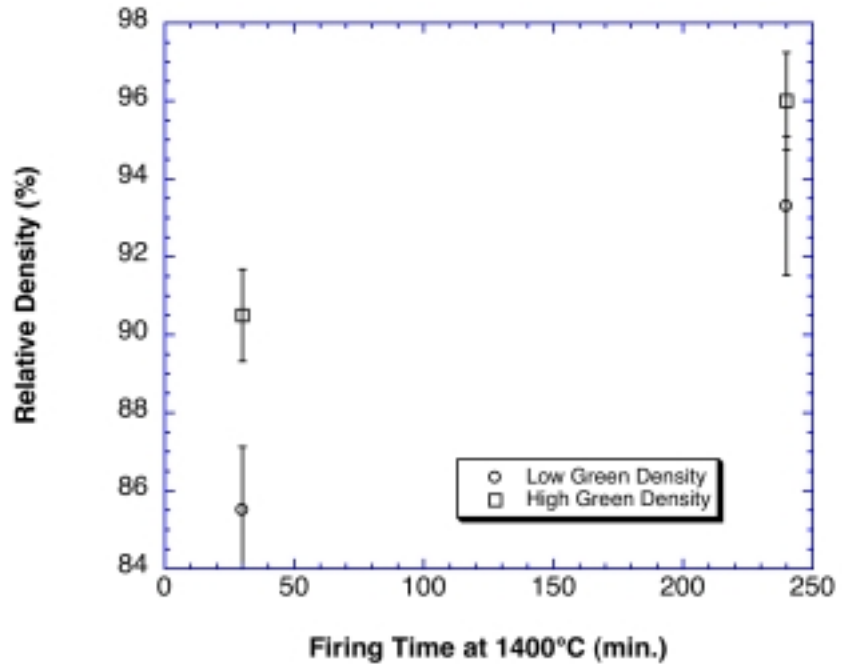

Figure 4. The average bulk density of TiO$_2$ pellets sintered at 1400°C for 30 or 240 minutes.
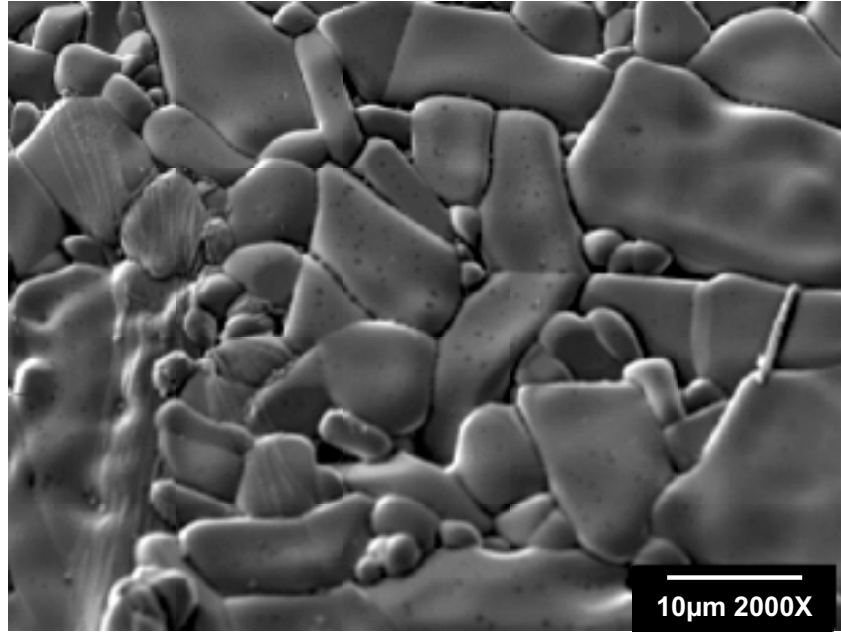
Figure 5.   A representative micrograph of the surface of a high green density TiO_2 pellet fired at 1400°C for 30 minutes
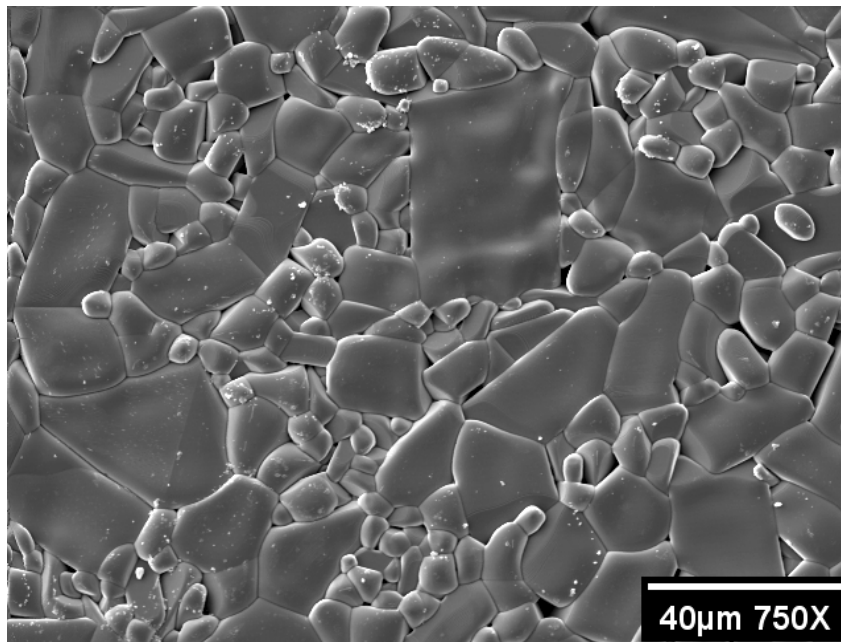

Figure 6.   A representative micrograph of the surface of a high green density TiO_2 pellet fired at 1400°C for 4 hours.
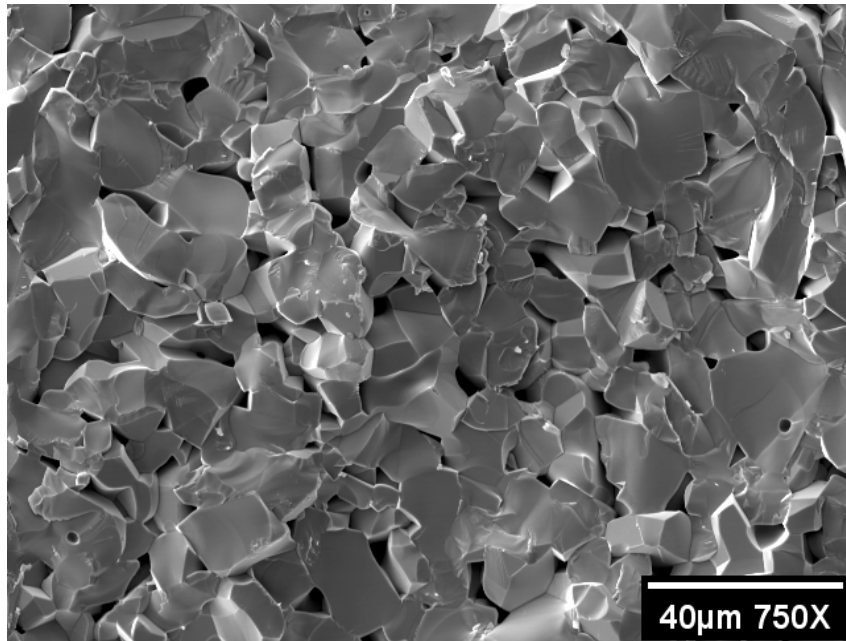
Figure 7.   A representative micrograph of a fracture surface of a TiO$_2$ pellet fired at 1400°C for 4 hours.

Discussion of Results

The Effect of Green Density

    Two different pressing pressures were used to prepare pellets for this study, 7 MPa (1000 psi) and 70 MPa (10,000 psi). Between these limits, pellets were defect-free and had sufficient green strength for handling. Below 7 MPa, it was difficult to reproduce the load on the press, resulting in variations in green density. Above 70 MPa, pressing defects, mainly capping, were present in most of the pellets. At 7 MPa, the average green density was 40.0% with a standard deviation of 0.31. At 70 MPa, the average density was 44.6% with a standard deviation of 0.29. The variability at the higher pressure is less, presumably due to the fact that the same absolute error in the press load at 70 MPa produces a lower percentage variability than the same error in load at 7 MPa. In other words, if the gauge on the press has an accuracy or reproducibility of ±1 MPa, the error is ±14% at 7 MPa but only ±1.4% of 70 MPa. The green density data for individual pellets is given in Tables II and III.

    The green density had a significant effect on the fired density of pellets. In Figure 2, the fired density is given as a function of green density. At all of the firing times and temperature, pellets with a higher green density had a higher fired density. For example, the average green density of pellets fired at 1400°C for 30 minutes was 40.1% for those pressed at 7 MPa and 44.6% for those pressed at 70 MPa. After firing at 1400°C for 30 minutes, the low pressure pellets fired to an average density of 85.5%, but the high green density pellets fired to 90.5%. The same is true for each firing time and temperature. The density increase is thought to be due to more complete and more uniform compaction at the higher pressing pressure. Green density measurements show that the high pressure pellets have a higher green density. Examination of the

microstructure of green pellets could confirm or refute the assertion that they have a more uniform microstructure, but that was beyond the scope of this study.

The Effect of Sintering Temperature

The sintering temperature had a dramatic effect on the final density of fired TiO_2 pellets. After sintering at 1250°C for 30 minutes, the average density was 73% for pellets pressed at 70 MPa. High green density pellets sintered at 1400°C for 30 minutes had an average density of 91%. The effect of firing temperature is summarized in Table VII and shown graphically in Figure 3. Archimedes' density data show a significant amount of open porosity in the 1250°C samples, an average of almost 30% by volume, with no closed porosity. In contrast, samples sintered at 1400°C had no open porosity and less than 10% by volume closed pores. Figure 1 shows a fracture surface of a pellet with high green density sintered at 1400°C for 240 minutes. The fracture surface shows all closed porosity. No evidence for open porosity or connected pore channels was found in samples sintered at 1400°C for 30 or 240 minutes either on fracture surfaces as shown in Figure 7 or on the sintered surfaces shown in Figures 5 and 6.

The Effect of Firing Time

An increase in the firing time from 30 to 240 minutes at 1400°C increased the average density by approximately 5%, shown in Table VII and Figure 4. Again, samples that had a higher green density had a higher fired density. In this case, the pellets with a high green density that were sintered at 1400°C for 30 minutes had about the same fired density as pellets with a low green density that were fired at 1400°C for 240 minutes.

Increasing the firing time also increased the average grain size of the pellets. For high green density pellets fired at 1400°C, the average grain size was 7.9 μm for pellets fired for 30 minutes, but that increased

to 15.3 μm for pellets fired for 240 minutes. The average grain size was determined by the lineal intercept method counting at least 200 intercepts using the micrographs presented in Figures 5 and 6. Note that the magnification of the micrograph in Figure 5 is much greater than that used for Figure 6.

The Summary and Conclusions should highlight your most important results. Tell us what you did and why it is significant. Include specific values from your results and discussion in the summary. For example, instead of saying "TiO₂ density increased as sintering temperature increased" try adding data to say that "the density of TiO₂ pellets increased from ~70% after sintering at 1250°C to more than 90% for sintering at 1400°C."

A true summary is a simple recap of the highlights of the study. If you give this section the title of "Summary," you should not make any statements that you have not already made in the body of the report. You should simply summarize what you have written, focusing on the most important parts. If you title this section "Conclusions" you can then draw conclusions from the results and discussion. The difference is subtle in some cases.

Summary and Conclusions

The density and grain size of sintered TiO_2 is affected by the green density of the pellets as well as the sintering time and temperature. Pellets with higher green density sintered to higher density at the same time and temperature. Increasing the sintering temperature from 1250°C to 1400°C increased the sintered density dramatically, from ~70% to over 90%. The increase in relative density was accompanied by a reduction of the open porosity from around 30% to essentially 0. Finally, an increase in the firing time from 30 minutes to 240 minutes at 1400°C increased the sintered density of TiO_2 from 90% to 95%, but increased the average grain size by a factor of 2. The parameters in this study show how to control the microstructure of TiO_2 by varying the green density, firing time, and firing temperature. TiO_2 with the same fired density was prepared by firing high green density pellets at 1400°C for 30 minutes or low green density at 1400°C for 240 minutes. The difference was a doubling of grain size.

References

References should give the reader a roadmap to find the supplemental materials that you have cited. The preferred style is to call the references throughout the text with superscripted numbers and include a list with corresponding numbers at the end of the text. Several representative examples of full bibliographic citations are given.

1. J.S. Reed, Principles of Ceramic Processing, 2nd Ed., Wiley-Interscience, New York, 1995.

2. M. Barsoum, Fundamentals of Ceramics, Chap. 10, McGraw-Hill, New York, 1997.

3. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, Introduction to Ceramics, 2nd Ed., Chap. 10, John Wiley and Sons, New York, 1976.

4. Handbook of Chemistry and Physics, 62nd Ed., p. B-162, The Chemical Rubber Company Press, Boca Raton, FL, 1983.

5. Authors, Lab Group Number, "Die Pressing," Ceramic Engineering 111 Laboratory Report, University of Missouri-Rolla, Fall 1999.

6. N.A. Pratten, "The Precise Measurement of the Density of Small Samples," Journal of Materials Science, **16**, 1737-1747, 1981.

General Comments

Based on lab reports from previous years and feedback from TA' s, professors, and students, I have compiled a list of helpful hints for preparing reports. These are in no particular order.

1. For technical writing, you should write in the third person using past tense and an active voice (see the report writing handout for examples). For this class, you can use phrases like "we did" or "our group found" without penalty. However, it is generally regarded as boastful or egotistic if you do this when preparing a technical paper for presentation or for reports to superiors in industry.

2. The procedure section should not read like an instruction manual. Do not tell the reader what to do. Give a detailed explanation of what you did and the resources (equipment, raw materials) that you used.

3. Whenever you use an acronym or abbreviation, make sure to spell out the entire phrase before you use the shortened version. Examples are given in the body of this document.

4. Try to write your report for an audience that is technically literate, but one that has not just completed this work. If it helps, try to imagine that you are writing for a boss or someone else who is familiar with your field, but that does not know what you do on a day-to-day basis.

5. Try to be concise. You want your report to include all the necessary details, but don't be excessively wordy. Be as descriptive as you can, but don't make it too long.

6. Proofread your work. The spell checker will not catch everything.