

1999-08-16

Synthesis Effects on Grain Size and Phase Content in the Anatase-Rutile TiO₂ System

Kimberly A. Farrell
Worcester Polytechnic Institute

Follow this and additional works at: <https://digitalcommons.wpi.edu/etd-theses>

Repository Citation

Farrell, Kimberly A., "Synthesis Effects on Grain Size and Phase Content in the Anatase-Rutile TiO₂ System" (1999). *Masters Theses (All Theses, All Years)*. 937.

<https://digitalcommons.wpi.edu/etd-theses/937>

This thesis is brought to you for free and open access by Digital WPI. It has been accepted for inclusion in Masters Theses (All Theses, All Years) by an authorized administrator of Digital WPI. For more information, please contact wpi-etd@wpi.edu.

Synthesis Effects on Grain Size and Phase Content in the Anatase-Rutile TiO₂ System

A Thesis

Submitted to the Faculty

of the

Worcester Polytechnic Institute

in partial fulfillment of the requirements for the

Degree of Master of Science

in

Materials Science and Engineering

by

Kimberly A. Farrell

February 2001

Chrysanthe Demetry, Major Advisor

Richard D. Sisson, Jr.

Materials Science and Engineering Program Head

1. Abstract

The phase content and grain size of titanium dioxide often have a strong influence on properties for a variety of applications. In many cases it would be desirable to produce the stable rutile phase with an ultra-fine particle size (<10nm), but most low temperature synthesis methods produce predominantly the metastable anatase phase. The anatase-rutile transformation in TiO₂ is known to be affected by dopant type and concentration, as well as the titanium precursor used in solution chemical synthesis. Recently, use of cavitation in the synthesis process has been shown to yield smaller grain size for a variety of oxides. However, the relative importance of these synthesis variables on the grain size and phase content of TiO₂ is not well understood. In this study, Taguchi analysis was used to determine the relative effects of dopants (Sn), titanium precursor (butoxide, sulfate, chloride), and cavitation power on grain size and phase content. Precursor residuals were also measured by analytical chemistry. Grain size and phase content results were analyzed statistically to determine whether there is a size dependence of the anatase-rutile transformation. Results show that grain size is strongly dependent on the concentration of chlorine. Absent chlorine, a definite grain size-phase content correlation exists; rutile content increases as grain size decreases. An L-4 orthogonal Taguchi analysis shows chlorine content and tin content as the major influences on the final product. With minimum grain size and maximum rutile content being considered optimal, our best result was 100% rutile and an average grain size of 5nm, which was achieved by acoustic synthesis with 3% tin dopant and low residual chlorine.

Table of Contents

1. ABSTRACT.....	2
TABLE OF CONTENTS	3
LIST OF FIGURES.....	4
LIST OF TABLES.....	4
2. INTRODUCTION	5
3. LITERATURE REVIEW	8
3.1 TITANIUM DIOXIDE.....	8
3.2 ANATASE-RUTILE TRANSFORMATION	9
3.2.1 <i>Effect of Impurities/Dopants</i>	11
3.2.2 <i>Effect of Atmosphere</i>	13
3.2.3 <i>Effect of Precursor</i>	15
3.3 EFFECT OF PARTICLE SIZE ON PHASE TRANSFORMATIONS	16
3.4 CAVITATIONAL SYNTHESIS.....	20
3.5 SUMMARY	22
4 EXPERIMENTAL METHODS.....	23
4.1 PREPARATION OF PRECURSOR SOLUTIONS	23
4.1.1 <i>Titanium Precursors</i>	23
4.1.2 <i>Tin Dopant</i>	24
4.2 POWDER PROCESSING.....	25
4.2.1 <i>Classical Synthesis</i>	25
4.2.2 <i>Acoustic Cavitation Synthesis</i>	26
4.2.3 <i>Post-Synthesis Processing</i>	27
4.3 CHARACTERIZATION OF POWDERS	28
4.3.1 <i>X-Ray Diffraction</i>	28
4.3.2 <i>Analytical Composition</i>	29
5 RESULTS AND DISCUSSION	30
5.1 EFFECT OF TITANIUM PRECURSOR.....	30
5.2 EFFECT OF DRYING METHOD.....	31
5.3 EFFECT OF CAVITATION SYNTHESIS	32
5.4 EFFECT OF TIN CONCENTRATION.....	34
5.5 EFFECT OF CHLORINE IMPURITIES.	38
5.6 RELATIVE IMPORTANCE OF SYNTHESIS VARIABLES	42
5.7 ANALYSIS OF POSSIBLE CORRELATION BETWEEN GRAIN SIZE AND RUTILE CONTENT	43
6 CONCLUSIONS	45
7 REFERENCES.....	47
APPENDIX A - SYNTHESIS AND SAMPLE INFORMATION.....	50
APPENDIX B - TAGUCHI ANALYSIS AND APPLICATION	51

List of Figures

Figure 1. A diagram of the anatase crystal [15]	8
Figure 2. A diagram of the rutile crystal [15]	9
Figure 3. Free energy of formation of the anatase and rutile phases of TiO ₂ , as a function of temperature [16]	10
Figure 4. Phase diagram of the SnO ₂ - TiO ₂ system. (The temperatures specified are in °C) [20]	13
Figure 5 - Schematic of experimental setup	26
Figure 6 - XRD plot of the powders from various precursors, after calcining.	31
Figure 7 - Percent rutile present dependent upon synthesis method	34
Figure 8 - Grain size as a function of tin concentration, in samples with high residual chlorine.	35
Figure 9 - Grain size as a function of tin concentration, in samples with low residual chlorine.	36
Figure 10 - Rutile content as a function of tin concentration.	37
Figure 11 - Grain size as a function of chlorine impurities present, high excess chlorine and varying tin content.	38
Figure 12 - Grain size as a function of chlorine impurities present, low excess chlorine and varying tin content.	40
Figure 13 - Rutile content as a function of weight % chlorine, with varying tin.	41
Figure 14 - Rutile content as a function of grain size for variable chlorine and tin concentrations.	44

List of Tables

Table 1 - Powder Characteristics resulting from freeze-drying and thermal-drying the same sample	32
Table 2 - Grain size as a function of synthesis method	33
Table 3 - Taguchi method results	42

2. Introduction

Titanium dioxide as a raw material supports industries worth \$3 billion annually in the United States alone [1]. Although used primarily in the pigment industry for paints and varnishes, paper, cosmetics, and plastics, TiO₂ is also used in catalysts, ceramics, coated fabrics, and roofing granules. The two most common and important phases of TiO₂ are anatase and rutile. Most commercially available titanium dioxide powders are either one of those two phases or a mixture of the two. Since the optical and electrical properties of anatase and rutile are different, it is desirable to be able to control the phase content. While previous studies have shown that method of preparation [2], dopant concentration [3,4], atmosphere [5], and particle size [6,7] can influence the anatase-rutile phase transformation, results have often been contradictory and the relative importance of these variables is not known.

In addition to controlling the phase content, control of grain size is also critical. In recent years, the benefits of nanocrystalline powders have been touted [8,9]. The desire for small-grained rutile powders is driven by their unique material properties, which are desirable in a large variety of industrial applications. Nanocrystalline ceramics have higher electrical conductivity, enhanced ductility, toughness, and formability than their counterparts with larger grain size, as well as increased luminescent efficiency when used in semiconductor applications [9]. Furthermore, since a larger fraction of atoms are at the surface of nanocrystals, they show increased reactivity, which can be applied to oxide sensing devices and catalysts, a field of growing investigation that includes titanium dioxide [10]. While synthesis of anatase with a grain size of less than 15nm is reported fairly often, synthesis of 100% rutile of this grain size is unusual, however.

Thus, both phase content and grain size are important characteristics of titanium dioxide powders. These variables may not be independent, however. A classic study by Garvie [11] showed that phase transformations may have a grain size dependence. He found that the relative stability of the tetragonal and monoclinic phases in the ZrO_2 system is affected by grain size. A critical grain size was proposed to exist, below which the higher temperature tetragonal phase could be made to exist instead of the low temperature monoclinic phase, if the surface free energy of the tetragonal phase were lower than that of the monoclinic phase. While the grain size and amount of rutile present in TiO_2 powders have often been reported in past studies, there are no consistent references in the literature to a possible correlation or interdependence between grain size and the anatase-rutile phase transformation.

Therefore, the goals of this work are two-fold: to improve the understanding of the relative effects of synthesis variables on the phase content and particle size of TiO_2 , and to explore whether there is a grain size dependence of the anatase-rutile phase transformation.

Since there are a multiplicity of synthesis variables that could be studied, the focus had to be narrowed. A solution chemical synthesis method was chosen due to its relative simplicity. The effects of the type of titanium precursor, amount of tin dopant, and drying method were investigated. Tin was chosen as the dopant of most interest due to a past study suggesting that it facilitated the anatase-rutile transformation [12].

Finally, the effect of a relatively new advance in processing – cavitation – was investigated since it has been shown to influence the particle size of other metal oxides [24].

The approach of this study was to synthesize titania powders, measure grain size and phase content, analyze the results to determine the relative influence of the variables, and then to explore any possible correlation between grain size and phase content.

3. Literature Review

3.1 Titanium Dioxide

Titanium dioxide is a ceramic material, commonly known as titania. Although generally used as a white pigment or opacifier, titania can also be applied in enameling and catalysis [13]. Three polymorphs of titanium dioxide exist: brookite, anatase, and rutile. All possess the same empirical chemistry, TiO_2 , but each has a different crystal structure.

Brookite has an orthorhombic crystal structure and spontaneously transforms to rutile around 750°C [13]. Its mechanical properties are very similar to those of rutile, but it is the least common of the three phases and is rarely used commercially.

The predominant commercial phase of titanium dioxide is anatase, although it is rarely found in ore form. It is metastable with respect to rutile under all conditions of temperature and pressure and reverts spontaneously to rutile at temperatures above 915°C [14]. Anatase has a tetragonal crystal structure in which the Ti-O octahedra share four corners, as shown in Figure 1.

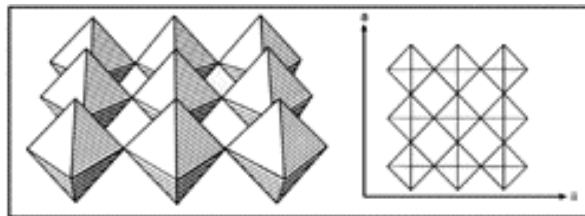


Figure 1. A diagram of the anatase crystal [15]

The stable form of titania is rutile, to which the other forms of titania transform at sufficiently high temperatures. Rutile has a crystal structure similar to that of anatase, with the exception that the octahedra share four edges instead of four corners. This leads

to the formation of chains, which are subsequently arranged in a four-fold symmetry, as shown in Figure 2.



Figure 2. A diagram of the rutile crystal [15]

A comparison of Figure 1 and Figure 2 shows that the rutile structure is more densely packed than anatase. As a point of reference, the densities of the anatase and rutile phases are known to be 3.899g/cm^3 and 4.250g/cm^3 , respectively [14].

3.2 Anatase-Rutile Transformation

The anatase to rutile transformation in titanium dioxide is believed to be spontaneous (i.e., the free energy of rutile is lower than that of anatase at all temperatures), but it is kinetically unfavorable at low temperatures. In a 1967 study, Navrotsky and Kleppa measured the enthalpy of the anatase to rutile transformation and found it to be negative. Since the volume change for the anatase-rutile reaction is always negative, they reported that anatase is metastable with respect to rutile under all conditions of temperature and pressure [14]. This is reinforced by JANAF thermochemical data, which is shown in Figure 3. The JANAF data shows that the free energy of rutile is always less than that of anatase, making rutile the more stable structure at all examined temperatures.

The generally accepted theory of the phase transformation is that two Ti-O bonds break in the anatase structure, allowing rearrangement of the Ti-O octahedra, which leads to a smaller volume and the rutile phase. The breaking of these bonds is accelerated by

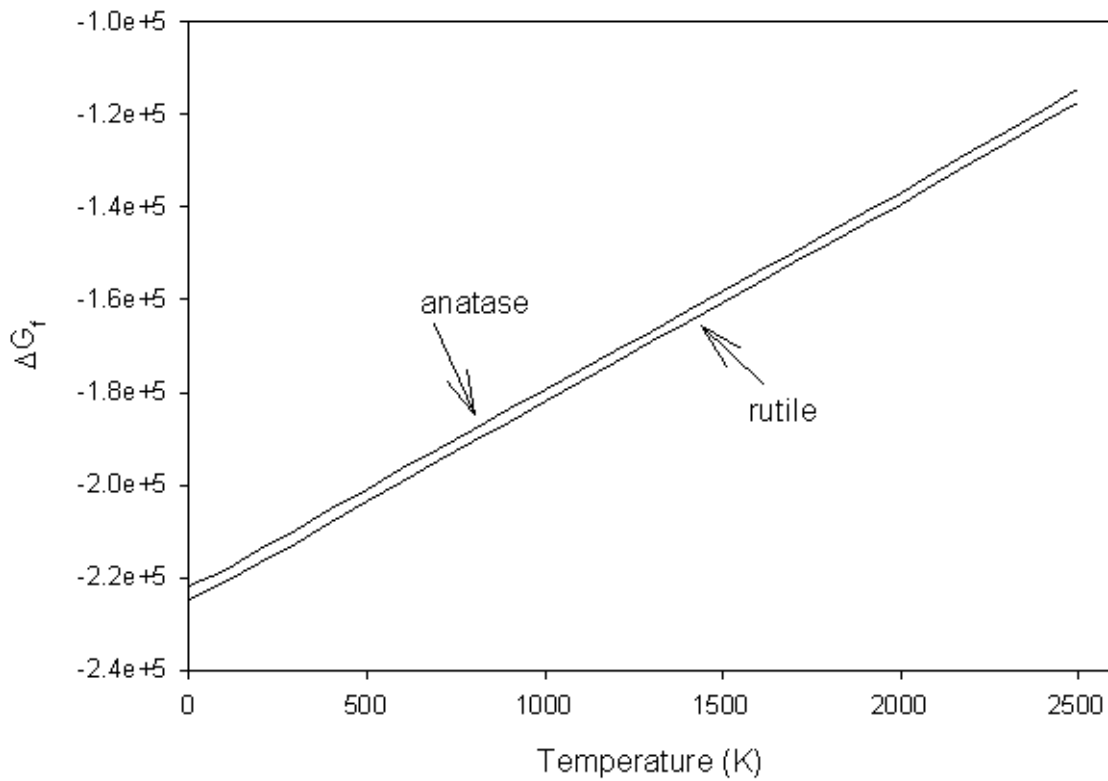
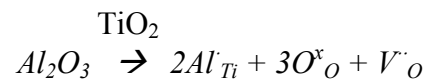


Figure 3. Free energy of formation of the anatase and rutile phases of TiO₂, as a function of temperature [16]

lattice disruptions, which can be introduced in a number of ways, including the addition of dopants, variation in the atmosphere (oxygen partial pressure), and method of synthesis. Past research on the effects of each of these variables will now be summarized.

3.2.1 Effect of Impurities/Dopants

The influence of impurities on the nucleation and growth of rutile from anatase was studied by Shannon and Pask [17]. They concluded that processes that create oxygen vacancies, such as the addition of acceptor dopants (ions with a lower valence than Ti^{4+}) and use of reducing atmospheres accelerate the anatase-rutile transformation. Conversely, processes that increase the concentration of titanium interstitials, such as the addition of donor dopants, inhibit the transformation. Shannon and Pask hypothesized that an increase in the concentration of oxygen vacancies reduces the strain energy that must be overcome before the rearrangement of the Ti-O octahedra can occur, and that cations with a valence less than that of titania (4+) will increase the concentration of oxygen vacancies, due to the necessity for charge balance. For example, the addition of Al_2O_3 as a dopant in TiO_2 may influence the defect chemistry in the following way:



This defect chemical reaction shows that for every mole of Al_2O_3 introduced into the system, one mole of doubly ionized oxygen vacancies are created for charge compensation. (This is only one among many possible defect chemical reactions.)

MacKenzie [3] proposed a rank-ordered list of dopants effective in accelerating the anatase-rutile transformation, on the basis of data collected from the literature. He reported that monovalent ions are more effective than divalent or trivalent ions. When ions of lower valency replace Ti^{4+} in the lattice, anion vacancies that compensate for the different charge disrupt the lattice. Thus, more oxygen vacancies would need to be created for monovalent dopants compared to divalent or trivalent. This effect is offset to

some extent by the greater ease with which higher-charged and consequently smaller ions can fit into the lattice. MacKenzie also reported that the effectiveness of dopants increased with their concentration, up to about 1mole%. The agglomerate size of rutile, as measured by scanning electron microscopy, was seen to be related to additives as well. A possible explanation for this effect is that when rutile nucleates more readily, it has more time to grow and agglomerate than it otherwise would. Agglomerate size is also affected by sintering temperature and time, as well as potential segregation of additives [3].

Seemingly in contradiction to the above studies, Rao et al. [18] reported that the presence of all dopants, both donor and acceptor cations as well as anion dopants, inhibits the anatase-rutile transformation by stabilizing the anatase phase. A correlation between the degree of inhibition and the size of the ions was found, as well as the ionic character of the dopants. Additives with a higher charge seemed to stabilize the anatase phase more strongly than those with a lower charge.

Tin oxide has been used previously as a dopant in titania systems [4]. The coordination number of tin and titanium are the same, and the cation to anion radius ratios are nearly identical, being 0.51 and 0.49, respectively [13]. Since Sn and Ti are isovalent, the addition of SnO₂ does not influence the defect chemistry of TiO₂. However, SnO₂ has a rutile tetragonal crystal structure with no anatase analog and thus can be expected to stabilize the rutile phase in TiO₂. The TiO₂-SnO₂ binary system shows spinodal decomposition with considerable solubility of SnO₂ in TiO₂ at elevated temperatures, as shown in Figure 4.

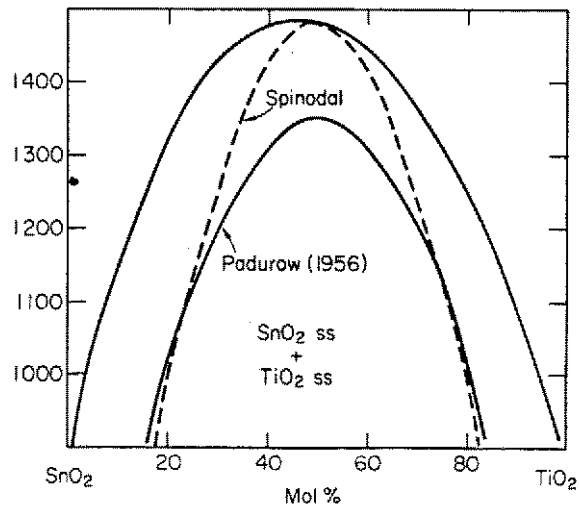


FIG. 5259.—System SnO₂-TiO₂.
D. Garcia and D. Speidel, *J. Am. Ceram. Soc.*, 55 [6] 322 (1972).

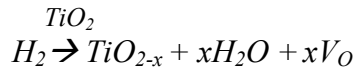
Figure 4. Phase diagram of the SnO₂ - TiO₂ system. (The temperatures specified are in °C) [20]

However, the solubility of Sn in TiO₂ appears to be quite low at the lower temperature (500°C) used in this study, at least for coarse-grained TiO₂. Past work has shown that nanocrystalline grain size can considerably enhance the solubility of dopants, however [19].

3.2.2 Effect of Atmosphere

Several researchers have studied the effects of different atmospheres on the anatase-rutile phase transformation, with somewhat conflicting results. MacKenzie found that reducing atmospheres such as steam, a H₂/N₂ mixture (5%-95%, respectively), and vacuum (10⁻¹Pa) yield the formation of large aggregates of rutile [3]. He again proposed the common theory that these atmospheres enable easier rupturing of two of the six Ti-O bonds in the anatase structure, again by introduction of oxygen vacancies. The

following chemical reaction was proposed to explain the effectiveness of the H₂/N₂ atmosphere:



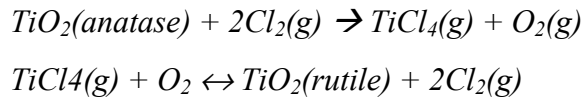
The water vapor evolved from the reaction facilitates the rupture of two of the six Ti-O bonds in the octahedral structure, while the oxygen vacancies provide pathways for the diffusion of ions. MacKenzie found that the use of the H₂/N₂ atmosphere yielded up to 97% rutile with an aggregate size of 3.5µm, while the vacuum and steam atmospheres yielded between 20% and 30% rutile with an aggregate size of 2µm. Similar reactions in air yielded less than 10% rutile. MacKenzie also reported a nearly linear relationship between % rutile in the samples and aggregate size as measured by scanning electron microscopy, such that aggregate size increased with an increasing amount of rutile.

MacKenzie's results are contradicted by those of Czanderna et al, who found that the rate of the anatase-rutile transformation was unaffected by the presence of a vacuum. Furthermore, Shannon and Pask reported that the anatase-rutile transformation was retarded in a vacuum [17]. They proposed that titanium interstitials were created rather than oxygen vacancies, thus inhibiting the transformation instead of facilitating it.

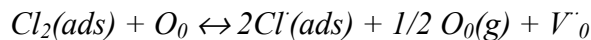
Gamboa and Pasquevich reported on the effect of air/Ar and Cl₂/Ar atmospheres on the anatase-rutile transformation [5]. The samples were calcined in the different atmospheres for a range of times. At 950°C the anatase-rutile transformation was found to be 300 times slower in the air/Ar atmosphere than in the Cl₂/Ar atmosphere. Gamboa and Pasquevich reported that after four hours in either air or Ar, only up to 5% of the anatase transformed to rutile, and that even after 48 hours the transformation was not

complete. This is contradicted in part by the studies of MacKenzie that show 10-15% transformation to rutile within 30 minutes in an air-Ar atmosphere, at 1000°C.

Gamboa and Pasquevich proposed that chlorine assists both vapor mass transport, which is a possible mechanism for nucleation on the solid surface, and oxygen vacancy formation, which assists nucleation and growth in the bulk material. They proposed that when the chlorine partial pressure is sufficiently high, it might assist dissolution of anatase and recrystallization of rutile by the following mechanism:



Therefore, TiCl₄ in the vapor phase may assist nucleation of rutile. When very small quantities of chlorine, on the order of a tenth of a weight percent, are present, however, the amount of TiCl₄ formed is negligible and the following mechanism was proposed in its place:



The idea of oxygen vacancy formation catalyzing the anatase-rutile transformation was discussed earlier, and this again was the mechanism proposed by Gamboa and Pasquevich to explain the observed effects of adsorbed chlorine on the system.

3.2.3 Effect of Precursor

Study of the effects of preparation method and titanium precursor on the resulting titania crystal structure has not been comprehensive. The effects of sulfate and chloride solutions were studied and reported by Wilska in 1954 [2]. He found that although the

initially dried products were always amorphous, the first crystalline forms present varied with preparation method and precursor solution. Samples originating from sulfate solutions always gave the anatase structure, while samples produced from the boiling of chloride solutions always gave the rutile structure. Other methods of synthesis such as hydrolysis of phosphate solutions or hydrolysis at room temperature gave either the anatase structure or a mixture of both the anatase and the rutile structure. Wilska found that an amorphous phase always existed prior to the crystalline phase, even in the cases of direct rutile formation. No mechanism was proposed to explain the different effect of sulfate and chloride precursors on the phase transformation.

3.3 Effect of Particle Size on Phase Transformations

There are two main effects of particle size on phase transformations that will be discussed in this section. The "critical particle theory" is a general thermodynamic theory first explained by Garvie in reference to the zirconia system [11]. The theory has been applied to the titania system by Kumar [7]. In addition, a kinetic effect of particle size on the anatase-rutile phase transformation has been proposed by Gribb and Banfield [7].

In the zirconia system, which is in many ways analogous to the titania system, there is a tetragonal to monoclinic phase transformation. A critical size effect theory is presented by Garvie [11]. The free energy of an individual crystal of ZrO_2 is given as:

$$G_T = 4/3 \pi r^3 G_{VT} + 4\pi r^2 \gamma_T \quad (1)$$

where G_T is the free energy of the tetragonal phase, G_{VT} is the volume free energy of the tetragonal phase, r is the radius of the particle, and γ is the surface energy. If a similar expression is written for the monoclinic phase, the difference in free energy is given as:

$$\Delta G = 4/3 \pi r^3 \Delta G_V + 4\pi r^2 \Delta \gamma \quad (2)$$

When the tetragonal and the monoclinic phases are in equilibrium, $\Delta G=0$ and the radius is given as

$$r = \frac{-3\Delta\gamma}{\Delta G_V} \quad (3)$$

Given the definition of volume free energy as

$$\Delta G_V = \Delta H - T\Delta S \quad (4)$$

and the knowledge that $\Delta G_V=0$ at the equilibrium transformation temperature, T_b , the entropy of the transformation is given as

$$\Delta S = \frac{\Delta H}{T_b} \quad (5)$$

Equations 4 and 5 can be combined to produce

$$\Delta G_V = \Delta H - \frac{T\Delta H}{T_b} \quad (6)$$

From equations 3 and 6, Garvie identified a critical particle size:

$$r_c = \frac{-3\Delta\gamma}{\Delta H(1 - T/T_b)} \quad (7)$$

Garvie's critical particle size is defined as the particle radius that prevents transformation of the tetragonal to the monoclinic phase. This is dependent upon the tetragonal phase having a lower surface free energy than the monoclinic phase. Otherwise, there would be no size effect.

Although Srinivasan et al [21] discount the critical size effect and attribute the stabilization of zirconia to chemical factors, they acknowledge that the theory would hold if the minimum particle size were smaller than they calculated. Becher and Swain [21] observed that the rate of tetragonal to monoclinic transformation consistently accelerates with increasing grain size. They explain this phenomenon by the probability that a nucleus capable of transforming exists increases with an increase in volume of the tetragonal phase, translated as larger particle sizes. Another explanation offered is that with grain growth tensile stresses tend to appear, which are known to promote this tetragonal to monoclinic phase transformation [22].

The critical size effect as it applies to titanium dioxide is summarized by Kumar [6], who used it to explain the initiation of the anatase-rutile transformation. Kumar found that both the grain sizes of rutile and the rutile content increased with increasing time and temperature of calcination. The total free energy change upon nucleation/growth processes can be expressed as

$$\Delta G = 4/3 \pi r^3 g_v + 4 \pi r^2 g_s + 4/3 \pi r^3 g_e \quad (8)$$

where r is the radius of the nucleus, g_v is the difference in volume free energy (per unit volume), g_s is the energy required to make a new surface (per unit area), and g_e is a free energy term which accounts for mechanical and environmental stress effects. Under the critical nuclei size effect theory, a nucleus will only be stable when it reaches a critical

size, r_c . Given that all else is constant, critical nucleus size depends only upon the transitional energies involved, as shown:

$$r_c = -2g_s / (g_v + g_e) \quad (9)$$

Kumar uses this to explain the observed increase in rutile grain size upon metastable-to-stable transformation from anatase, considering a stress-free environment such that $g_e \leq 0$, which is possible due to the volumetric decrease upon phase transformation of 8%.

In addition to the thermodynamic effect as studied by Kumar and Garvie, Gribb and Banfield investigated the kinetic effect of particle size [7]. They found significant particle-size effect on the anatase-rutile transformation rate in nanocrystalline titania whereby an increase in reaction rate was associated with a decrease in particle size. Three rate-limiting factors were offered as explanation, each relating particle size to a change in reaction rate:

1) Potential Nucleation Sites. Due to purely geometrical effects, the overall number of potential surface nucleation sites per unit volume increases with a decrease in particle size. As the number of potential sites per unit volume increases, it would logically follow that the number of surface nuclei increases, increasing the rate of phase transformation.

2) Driving Force. The driving force for a phase transformation is the difference in free energies between the reactant and product phases. Gribb and Banfield cited experimental evidence suggesting that anatase has a lower surface energy than rutile and therefore would imply that as crystallite size decreases, so does the driving force, which would result in a reduced reaction rate. This is inconsistent with the experimental data provided by Gribb and Banfield and was therefore discounted as a reasonable explanation.

3) Strain Energy. Since the molar volume of rutile is 8-10% less than that of anatase, there is likely to be strain energy associated with the phase transformation. Because of differences in surface tension and hydrostatic-like pressure on smaller crystallites, this strain energy may be affected by particle size. As particle size decreases, the surface tension and hydrostatic-like pressures would potentially reduce the strain energy, reducing one of the barriers to transformation.

Upon consideration of experimental data that included the examination of both nanocrystalline and macrocrystalline titanium dioxide, Gribb and Banfield concluded that the number of nucleation sites was the most probable cause of the increase in reaction rate with decreasing particle size.

3.4 Cavitation Synthesis

Synthesis methods for the production of nanostructured materials vary widely between laboratories and researchers. One common approach, however, is to combine a metal salt solution with a precipitating agent. The result is a precipitant slurry containing a mixture of solid particles suspended in a liquid. In the conventional case, the particles are an oxide precursor, such as a hydroxide, which can then be converted to the oxide by calcining at elevated temperatures [24, 25]. One method that can potentially produce nanometer-sized grains in the solid oxide involves exposing those particles to a tremendous amount of shear stress and *in situ* calcination. The effect of shear is to produce a nanometer-sized, fine, crystalline solid. *In situ* calcination causes the

decomposition of any residual salts such as sulfates, nitrates, and chlorides [25]. The result is a metal oxide slurry which can be dried to a powder. Most of the research conducted in order to accomplish this strategy has focused on the use of cavitation to provide both the shear force and the in situ calcination.

Suslick and co-workers [23] performed much of the early work exploring the effects of acoustic cavitation on materials synthesis. Using ultrasound, Suslick generated acoustic waves to produce the desired cavitation effects. His studies provide insight into the microscopic effects of cavitation on solid particles. Suslick asserts that the effects of ultrasonic-induced cavitation on metal powders are radical changes in particle morphology, significant agglomeration of particles, and a reduction in passivating surface oxide coatings.

Cavitation in liquids generates implosive bubble collapse and associated shock waves. If the bubbles collapse near an extended solid surface, localized high-speed jets of liquid impinge on the surface of the solid. If small solid particles exist in a slurry these smaller particles do not interrupt the cavitation process. Essentially the solid is suspended on the surface of the bubble before the bubble implodes. Normal cavitation collapse occurs. As this occurs, solid particles suspended on the surface of the bubble collide. The collisions that occur as results of cavitation afford a tremendous amount of in situ thermal treatment and an exceptional degree of shear leading to good mixing. Suslick reports temperatures as high as 5000°C when using a high powered ultrasonic probe to induce cavitation effects [23]. Cavitation has also been shown by Moser to produce smaller grain sizes in a variety of oxide systems, but only in the case of mechanically induced cavitation, not acoustic [24].

The effect of acoustic cavitation on the grain size of nanostructured metal oxides was studied in depth by Emerson et al [25] using a synthesis technique similar to the one used in this study. Emerson found that while acoustic cavitation generally has a minor effect on the grain size and phase purity of most metal oxide catalysts, it has a more dramatic, yet still minor, effect on the grain size of titania. The observed effect was a 1-2nm reduction in grain size upon exposure to the ultrasound. Since this contradicts other results in the literature, Emerson offered a few explanations for his observations. Firstly, the rate of precipitation in the studied systems is very high. Since one of the major benefits of acoustic cavitation is an increased precipitation rate, acoustic cavitation would be less effective on a system with an already high precipitation rate. Secondly, acoustic waves from the tip of the ultrasonic probe have a tendency to propel objects away from the tip, so it is not inconceivable that precipitates are pushed from the probe and avoid the effects of cavitation [25].

3.5 Summary

The anatase-rutile transformation has been shown in the literature to be affected by a large number of processing variables, including dopants and impurities, atmosphere, precursor, particle size, and synthesis method. However, this review of the literature showed that results from previous studies are often contradictory. Furthermore, the relative influence of each of these variables appears not to have been studied. Therefore, the focus of this work was the exploration of these variables and their individual as well as group effects on the phase transformation and on particle size.

4 Experimental Methods

The focus of the experimental phase of this work was the variation of process variables and determination of each variable's effect on the resulting powders. The independent variables included the type of titanium precursor, the synthesis method (classical or with acoustic cavitation), tin dopant concentration, and drying method. The grain size of rutile in the product and the phase content of the product were characterized as dependent variables. Another variable that became an issue was the analytical composition of the entire sample, especially the residual chlorine content. This chapter describes details of powder synthesis and characterization.

4.1 Preparation of Precursor Solutions

4.1.1 Titanium Precursors

Titanium sulfate, titanium butoxide, and titanium tetrachloride were the three precursors examined in this work. Titanium sulfate (Alfa Aesar, 99.999% metals basis) was mixed into deionized water and stirred with a magnetic stirbar for approximately 30 minutes prior to synthesis. Deionized water was added such that the total volume of the solution was 100mL, and this led to a dilution of 0.125g/mL. Since titanium butoxide has a tendency to crystallize in water, isopropyl alcohol (Alfa Aesar, pure) was used instead of water. Isopropyl alcohol was added such that the total volume of the solution was 100mL, and this led to a dilution of 0.125g/mL.

Titanium tetrachloride (Alfa Aesar, 99.999% metals basis) was poured over a mixture of ice and water to form an aqueous solution, and left to stir overnight up to 12

hours, to ensure clarity and complete dissolution. The ice water was made from de-ionized water, and approximately 30gTiCl₄:120g ice was the optimal ratio as previously determined by C. Demetry [12]. The ice water was required since the reaction of titanium tetrachloride is strongly exothermic; the melting of ice helped to absorb the generated heat. Additional dilution by de-ionized water immediately prior to the processing resulted in a final dilution of 0.125g/mL to standardize the volume for synthesis.

4.1.2 Tin Dopant

Tin oxide was the dopant used in this study, for several reasons. SnO₂ is isostructural with rutile and thus can be expected to promote the formation of the rutile phase in TiO₂. A prior study confirmed this to be the case [12]. Tin is isovalent with titanium and has a similar ionic radius, both of which suggest that tin will have some solid solubility in TiO₂. A range of 0-4% Sn, weight metals basis, was used. The tin solution was prepared similarly to the titanium tetrachloride solution, as described in the previous section. The tin was obtained as tin tetrachloride and poured over a de-ionized water/ice mixture to make a stock solution which was used over the course of this work. Prior to each use the solution was stirred for approximately 30 minutes to ensure homogeneity.

4.2 Powder Processing

Titanium dioxide precursor slurries were synthesized from the titanium salt precursor solutions by two methods, which will be referred to as "classical synthesis" and "acoustic cavitation" synthesis. In both cases the fundamental mechanism is a co-precipitation reaction that occurs when the highly acidic Ti-Sn solution comes in contact with a basic solution, exceeding the solubility of the metals in solution. A table that lists the composition and preparation method of each sample is included in Appendix A.

4.2.1 Classical Synthesis

The driving solution for the precipitation reaction in classical synthesis was ammonium hydroxide (2M, Alfa Aesar). Dissolution of all species in the precursor solutions is critical, and when ammonium hydroxide meets the precursor solution immediate precipitation occurs.

The precursor solution, a mixture of the titanium salt solution and the tin salt solution, was metered into the interaction zone, as shown in Figure 5, at a rate of 3mL/min, resulting in a run time of approximately 30 minutes. The titanium solution comes into contact with the ammonium hydroxide solution in the interaction zone, causing immediate precipitation. The product is pulled by vacuum application into the flask holding the ammonium hydroxide, where it is mixed with the ammonium hydroxide and again fed into the interaction zone in a recycle stream. This cyclic process was used in order to come as close as possible to achieving complete precipitation of the metal species.

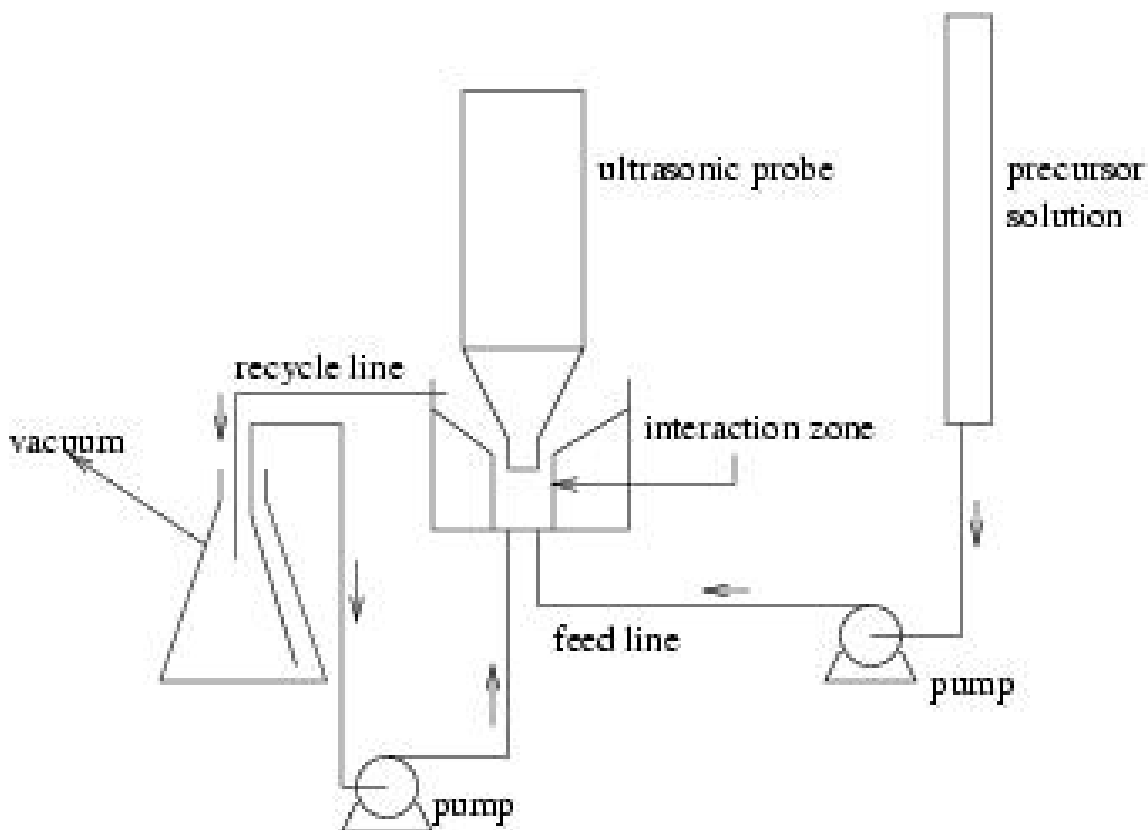


Figure 5 - Schematic of experimental setup.

4.2.2 Acoustic Cavitation Synthesis

With the acoustic method, the ultrasonic probe, a 20kHz, 600-Watt Sonics & Materials Vibracell that is shown in Figure 5 was turned on to an amplitude of 100%. The remainder of the synthesis was identical to the classical synthesis, and the recycling process exposed both freshly precipitated and cycled product to the interaction zone, where the ultrasonic waves are focused.

4.2.3 Post-Synthesis Processing

After synthesis processing, the product slurry was washed and dried. Washing was done to remove the excess ammonium hydroxide and chlorine left in the system after synthesis, and to dissolve any ammonium chloride that precipitated. Washing was carried out over a number of days with de-ionized water and mechanical stirring. Cycles were approximately 8 hours of mixing then 16 hours of settling, at which point the supernatant was withdrawn by pipet and more de-ionized water was added to continue the washing. This was originally done only once, but upon receipt of initial analytical results that contained an excess of chlorine, the washing step was increased such that the washing was repeated for five cycles.

Two methods of drying the resultant product slurry were used. Thermal drying, which involved baking the slurry in a furnace at 100°C for 24 hours, resulted in a cake of product, which was hard and difficult to work with. Freeze drying, which is a lengthy process by which the product slurry is frozen and the water is slowly sublimed, yielded a light powder which could be easily handled for x-ray diffraction analysis or chemical analysis. Both methods were examined initially, but freeze-drying was used predominantly throughout the study since it yielded smaller grain sizes and due to the ease with which its product was handled.

In order to freeze-dry the slurry, the solution must be pre-frozen to at least -40°C. To achieve this and to assure compositional homogeneity of the solution, the slurry was sprayed into a pan of liquid nitrogen prior to the freeze-drying cycle. A Virtis model Genesis 25EL freeze dryer was used. A typical run was at a pressure of 20-30mtorr and

started at -30°C. Approximately every 2 hours the temperature was increased by five degrees until the temperature had reached 30°C. After drying, all powders were calcined at 500°C for one hour in air.

4.3 Characterization of Powders

4.3.1 X-Ray Diffraction

X-Ray diffraction (XRD) was used to measure two characteristics of the powders: the grain size and the phase content. The XRD patterns were collected on a Rigaku 2000® diffractometer using a $\text{CuK}\alpha$ ($\lambda=1.5418$ angstroms) radiation source with a nickel filter over a 2θ range of 5-90° with a step size of 0.1° and a collection time of 4 seconds. The spectra were plotted and compared with data from the Joint Committee Powder Diffraction Standards (JCPDS) for analysis. The (101) peak ($2\theta=25.28^\circ$) of anatase and the (110) peak ($\theta=27.42^\circ$) of rutile were used for analysis.

Grain size can be estimated from an XRD line broadening analysis using the Scherrer equation or from direct observation by transmission electron microscopy (TEM). The grain sizes reported in this research were measured by XRD analysis and the Jade software associated with the Rigaku diffractometer. The Jade software estimates the grain size by a variation of the Scherrer equation that accounts for instrumental broadening. All grain sizes reported in this study are of the rutile phase only. In a few cases there was only anatase present, so no grain size is reported.

The phase content, defined as the weight percent of anatase in the sample, was determined from the ratio of peak heights in the XRD data. Spurr and Meyers showed

that the anatase-rutile weight ratio is proportional to the ratio of their integrated peak intensities. Spurr and Meyers [26] derived the resulting weight fraction to be:

$$X_a = \frac{1}{(1 + I_r/kI_a)}$$

where k was found to be 0.68 in the region where $X_a \leq 0.2$. I_r and I_a are the integrated intensities of the rutile and anatase peaks, respectively. Although Spurr and Meyers used the integrated intensities of the peaks, this study used the relative intensities of the peaks and found only a slight (<5%) difference.

4.3.2 Analytical Composition

NSL Analytical Services, Inc., of Cleveland, Ohio, conducted the chemical analysis of selected samples. The samples were tested for titanium, tin, chlorine, silicon, aluminum, and balanced for oxygen. Titanium and tin were tested due to their intentional inclusion in the synthesis. Chlorine was tested due to its presence in the precursor solution, and silicon and aluminum were tested due to potential impurities in the original 99.999% pure titanium tetrachloride ordered from Aesar. NSL chose photoemission to test for tin, silicon and aluminum, and ion chromatography to test for chlorine. In order to check the precision of NSL's techniques, one batch of powder was split into two lots and sent for testing.

5 Results and Discussion

The results and discussion are presented here in three stages. First, the effects of the multiple variables will be presented and discussed. Second, the relative importance of select variables with respect to each other will be analyzed. Finally, we will explore possible correlations between the grain size and the phase content.

5.1 Effect of Titanium Precursor

Three solutions were examined for use as the titanium precursor. The optimal precursor would yield a large amount of the rutile phase, which could potentially be increased further by manipulating other process variables. Titanium sulfate, titanium butoxide, and titanium tetrachloride were chosen due to availability, familiarity, and results of studies in the literature.

Titanium sulfate precursor yielded an anatase powder, consistent with literature results [2]. Titanium butoxide, which has not been discussed in the literature, also gave an anatase powder. Titanium tetrachloride precursor, however, resulted in a powder that was 41% rutile. For this reason, titanium tetrachloride was the precursor used for the remainder of the study. This is consistent with Gamboa and Pasquevich's theories on adsorbed chlorine assisting the anatase-rutile phase transformation, as discussed previously in section 3.2.2. The X-ray diffraction patterns are shown in Figure 6. Note the lack of rutile peaks at $2\theta = 27.42$ in both the butoxide and the sulfate samples.

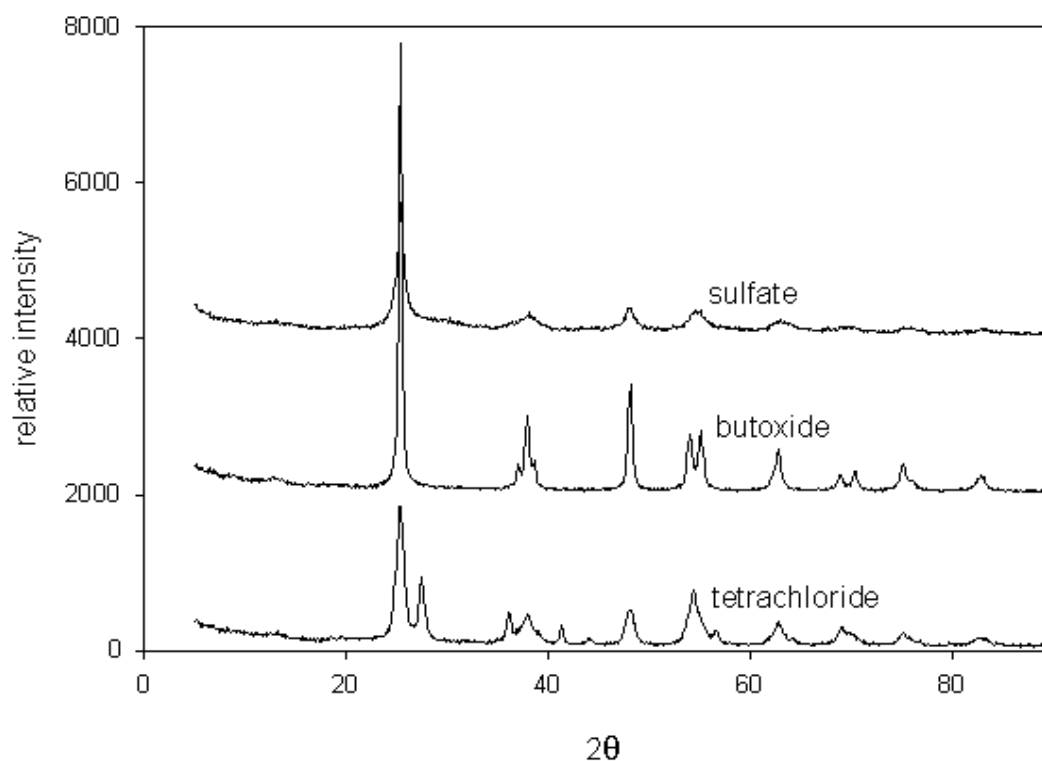


Figure 6 - XRD plot of the powders from various precursors, after calcining.

5.2 Effect of Drying Method

Two drying methods were examined: thermal drying and freeze-drying. Thermal drying was a relatively quick process in which the product slurry was heated in an oven at 100°C for 24 hours. The result was a tough cake that had to be ground by mortar and pestle into a powder for further analysis. Freeze drying was lengthier and involved spraying the product slurry into liquid nitrogen, reducing the temperature and pressure, and gradually increasing the temperature until the slurry was completely dried. The result was a light, fluffy powder. To quantify the effect of the drying method on powder characteristics, the slurry from one process run (1 weight% Sn, acoustic cavitation synthesis) was divided in half, dried by the two methods, then given identical calcining

treatments (500°C, 1 hour). Characteristics of the resulting powders are compared in Table 1. Freeze-drying was the method chosen for the remainder of the study, since it yielded more rutile with a grain size about half that of the thermal drying method.

Table 1 - Powder Characteristics resulting from freeze-drying and thermal-drying the same sample.

Drying Method	% Rutile	Grain Size
freeze-dry	87%	9nm
thermal	55%	18nm

Grain coarsening is a common occurrence in calcined titania; particles grow with the application of heat over time. Although the thermal drying took place at a lower temperature than that at which calcining normally occurs, it would seem a plausible explanation that the grain sizes of the thermally dried samples are larger due to the additional thermal treatment they received.

5.3 Effect of Cavitation Synthesis

Two synthesis methods were examined throughout this work: classical synthesis and acoustic cavitation synthesis. The only difference between the two is the presence of ultrasonic waves in the acoustic synthesis, which has been shown in previous studies to reduce particle agglomeration [23].

For the thoroughly washed powders, the grain size of rutile was largely unaffected by cavitation, as is shown in Table 2. Samples with no tin dopant were also synthesized, but since there was no rutile in the powder a rutile grain size for the two methods could

not be measured. These data reinforce work by Emerson *et al* [25] in which the differences in grain size between acoustically prepared and classically prepared materials were found to be small, on the order of 1-2nm. Since the coarsening of a powder would be assisted by agglomeration of its constituent particles, it is not surprising that the cavitation slightly inhibits the growth of the titania particles, if indeed cavitation breaks up agglomerates.

Table 2 - Grain size as a function of synthesis method.

Tin (weight %, metals basis)	Classical	Acoustic
1%	10nm	9nm
2.2%	7nm	7nm
4.5%	6nm	6nm
5.6%	7nm	7nm

For the thoroughly washed samples, there was no significant effect of the acoustic method on phase content, as shown in Figure 7.

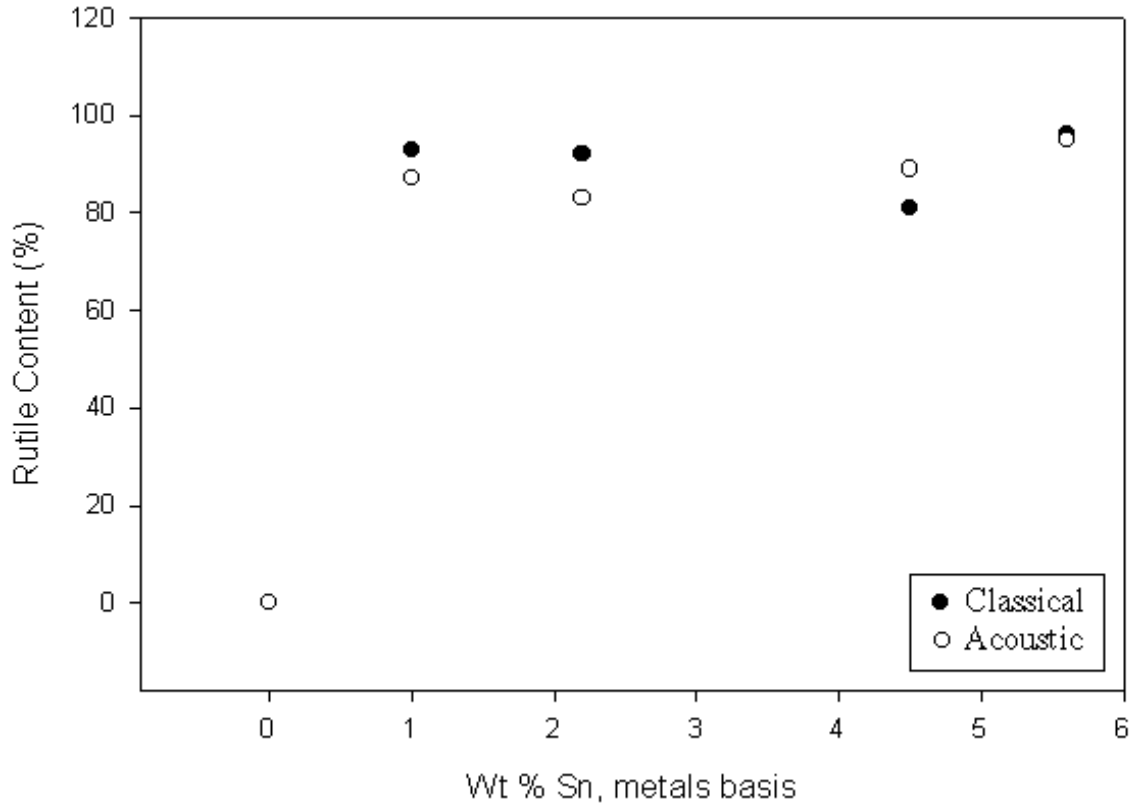


Figure 7 - Percent rutile present dependent upon synthesis method.

5.4 Effect of Tin Concentration

The tin dopant concentration in the titania was a variable expected to affect both the grain size and the rutile content significantly. The tin concentrations referred to in this section are those measured analytically by NSL, converted to weight % on a metals basis. We believe the data from NSL to be reliable, after a double-sample was sent for identical analysis and the results were similar, to within 2%.

The samples with high residual chlorine concentration exhibited minimal correlation between tin concentration and grain size, due to the overwhelming effect of chlorine, as shown in Figure 8.

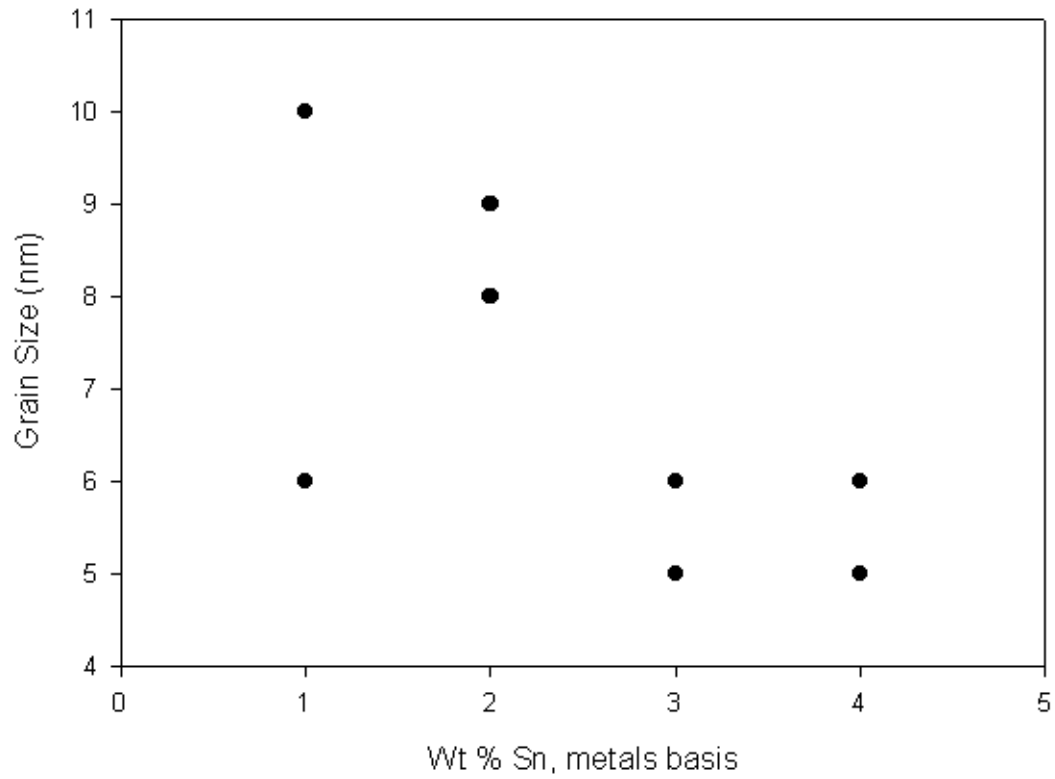


Figure 8 - Grain size as a function of tin concentration, in samples with high residual chlorine.

Those samples with low residual chlorine showed a stronger correlation, as shown in Figure 9.

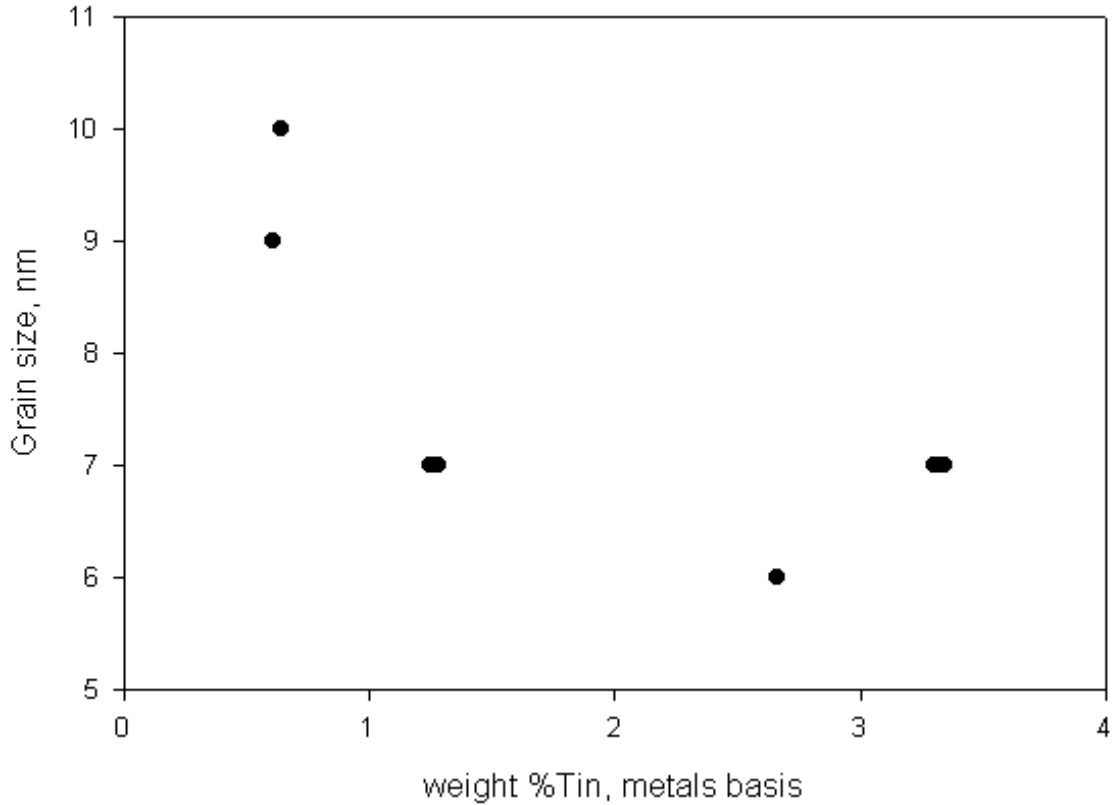


Figure 9 - Grain size as a function of tin concentration, in samples with low residual chlorine.

Both acoustic and classical samples are included in Figure 9, but due to the minimal effects of cavitation discussed in Section 5.3, they are not distinguished. Above a tin content of 1wt% there is a lower limit in the minimal grain size of titania, since the difference between 6nm and 7nm is experimentally indistinguishable. It can be argued that above this tin concentration the effect of the dopant has reached a plateau. Possible precipitation of tin oxide in the samples was not significant enough for it to be detected upon XRD analysis, yet the possibility of tin exceeding the solubility limit and precipitating out of the titania is a potential explanation for the decrease in effectiveness at minimizing the growth of the rutile phase.

The presence of tin did appear to affect the phase content of rutile, but only in the samples with a high level of residual chlorine, as shown in Figure 10. The combination of tin and chlorine as dopants in the titania system has not been previously studied. This effect could be explained by the presence of chlorine alone, as there is not enough evidence to study the effect of Sn alone.

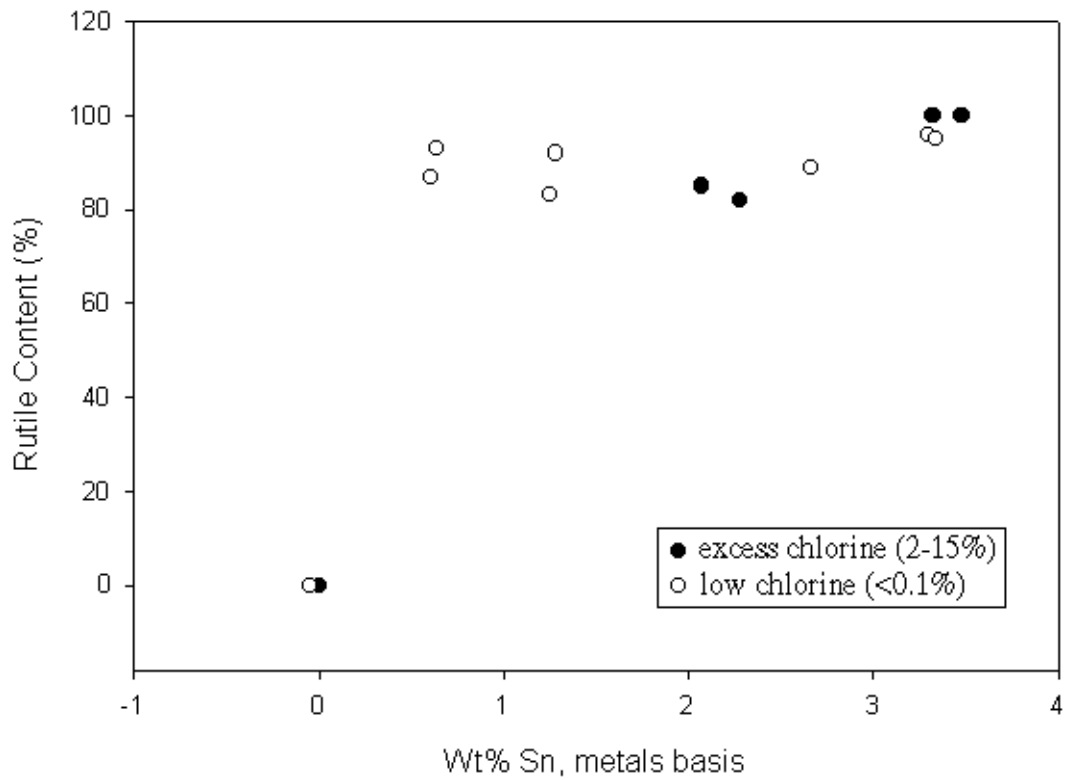


Figure 10 - Rutile content as a function of tin concentration.

5.5 Effect of Chlorine Impurities

Chlorine impurities are likely from this synthesis method due to the choice of titanium tetrachloride as the titanium precursor. The thoroughness of the washing step was examined as a variable in the process. The variation of the washing step led to a range of levels of residual chlorine.

In samples with excess chlorine, there appears to be a correlation between chlorine concentration and grain size. This can be seen in Figure 11, which shows a decrease in grain size as chlorine concentration decreases. Chlorine is often referred to as a dopant in the literature [7,24] and this data reinforces that the presence of chlorine does

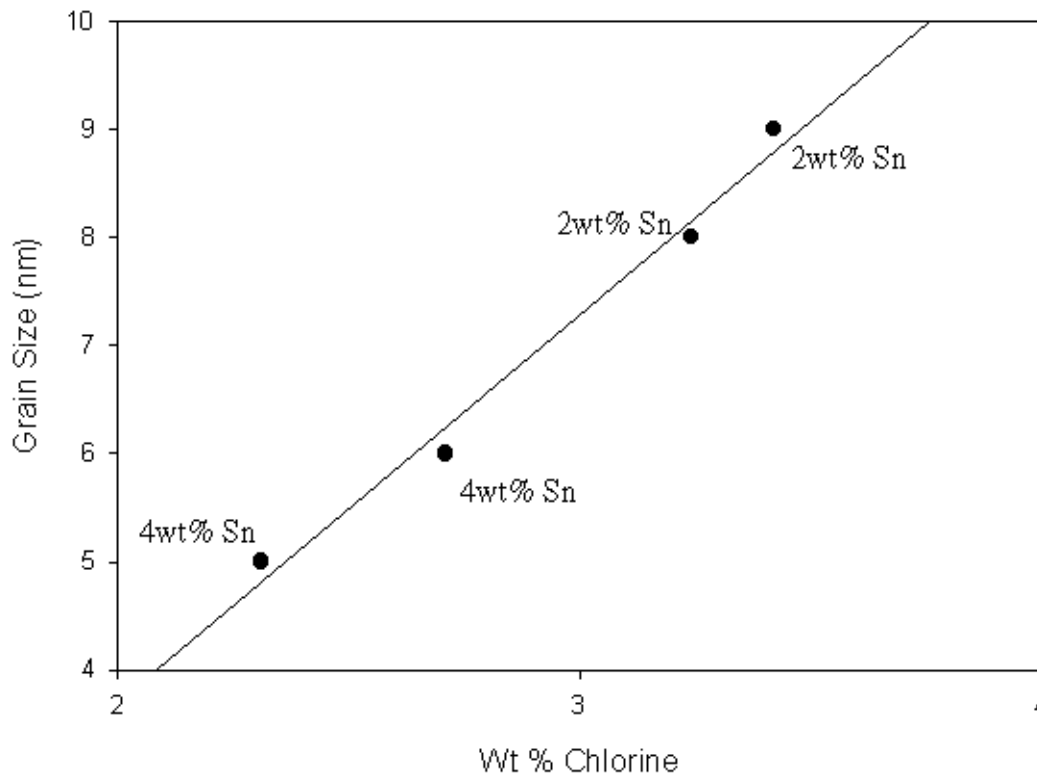


Figure 11 - Grain size as a function of chlorine impurities present, high excess chlorine and varying tin content.

indeed have an effect on the grain size. As the chlorine concentration increases, the potential for segregation of the chlorine also increases and could hereby have less effect on the main phases (anatase, rutile) of the system. Although no non-TiO₂ phases were detected in the XRD spectra, it is also known that phase inclusions of less than 5% often are not detected by XRD. If chlorine-containing phases were present, this could invalidate any chlorine-dependency we'd see, since chlorine present in a distinct phase potentially would have a different effect.

The samples that were thoroughly cleaned of chlorine showed the opposite correlation between grain size and chlorine content, as seen in Figure 12. This data, while not as strong a correlation as Figure 11, does show a trend that supports the presence of chlorine as a dopant that can minimize the grain size of rutile. There is an apparent contradiction in these distinct sample groups of excess and minimal chlorine content. There seems to be a minimum grain size that titania can reach with the presence of chlorine, at approximately 6nm. With an impurity content between 0.7wt% and 2wt% chlorine, a minima is approached. This trend is by no means solely attributable to the chlorine content, however. The tin content, as labeled in Figures 11 and 12, appear to correlate strongly with grain size as well. This was discussed in Section 5.4, but the correlation was ambiguous due to the variation in both tin and chlorine.

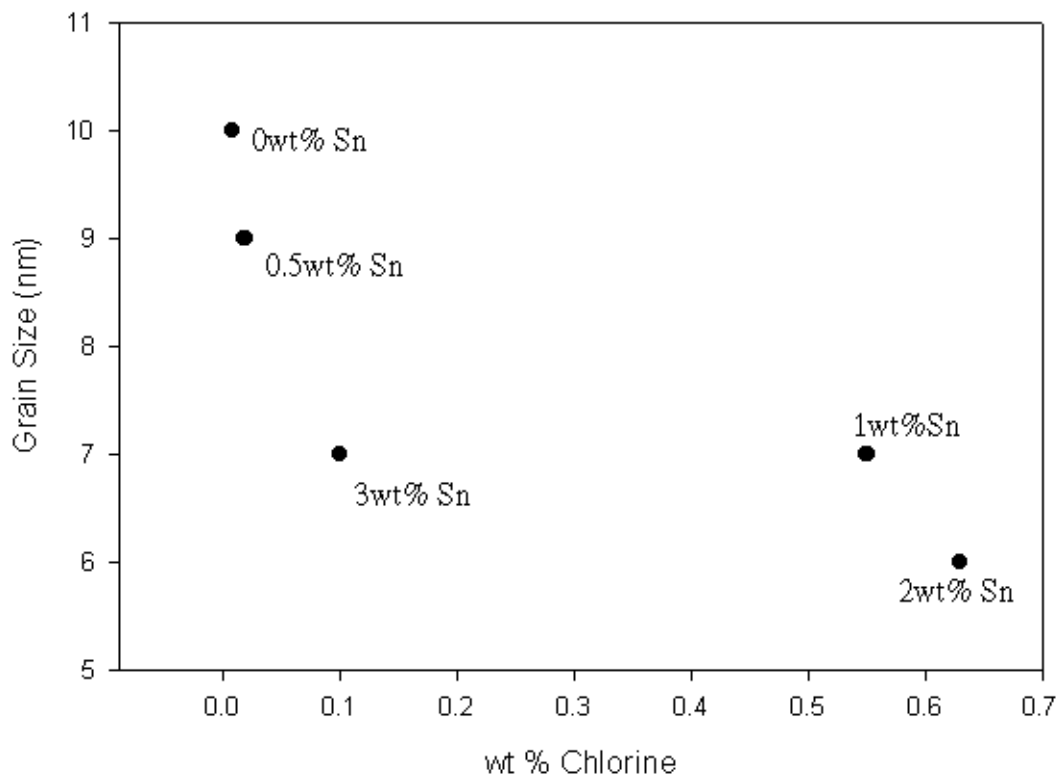


Figure 12 - Grain size as a function of chlorine impurities present, low excess chlorine and varying tin content.

While the chlorine impurities clearly affect the grain size of rutile in titania, they showed much less effect on the phase content, as can be seen in Figure 13. There seems to be no correlation at all between chlorine content and rutile content when all the results are considered together. However, considering only those powders with high excess chlorine (>2wt%), there is a potential inverse correlation between rutile content and chlorine content but again, this could be explained by the tin content just as well. An inhibitory effect of excess chlorine on the production of rutile would contradict the results of Gamboa and Pasquevich, but their results were in the presence of gaseous chlorine involving adsorption and our excess chlorine could be in solid solution in the titania. The presence of excess chlorine in solution may inhibit the anatase-rutile

transformation. If the excess chlorine is in such a state that it could be treated as a donor-dopant, it might increase the concentration of titanium interstitials, which inhibits the transformation as noted by Shannon and Pask [17].

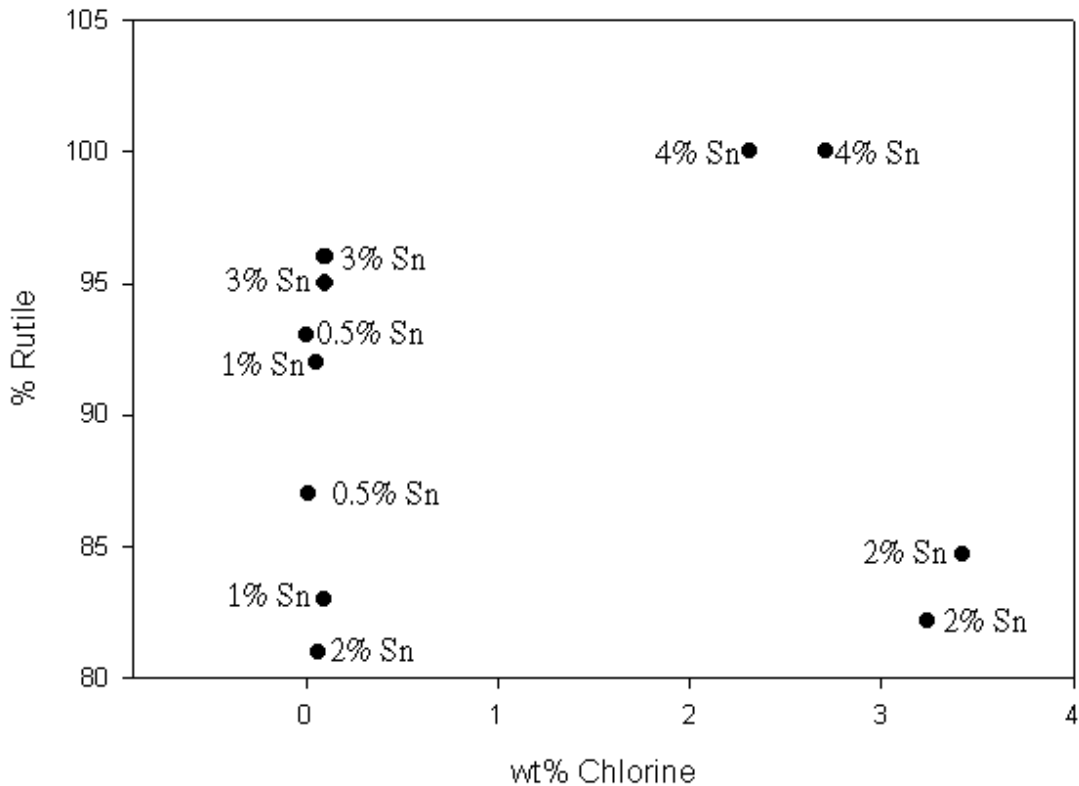


Figure 13 - Rutile content as a function of weight % chlorine, with varying tin.

We have thus far presented a wide array of results, which would benefit from summary. Titanium sulfate was chosen as the precursor to titanium dioxide, since neither titanium sulfate and titanium butoxide yielded any rutile. Freeze-drying was shown to be preferable to thermal drying, owing to smaller grain sizes and greater rutile content. Chlorine impurities had two effects on grain size, increasing with increasing chlorine content for high chlorine content, and increasing with decreasing chlorine content for low

chlorine content. Acoustic/ultrasonic vs. classical synthesis methods showed really no difference within experimental parameters. Tin concentration seemed to have some effect, but was indistinguishable from the chlorine effect. Since the effects are so intertwined, calculations have been done to distinguish the relative importance of a few effects.

5.6 Relative Importance of Synthesis Variables

The problem of determining the relative importance of synthesis variables was a complex one, and analyzed using a Taguchi analysis. An L-4 orthogonal Taguchi array was compiled to focus on the three major variables: synthesis method, chlorine content, and tin content, and their effects on both the phase content and the grain size dependence. Other variables were not chosen due to design-of-experiment constraints. Details of the Taguchi method and analysis are included in Appendix B. The results are shown in Table 3.

Table 3 - Taguchi method results.

Factor Effects	Phase Content	Grain Size
Synthesis Method acoustic vs. classical	12%	0%
Tin Content	40%	0%
Chlorine Content	48%	100%

This ranking of variables' importance to the final TiO₂ product highlights again the influence of dopants above preparation method on results. Chlorine and tin affect phase content similarly, yet it appears that the sole factor in grain size determination is the chlorine content. The strength of chlorine as a dopant has been previously studied

and shown to be instrumental. The heavily skewed factor effect in grain size is a result of both the small sample size and the large relative margin of error in measuring grain size.

Further explanation of the Taguchi method is included in Appendix B.

5.7 Analysis of Possible Correlation Between Grain Size and Rutile Content

Given an examination inclusive of the entire body of data collected over the course of this work, no direct relationship between grain size and rutile content could be shown. However, among the data taken only from the samples with low residual chlorine content, there is a definite correlation. Figure 14 shows both the low- and high- residual chlorine data. The rutile phase content clearly increases with decreasing grain size for the samples with low residual chlorine. Gribb and Banfield, whose data showed a marked increase in the rate of anatase-rutile transformation when the anatase used was finely crystalline, confirm these results. Gribb and Banfield, as explained in section 3.3, attributed their results to the geometrical effect of an increase in the number of nucleation sites per unit volume as particles decrease in size.

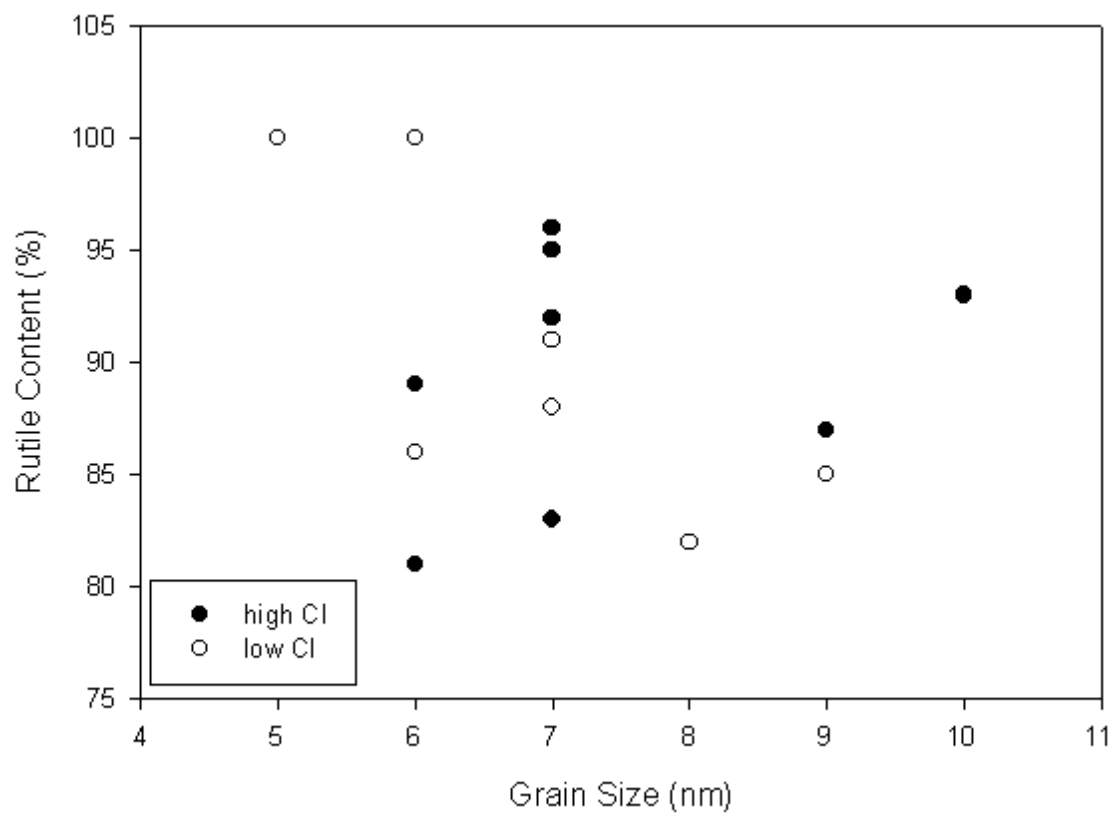


Figure 14 - Rutile content as a function of grain size for variable chlorine and tin concentrations.

6 Conclusions

The primary objectives of this work were to determine the relative effects of synthesis variables on the phase content and particle size of TiO₂ as well as to examine a potential relationship between phase content and particle size.

Choice of the titanium precursor was very important in regard to whether the rutile phase could even be produced, and titanium tetrachloride proved to be optimal in that regard, yielding between 41% and 100% rutile, compared to 0% for sulfate and butoxide precursors. It was also shown that powders from the same synthesis batch had smaller grain size and rutile content upon freeze-drying than upon thermal drying.

We have shown that although the synthesis method (acoustic or classical) is expected to have an effect on either the grain size or the rutile content, it had neither when comparing a classical and ultrasonic cavitation synthesis. Synthesis conducted simultaneously with ultrasonic cavitation had a minimal effect on grain size and rutile contents.

The most influential variables on grain size and rutile content were found to be the concentrations of tin dopant and residual chlorine from the chloride precursor. By the relative interaction of chlorine, tin, and grain size, we found chlorine to affect the grain size of the rutile phase slightly more than tin. The strong effect of residual chlorine has tremendous repercussions for processing of powder by this method; the reproduction of the washing step (or lack thereof) will have a large influence on powder characteristics from batch to batch.

A potential relationship between the grain size of rutile and the amount of rutile phase present was explored. Only in samples with low residual chlorine was a

correlation found that rutile content was shown to increase with decreasing grain sizes. There could be a size effect of the phase transformation similar to that for ZrO_2 .

Further study into the anatase-rutile phase transformation could be taken in two primary directions. First for conclusive study would be the mechanism by which chlorine affects the phase transformation. Second for further academic and applicable knowledge, would be an examination of the potential size effect of the phase transformation itself, whether it be kinetic or thermodynamic.

7 References

- [1] <http://minerals.er.usgs.gov/minerals/pubs/commodity/titanium/index.html#mcs> U.S. Geological Survey, Minerals Information. October 10, 2000
- [2] Wilska, Seppo, "An X-Ray Diffraction Study to Determine the Effect of the Method of Preparation Upon the Crystal Structure of TiO₂," *Acta Chemica Scandinavica* **8** (1954)
- [3] MacKensize, K.J.D. "The Calcination of Titania: The Effect of Additives on the Anatase-Rutile Transformation"
- [4] Banfield, Jillian F.; Bishoff, Brian L; and Marc A. Anderson, "TiO₂ accessory minerals: coarsening, and transformation kinetics in pure and doped synthetic nanocrystalline materials," *Chemical Geology* **110** (1993)
- [5] Gamboa, Julio A. and Daniel M. Pasquevich, "Effect of Chlorine Atmosphere on the Anatase-Rutile Transformation," *Journal of the American Ceramic Society* **75** (1992)
- [6] Kumar, Krishnankutty-Nair, "Growth of Rutile Crystallites During the Initial Stage of Anatase-to-Rutile Transformation in Pure Titania and in Titania-Alumina Nanocomposites," *Scripta Metallurgica et Materialia* **32** (1995)
- [7] Gribb, Amy A. and Banfield, Jillian F. "Particles size effects on transformation kinetics and phase stability in nanocrystalline TiO₂" *American Mineralogist* **82** (1997)
- [8] Ashley, Stephen, "Small-scale structure yields big property payoffs" *Mechanical Engineering* February 1994
- [9] Gell, Maurice, "Application opportunities for nanostructured materials and coatings" *Materials Science & Engineering*, **A204** (1995)
- [10] Rittner, Mindy and Thomas Abraham, "Nanostructured Materials: An Overview and Commercial Analysis," *Journal of Powder Metallurgy*. **34** (1998)
- [11] Garvie, R.C., "Stabilization of the Tetragonal Structure in Zirconia Microcrystals," *The Journal of Physical Chemistry* **82** (1978)
- [12] Terwilliger, Chrysanthe, "Excess Thermodynamic Properties and Size-Dependent

- Segregation Phenomena in Ultrafine-Grained Titanium Dioxide," PhD. Thesis, *Massachusetts Institute of Technology* (1993)
- [13] McColm, I.J., "Ceramic Science for Materials Technologists," Leonard Hill, Chapman and Hall, New York. 1983.
- [14] Navrotsky, A. and O.J.Kleppa, "Enthalpy of the Anatase-Rutile Transformation," *Journal of the American Ceramic Society* **50**
- [15] <http://www.nl-ind.com/kronos/na/titanium3.html> Kronos, Inc., NL Industries June 10, 1999.
- [16] Stall, D.R., "JANAF Thermochemical Tables," Joint Army-Navy-Air Force-ARPA -NASA Thermochemical Working Group. (1996)
- [17] Shannon, Robert D. and Joseph A. Pask, "Kinetics of the Anatase-Rutile Transformation," *Journal of the American Ceramic Society* **48** (1965)
- [18] Rao, C.; Turner, A.; and J. Honig, "Some Observations Concerning the Effect of Impurities on the Anatase-Rutile Transition," *J. Phys. Chem. Solids.* **11** (1959)
- [19] Terwilliger, C.D. and Yet-Ming Chiang, "Size-Dependent Solute Segregation and Total Solubility in Ultrafine Polycrystals: Ca in TiO₂," *Acta Metall. Mater.* **43** (1995)
- [20] Roth, Robert; Negas, Taki; and Lawrence Cook. "Phase Diagrams for Ceramists, Volume IV" *American Ceramic Society, Inc.* (1981)
- [21] Srinivasan, Ram; Rice, Larry; and Burton Davis. "Critical Particle Size and Phase Transformation in Zirconia: Transmission Electron Microscopy and X-Ray Diffraction Studies" *J. Am. Ceram. Soc.* **3** (1990)
- [22] Becher, Paul and Michael Swain, "Grain-Size-Dependent Transformation Behavior in Polycrystalline Tetragonal Zirconia," *J. Am. Ceram. Soc.* **73** (1990)
- [23] Suslick, Kenneth, "Sonochemistry," *Science* **247** (1990)
- [24] Moser, W.R., et al. "The Synthesis and Characterization of Solid-State Materials Produced by High-Shear Hydrodynamic Cavitation," *Journal of Materials Research* **10** (1995)
- [25] Emerson, S.C. et al "The Ultrasonic Synthesis of Nanostructured Metal Oxide Catalysts," *Stud. Surf. Sci. Cata.* **118** (1998)
- [26] Spurr, R.A. and H. Meyers, "Quantitative Analysis of Anatase-Rutile Mixtures With

an X-Ray Diffractometer," *Analytical Chemistry* **29** (1957)
[27] <http://www.cnde.iastate.edu/staff/bforoura/HTML/taguchi.html> Center for
Nondestructive Evaluation, Iowa State University. February 7, 2000.

Appendix A - Synthesis and Sample Information

sample I.D.	Synthesis Method	Precursor	%Tin	%Rutile	Grain Size (nm)	NSL (analytical) RESULTS				
						Al	Cl	Si	Sn	Ti
k00402	classical	tetrachloride	0	0	n/a					
k00801	acoustic	tetrachloride	0	19	n/a					
k01001	classical	tetrachloride	0	0	n/a	0.004	14.8	0.021	<0.01	41.15
k01002	acoustic	tetrachloride	0	3.6	n/a	0.004	10.35	0.006	<0.01	39.96
k01401	acoustic	tetrachloride	0	41	n/a					
k01402	acoustic	butoxide	0	1	n/a	0.005	0.14	0.034	<0.01	44.64
k01403	acoustic	sulfate	0	7	n/a	0.009	0.01	0.03	<0.01	34.61
k01701	classical	tetrachloride	2	85	9	0.001	3.42	0.032	1.41	39.96
k01702	acoustic	tetrachloride	2	82	8	0.001	3.24	0.047	1.09	36.9
k01703	classical	tetrachloride	1	72	10					
k01704	acoustic	tetrachloride	1	86	6					
k01801	classical	tetrachloride	4	100	6	0.002	2.71	0.18	1.76	35.32
k01802	acoustic	tetrachloride	4	100	5	0.002	2.31	0.16	1.8	33.73
k01803	classical	tetrachloride	3	100	6					
k01804	acoustic	tetrachloride	3	100	5					
k02201	classical	tetrachloride	0.5	88	7					
k02202	acoustic	tetrachloride	0.5	91	7					
k02501	classical	tetrachloride	2	81	6	0.03	0.063	0.06	2.66	57.1
k02502	acoustic	tetrachloride	2	89	6					
k02901	classical	tetrachloride	1	92	7	0.006	0.055	0.13	1.28	57.13
k02902	acoustic	tetrachloride	1	83	7	0.001	0.099	0.083	1.25	57.71
k02903	classical	tetrachloride	3	96	7	0.001	0.1	0.019	3.3	56.38
k02904	acoustic	tetrachloride	3	95	7	<0.001	0.1	0.016	3.34	55.83
k03103	classical	tetrachloride	0.5	93	10	<0.001	0.007	0.019	0.64	58.8
k03104	acoustic	tetrachloride	0.5	87	9	0.001	0.018	0.017	0.61	58.15
k03104d	acoustic	tetrachloride	0.5	55	9					

Please note that grain size measurements are inaccurate or not possible on samples with less than 50% rutile present.

Appendix B - Taguchi Analysis and Application

The Taguchi method of analysis is a classic screening method for variable interaction in a multi-variable system. In its simplest application, we assign one of two values to a variable - "on" and "off", or "high" and "low". By controlling the design of experiments such that each particular variable is "on" or "off" in specific combinations, we can observe the interaction of the variables.

The Taguchi method is most often applied in robust design, as a methodology for improving process stability [26]. The essential steps include both planning and analysis.

Planning an experiment requires knowledge of the process variables. Once the process variables are known, they can be designed into an experimental matrix that will facilitate analysis. Standard orthogonal arrays are available that are applicable to nearly any situation [26].

Analysis of variance (ANOVA) is the method by which the relative importance of various factors is calculated. Each factor's sum of squares in ratio to the total sum of squares gives us the factor effect. This is shown in Table A1, applied to data culled from this study.

The variables that were possible to set at a high/low or on/off level were determined to be tin content, chlorine content, and classical vs. acoustic synthesis method. The array was laid out as shown in Table A1. Each row is taken as one experimental run. The zeroes and ones refer to the level of the variable, as "high" or "on" for a one and "low" or "off" for a zero.

synthesis method	chlorine content	tin content
0	0	0
0	1	1
1	0	1
1	1	0

Table A1 - Taguchi experimental matrix.

Synthesis method zero referred to a classical synthesis, while synthesis method one referred to an acoustic synthesis. Chlorine content low referred to a residual chlorine content $<0.5\%$ and chlorine content high referred to residual chlorine content $>2\%$. Low tin content referred to content $<0.5\%$, while high tin content referred to content $>2\%$. Representative samples were taken from the data collected in the study for analysis. The grain size and phase content of each sample was recorded and the effect on each of these was calculated separately. The factor effect in each case was calculated by taking the ratio of the sum of squares due to each factor (SSF) to the total sum of squares (TSS). In the case of phase content dependence on each variable, the overall mean came to 93 and the total sum of squares to 332. The results of the calculations are shown in Table A2.

	synthesis method	chlorine content	tin content	% rutile
kf2901	0	0	0	92%
kf1801	0	1	1	100%
kf2502	1	0	1	89%
kf2202	1	1	0	91%
degrees of freedom	1	1	1	
sum of squares	40	134	158	
total sum of squares	332			
factor effect	0.12	0.40	0.48	

Table A2 - Phase content Taguchi results.

The grain size results were calculated similarly, with a mean of 6.5 and a total sum of squares of 2. The results are shown in Table A3. The results aren't as definitive with the grain size dependence, owing to both the small sampling taken for this analysis and the resolution of the grain size measurement, and the results are therefore suspect.

	synthesis method	chlorine content	tin content	grain size
kf2901	0	0	0	7nm
kf1801	0	1	1	6nm
kf2502	1	0	1	7nm
kf2202	1	1	0	6nm
degrees of freedom	1	1	1	
sum of squares	0	1	0	
total sum of squares	1			
factor effect	0	1	0	

Table A3 - Grain size Taguchi results.