The Synthesis of Nano TiO₂ Particles Using a DC Transferred Arc Plasma Reactor

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© Xiaohong Liao, April 2011
TO MY MOTHER,

MY HUSBAND,

MY SON,

MY DAUGHTER

AND IN MEMORY OF MY FATHER
ABSTRACT

The effect of quench conditions on the properties of titanium dioxide produced using a transferred arc process was studied. Rutile phase TiO$_2$ in the form of micron sized powder was decomposed and vaporized in a continuous feed DC transferred arc system. The hot gas stream exiting the reactor contained a mixture of the decomposition products of titania including titanium suboxides (TiO, Ti$_2$O$_3$), argon (Ar), and oxygen (O$_2$). Rapid quenching of this gas stream with dry air resulted in the production of a titania aerosol. Collection of the product took place in the filtration system. The quench conditions studied included pre-quench temperature, $T_1$, quench rate, $R_q$, residence time, $\tau$, and operating power, $P_{torch}$. The characterization of particles includes phase identification, phase content calculation, size distribution analysis, elemental composition analysis, and morphology examination.

The range of quench conditions studied were as follows, $1300 < T_1 < 1700$K, $8000 < R_q < 18000$K/s, $50 < \tau < 80$ms, $7.6 < P_{torch} < 12.0$kW. In general, high quench rate produced small size and high surface area products. Residence time had no obvious effect on product size and crystal phase formation. Low operating power produced a high anatase fraction product. In all cases, spherical particles of a polymorphous mixture of anatase and rutile with no evidence of sintering were produced. Particle size ranged from less than 10 to 300nm. A representative sample has the mode of 22.3nm, median of 28.1nm and geometric standard deviation of 1.6nm.
RÉSUMÉ

L'effet des conditions de trempe sur les propriétés du dioxyde de titane produit par un procédé à arc transféré a été étudié. Des poudres de TiO$_2$ de la phase rutile et de taille micrométrique ont été alimentées en continu dans un arc à courant continu (CC), décomposées et vaporisées. Le flux de gaz chauds sortant du réacteur contenait un mélange de produits de décomposition : notamment de l'oxyde de titane (TiO), du Ti$_2$O$_3$, de l'argon (Ar) et de l'oxygène (O$_2$). Une trempe rapide de cet écoulement de gaz avec de l'air sec a abouti à la production d'un aérosol d'oxyde de titane qui fût ensuite récupéré avec l'aide d'un système de filtration. Les conditions opératoires étudiées comprenaient la température initiale avant la trempe, $T_1$, la vitesse de trempe, $R_q$, le temps de résidence, $\tau$, et la puissance de l'arc, $P_{torch}$. La phase, la teneur de la phase, la distribution de taille, la composition élémentaire ainsi que la morphologie des poudres produites ont été obtenus.

La gamme de conditions de trempe étudiées était la suivante : $1300 < T_1 < 1700$ K, $8000 < R_q < 18000$ K/s, $50 < \tau < 80$ ms, $7.6 < P_{torch} < 12.0$ kW. En général, les taux de trempe élevés ont généré des poudres de petite taille et surface spécifique élevée. Le temps de résidence n'a eu aucun effet évident sur la taille des poucres ainsi que sur la formation de la phase cristalline. Une faible puissance d'opération de la torche mène à la formation de poudres ayant une forte proportion de la phase anatase. Dans tous les cas, des poudres sphériques constituées d'un mélange polymorphe d'anatase et de rutile, sans apparence de frittage, ont été produites. La taille caractéristique des poudres varie de 10 à 300 nm. Un échantillon représentatif a montré un mode de 22.3 nm, une médiane de 28.1 nm et une écart type géométrique de 1.6 nm.
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NOMENCLATURE

Abbreviations

BET       Brunauer, Emmett, and Teller technique
CVD       Chemical Vapor Deposition
DAS       Data Acquisition System
DC        Direct Current
EDS       Energy Dispersive X-ray Spectroscopy
FE-SEM    Field Emission Scanning Electron Microscope
FWHM      Full Width at Half Maximum
ICP       Inductively Coupled Plasma
I.D.      Inside Diameter
lpm       Litres Per Minute
O.D.      Outside Diameter
RF        Radio Frequency
SEM       Scanning Electron Microscope
slpm      Standard Litres Per Minute (20 °C, 101.3kPa)
TEM       Transmission Electron Microscope
XRD  X-ray Diffraction

Roman Letters

A  Surface area (m$^2$)

$D_A$  Average particle diameter (surface based diameter) from BET surface area measurement (nm)

$D_v$  Average particle diameter (volume base diameter) from XRD spectrum measurement (nm)

$f_a$  Fraction of TiO$_2$ anatase

$f_r$  Fraction of TiO$_2$ anatase

$I$  Current (A)

$I_a$  XRD spectra intensity of anatase signal (counts)

$I_r$  XRD spectra intensity of rutile signal (counts)

$l_q$  Length of quench region (cm)

$n$  Total molar flow rate (mole/m)

$P$  Pressure (psi)

$P_{torch}$  Power of the torch (kW)

$Q$  Volumetric flow rate (slpm)

$Q_{air}$  Volumetric flow rate of quench air (slpm, at 1 atm, 298K,)
\( Q_f \)  Volumetric argon flow rate of feeder (slpm, at 1 atm, 298K.)

\( Q_{pq} \)  Volumetric argon flow rate before quench (slpm)

\( Q_t \)  Volumetric argon flow rate of torch (slpm, at 1 atm, 298K)

\( Q_{g0} \)  Volumetric gas flow rate (slpm, at 1 atm, 298K)

\( Q_{vi} \)  Volumetric gas flow rate at \( i \)th thermocouple location along the quench pipe (slpm)

\( Q_w \)  Volumetric argon flow rate of observation window (slpm, at 1 atm, 298K)

\( R \)  Gas constant (8.314 J·K\(^{-1}\)·mol\(^{-1}\))

\( R_q \)  Quench rate (K/s)

\( r \)  Pearson’s correlation coefficient

\( r^* \)  Critical radius (m)

\( t \)  Time (s)

\( T \)  Temperature (ºC)

\( T_m \)  Melting temperature (ºC)

\( T1 \)  Pre-quench temperature (ºC)

\( T2 \)  Quench temperature (ºC)

\( T3 \)  Growth zone point 3 temperature (ºC)

\( T4 \)  Growth zone point 4 temperature (ºC)
$T5$ Temperature of the gas entering the filter bag (°C)

$V$ Voltage (V)

$v$ Velocity of gas flow (m/s)

Greek letters

$\Delta G^*$ Free energy formation of critical radius (J)

$\Delta H_s$ Enthalpy of sublimation (KJ·mol$^{-1}$).

$\Delta T$ Change of temperature (K)

$\theta$ The diffraction angle (°)

$\rho$ Density (g/cm$^3$)

$\rho_a$ Density of TiO$_2$ anatase (g/cm$^3$)

$\rho_p$ True density of TiO$_2$ mixture particle (g/cm$^3$)

$\rho_r$ Density of TiO$_2$ rutile (g/cm$^3$)

$\sigma$ Surface tension (N/m)

$\tau$ Residence time (ms)
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Chapter 1  Introduction

Titanium dioxide, also known as titania, is a naturally occurring oxide. The crystal structure of titanium dioxide exists in three morphologies: rutile, anatase and brookite. The rutile structure is the most thermally stable structure in bulk, while in nano scale (<10nm) metastable anatase is dominant. Both rutile and anatase are tetragonal despite having different structures; while brookite is orthorhombic. As shown in Figure 1, anatase structure repeats the orientation without twisting the angle like rutile structure; therefore, it is more loosely packed compared to rutile leading to a higher surface area.

![Crystalline structure of rutile and anatase](image)

Figure 1: Crystalline structure of rutile and anatase (Gaffet, 2007).

Titanium dioxide is one of the most widely used materials from daily life to high-tech field; its applications include:

- Paints, coatings and inks
- Plastics and paper
- Food
Chapter 1 Introduction

Medicine

Cosmetics

Construction

Semi-conductor materials

Energy production

Waste water remediation

The most noteworthy application of the titanium dioxide rutile structure is as the white pigment in a micron sized powder form. Due to its high refractive index, it provides the whiteness and opacity. Since 1916, commercial production of titanium dioxide pigments has been pioneered by KRONOS Worldwide, Inc. and its predecessors using the sulfate method. The company developed the chloride process to reduce the environmental impact of the sulfate process and the first chloride process plant was commissioned in 1970’s. Nowadays, two thirds of pigments are produced by the chloride process.

1.1 Properties of Nano Titania

With the development of nanotechnology, nano-scale titanium dioxide attracts great attention in the photochemical field and the photoelectrical field. Titania, either as a catalyst support or catalyst itself, has been extensively studied in recent years, (Anopo, 2004) (Arabatzis, 2003) (Gao, et al., 1999) (Herrmann, et al., 1997) (Chun, et al., 2009) (Jung, et al., 2005) (Bankmann, et al., 1992). Titania thin film coating on outdoor building materials such as glass, tile and stone has drawn a great deal of attention; and now these products are commercially available and referred to as self-cleaning products. The self-cleaning effect originated from the
nano effect properties. Nanoscale titania can decompose organic contamination by the oxidation process under ultraviolet irradiation; and due to its hydrophilic behavior, it can sheet water to wash off any debris and dust. Furthermore, nano titania reflects the harmful UV light by about 98%, which means these self-cleaning products can also act as a UV filter providing necessary protection from UV hazards. Thus, it is extensively applied to various products like lamps, anti-fogging mirrors, tents, car windows and car bodies etc. Efforts have been made to shift the photocatalytic activity of nano titania under visible light irradiation for indoor applications. By doping with atoms like nitrogen and transition metal ions, this goal can be achieved effectively (Asahi, et al., 2001). In recent years, titania has been considered for the production of renewable energy. Nanocrystalline titania was found to be one of the valuable media to convert sunlight into electrical energy in the development of solar cells (Ito, et al., 2006).

1.2 Titania Photo Catalytic Activity

Another environmentally important application of nano titania is to use nanocrystalline titanium dioxide to treat waste water by suspending the nanopowder in waste water and exposing it to sunshine. Research showed that anatase titanium dioxide has significantly higher efficiency than the rutile form in terms of decomposition rate of organic compounds due to the higher surface to volume ratio and larger conducting band gap.

To our knowledge, two types of nano sized titania, which have surface area greater than 50 m²/g, are commercially available. Degussa’s P25 TiO₂ is fumed titania through the flame hydrolysis of TiCl₄ (Kloepfer, 1953) and Rhône-Poulenc’s DT51 TiO₂ is precipitated titania produced by the sulfate route. The properties of these two types are listed in Table 1 (Bankmann, et al., 1992). As shown in the table, the purity of Degussa’s P25 is greater than 95% and 32% of particles are in the range of 2nm to 30nm. The surface area is about 55 m²/g in crystalline phase of about 20-30 %
rutile and 80-70% anatase. The crystalline form is the result of high temperature and short residence time in the hot zone during synthesis. Precipitated Rhône-Poulenc’s DT51titnia has a higher surface area (100 m²/g) due to the ring-shaped open structure of the particles in the pure form of anatase with a wider size distribution compared to Degussa’s P25. The different morphologies can be distinguished by TEM analysis as shown in Figure 2.

### Table 1: Properties of P25 and DT51

<table>
<thead>
<tr>
<th>TiO₂ Properties</th>
<th>Degussa’s P25</th>
<th>Rhône-Poulenc’s DT51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical purity/impurity</td>
<td>Purity &gt;99.5%</td>
<td>Impurity sulfate&lt;2wt%</td>
</tr>
<tr>
<td>D&gt;300nm</td>
<td>2%</td>
<td>14%</td>
</tr>
<tr>
<td>D=2-30nm</td>
<td>32%</td>
<td>26%</td>
</tr>
<tr>
<td>Pore volume[ml/g]</td>
<td>0.34</td>
<td>0.40</td>
</tr>
<tr>
<td>BET surface area[m²/g]</td>
<td>55</td>
<td>100</td>
</tr>
<tr>
<td>XRD Crystalline phase</td>
<td>70-80% Anatase, 30-20 % Rutile</td>
<td>100 % Anatase</td>
</tr>
</tbody>
</table>

**Figure 2:** Comparison of fumed and precipitated TiO₂ powder by TEM analysis (Bankmann, et al., 1992)
To decompose the organic waste effectively, the uniform suspension of a photo catalyst is preferred to provide the maximum contact surfaces, which speeds up the chemical reactions. However, titania tends to aggregate in water; as a result, the surface area is reduced and the efficiency of photo catalytic activity will be lost or reduced significantly. A simple way to solve this problem is to coat the titania with a thin layer of silica (Mchida, et al., 1999) (Yang, et al., 2009). It is simple and economical, however, difficult to recycle the suspended catalysts. Liao et al. tried to use nanometer-sized Fe₃O₄ as the support to make a hybrid titania catalyst that has good magnetic properties for recovery; the experimental results showed a great improvement of recycling efficiency (Liao, et al., 2004).

1.3 Objectives

This research project is a continuation of Altenhoff’s work (Altenhoff, 2009) under the supervision of Prof. Munz (McGill University Plasma group). He demonstrated the technical feasibility of making nano TiO₂ using transferred arc plasma technology in a batch mode. However, he was not able to study the effect of the operating parameters to the product properties.

In the present work, the primary goal is to demonstrate the feasibility to synthesize nano titania continuously using DC transferred arc plasma reactor and to optimize the reaction parameters, like operating voltage, current, feeding rate, quench rate, and quench temperature, to maximize content of anatase phase nano titania under steady state while minimize the contaminations.

The second goal is to produce SiO₂ coated nano titania as the photocatalyst by introducing the SiCl₄ vapor in the quench gas. The influence of operating parameters, such as
Chapter 1 Introduction

quench temperature and quench rate of SiCl₄, to the resulting TiO₂/SiO₂ composition will be focused under the optimized condition obtained from the production of pure anatase titania in the first experiments. However, due to the Si contamination present in the produce, addition of SiCl₄ is not necessary.

The third goal is to characterize the powder produced and their properties. The morphology of products will be analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM); the phase formation and composition will be analyzed using X-ray diffraction (XRD); the surface area will be analyzed by specific area measurements (BET); and the elemental composition will be analyzed by energy dispersive X-ray spectroscopy (EDS or EDX). Correlation of the effect of operating conditions with product properties and comparison of the results with the properties of AEROXIDE TiO2 P25, a commercial product of Degussa, should be completed.
Chapter 2  Literature Review

This section gives a brief review of the various synthesis methods of nano titania powder. Synthesis includes gas phase and liquid phase methods. The liquid phase method is dominated by the gel-sol method. Gas phase methods include flame hydrolysis process and plasma processes. The flame hydrolysis process is a widely used and efficient method that belongs to chemical vapor deposition (CVD) process. The plasma approach includes CVD and simple physical evaporation corresponding to liquid/gas precursor and solid phase precursor, respectively. However, since plasma has higher energy than flame, it can offer two extreme reaction conditions for evaporation and super-cooling, which leads to ultrafine particles.

2.1  Sol-Gel Process

More attention was paid to the solution–based synthesis of nano particles in the last decade, since it can produce a smaller size, a narrower size distribution and about twice the surface area of the flame hydrolysis method. As mentioned before, the surface area is almost two times larger than the flame method because the product from this process has an open ring structure. It normally starts from titanium containing organic compounds and passes through a series of reactions to produce an amorphous or low crystalline intermediate; then through careful heat treatments the intermediate is converted to the desired crystalline nano powder. The main drawback is that the heating process will cause a significant coagulation of initially extremely fine particles. Furthermore, the wet chemical process is not suitable for large scale production in the sense of requiring expensive treatments of the waste and having potential environmental hazards. The following schematic of sol-gel synthesis demonstrates a stepwise chemical additions and treatments. As we can see, it involves four sequential chemical reactions and more
than two days to get the final product. Every single step will introduce potential contamination resulting in poor yield or poor purity of product. In industry, more steps also mean more labor costs and less daily output. Another drawback of the gel-sol method is the starting material. Since it is an organic complex, other issues, like safety, environment compact, and cost, will be considered.

![Diagram of the synthesis of TiO$_2$ powder by a sol-gel method](image-url)

Figure 3: Schematic diagram for the synthesis of TiO$_2$ powder by a sol-gel method (Pookmanee, et al., 2009).
2.2 Flame Hydrolysis Process

The main process used industrially to produce fumed titania is the flame hydrolysis process, also known as the Aerosil® process. The overall reaction in the process is,

\[
TiCl_4(g) + O_2(g) \rightarrow TiO_2(g) + 2Cl_2(g)
\]  

(1)

The method was first employed by Degussa in 1942. The precursor is introduced into hydrogen-oxygen diffusion flame forming molecular or cluster compounds in the gas phase.

Figure 4: The basic steps of particle formation and growth by gas-to particle conversion adapted from (Pratsinis, 1998)
Chapter 2 Literature Review

Shown in Figure 4 are the particle formation mechanisms in the flame hydrolysis method. As the aerosol stream leaves the hot temperature zone and cools down, particles are formed through homogeneous nucleation from supersaturated vapor. On the way to the collection zone, particles continuously grow through condensation, surface reactions, and coagulation and aggregation mechanisms. Post-processing like the calcination stage is performed before product collection due to chlorine gas absorption by titania. Finally, particles are collected in a baghouse filter, electrostatic precipitator or cyclone separator. Serious operational problems can exist during transport: for example, the particles can be removed from the process stream by diffusion and thermophoresis to the reactor walls, (Pratsinis, 1998). The flame synthesis normally results in micron sized particles, thus careful controls and post treatments are required to get nano particles. That makes it not practical in industry.

2.3 Plasma Process

2.3.1 Introduction of Plasma

Plasma, also called the forth state of matter, represents greater than 99% of the mass of the universe. The term plasma was first defined by Langmuir. He wrote “Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the name plasma to describe this region containing balanced charges of ions and electrons (Langmuir, 1928).” The definition accurately stated the electrical quasi-neutrality of plasma; furthermore, because of these free charged particles, a plasma gas is distinguished from an ordinary gas in term of its high electrical conductivity. Furthermore, the high energy content of the plasma makes it an ideal source for processing.
Processing plasma can be either thermal or non-thermal in terms of the electron temperature. When the temperature of heavy atoms is equal to the temperature of electrons, in other words, they are in the kinetic equilibrium state; we call this type of plasma thermal plasma. Thermal plasma technology is widely used in the fields like: plasma deposition, plasma synthesis of fine powders, plasma decomposition, plasma metallurgy, plasma densification and plasma welding and cutting, where high temperature is desired. In contrast, plasmas with strong deviations from kinetic equilibrium are called non-thermal plasma. For instance, in non-thermal plasma, the temperature of electrons can be greater than 1eV (11 600K), while the temperature of heavy atoms remains in the room temperature range. This property has a great advantage for the treatment of temperature sensitive materials where only the high temperature of electrons is desired to process chemical reactions. Therefore, it is widely used in the field like surface cleaning or sterilization, surface modification by ion implantation and diffusion, thin–film deposition by evaporative condensation and sputtering, plasma chemical vapor deposition and plasma etching.

Figure 5: Classification of plasmas.
Chapter 2 Literature Review

In thermal plasma, the DC plasma and RF plasma are classified by the different torch types. In DC plasma, torch designs can further classified to transferred arc and non-transferred arc types according to the usage of electrodes. The position of the transferred arc reactor employed in this project in the classification of plasma device is shown in Figure 5.

As shown in Figure 6, transferred arc plasma devices use the work piece as the anode. However, to start, it usually utilizes an auxiliary electrode (nozzle) to generate the initial arc between cathode and nozzle; then this arc is transferred from the nozzle to the work anode, which is the material to be processed. Because of this configuration, the material has to be electrically conductive in order to sustain the plasma. While in non-transferred arc plasma devices, the nozzle remains as the main anode to sustain the plasma throughout the whole process; therefore, no conductivity requirement for the work piece.
2.3.2 Thermal Plasma Synthesis of Fine Powder

In the thermal plasma synthesis of fine powder, the chemical mechanism is essentially the same as the gas-to-particle conversion shown in Figure 4. The differences are the source of energy to convert a precursor to reactive vapor in the first place and temperature gradients the system can provide. The high energy source of thermal plasma is used to generate active species for the chemical reaction in the vapor phase, and then the vapor is cooled down rapidly to nucleate particles. The quenching rate, vapor concentration and residence time are the major controllable parameters to determine size distribution, morphology as well as chemical composition and surface properties. Ceramic powders such as carbides, nitrides, and oxides have...
been successively synthesized in thermal plasma reactors. Research in thermal plasma synthesis of fine powder has concentrated on designing novel reactors and processes to enhance the powder quality. These novel designs include the RF-DC hybrid reactor, the reactive submerged arc (RSA), multiple plasma jets, and counter flow liquid-injection plasma reactors, (Pfender, 1999).

The great advantages of thermal plasma are its very high temperatures and steep temperature gradients, which provide the huge driving force for particle condensation (homogeneous nucleation) resulting in very fine particles due to the degree of supersaturation of the vapor species. Compared with the liquid method, the plasma method produces nano powders by one-step process and without post-processing.

The challenge of synthesis of nano particle like titania using plasma relies on a few controllable parameters, for instance, quenching rate, quenching gas injection, quenching gas, residence time, non-equilibrium electron population etc. The plasma temperature gradient is a function of the plasma gas, plasma flame stability, pressure inside the reactor, as well as the design of the torch. In some plasma devices, the particle formation starts at the tail of the plasma flame. Thus, synthesis of nano-particles using thermal plasma is really limited by the chemical and physical properties of precursors and products themselves.

Again, the chemical mechanism of plasma synthesis of nano titania is very similar to flame hydrolysis method, but with more efficient vaporization and ionization process in the plasma flame than in a combustion flame. The residence times of precursor and temperatures of plasma flame are roughly two to three times greater than those found in the hottest combustion flames (acetylene/nitrous oxide ) leading to total atomization and ionization (Skoog, et al., 1998).
These active species in the vapor phase at high temperatures lead to high reaction rates even in the case of very endothermic processes. The gas exiting the flame is then quenched rapidly. Because of the large drop in temperature, the vaporous product becomes supersaturated and nucleates out of the vapor phase homogeneously. This causes the formation of very fine particles in one step with the desired crystalline structure while in the Gel-sol method as shown in Figure 3, the initial product of titania is suspended in the solution. Through drying, the solution is converted into gel. Following the calcination at the proper temperature, the nano anatase powder is obtained. However, during the calcination, the initial fine powder inevitably aggregates. Furthermore, the initial formation of titania crystalline is rutile; it is impossible to directly use for photo catalysis without calcination.

2.3.2.1 RF Induction Plasma

Ishigaki, et al. investigated RF plasma synthesizes TiO$_2$ from liquid precursors or solid starting materials, (Li, et al., 2006) (Li, et al., 2007) (Oh, et al., 2005) (Ishigaki, et al., 2007) (Li, et al., 2004). They demonstrated the feasibility of synthesizing nano titania from inorganic TiN, TiC and TiCl$_4$, organic mixtures of titanium butoxide and diethanolamine solution. Experimental results showed that the direction of quench gas and the type of quench gas had effects in controlling the particle size. Transverse argon gas injection (Figure 7) of 100 l/min produced a $d_{50}$ value of ~52nm; while, with the same injection, Ar counter-flow produced a significantly finer powder $d_{50}$ value of ~34nm. Experimental setups for these two injections are shown in Figure 7. Helium possesses a higher thermal conductivity than argon in the temperature range 1500-3000K, where the nucleation and particle growth occur; it can enhance the rapid quenching to obtain smaller particles. Nevertheless, their studies were not practical in term of relatively expensive powder materials or complicated preparation of liquid precursors and the high power
consumption (~1900 kW/kg). Furthermore, size distribution of nano particle is crucial for most of the applications; however, RF plasma generated nano titania has sizes ranging from several nanometers to about 200nm.

![Figure 7: The experimental setups for transverse injection (a) and counter-flow injection (b) of quench gases (Li, et al., 2007)](image)

2.3.2.2 Plasma (Non-Transferred Arc)

DC plasma jet synthesis of nano titania was also studied by several groups (Lee, et al., 2004) (Kakati, et al., 2007) (Vijiay, et al., 2009) (Oh, et al., 2001). The problems associated with the plasma jet synthesis are the very short residence time and the difficulty of introducing precursor into plasma jet. A successful case study was done by Kakati et al. (Kakati, et al., 2007) using a multi-segment (cascaded) arc plasma torch based reactor, with the precursor-laden plasma beam expanding supersonically in to a low-pressure chamber to obtain nano scaled titania from oxidation of TiCl₄. The plasma torch consisted of a cathode and a stack of four copper ring segments separated by insulating rings and a copper anode as shown in Figure 8. The main contribution of this work was the narrower size distribution of 15 to 45nm, with an average of 20nm, compared to RF thermal plasma synthesis. The torch design greatly increases the electron density in the plasma column and residence times for the molecules. However, this also
means the corrosion of torch will be extremely high. Other limitations of this study are the complex reactor set-up and operating procedures. It requires a carefully controlled vacuum chamber, high speed pumps, and desired shock patterns at different stages of reaction.

Figure 8: Drawing of the basic reactor, where segmented torch is connected to the injection-section, nozzle combination (Kakati, et al., 2007)

2.3.2.3 DC Plasma (Transferred Arc)

Transferred arc DC plasma reactor design by Munz et al. of McGill University was
extensively used for synthesis of nano particles like fumed silica and aluminum nitride; and the quality of those products were comparable to commercial grades.

The synthesis process includes three major steps: the evaporation step, the quenching step, and the sample collection step. The design of this device enables completely separated regions for evaporation and quenching (see section 3.1 for details), which provides the possibility of controlling the chemical reactions or particle formations by adjusting the quench rates, vapor concentrations, or by changing quench gases or vapors. The operation of this reactor is simple and economical. The gas flow can be very small compared to the RF plasma device or plasma jet device. The reactor is operated under the atmospheric pressure; therefore, no expensive vacuum pump and no strict sealing are required. Furthermore, the reactor can be easily scaled up by increasing the current for large quantity production. The transferred arc plasma reactor has other advantages in common with all other transferred arc devices. For example, the high temperature of the arc root (>10,000K) can evaporate the starting material without any problem, since the arc strikes directly on the materials. Secondly, the energy efficiency for transferred arc system can be extremely high. In theory, the energy losses can be limited under 5 percent at the cathode only; other energy losses within the anode will evaporate the work material (Munz, et al., 1999). With the proper insulation, the convective heat losses to the reactor wall can be limited to a negligible level. However, efficiency is not the only concern. Material limitations for building up the devices are the major drawback for all the thermal plasma devices. Electrode erosion is a serious problem leading to the contamination of product, short life time of electrodes, sheathing gas restriction etc. In the transferred arc plasma reactor, the anode is the processing material, thus anode contamination and corrosion can be eliminated in the continuous synthesis system at the steady state, when evaporation rate and feeding rate are equal. At such conditions, arc always
strikes only on the surface of the molten material. The surface material evaporates rapidly, which is desirable, the loss is balanced by the feed, and the graphite crucible under the molten material remains intact. The transferred arc configuration relies on the material’s electrical conductivity at the process condition, since work piece itself will be one of work electrodes. A potential problem in working with most metal oxides is that they are electrical insulators at low temperatures and thus a special method is needed to start the system. Turner, et al. (2000) have patented an ignition method to solve this problem. Once the titania is molten at high temperature it has a good conductivity. Previous experiments done by Altenhoff (2009) using the transferred arc plasma reactor showed the feasibility of using the transferred arc plasma to produce nano titanium from micrometer scaled titania. This micron sized pigment grade rutile titanium powder is cheap and safe to handle. It is also clean to the environment without hazardous by-products to be handled. The chemical reactions involve the decomposition of titania to sub-oxides like TiO or Ti₂O₃ which are re-oxidized to titania by dry air as following,

\[ TiO_2(g) \rightarrow TiO(g) + \frac{1}{2} O_2(g) \]  

\[ 2TiO_2(g) \rightarrow Ti_2O_3(g) + \frac{1}{2} O_2(g) \]  

\[ TiO(g) + \frac{1}{2} O_2(g) \rightarrow TiO_2(g) \]  

\[ Ti_2O_3(g) + \frac{1}{2} O_2(g) \rightarrow 2TiO_2(g) \]

Decomposition reactions occur inside the plasma reactor; oxidation reaction occurs in the quench zone.
Chapter 3 Apparatus

3.1 Plasma Reactor

The transferred arc plasma reactor used in this project is the same as the one Addona used for his Master’s degree; the detailed design can be found in his thesis (Addona, 1993). The whole system configuration with power supply is shown in Figure 9. The main components consisted of the following:

1. Power supply and control console
2. Arc ignition and transfer system
3. Plasma gas flow instrumentation
4. Cooling water flow instrumentation
5. Transferred arc plasma torch
6. Reactor assembly
7. Feeding vibration chute
8. Quench manifold
9. Baghouse filter
10. Inline cartridge filter
11. Vacuum pump
12. Data collecting instrumentation
Figure 9: Transferred arc plasma reactor configuration (Addona, 1993)

The system can be divided into three regions according to the chemical reactions involved in the production of nanoparticles.

1. Evaporation zone (Reactor assembly): including detachable graphite chamber, crucible to load the bath material, cathode, nozzle and anode. In this zone, the initial raw material was loaded and evaporated by the transferred arc. The feeding material was added through the top
Chapter 3 Apparatus

flange of the reactor. By gravity, the feeding pellets fall into the crucible to maintain the consistent molten level.

2. Quench zone: including quench gas inlets, water cooling zone, air cooling zone and thermo-couples at different sites along the quench zone to monitor temperature profiles of the reaction. The hot gas stream left the reactor towards the quench zone, passing through the radially injected cold quench gas, further cooled by the water and air cooled tube wall in sequence. Thermocouples were located at different tube sites to monitor the temperature profile of process.

3. Sample collection zone: including air inlet for further cooling to the temperature that is safe to the filter, by-pass path of baghouse filter for the undesired exhaust, baghouse to hold the filter bag, inline filter cartridge, and vacuum pumps at the end of exhaust line to avoid building up pressure in the system and back flow of air into plasma reactor chamber.

As the temperature of thermal plasma is high enough to melt the construction pieces, water cooling is heavily employed for all the parts that are exposed to heat flux, for example, reactor wall, starting section of quench tube, cathode, nozzle, anode and window.

**Reactor Chamber Assembly**

The complete reactor assembly is shown in Figure 10. The reactor wall is made of stainless steel to give durability and electron magnetic interference shielding. Inside the wall, silica cloth (UC100-28, Armil C.F.S. Inc.) and alumina layers (blanket type ASB-2600, Zircar Fibrous Ceramics; blanket type RS-3000, Zircar Refractory Composites, Inc.) give both electrical and heat insulation. Further inside the reactor chamber, graphite felt (grade GFA10, SGL Carbon Corp.) and graphite chamber (grade HLM extrude, SGL Carbon Corp.) provide...
additional isolation to minimize the heat loss thus increase the energy efficiency.

The reactor has two openings on the top to let the torch and the feeding tube (ceramic pipe) in (Dia. 2.0 cm and 1.5 cm, respectively). The openings for the exit tube (Dia. 3.6 cm) and the observation window (Dia. 3.6 cm) are located on the side wall of the reactor graphite chamber.

Figure 10: Transferred arc plasma reactor cut view (Altenhoff, 2009)

**Torch**

Torch assembly is shown in Figure 11. The nozzle is made of copper, which has great heat conductivity for effective cooling and protecting the cathode. Inside the nozzle is a conical, concentric cathode made of 2% thoriated tungsten for electron emission. It is set into a heavily cooled copper tube.
The arc ignition and transfer system is shown schematically in Figure 12. The system consists of a high frequency generator, a high current 1 ohm resistor and a switch to open and close the circuit. Once activated, the generator could supply a high voltage spark.
The tip of cathode is designed to be the shortest distance (0.3 cm) to the bottom hole of nozzle as shown in Figure 12. This design ensures the arc is generated initially between the tip of cathode and the edge of nozzle hole only, and this arc will later be transferred to the anode which can be several centimeters away from the cathode. The auxiliary anode is to reduce the electrical
breakdown voltage of the plasma for both ease of ignition and safety. According to the Paschen curve, to breakdown neutral argon gas into plasma gas at atmosphere pressure, per centimeter gap between the electrodes will require 30kV voltage. For example, if we want to have a plasma column of 3cm, 90 kV voltage has to be supplied at the beginning. By shortening the gap to 3 mm, the initial voltage requirement reduces tenfold. After ignition, the voltage normally will drop to some tens of volts since the plasma gas is conductive; thus, a much lower power supply voltage can be used for sustaining the plasma. In practice a high voltage power supply increases potential hazards and cost.

**Product Collection**

The filter baghouse is shown in Figure 13. Three types of filter bag were tried.

![Figure 13: Schematic drawing of the filter baghouse..](image)
1. Nomex filter bag (Filtration Quebec: Nomex® 30cm diameter × 48cm long)

2. Polyester filter bag (Filtration Quebec: Polyester 12cm diameter × 22cm long)

3. Teflon membrane coated woven glassfiber filter bag (Filtration Quebec: 30 cm diameter × 24 cm long)

The Teflon membrane coated filter coated bag has the highest efficiency to collect our products.

![Diagram of filter cartridge and retainer disc of Model 30 housing](image)

Figure 14: Filter cartridge and retainer disc of Model 30 housing (Dow11).

The inline cartridge filter (Balston® Model 30 filter housing) is shown in Figure 14. In the Model 30 housing, the filter cartridge is sealed in place by a stainless steel spring acting on a lightweight stainless retainer disc. The retainer disc is pressed firmly into the end of the filter cartridge. When the filter is in service, flow through the filter cartridge is inside-to-outside so that even large solid particles which fall off the filter cartridge are held in the cartridge-disc assembly. Grade DH filter cartridge (temperature resistance up to 482°C) is used, which has
Chapter 3 Apparatus

Retention efficiency of 93% for particles at 10nm. Filter cartridge material consists of glass fiber, quartz fiber, and high performance polymers etc.

3.2 Measurement Techniques and Instrumentation

Important operating parameters including pressure, current, voltage, gas flow rate and temperatures are measured during the experiment.

Pressure Gauge

In order to monitor the pressure changes during the experiment, pressure gauges are installed at the reactor and baghouse. The experiment was conducted around one atmosphere, and the pressure was controlled less than 5 psi gauge. This limit was set by the gas leakage test. Negative gauge pressure was avoided at all the times to avoid potential inflow of air which would react with the graphite parts of the plasma reactor and reduce evaporation of titanium compounds.

Rotameter

Gas flow rates were measured by calibrated rotameters. Calibration of these rotameters was done with Gilian Gilibrator-2 air flow calibrator, under the identical conditions to that of the actual sampling. The rotameter reading can be converted into actual gas flow rate using the corresponding calibration curve.

ICP-DAS data acquisition system (DAS)

The DAS system consists of an input module and a computer. The input module used is ICP-DAS model I-7091R (Hoskin Scientific LTD). The module is an 8-channel voltage, current, and thermocouple analog input module, with the ability to connect various types of inputs to a
single module (Figure 15). It is designed for industrial plant environments and has special input circuits to provide ±240Vrms continuous overload protection. The analog signal was converted to a digital signal by I-7520: RS-232 to RS-485 converter for connection to a PC. The raw data were processed by the Labview 6.1 interface and recorded as the temperatures in °C, current in A and voltage in V. The rate of data acquisition was set at 60 samples per minute. The instrument accuracy is ± 0.15% of full scale reading.

![Terminal assignment of I-7019R model (Use11).](image)

Temperatures measured include (see Figure 18 for locations):

- **T1** (type C (0 to 2320 °C) thermal couple) pre-quench temperature, reactor exit gas temperature;

- **T2** (type K (-200 to 1250 °C) thermal couple) quench temperature where quench air is injected;

- **T3** (type K thermal couple) particle growth zone temperature point 3;
Chapter 3 Apparatus

$T_4$ (type K thermal couple) particle growth zone temperature point 4;

$T_5$ (type K thermal couple) temperature of gas entering the filter bag.
Chapter 4 Experimental Procedure

4.1 Material

The starting bath material for plasma production of nano titinia powder was rutile titania (99.5% min, metals basis) bought from Alfa Aesar (USA). The feeding material (99.5%, metals basis) was bought from Guangdong Huazhou TiO\textsubscript{2} Inc. (China).

The feeding pellets were prepared by a TDP-single tablet press (Mode Dia. 3mm, Max Pressure 20MPa, Shanghai Tianxiang & Chentai pharmaceutical machinery Co. LTD); the formed pellets have a diameter of 3mm and length of 2 mm.

4.2 Preparation of Reactor

The reactor was cleaned after each experiment. The condensed residue was removed from the reaction chamber and exit tube. The crucible was replaced with a new one for every experiment. The insulation was replaced once visual damage was observed. The resistance of graphite reactor chamber to the outside stainless steel wall was checked to make sure these parts were electrically insulated before closing the reactor. The detailed preparation procedure is described in the pre-experimental procedure section of Appendix D.

4.3 Experiments

The general experimental procedure was summarized as the following steps (Detail procedures were shown in experimental procedure section of Appendix D):

1. Clean the reactor and replace damage parts

2. Load the bath material
3. Check the isolation of the reactor inside chamber from the outside reactor wall

4. Close the reactor

5. Load the feed material

6. Connect the water pipes, gas lines check for leakage and gas pressure

7. Purge the system for 1 hour with argon at 10 slpm

8. Bypass the system (to avoid collection of not pseudo steady state product)

9. Ignite the plasma

10. Inject quench air

11. Start vacuum pumps

12. Start the data acquisition system to collect experimental data

13. Start feeding the titania pellets

14. Switch to baghouse after the system has reached steady state temperature

15. Shut down the system when finishing the experiment

16. Shut down the data acquisition system

17. Cool down the system to room temperature before shutting down the cooling water

18. Collect the product powder
Chapter 5  Analytical Methods

5.1  Instrumental Analysis

5.1.1  XRD

The X-ray diffraction instrument used in this study was a Philips PW 1710 diffractometer with monochromatic radiation under Bragg-Brentano geometry. X-ray diffraction is one of the most important non-destructive methods to identify and characterize the solid samples. It is widely used for phase identification, quantitative volume fraction analysis, crystallinity analysis, residual stress analysis, texture analysis etc. In our study, XRD is used to identify the crystal structure, composition, as well as crystalline size of the titania particles produced. Diffraction patterns (Figure 23) were collected with Cu Kα radiation (40kV, 20mA) in the step scanning mode. The scanning 2θ range was 10° to 100° with step size of 0.02° and collecting time of 1s per step.

The obtained spectra were processed by HighScore software as the following: identifying the background, eliminating outlier, stripping the Kα2 lines, and searching peak. The peaks were then compared to the literature data searching for candidates; and the best matched patterns were accepted.

Taking the full width at half maximum (FWHM), we also can estimate the crystallite size of the sample according to Scherrer formula,

$$D_c = \frac{f\lambda_{Cu}}{W_1 \cos \theta_B}$$

(5)
where $D_c$ is the crystallite size, $f$ is a dimensionless shape factor evaluated to 0.9, $\lambda_{Cu}$ is the X-ray wavelength ($\lambda_{Cu} = 1.5406 \text{Å}$ produced by copper anode), $W_1/2$ is the peak width at half the maximum intensity (in radians) and $\theta_B$ is the Bragg angle (in radians). The standard deviation of crystalline size was calculated based on all the peaks matched with the same reference code in the spectrum.

### 5.1.2 BET

BET is an important analysis technique for the specific surface area measurement of a solid sample. It is based on Langmuir isotherm of the monolayer gas adsorption, and extended to multilayer gas adsorption. Adsorption is the consequence of surface energy minimization. In BET theory, the adsorption mechanism concerned is physical adsorption, which is a function of temperature, gas pressure, interactions between the surface and the gas (e.g. vapor pressure), and surface area. Therefore, at a given pressure and temperature, the amount of gas adsorbed on a solid surface can derive the surface area of the solid. From the surface area measurement, a representative average particle size can be obtained using the following equation (2), assuming the particle to be spherical.

\[
D_{av} = \frac{6}{\rho_p A}
\]

where $\rho_p$ is the true density of the particle and $A$ is the specific surface area given in m$^2$/g. Since the product we produced is the mixture of anatase and rutile, the relative density is calculated from the following (3)

\[
\rho_p = f_a \rho_a + f_r \rho_r
\]
where $f_a$ and $f_r$ denote fraction of anatase and rutile, and $\rho_r$ and $\rho_a$ denote density of anatase and rutile, respectively.

The equipment used for BET analysis in this study was a TriStar 3000 analyzer, which uses physical adsorption and capillary condensation principle to obtain information about the surface area and porosity of a solid material. It consists of three units: a degas unit for preparation of a clear sample, a surface area measurement unit including three independently sample stations and four gas transducer, a computer control unit for setup of the parameters, recording data and performing calculations. The sample measurement cycle includes cooling the sample tubes to 77 K (temperature of liquid nitrogen at atmosphere), then exposing the sample to analysis gas at a series of precisely controlled pressures. As the pressure is increased stepwise, the ratio of equilibrium pressure and saturated pressure is recorded along with the amount of gas absorbed at each equilibrium pressure. During the adsorption process, the micropores will be filled first, and then the free surface will be covered completely. The larger pores will be filled last by capillary condensation of the analysis gas. After that, a reverse process of adsorption, desorption will be proceeded in the reverse fashion. Pressure is decreased stepwise allowing the release of the gas; the quantity of gas liberated at each equilibrium pressure is recorded. From these two sets of data, adsorption and desorption isotherm can be plotted, and the surface area porosity of the sample can be derived. These calculations are done by the computer, a detailed report can be obtained including the operating conditions (for example, relative pressure, absolute pressure, quantity adsorbed, time and saturation pressure) at each step, isotherm linear plot, isotherm log plot, BET surface area report, and BET surface area plot. Figure 16 showed the Tristar 3000 BET analyzer used in this study.
5.1.3 SEM

The scanning electron microscopy (SEM), Hitachi S-4700 FEG-SEM (Field Emission Gun) was employed to exam the morphology, size distribution and chemical composition in this study. The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals derived from electron-sample interaction reveal information about the sample such as external morphology by means of secondary electron emission and chemical composition by means of energy dispersive X-ray emission (EDS). The SEM is also capable of performing analysis of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS).

In our study, the produced nano titanium dioxide powder was dusted onto a conductive double-sided adhesive carbon tape. While doing so, the particles were dispersed as widely as possible and excess powder was removed by compressed air. This sample preparation method allowed us to observe a relatively large number of nano particles in one analysis, which could represent the real sample morphology. However, charging occurred as nano titania is not
conductive at room temperature. Impinging electrons are trapped within the sample and these accumulated electrons on the surface will distort the image by deviating electron probes and secondary electrons arising from repulsion. Therefore, a low accelerating voltage (2kV) with current of 10 μA was used in the study of morphology to obtain fairly good images. A high accelerating voltage of 10 kV with a current of 10 μA was used for the elemental composition study in EDS.

5.1.4 TEM

The transmission electron microscope (TEM) is capable to study the size, shape and arrangement of the particles with atomic scale resolution using a high energy electron beam transmitted through a very thin sample. Philips CM200 200 kV FEG-TEM was employed to study the morphology and composition of plasma produced particles in this study. The schematic outline of a TEM is shown in Figure 17. The electrons are focused with electromagnetic lenses and the image is observed on a digital camera. The electrons accelerated at 200kV have a wavelength of 0.025Å; therefore in theory, it could resolve the image close to this range. However, the resolution of TEM is limited by aberrations inherent in electromagnetic lenses, to about 1-2 Å. For our purpose, this is fine enough to study the morphology, crystal lattice, and defects of the crystal produced. The TEM is also capable of forming a focused electron probe, as small as 20 Å, which can be positioned on a specific particle in the sample for microdiffraction information or analysis of x-rays for compositional information.

Different from SEM sample preparation-dusted directly on the carbon tape, particles were dispersed in acetone first, then a few drops of suspension were dribbled on the copper grid (G200 square mesh with carbon film coating) placed on the Kim wipes to absorb acetone. The grid was air dried for more than 10 minutes before analysis to ensure the acetone was totally evaporated.
5.2 Calculation of Operating Parameters

Important operating parameters including pressure, current, voltage, gas flow rate and temperatures are measured during the experiment.

5.2.1 Power ($P_{torch}$) Calculation

Power was calculated through measured current ($I$) and voltage ($V$) by the following equation

$$P_{torch} = IV \quad (8)$$
5.2.2 Quench rate ($R_q$) Calculation

In the different sites of plasma reactor system, the pressure and temperature have been measured as shown in Figure 18. The pressures of plasma reactor and exit tube after cooling are named $P_{V1}$ and $P_{V2}$, respectively. There are 5 sites for measuring temperature. Site 1 is located at the exit of reactor, its temperature $T1$ is referred as pre-quench temperature. Site 2 is the injection point of compressed dry air, its temperature $T2$ is really the mixing temperature. Site 3 is arranged after water-cooling, its temperature $T3$ also referred to quench temperature. $T4$ is the temperature of the site with the heat loss to room air through the pipe wall by convection; $T5$ is the site with the injection of compressed dry air before the hot gas stream entering the filter baghouse.

![Figure 18: Schematic drawing identifying the sites of pressure and temperature measurement in the plasma reactor system.](image)

The quench rate ($R_q$, $K/s$) is denoted as the change of temperature ($\Delta T$, $K$) during the quench time ($\Delta t$, s), it is shown in Equation (9).
Chapter 5 Analytical Methods

\[ R_q = \frac{\Delta T}{\Delta t} \]  \hspace{1cm} (9)

where, \( \Delta T \) is the change of temperature between site 1 and site 3, i.e. \( \Delta T = T_1 - T_3 \), then \( \Delta T \) is the residence time of mixture gas between site 1 and site 3, the calculation of \( \Delta T \) is shown in Equation (10),

\[ \Delta t = \frac{\Delta l}{\frac{Q_{v1} + Q_{v3}}{2S}} \]  \hspace{1cm} (10)

where \( \Delta l \) is the distance of quench process from site 1 to site 3; \( Q_{v1} \) and \( Q_{v3} \) are volumetric flow rates of the gas at site 1 and site 3 respectively; \( S \) is the inner cross-sectional area of exit tube. We assume that the high-temperature gas obeys the ideal gas law,

\[ P_v Q_v = nRT \]  \hspace{1cm} (11)

where \( P_v \) is the pressure in the reactor, \( n \) is the total molar flow rate, \( R \) is the gas constant, and \( T \) is the temperature at the different measuring points.

Assume the pressure and total mass of gas are constant inside the reactor, then,

\[ \frac{Q_{v0}}{Q_{vi}} = \frac{T_0}{T_i} \]  \hspace{1cm} (12)

The subscripts \( i \) indicate the different temperature sites inside the plasma reactor system. \( T_0 \) means the initial condition of gas at the room temperature (298K); and \( Q_{v0} \) is the gas flow rate from compressed cylinder to the reactor.

\[ Q_{v1} = \frac{(Q_i + Q_v + Q_f) \times T_i}{T_0} \]  \hspace{1cm} (13)
where $Q_t$, $Q_w$ and $Q_f$ is for volumetric gas flow rate of observation torch, window, and feeder, respectively.

### 5.2.3 Residence time ($\tau$) Calculation

Residence time ($\tau$) is denoted as the time of high-temperature mixing gas during the pre-quench and a specific temperature. It is shown in Equation (14),

$$
\tau = \frac{\Delta l_r}{Q_{v1} + Q_{v3} \over 2S}
$$

where $\Delta l_r$ is the distance of nanocrystalline growth or crystal phase transformation from site $T_1$ to $T_3$ point; $Q_{v3}$ is volumetric flow rate of the gas at specific $T_3$ point.

### 5.2.4 Anatase ratio Calculation

The anatase ratio was calculated from the generated calibration curve, according to the ratio of the strongest anatase peak to the strongest rutile peak. For a given sample, the ratio ($I_a/I_r$) of the intensity of the strongest anatase reflection to the intensity of the strongest rutile reflection is independent of fluctuations in diffractometer characteristics. This ratio therefore provides a useful index of sample composition (Spurr, et al., 1957). The calibration curve was generated by measuring XRD spectra (three replicas) of six known ratios of anatase and rutile mixtures and then plotting the ratio of the intensity at $2\theta$ of 23.5° (101 diffraction peak) for anatase and 25.7°(110 diffraction peak) for rutile with respect to reciprocal of rutile fraction. Through the linear regression, a calibration curve of reciprocal of rutile fraction ($1/f_r$) was obtained. The anatase ratio was then obtained assuming no other content present using the following equation.

$$
\text{Anatase fraction} = 1 - \text{Rutile fraction}
$$

(15)
Chapter 5 Analytical Methods

Standard deviation of anatase ratio was calculated from background influence of peak height. Two sets of peak height were obtained based on the computer defined base line and absolute zero line, respectively.

The resulting calibration curve of reciprocal of rutile weight fraction was shown in Figure 19. The linear relationship was obtained between the ratio of intensity of anatase and intensity of rutile ($I_a/I_r$) versus reciprocal of rutile weight fraction ($1/f_r$) in sample. The slope of the function is 0.6843 with the intercept of 0.9777. The data fit nicely for the linear function with R-square value of 99.83%. The empirical data of $I_a/I_r$ obtained from XRD spectra were within the calibration range, thus the calibration function was valid for the calculation of anatase/rutile fraction.

![Figure 19: Calibration curve for anatase and rutile ratio calculation.](image)
Chapter 6  Results and Discussion

6.0  Summary of Experimental Conditions

Different quench conditions were studied by varying the torch gas flow, the quench air flow and current to find the optimum conditions for the production of a high anatase: rutile ratio, which is close to Degussa P25. The torch position was located 3 cm above the crucible for all the experiments. The arc length was around 4-8 cm depending on the melt height in the crucible. The torch gas used was pure argon (99.9%) from MEGs. Dry air from the lab line was used for quench air. The successful experiments are summarized in Table 2. A total of 24 experiments were conducted, however due to various reasons only ten experiments yielded full results. The experiments were grouped according to total argon flow rate and quench air flow rate. For runs xl-05 to xl-07, the feed consisted of irregularly shaped pellets (1-1.7 mm pieces) and the initial titania loaded into the crucible was 150-200 g. For runs xl-17 to xl-24, the feed was uniform cylindrical round pellets (Diameter 3 mm × Length 2 mm), and the crucible loading was 250 g. The duration of the experiments depended on the process conditions. The weight loss during the experiment was not recorded for each experiment, due to the difficulty of removing the reaction chamber to make the measurement. After each experiment, the reaction chamber stuck to the exit tube by the condensation of vapor, separating the parts by force might damage them.
## Table 2: Summary of successful experiments

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<th>Voltage (V)</th>
<th>$Q_{\text{argon}}$ (slpm)</th>
<th>$Q_{\text{air}}$ (slpm)</th>
<th>$T_1$ (°C)</th>
<th>$T_2$ (°C)</th>
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Notes:
- (A) = Amperes
- (V) = Volts
- (slpm) = Standard liters per minute
- (°C) = Degrees Celsius
- (min) = Minutes
6.1 General Observations and Discussion

The currents, voltages and temperatures reported here were averages at the pseudo-steady state conditions during which product was collected. The experiments could be divided into two periods, the preliminary testing period as runs xl-05 to xl-07 and formal experimental period as runs xl-17 to xl-24.

In the preliminary testing period, we encountered the particle collection problems. The particles were removed from the filter bag by blowing air into the filter bag to force the trapped powder out of the filter bag. We also collected the particles from the inside wall of the baghouse; this powder had bypassed the filter bag.

The results from the formal experimental period were considered more representative. In these runs, we overcame all the difficulties. Every experiment was successful and under control. The particles were all collected from either the filter cartridge or inside filter bag, which limited the contamination.

Voltage

Voltage was influenced by the feeding rate and melting process of the bath material, and it was very stable (±1V) once the pseudo-steady state was established. It was also used as a warning if the level of molten titania in the crucible was too low (sudden lowering of voltage), under these circumstances the feed rate would be increased.

Current

During the experiment, current was a major controllable parameter to yield a desirable pre-quench temperature. Higher currents resulted in higher pre-quench temperatures at pseudo
steady state operation; this provided a range of operating temperatures to test the effect of quench rate by changing the quench air flow rate. The upper limit of the current was set by other factors such as graphite crucible tolerant temperature, insulation material tolerant temperature, as well as the smoothness of the melt vaporization process (to avoid overflow). It was found that 160A is an ideal operating current. It provides pre-quench temperature of about 1200°C and smooth vaporization in the crucible. Furthermore, it was found it was better to start at a low current (ie.150A) for heating up the reactor without losing bath material too soon. The current was adjusted to the desired value when the exit gas temperature reached 1000°C. While feeding the titania pellets, the currents would oscillate slightly; therefore, the average current during the powder collection period was reported for each run. It was rounded to the nearest ten amps, which was limited by the sensitivity of the current measurement.

It is worth mentioning that the power control is a key obstacle to repeat an experiment due to two factors:

1. The precision of the ammeter was ±10 A, a slightly touch of the current knob will result in a huge oscillation of 10 to 20 A that corresponds to 5-10% of the operating current.

2. The voltage of pseudo- steady state was established according to feed rate, evaporation rate and the melt left in the crucible. To maintain all these factors the same as that of the former experiment is very hard.

**Quench Air**

Quench air is another important parameter which needs to be controlled. It determined the quench rate and completeness of oxidation, and thus determined the size of nano particles and phase composition of crystalline structure. The quench air flow rate varied from 15 to 55
slpm. The optimum quench air flow rate was 30 slpm that can produce particles around 30nm. The optimization considered the complete oxidation reactions, the narrow particle size distribution, as well as the safe operating pressure.

**Total Argon Flow Rate**

In column 4 of Table 2, one can see the total argon flow rates decreased from 35 slpm to 25 slpm after run xl-17. The window and feeder argon flow rate were kept the same. The torch argon flow rate was decreased from 25 slpm to 15 slpm. We intended to lower the energy flux to the anode surface under the arc in order to evenly heat the whole titania bath. The net local energy flux from the plasma to the anode surface includes the contribution due to convection, radiation and the electron acceleration and ‘condensation’. According to Chen, et al., (2001) 68.6% of the total heat flux from the plasma to the anode can be attributed to convection, 23.7% to electron condensation and acceleration while 7.7% is due to the radiation from the plasma to the anode surface. After decreasing the torch argon flow rate and initial current, less local damage of the crucible was observed indicating more uniform heating and a better circulation of the melt. Because the effects of arc current and torch flow rate are connected, no conclusion could be drawn regarding the effects of the individual parameters.

**Quench Temperature \((T_2)\)**

Quench temperature was measured just after the air injection point. It was controlled by the quench air flow rate. The higher quench air flow rate, the lower the temperature reported.

**Pre-quench Temperature \((T_1)\)**

Pre-quench temperature was measured in the reactor exit tube. It was determined by two
Chapter 6 Results and Discussion

factors: power of the system and the total argon flow rate. Increasing the power of the system should lead to a higher temperature, and this was consistent with the experimental observations shown in Figure 20. The error bars in this figure represent the standard deviation of one set of replicates. The correlation between temperature and power is medium (Pearson’s coefficient $r = 0.604$) because of the influence of other variables. The total argon flow rate has a lower but non negligible effect in our experiment compared to the power effect. For instance, xl-07 and xl-21 were very similar in operating power; however, xl-21 with low argon total flow rate has a higher pre-quench temperature. The insulation influence was not considered as a critical factor in this case, since the insulation was replaced once damage was observed; and we assume the insulation efficiency was all the same for each run.

![Graph](image)

Figure 20: System operating power versus pre-quench temperature.

Experiment Duration Time

The duration time includes two periods: the system bypass period and powder collection period. The number reported was the total reaction time and parentheses indicate the powder
collection time.

**Product Yield**

The product yield is low because of the very high evaporation temperature of TiO\textsubscript{2} and its sub-oxides. Although considerable material is evaporated, it does not leave the reactor chamber as shown in Figure 21. A thick crust consisting of TiO\textsubscript{2} sub-oxides, mainly Ti\textsubscript{2}O\textsubscript{3} and TiO, (see Figure A-4 XRD spectrum of residue in Appendix A) was observed on the reactor walls after each experiment.

**Optimized parameters**

Parameters used for experiment run xl-19 were believed to be the optimum situation since the product obtained for this run is very similar to Degussa P25 in crystal structure and particle size. Detailed comparisons are present in the product characterization section. Figure 21 shows the reactor chamber and crucible after the experiment. From Figure 21, it can be seen that the molten TiO\textsubscript{2} sub-oxides had covered the bottom of the crucible, and the melt and crucible
were separable. After removing the melt, the crucible was intact with no sign of arc damage but some signs of erosion due to the high temperature. It is very important to the process that the arc strike the melt rather than the crucible surface; the arc is intense enough to damage the crucible and this leads to contamination of the product by carbon. Also, since a great deal of energy is released at the arc root from the anode fall and resistance heating within the melt, it is far more energy efficient to have the arc to strike the melt.

6.2 Experimental Problems

6.2.1 Problems with Product Collection

The first problem encountered was the efficiency of the particle collection system. Since there is no filter bag specifically designed for nano particle collection, a Nomex® fiber filter bag was used. The nano powder was expected to go into the filter felt, block the holes and form a powder cake on the surface of filter bag; further collection would then build up on this cake. However, the surface area of the initial filter bag (Filtration Quebec: Nomex® 30cm diameter × 48cm long) was too large to form the collectable powder cake on the surface of filter bag during a single experiment, due to the small amount of powder produced. The filter bag house was remodeled to hold a small filter bag (12cm diameter × 22cm long). However, the seal of small filter bag holder was very poor due to thermal deformation of the old baghouse; considerable gas bypassed the filter bag and no improvement was obtained.

An inline filter (Balston® Model 30 filter housing, Grade DH Filter Cartridge) was installed after the bypass line. This cartridge filter system was able to collect a fair amount of particles within a short collecting time (i.e. 5 min). Only the particles produced during pseudo-steady-state operation were collected by inline cartridge and had less contamination of carbon.
Nevertheless, there were three drawbacks. First of all, pressure could build up during the powder collection because of the much smaller filtering area. The system must be kept below 5 psi gauge due to safety concerns and this restriction normally limited the particle collection period to 10 minutes. Secondly, since the filter cartridge was made of glass fiber, it might be a source of silicon contamination. The study was attempting to produce titania with silica coating; therefore, silica contamination should be strictly controlled. The last drawback was the high cost of cartridges compared to the filter bag cost.

A compromise solution was to use Teflon coated filter bags to collect the powder using the original filter bag holder. To increase collection efficiency and reduce the surface area of the filter bag, the bag length was reduced from 48cm to 24cm. Since the filter bag has Teflon coating, the most of produced powder was trapped on the filtering surface and ready for collection. A problem of contamination of the product by carbon remained. Because the bypass valve was located after the filter, transient pressure changes at the beginning of the experiments caused some dirty gas to flow into the baghouse. This gas contained some graphite from arc ignition and some graphite felt fibers from the reactor insulation.

### 6.2.2 System Related Limitations

1. The current plasma reactor system was very successful for synthesizing fumed silica. However, a much higher temperature is needed to decompose and vaporize titania. Quenchable TiO gas is formed ca. 3300-3700 K (Altenhoff, 2009) and plasma chamber wall temperature ranged from 1375 K to 1975 K (Addona, 1998), which means that much of the vapor product was condensed before reaching the quench section. This is consistent with the experimental observation as shown in Figure 21.
2. The higher required temperatures caused partial vaporization of some high silica insulation along the inner walls of the reactor and possibly contaminated the product with silica. Silica is much more volatile than titania, and will have a cumulative effect.

3. The higher power levels needed to vaporize titania caused local overheating of the molten anode leading to boiling and overflow of the melt.

4. The boiling behavior of the melt sometimes led to contact of the melt with the cathode sheath and cathode and damage to the torch. This limited the currents that could be used to about 190 A.

Figure 22: Crucible and chamber after 5 min reaction without feeding.

Figure 22 shows the crucible after 10 min of arc striking. It is a good example of local overheating when 200A was applied. Titania under the arc contact region was completely evaporated, and the bottom of graphite crucible was exposed. A splash of melt was observed on the wall of the reactor chamber; however, the graphite rod remained intact. These observations indicated that titania surrounding the arc was melted and evaporated quickly, and the arc was in direct contact with the bottom of the crucible to maintain a transferred arc without the help of the
graphite rod. This is also the reason for us to start the reactor at a lower current (150A) to warm up the crucible and reactor chamber gradually. The desired current was adjusted when the bath titania melted.

### 6.2.3 Other Problems

1. Torch failure

   Tungsten tip of the torch was worn during the experimental period, and no longer protruded out of the nozzle hole. In the worst situation an initial unstable arc would contact the nozzle and melt the contact point causing water leakage.

2. Feeding tube blockage

   The tube diameter inside the vibrating chute (6 mm) is only two times larger than the pellets size (Dia. 3mm× Length. 2 mm). Once several particles stacked together, the loose powder produced upon handling and feeding would fill up the gaps and block the path totally. This could be solved by blowing argon into the vibration chute from below the feed tube, when blockage happened. Also, drying the material before the experiment was also useful to reduce the tube blockage.

   The tip of the feeding tube inside the reactor should be kept as far away as possible from the arc to avoid accumulating of excess condensation, which would lead to a blockage of the feeding tube opening. The feeding tube inside the reactor had to be cleaned and polished after each experiment to avoid blockage.

### 6.3 Product Characterization

In spite of the above difficulties we were able to identify the operating conditions for
producing a high content of anatase (70.8%) with the average diameter of 38.6±0.6nm (run xl-19, based on BET analysis). The following Table 3 shows the comparison of our samples withDegussa P25. The experiments were divided into five groups with the same argon flow rate and same quench air flow rate for later comparison. The product analysis of TEM and SEM were focused on the experiment xl-23 and xl-24, these last two runs had minimum contamination. Temperature profiles of these two runs as well as xl-19 are shown in Appendix C. The plateau region of the temperature profile demonstrates the pseudo-steady state achieved during the synthesis.

Table 3: The summary of experiment results

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<td>0.4</td>
<td>83.2898</td>
<td>1.4700</td>
</tr>
</tbody>
</table>

6.3.1 Crystallographic Structure

The XRD pattern analysis identifies the crystallographic structure of the produced powder. XRD spectra of the powder produced were reproduced in the same scale on one graph for comparison (Figure 23). It was noticed that a mixture of anatase and rutile crystal structure was obtained in all cases. Characteristic peaks at 20 of 25.3° and 27.5° represent strongest
reflection of the anatase and rutile phases, respectively. Peak heights indicate the phase ratio semi-quantitatively.

The peak pattern of our sample is very similar to Degussa P25. The different peaks were marked by the vertical dashed lines in Figure 23. The 1\textsuperscript{st}, 3\textsuperscript{rd} and 4\textsuperscript{th} lines are the rutile peaks, which missed in Degussa P25 and showed up in all plasma produced samples. The 2\textsuperscript{nd} line is also a rutile peak. It showed up in Degussa P25, but missed in our samples. This could due to the different synthesis methods resulting in different defects, which are detectable by XRD. An example is that the XRD spectrum of the natural occurring rutile is different from that of synthesized rutile.

![XRD spectra of products compared with P25.](image)

Figure 23: XRD spectra of products compared with P25.

The peak list of the powder produced in run xl-19 was shown in Figure 24 as an example.
Chapter 6 Results and Discussion

The top graph was the total peak list identified in the XRD spectrum. The following graphs were the best matched structures labeled with the reference codes. It was observed that all the lines in peak list can be matched to a reference line indicating no crystalline structures other than anatase or rutile were present in this sample. The line spectra of xl-23 and xl-24 are shown in Appendix A.

Figure 24: Peak list of powder produced in run xl-19 with reference peak list of anatase and rutile.

Figure 25: Peak list of powder produced in run xl-17 with reference peak list of anatase, rutile and graphite.
It is noticed that for run xl-17 and xl-20, a small peak was observed around 26.5° indicating graphite contamination as shown in Figure 23 and Figure 25. This is also consistent with lower peak height of our sample than that of P25, indicating less crystals in the sample.

The background of XRD spectrum for each sample was much higher than that of Degussa P25, which probably indicates some amorphous contents in the sample. A detailed discussion is in the elemental composition analysis section.

6.3.3 Particle Size Analysis

There are several ways to analyze the particle size and distribution of a powder. Due to the different theories, the particle sizes obtained are expected to be slightly different from different measurement techniques. Since our TiO$_2$ particles were not necessarily single crystals, XRD can only provide us an indication of the smallest crystal present in the sample.

BET measurement enables us to calculate the average particle size based on a relatively large sample. The larger sampling scale yields a closer representation of the real sample properties. However, BET analysis cannot distinguish TiO$_2$ particles from the contaminants. The average particle size is directly influenced by the particle size of contaminants. Summarized particle sizes obtained from XRD and BET measurements with its deviation can be found in Table 3.

Fortunately, TEM image provides us another method to study the particle size distribution. Size distribution may be obtained by counting particles in the TEM image. Also, the TEM image was able to distinguish contamination from TiO$_2$ by shape, particle darkness (reflecting density of material) and particle aggregation. Confirmed contaminations can be excluded from the calculation. (The results will be discussed in Section 6.3.3.3.)
6.3.3.1 Particle Size Calculated from XRD

XRD spectra provide us crystallite size of the particles that is volume-weighted average \( (D_v) \). The narrower the peak the smaller crystalline size it is indicated. The peaks identified were used to calculate the corresponding particle size using Equation (5), and by averaging the same phase, we got the rutile and anatase crystal size. Standard deviation was obtained from these data. The main diameter of the mixture of anatase and rutile was calculated as a mass average of the two component as shown in Equation (16).

\[
D_{\text{XRD, Average}} = D_{\text{XRD, Anatase}} \times f_a + D_{\text{XRD, Rutile}} \times f_r
\]  

(16)

Figure 26: Average crystallite sizes calculated from XRD spectra with the error bars based on standard deviation.

The crystallite size versus quench rate was plotted in Figure 26. It is noticed that within the error range, the crystallite size seems has no significant changes with the increasing quench rate. Through a linear regression analysis, the crystallite size versus quench rate has a nearly zero slope of \( 10^{-4} \text{ K/s} \), and intercept of 23.18nm. The Pearson’s correlation coefficient, \( r = -0.06 \), is
very close to zero, which mean no correlation. The fact that quench rate has a minor or no effect on crystallite size is normal, since it might only represent the smallest unit cell in a large particle. However, the quench rate has a considerable influence on particle size in our system as shown later in BET calculation of particle size.

The particle size obtained from XRD has a standard deviation ranging from 30 to 60%. The large deviation could come from the amorphous particle present in the sample, which shifts the background of spectrum and thus affects the accuracy of HWHM value. For a better result, an advanced profile fitting by individual peaks considering both instrumental broadening and specimen broadening effects is recommended. To do so, the specialized data analysis software like ‘MDI Jade’ is required. The Scherrer analysis assumes the particles have spherical crystallite shapes. From the TEM and SEM images of the plasma produced sample, we know this method is valid to estimate our samples; however, this assumption is not accurate according to TEM image of Degussa P25 (Figure 33), in which the particles are cuboids. This explains the large standard deviation of XRD based particle size for Degussa P25 analysis, in which there are no amorphous particles contributing to the background noise. Also, the large standard deviation probably suggests the existence of crystallite size dispersion in our sample.

Assuming each reflection peak of whole-powder-pattern represented for spherical crystallites with a lognormal distribution of diameters (Langford, et al., 2000), mass median diameter(MMD), surface median diameter(SMD), number median diameter(NMD), and geometric standard deviations were calculated and tabulated in similar for geometric standard deviation calculation. MMD was converted to SMD and NMD according to the following Equation (17) and (18), respectively.
\[ \ln MMD = \ln NMD + 3\ln^2 \sigma_g \]  \hspace{1cm} (17)

\[ \ln SMD = \ln NMD + 2\ln^2 \sigma_g \]  \hspace{1cm} (18)

The sequence of median size always follow MMD > SMD > NMD.

The relationship of MMD versus quench rate was plotted in Figure 27. Pearson’s correlation coefficient is 0.13 suggesting very weak correlation between quench rate and crystallite size.

![Figure 27: Crystallite size of the samples versus quench rate with geometric standard deviation.](image)

It is of interest to notice that in Table 4, geometric standard deviations for all the runs are close to 1.60nm except xl-18 and xl-22. This observation is consistent with size distribution computed from TEM number diameter in which \( \sigma_g \) is 1.62nm. This might suggest that the previous assumption is valid; the crystallite size obeys the lognormal distribution as the particle size for plasma produced titania. From the Table 4, comparing group xl-23/xl-21 and group xl-19/xl-24, it is noticed that with the same quench air flow rate and a similar quench rate the
crystallite size is larger when pre-quench temperature is higher. However, this trend is opposite as for xl-17/xl-18. The geometric deviation of xl-18 is 2.11nm, and much larger than the others. The result of experiment xl-18 might be an outlier. To confirm the conclusion, further repeat experiments should be done.

Table 4: Size distribution calculated from XRD spectra

<table>
<thead>
<tr>
<th>runs</th>
<th>$D_v$ (nm)</th>
<th>MMD (nm)</th>
<th>SMD (nm)</th>
<th>NMD (nm)</th>
<th>$\sigma_g$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>xl-17</td>
<td>27.6</td>
<td>26.5</td>
<td>20.34</td>
<td>11.98</td>
<td>1.67</td>
</tr>
<tr>
<td>xl-18</td>
<td>16.7</td>
<td>13.28</td>
<td>7.59</td>
<td>2.48</td>
<td>2.11</td>
</tr>
<tr>
<td>xl-21</td>
<td>24.1</td>
<td>21.4</td>
<td>16.63</td>
<td>10.05</td>
<td>1.65</td>
</tr>
<tr>
<td>xl-23</td>
<td>28.1</td>
<td>25.59</td>
<td>20.62</td>
<td>13.40</td>
<td>1.59</td>
</tr>
<tr>
<td>xl-19</td>
<td>18.7</td>
<td>16.73</td>
<td>13.30</td>
<td>8.42</td>
<td>1.61</td>
</tr>
<tr>
<td>xl-24</td>
<td>28.3</td>
<td>25.93</td>
<td>21.23</td>
<td>14.22</td>
<td>1.56</td>
</tr>
<tr>
<td>xl-20</td>
<td>31.1</td>
<td>29.55</td>
<td>23.48</td>
<td>14.82</td>
<td>1.62</td>
</tr>
<tr>
<td>xl-22</td>
<td>21.4</td>
<td>20.39</td>
<td>18.68</td>
<td>15.67</td>
<td>1.34</td>
</tr>
</tbody>
</table>

6.3.3.2 Particle Size Calculated from BET Surface Area Measurement

XRD provides a clue of crystallite size, however, particle size is of most interest in our case since we assume plasma produced powder is not a single crystal.

Average particle diameter ($D_A$) calculated from the BET versus quench rate is plotted. As shown in the Figure 28, the obtained particle size is decreasing with the increasing quench rate. Form the BET results in Table 3, it is noticed that the smallest $D_A$ obtained is 17nm and the biggest $D_A$ obtained from this plasma process is 68nm. The particle size obtained from BET is a surface-weighted mean diameter for spheres. The error bar represents the sum of the standard deviation due to the BET measurement and geometric standard deviation due to the crystallite
size dispersion, assuming particle size follows the same distribution as crystallite size. The decreasing average particle size was observed with the increasing quench rate, as the quench rate larger than 10 000 K/s. At the lower quench rate region, a rather random distribution was observed; however, the particle sizes in this region in spite of everything are greater than that in high quench rate region. The Pearson’s correlation coefficient for quench rate and average particle size is -0.82 suggesting a strong negative correlation. However, no conclusion should be made based on so few data. Further repeated experiments are necessary to investigate the relationship between quench rate and particle size.

![Graph showing average particle size based on BET measurement with deviation](image)

Figure 28: Average particle size based on BET measurement with deviation (sum of measurement error and geometric standard deviation).

### 6.3.3.3 Particle Size Obtained from TEM analysis

To confirm the assumption of lognormal distribution for the particle size, TEM analysis was performed. Figure 29 is the images taken from the two sites of sample xl-24 with magnification of 22 000X and 16 500 X of a) and b), respectively. These images are used to
count the particles. The total number of 660 particles was counted. The average particle size is 31.6nm with the standard deviation of 16.2nm.

![TEM images](image)

Figure 29: TEM images used for particle size calculation (a) Mag. 122 000X (b) Mag. 162 000X.

The size distribution data obtained from TEM were fitted by a lognormal function in Figure 30. From the particle distribution histogram, it is shown that particles were primarily distributed in the range of 10nm to 40nm (71.5%). Less than 2.5% of the particles were smaller than 10nm; and less than 4% of the particles were greater than 100nm. The largest particle found in this sample was 283.3nm, the smallest particles found in this sample was 6.59nm.
Figure 30: Size distribution histogram of titania particle obtained from TEM with the lognormal fitting and the corresponding cumulative distribution function.

From the fitted lognormal function, the mode is 22.3nm and median is 28.1nm ±1.6nm. The cumulative distribution function, also referred as cumulative fraction – less–than particle size in Figure 30, shows the NMD position at 28nm. It also shows that 77% of particles is less
than 40 nm and 95% of particles is less than 60 nm. The parameters denoted $\mu$ and $\sigma$, are the mean and standard deviation of the variable’s natural logarithm, are 3.3366 and 0.48254, respectively. It is noticed that the geometric standard deviation obtained from TEM is 1.6 nm and from XRD line fitting is 1.56 nm. The NMD, SMD and MMD obtained from TEM, are 28.1 nm, 44.76 nm and 56.48 nm; from XRD spectrum are 14.22 nm, 21.23 nm, and 25.93 nm, respectively. The different results show the difference of crystallite size and particle size, the particle size is almost double the crystallite size. The closely related geometric standard deviations for two analyses suggest that the particle size and crystallite size follow the same distribution pattern.

Table 5: Comparison of diameter calculated from TEM and XRD particle size analysis

<table>
<thead>
<tr>
<th>Analysis Method</th>
<th>MMD (nm)</th>
<th>SMD (nm)</th>
<th>NMD (nm)</th>
<th>$\sigma_g$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM</td>
<td>56.48</td>
<td>44.76</td>
<td>28.10</td>
<td>1.62</td>
</tr>
<tr>
<td>XRD</td>
<td>25.93</td>
<td>21.23</td>
<td>14.22</td>
<td>1.56</td>
</tr>
</tbody>
</table>
6.3.4 SEM analysis of Morphology of Titania Particles

SEM image can provide us with information about the shape of particles, size distribution and agglomeration of particles. Figure 31 (Mag. 50 000X) demonstrates four experimental results under three different quench flow conditions, 15slpm, 30 slpm and 55 slpm. It is clear that the produced particles are nearly spherical with some agglomeration (cloudy area). Most particles are around 50nm or smaller; a few particles are larger than 100nm. However, four sub-images look very similar in Figure 31; these images alone there support no conclusion about the relationship between quench air flow rate and particle size.

![SEM images of representative runs (Mag. 50 000 X).](image)

Figure 31: SEM images of representative runs (Mag. 50 000 X).
Figure 32: SEM images of representative runs (Mag. 110 000 X).

Figure 32 shows the images observed under high magnification (Mag. 110 000X). The four quench air flow rates were 15, 20, 30 and 55 slpm, respectively. Compared with previous Figure 31, we observe more details of small particles. The sphericity of particles is nearly complete and particles are distinguishable. There is no sign of strong sintering. It is clear that in Figure 32 (c) and (d) images contain more particles less than 50nm than that in (a) and (b) images. No particle is greater than 100nm due to the smaller view of high magnification.

6.3.5 TEM analysis of Morphology of Titania Particles

Since our particles are normally smaller than 100nm, TEM analysis with high resolution (down to 5nm) is helpful to observe more details of the particle morphology. In Figure 33, the
first image shows a TEM image of the sample obtained from the experiment xl-19; the second image shows a TEM image of the commercial product Degussa P25. In xl-19 image, we observed individual spherical or nearly spherical particles. The spherical shape of our sample indicated the formation of nano particle is from liquid to solid. No sintering observed. The same results were observed for the other plasma produced samples. This observation is also consistent with SEM observations. Particle size ranged from less than 10nm to over 100nm for this sample xl-19. The particles of P25 appear to be square shaped individual particles with no sintering observed. The size distribution of P25 from about 20nm to 50nm is more uniform than that of our sample.

Figure 33: TEM image of xl-19 (Mag. 29 600X) and P25 (Mag. 41 000 X)
The TEM image of Figure 34 shows the lattice spacing of particles. From the xl-23 image, we noticed grooves on the particle indicating the orientation of crystalline growth and the whole particle is crystallized. The xl-24 image marked 10 lattice distances of 3.78 and 3.79nm corresponding to 10 fold of lattice constant of anatase phase $a = 3.7845\,\text{Å}$ (Ana11). At the same time, not all the small particles appear to be crystallized; some parts of the small particles are amorphous. This is consistent with the elemental composition analysis in the later section. The small particles (Dia. < 20nm) consist not only of titania but also of other impurities like Si, C and P, which structure is amorphous.

6.3.6 Elemental Composition Analysis

6.3.6.1 SEM-EDS Analysis

Elemental composition analysis was performed on SEM-EDS for selected samples. Each sample was mapped over the whole captured area in SEM electron image unless otherwise
specified. Qualitative and quantitative results were present here. However, it is worth to mention that because the sample surface was not polished; the obtained results are at best semi-quantitative. The accuracy of SEM-EDS for particles, with rough surface is ±50% relative. Therefore, for a qualitative analysis using SEM-EDS, the identification of the major constituents of a sample can usually be done with a high degree of confidence, but, when minor (1-10%) or trace-level (<1%) elements are considered, errors in peak assignments can arise unless careful attention is paid to the problems of spectral interferences, artifacts, and the multiplicity of spectral peaks observed for elements of intermediate and high atomic number (Goldstein, et al., 2003).

Taking produced sample powder xl-24 as an example, Figure 35, Figure 36 and Figure 37 show the mapping results of the different sites, sub-images (A) (B) (C) and (D) show the SEM electron image for mapping, sum spectrum, quantitative table of elements, and graph of quantitative result plotted in weight percent, respectively. In sub-image (A), the particles in the SEM are shown in white and gray, the black region was the background of the carbon tape. The bright region is due to the charge built up on the surface of TiO$_2$ particles. It is noticed that different sites of the same sample xl-24 have different compositions of contaminations. Ti, O, C, Si, and P are found in all sites. Site 1 has V and W; site 2 has V; site 3 has no contamination of V and W at all. Assuming the Si and P contaminants are oxides, the rough ratio of compound SiO$_2$: P$_2$O$_5$: TiO$_2$ are 2:3:10, 1:2:20 and 2:3:11 for site 1, site 2 and site 3, respectively. All the results show that Ti and O are the dominant elements; P contamination is slightly higher than Si.

In Figure 37 (A), the sub-images in (A) show the maps of Ti, P and Si ions together with those of O and C. This figure revealed that while Ti, P, Si, and O are distributed equally on the selected area, C appears to show a weak signal. This might indicate that the C influence of
carbon tape is limited to a minimum by choosing this thick powder covered region.

Contaminant Si and P probably originate from the insulation layer - refractory material since both of them are found in the SEM-EDS spectrum, as shown in Figure B-2 in Appendix B. Although a high purity alumina layer was inserted between the graphite felt and silica/alumina refractory layer to limit the contamination, silica/alumina refractory is possibly exposed to the high temperature gas at the opening sites of the reactor, for instance, the top of reactor graphite chamber (two openings for the torch and feeding tube), exit tube joint and observing window joint. In addition the filter bag could be a source of contaminant Si, since the filter bag is made of glass fiber (shown in Figure B-3 in Appendix B).
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(A)

(B)

(C)

(D)

Figure 35: SEM-EDS mapping of the sample xl-24 over the SEM electron image (site 1).
Figure 36: SEM-EDS mapping of the sample xl-24 over the SEM electron image (site 2).
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(A)

(B)

(C)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
<th>Compd%</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>4.29</td>
<td>0.51</td>
<td>7.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si K</td>
<td>5.01</td>
<td>0.26</td>
<td>3.92</td>
<td>10.72</td>
<td>SiO2</td>
</tr>
<tr>
<td>P K</td>
<td>6.90</td>
<td>0.34</td>
<td>4.89</td>
<td>15.81</td>
<td>P2O5</td>
</tr>
<tr>
<td>Ti K</td>
<td>34.62</td>
<td>0.87</td>
<td>15.87</td>
<td>57.75</td>
<td>TiO2</td>
</tr>
<tr>
<td>O</td>
<td>49.18</td>
<td>0.92</td>
<td>67.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(D)

Figure 37: SEM-EDS mapping of the sample xl-24 inside the red rectangle SEM electron image (site 3).
Contaminant V may originate from the starting raw material as shown Figure B-1 in Appendix B. It may also be possible that the material identified as V was due to software error and not really present in the sample, as the V(K\text{α}) emission line (4.9 KeV) actually overlaps with the Ti(K\text{β}) emission line (4.9 KeV), the V(K\text{β}) (5.4 KeV) is buried in the background as shown in sub-image (B). Overlap peaks in the low energy region are even harder to resolve and to distinguish from element to element. W was likely from the tungsten tip of the torch, this is consistent with the observation of slight damage of the torch tip after each experiment. Since carbon tape was used as the adhesive media for the sample, the semi-quantitative result is not representative for carbon. Nevertheless, carbon was found in the sample when analyzing with TEM-EDS using the copper grid (Figure 38). The carbon contamination was from the graphite parts of reactor.

For the samples collected by inline filter cartridge, we observed contaminations of Ca, Al, Fe and K (shown in Figure B-6 in Appendix B). Ca may originate from the raw material or filter cartridge (Figure B-1, Figure B-4 in Appendix B), since Ca was identified in both materials. The source of K was from the filter cartridge. Al was from the insulation and/or the filter cartridge.

6.3.6.2 TEM-EDS Analysis

The elemental composition of selected samples was also analyzed using the TEM-EDS technique. In each sample several random sites were selected to determine the elemental composition. The typical results show five elements in a sample, Ti, O, C, Si, and P. Taking the sample xl-23 as an example in Figure 38, two extreme regions were selected to distinguish titania from contaminates, the large particle (>100nm) region and small particle (<20nm) region. The minimum probe diameter of the detector was 20nm; therefore, a single particle elemental composition could be identified for a large particle. In Figure 38, two different EDS spectra were
shown with the region A and region B in the TEM image of sample xl-23, respectively. In spectrum A, the characteristic peaks of Ti(Kα) and Ti(Kβ) appear between 4.10 -5.10 keV confirming the presence of titanium in the sample; the oxygen peak appears around 0.5 keV confirming the presence of oxygen; which means that the large particle is titanium oxide. This was corroborated by the lattice structure observed in TEM image (Figure 34) and XRD spectrum result (Figure 23). In the TEM image of sample xl-23, the lattice spacing was very obvious; and in the XRD spectrum of sample xl-23, the only crystalline material present was TiO₂. The copper peaks originated from the copper grid used to support the sample. The trace silicon peak is negligible. It is either originated from the surroundings of the large particle; or from the Si internal fluorescence peak. Si peak may be present to an apparent level of 0.2 wt% even though there is no Si in the sample under examination (Lyman, et al., 1988).

In spectrum B, except for the strong copper peaks originating from the copper grid, characteristic peaks for C, Si, P and Ti were present, similar to Figure 36. It shows that small particles were contaminated by C, Si, and P.
Figure 38: TEM-EDS elemental composition analysis of sample xl-23 of region A (top) and B (bottom) in the upper TEM image.
In conclusion, the collected samples were mainly TiO$_2$ with contamination by carbon, silicon and phosphorous, especially for the smaller particles. Carbon contamination could come from the two sources. One, from the vaporization and redeposition of graphite rod to ignite the reactor before the steady state was established; the first batch of dirty gas filled the filter bag despite the open bypass. In future work or in an industrial process this could be avoided by relocating the filter baghouse valve from behind the filter baghouse to the place before the filter baghouse in order to totally close the path that of the dirty gas into the filter baghouse at the beginning of the experiment. Another source of carbon might be from the wear of reactor chamber during the experiment. Again, in a commercial process this would be negligible when the vapor of TiO$_2$/TiO as a liquid film deposited on the reactor chamber acting as a physical barrier, or Ti$^{2+}$ reacts with graphite chamber forming stable TiC on the graphite chamber surface (Altenhoff, 2009) over a long time continuous reaction. Silicon and phosphorous material are more volatile than TiO$_2$ and thus these contaminants would build up in the product. The replacement of all Si/P containing refractory to high purity alumina (99%) should eliminate this source of contamination.

6.3.2 Anatase Formation Discussion

The anatase/rutile ratio of the product was calculated from the XRD spectra of samples and the calibration curve of known composition of micron sized samples. Rutile is known to be the thermodynamically stable structure for TiO$_2$ in larger particles. However, in nano scale (below ca. 14nm), anatase is more thermodynamically stable than rutile. If nanometer sized titania is heated, crystal growth leads to alteration of phase stabilities and, ultimately, conversion to rutile (Zhang, et al., 1998).

The formation of nanoparticles condensation process in our system probably includes
oxidation, nucleation, growth, particle coagulation and coalescence. The oxidation process occurs simultaneously with the nucleation process; the quench gas (dry air) consists of 21% oxygen. The high temperature (>1000°C) TiO gas stream encountered room temperature quench gas and formed TiO₂ through oxidation. At the same time, stable spherical nuclei (Mitchell, et al., 2003) (Balthasar, et al., 2005) were also formed due to supercooling and supersaturation through homogenous nucleation, and finally growth to the final particle size.

Studies showed that TiO₂ is more stable as anatase at sizes under 14nm (Gribb, et al., 1997) (Zhang, et al., 1998) and at the low temperature. Very likely, the initially formed stable nuclei are anatase at the low quench temperature (~100-200°C); these then grew until thermodynamic equilibrium is restored. TiO₂ crystalline phase transition probably occurs during the process of the restoration of thermodynamic equilibrium. Gribb et al demonstrated that the pure anatase nano crystallites sample (~6nm, spherical particles) had 9.6% conversion to rutile when held at 525.8 °C for 1.2h. As the residence time of quenching zone (from T1 to T3) is no more 100ms (2.78×10⁻⁵h), it is likely that the crystalline phase of nano TiO₂ particles is formed during the quench/mixing process; in other words, phase transformation occurs simultaneously with nucleation depending on local thermodynamic and/or reaction equilibrium. No later conversion from anatase to rutile or vice versa, once the particle stops growth.

As shown in Figure 39, there is little correlation between residence time and anatase fraction of the TiO₂ product (Pearson’s correlation coefficient r = 0.55). At the residence time 69 ms, both high (0.71) and low (0.24) anatase fraction are observed. In this very short time range (from 55 to 80ms), the anatase fraction is between 0.10 and 0.71.
Figure 39: Anatase fraction of the product versus residence time.

The anatase fraction versus quench rate is plotted in Figure 40. There is weak correlation ($r = 0.34$) within the studied quench rate range. Unfortunately, the experiments have no replicates; several repeated experiments are useful to obtain valuable conclusions with the consideration of system error. The error bars present in Figure 39 and Figure 40 is based on XRD calculation error only.

Figure 40: Anatase fraction of the product versus quench rate of the system.
The operating power influences not only the pre-quench temperature but also the evaporation rate of titanium species and thus the composition of the reactor exit gas. It is thus expected to influence the anatase fraction in the produce. The plot of operating power versus anatase fraction of the product in Figure 41 shows a reduction of anatase fraction of the product as the operating power increases (Pearson’s correlation coefficient $r = -0.74$). It is interesting to note that experiments with the same operating power obtained different anatase phase fraction as 0.350 vs. 0.661 at 9.1kW and 0.233 vs. 0.566 at ~9.5kW. These differences might suggest two things:

1. Other factors contribute to the TiO$_2$ crystalline phase formation.

2. The uncertainty in determining or controlling the fraction of anatase is relatively large.

Despite the difference, the overall trend observed suggests that low temperature favors high anatase phase content formation.

![Figure 41: The anatase fraction of the produce versus operating power.](image)
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Comparing experiments xl-17 and xl-18 in Table 6, those with the same gas volume of argon and quench air, 25slpm and 20slpm respectively, we found that the anatase fraction of xl-18 is only 0.098 with 1286°C pre-quench temperature, very different from 0.35 with 1145.5°C pre-quench temperature, the result of xl-17. The anatase fraction decreases with the increasing pre-quench temperature at the same gas flow rate and quench flow rate. This trend can also be obtained from other experiment groups with similar operation conditions, xl-19 and xl-24, xl-21 and xl-23, respectively.

With the same flow rate, high pre-temperature indicates large change of temperature. The greater the supercooling, the smaller the critical nucleus size and the less energy required to form it as shown in the following equations according to classic homogeneous nucleation theory

\[
r^* = \frac{2\sigma T_m}{\Delta H_S} \frac{1}{\Delta T}
\]  \hspace{1cm} (19)

\[
\Delta G^* = \frac{16\pi\sigma^3 Tm^2}{3\Delta H_S^2} \frac{1}{(\Delta T)^2}
\]  \hspace{1cm} (20)

where \( r^* \) is the critical radius, \( \Delta G^* \) is the free energy formation of critical radius, \( \sigma \) is the surface tension, \( T_m \) is the melting temperature, \( \Delta H_S \) is the enthalpy of sublimation, and \( \Delta T \) is the change of temperature. These equations only provide us information of the relative ease of homogenous nucleation and how small the critical radius could be with the increasing \( \Delta T \). But, how the change of temperature is connected with TiO\(_2\) crystalline phase formation and why the lower temperature favors higher anatase content in the plasma synthesis process remain unclear.

The anatase-rutile transformation has been shown in the literature to be affected by processing parameters like dopants and impurities (Okada, et al., 2001) (Chen, et al., 2007), atmosphere (Gamboa, et al., 1992), particle size (Zhang, et al., 2007), and synthesis method (Iida, et al.,
Results have often been contradictory and the relative importance of these variables is not known.

Table 6: Comparison of pre-quench, quench temperature with the anatase fraction

<table>
<thead>
<tr>
<th>Run #</th>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>Q_{argon} (slpm)</th>
<th>Q_{air} (slpm)</th>
<th>T1 (°C)</th>
<th>T2 (°C)</th>
<th>f_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>xl-17</td>
<td>170</td>
<td>53</td>
<td>25</td>
<td>20</td>
<td>1145.5</td>
<td>221.9</td>
<td>0.350</td>
</tr>
<tr>
<td>xl-18</td>
<td>200</td>
<td>60</td>
<td>25</td>
<td>20</td>
<td>1286.5</td>
<td>245.9</td>
<td>0.098</td>
</tr>
<tr>
<td>xl-19</td>
<td>160</td>
<td>48</td>
<td>25</td>
<td>30</td>
<td>1206.6</td>
<td>151.9</td>
<td>0.708</td>
</tr>
<tr>
<td>xl-24</td>
<td>160</td>
<td>60</td>
<td>25</td>
<td>30</td>
<td>1256.9</td>
<td>136.5</td>
<td>0.566</td>
</tr>
<tr>
<td>xl-21</td>
<td>160</td>
<td>56</td>
<td>25</td>
<td>15</td>
<td>1120.8</td>
<td>191.2</td>
<td>0.661</td>
</tr>
<tr>
<td>xl-23</td>
<td>170</td>
<td>58</td>
<td>25</td>
<td>15</td>
<td>1255.8</td>
<td>206.1</td>
<td>0.233</td>
</tr>
<tr>
<td>xl-20</td>
<td>170</td>
<td>57</td>
<td>25</td>
<td>45</td>
<td>1186.7</td>
<td>110.6</td>
<td>0.383</td>
</tr>
<tr>
<td>xl-22</td>
<td>180</td>
<td>57</td>
<td>25</td>
<td>55</td>
<td>1216.0</td>
<td>78.91</td>
<td>0.537</td>
</tr>
</tbody>
</table>

Generally speaking, the anatase fraction of the product is a result of multiple factors like temperature, atmosphere, quench rate, seed size, concentration of quenchable gas, and impurities in our case. Based on partial results without theoretical foundation, no conclusion can be made. Further study of kinetic and thermodynamic analysis is necessary to explain the mechanism and experimental data.
Chapter 7 Conclusions

The synthesis of nano titania using a laboratory scale transferred arc device with continuous feed of TiO$_2$ pellets feeding was studied: nanosized titania particles were successfully synthesized. Through the XRD, BET, TEM, SEM, and EDS analysis, the following conclusion could be made.

1. The obtained TiO$_2$ particles are a polymorphous mixture of anatase and rutile. The highest anatase fraction obtained is 0.708±0.024.

2. The highest surface area of the product TiO$_2$ is 83.3 m$^2$/g.

3. The TiO$_2$ particles are individual spherical particles with NMD between 20-30nm.

4. TiO$_2$ crystalline size is smaller than particle size for plasma produced powder.

5. The TiO$_2$ particle size decreases as the quench rate increases; residence time has no obvious influence on particle size in the range studied.

6. Size distribution of the crystallite size and particle size follows a log-normal distribution with geometric standard deviation around 1.6nm.

7. The temperature, residence time and quench rate has very weak correlation on phase content of anatase in the range studied.

8. The product was somewhat contaminated with C, Si and P which came from graphite rod and refractory material. Due to the poor insulation of the laboratory device, large heat losses and short reaction time limited the production rate. Much of the evaporated material recondensed within the plasma chamber.
The study has demonstrated the technical feasibility of the proposed process and has led to suggestions for modifications to the equipment and process which will enhance the economic viability.
Chapter 8  Suggestions for Future Work

The current device has the filter baghouse located before the bypass line, and the control valve is after the baghouse. This setup allows transient exit gas to enter the baghouse during the time in the run that the pressure is increasing, thus contaminating the filter bag. Reversing the order of the bypass and baghouse and placing the control valve before the baghouse entrance would solve this problem.

In our experiments, the collection system was normally bypassed for 45 min, and the powder collecting time was normally 20-30 min. A large amount of material was consumed during the steady state establishment stage; however, we have no idea about the system behavior during this period. We could install an extra baghouse to collect the transient particles, which could be useful to help us understand system behavior throughout the course and obtain information like mass balance and reaction rate.

The quench zone has only a short length of water cooling region, to protect the filter bag from high temperature damage; extra cooling air was injected before the hot gas stream entering the baghouse. However, this injection of air increases the pressure of the baghouse/system and limits the maximum quench air can be used is 55 slpm. It might necessary to extend water cooling region to whole quench pipe. A cooling coil around the current quench pipe could improve the operation with minimal changes. If no extra cooling air injected, the pressure change of the baghouse or system was purely due to the TiO$_2$ reaction system. Possible influence of pressure with the product properties could be studied. Also, extreme condition with higher quench air flow rate (up to 100 slpm) can be studied.
In our experiments considerable raw material was evaporated but never reached the quench zone of the tubular reactor; it condensed within the plasma chamber. Attempts should be made to better insulate this chamber with suitable high temperature materials to increase the material and thermal efficiency of powder production. This might be difficult in a small scale laboratory reactor but easier in a higher power pilot scale or commercial reactor.


Anatase. (n.d.). Retrieved 03 14, 2011, from the mineral and locality database:
http://www.mindat.org/min-213.html


http://www.balstonfilters.com/pdf/SampleFilters.pdf


www.cnam.fr/servlet/com.univ.utils.LectureFichierJoint?CODE...0

REFERENCES


REFERENCES


92


REFERENCES


APPENDIX

Appendix A: XRD Phase Identification

XRD line spectra showing here are sample xl-23, sample xl-24, Degussa P25 and residue from the reactor chamber.

Figure A-1: XRD line spectrum of run xl-23 shows the rutile and anatase crystalline phase with the ‘best’ matched reference code.

Figure A-2: XRD line spectrum of run xl-24 shows the rutile and anatase crystalline phase with the ‘best’ matched reference code.
Appendix A: XRD Phase Identification

Figure A-3: XRD line spectrum of Degussa P25 showing the crystalline phase of anatase and rutile only.

Figure A-4: XRD line spectrum of residue in the reactor showing compounds of TiO, Ti₂O₃ and TiC present in the reactor chamber after the experiment.
Appendix B: SEM-EDS Analysis

SEM-EDS was employed to identify the resource of contaminants of Si, P and K.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>19.03</td>
<td>26.86</td>
</tr>
<tr>
<td>S K</td>
<td>0.32</td>
<td>0.17</td>
</tr>
<tr>
<td>Ti K</td>
<td>17.17</td>
<td>6.08</td>
</tr>
<tr>
<td>V K</td>
<td>0.33</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn L</td>
<td>0.21</td>
<td>0.05</td>
</tr>
<tr>
<td>O</td>
<td>62.94</td>
<td>66.72</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Figure B-1: SEM-EDS mapping of raw TiO$_2$ material over the whole SEM electron image showed the trace amount of V, S and Zn present in the sample.
Figure B-2: SEM-EDS mapping of the refractory material showed the resource of Si and P contamination.
Figure B-3: SEM-EDS mapping of the Teflon coated filter bag woven glass fiber showed contamination resource of Si and Ca.
Appendix B: SEM-EDS Analysis

Figure B-4: SEM-EDS mapping of inline filter cartridge material showed the contamination resource of Si, K, Na, Al and Ca.
Figure B-5: SEM-EDS line scan of the sample xl-24. The scan line crossed a glass fiber contaminant. The spectrum after 100μm showed the content of glass fiber and the particles on the surface of the glass fiber. Carbon is originated from the adhesive carbon tape.
Appendix B: SEM-EDS Analysis
Figure B-6: SEM-EDS mapping of xl-19 inside the marked areas where the nano powder present, respectively. (The minor contaminants like K, Na, and Al are mainly from inline cartridge filter material.)
Appendix C: Temperature Profile of the Experiment

The following temperature profiles showed the pseudo-steady state was achieved during the synthesis as shown in the plateau region in $T1$ (pre-quench temperature). The sudden decrease of temperature at the tail indicated the time when power was shut down.

![Temperature profile graph](image)

Figure C-1: Temperature profile of xl-24 shows that the pseudo-steady state achieved from 40 to 55 min.

![Temperature profile graph](image)

Figure C-2: Temperature profile of xl-23 shows that the pseudo-steady state achieved from 48 to 65 min.
Figure C-3: Temperature profile of xl-19 shows that the pseudo-steady-state achieved from 42 to 55min.
Appendix D: Experimental Procedure

Pre-experimental procedure

Preparation of the reactor and its peripheral devices

To start, make sure the power switch is off, gas valves and water faucets are closed

Check and fasten the external parts, gas lines, and water pipes

Clean the inside of the reactor (use brush and vacuum), dispose of waste to the proper container (use a suitable mask when cleaning)

Check the insulation and other internal parts, replace the damaged ones

Inspect and clean the torch

Clean and reassemble the exit tube, window, filter, powder feeder and feed line.

Weigh the empty crucible and feeder

Verify electrical isolation of the crucible and chamber

Press TiO$_2$ (99.5% purity) into crucible and weigh crucible with the TiO$_2$

Press TiO$_2$ (99.5% purity) into small tablet and place in the feeder and weigh the feeder with TiO$_2$

Pressure test

Turn on gas flow and build up a 4 psi pressure inside the reactor

Use soap solution to check the leakage
Turn off the gas flow and check if pressure remains constant for 5 min

Check the ground cables

Check resistance

Make sure resistance between cathode and ground and cathode and nozzle is at least 1MΩ

If not, the consequence is that the torch is not electrically isolated and must be repaired

Replace the electrical tape on the cathode and be sure the cathode tip and the nozzle do not touch each other

**Experimental procedure**

Use a check list for the experiment

Turn on the elephant trunk exhaust and place it at the exhaust gas exit

Turn on cooling water flows to the reactor and touch and check for leaks

The valves must be fully opened to give the maximum flow rates

Turn on the booster pump and check for leaks

check, if the water flow indicators for the cathode and the nozzle are working

Turn on the argon gas flows.

Before ignition of the arc, argon must flow for 1 hour with 5 slpm to purge the system of air (when air concentration reaches about $\sim 10^{-7}$, this is approximation in theory, no indicator installed)
Appendix D: Experiment Procedure

For the experiment, flows of 20 slpm argon gas for the torch and 4 slpm argon gas for the window and the feeder are used.

Check, if the exposed cathode section is covered with the plastic cover to avoid accidental human contact during the experiment.

Make sure, the cables from the power supply to the torch do not touch each other.

Plug in control panel and high frequency power cables.

Check, if the cables marked “transferred arc anode” (red plug) and “transferred arc cathode” (black plug) are attached to the grey box named “connection box” (located in the corridor between the laboratories 5310 and 5120, on top of the DC power supply system).

Check, if the cable labeled “transferred arc” is connected to the socket on the blue remote control box (located in the corridor between the laboratories 5310 and 5120, near the “connection box”).

Turn on the main circuit breakers marked 1&5, 2&6, 3&7, 4&8 (located in the corridor between the laboratories of 5310 and 5210).

Set the rheostat for the power control to zero (control panel, laboratory 5310).

Turn on the power switch and the high frequency power switch on the control panel.

Turn on the switch marked “DC power supply” on the control panel.

Release the emergency button (out position). The voltmeter on the control panel should indicate 600 V.

Press the auxiliary anode relay button (small red button located under the power supply rheostat).
Push the high frequency toggle switch (located under the knob labeled power supply rheostat) to the right. A spark is created, generating an arc between the cathode and nozzle, which then is transferred to the graphite rod in the center of the crucible. When this occurs, the nozzle relay is opened.

Increase the power to desired value (100-200 A) by adjusting the power supply rheostat slowly.

Turn slowly on the quench gas (air, taken from the pressure line).

Start the data acquisition system (approximately one minute after the arc ignition).

The power collection starts when the temperature in the exit tube is almost constant. The filter has to be set from bypass to inline.

Start feeding with TiO$_2$ tablets

**Shut-down procedure**

Prior to the termination of an experiment, particle feeding must be stopped and the filter must be bypassed again.

Turn off the quench gas

Reduce the argon flow of the torch, window and feeder.

Turn off the power switch and simultaneously set the rheostat to zero

Push the red emergency button (in position)

Turn off the control panel power switch and the high frequency power switch (down position)

Turn off the main circuit breakers marked 1&5, 2&6 and 4&8.
Appendix D: Experiment Procedure

Argon purge and cooling water flows must continue until the apparatus is cooled to normal temperatures (approximately 50 °C)

When reactor is cooled down, turn off the argon and water flows.

Turn off the elephant trunk.

Emergency situation

Push the red emergency button (in position) to remove D.C. power

Check and solve the suspected problem

In case of uncontrollable fire, leave the room as soon as possible after shut down the power, call McGill security immediately.

Potential hazard description and hazard handling and safety precautions

High voltages and currents

All parts of equipment except cathode are grounded.

Torch is surrounded with plastic cover to prevent human contact during the experiment.

During the experiment, I should be very cautious not touching devices and stay at least 0.5 m away.

High temperatures

High temperature exist only in the plasma chamber, which is heavily water cooled

High pressures
The argon cylinders are pressurized; they must be securely attached to an appropriate cylinder support.

The reactor itself is operated at atmospheric pressure (or slightly above, +4 psi)

**Other hazards**

TiO$_2$ causes violent exothermic reaction and development of heat as well as the risk of explosion if it is mixed with the following metals: aluminum powder, calcium, potassium, magnesium, sodium, lithium, zinc powder. These substances are not included in the system.

When handling with either TiO$_2$ powder as reactant or nanoparticle as the product, a dust mask/respiratory filter (particle filter P2 or P3, color code white) should be worn. Inhalation of TiO$_2$ dust may cause cancer.

TiO$_2$ irritates the eyes and skin, so half face mask and gloves should be worn all the time during handling the sample collection.

The arc plasma causes flash burn of the eyes by looking directly into it. To observe the arc plasma, welding glasses should be worn.
**Checklist of Transferred Arc Experiment**

**Pre-experimental procedure**

<table>
<thead>
<tr>
<th>Number</th>
<th>Procedure</th>
<th>Check</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Clean the reactor.</td>
<td>O</td>
</tr>
<tr>
<td>2</td>
<td>Replace damaged carbon parts &amp; insulation.</td>
<td>O</td>
</tr>
<tr>
<td>3</td>
<td>Clean &amp; inspect torch.</td>
<td>O</td>
</tr>
<tr>
<td>4</td>
<td>Clean &amp; reassemble the exit tube, the window, the filter, feeder and feeder line.</td>
<td>O</td>
</tr>
<tr>
<td>5</td>
<td>Weight the graphite crucible and feeder</td>
<td>O</td>
</tr>
<tr>
<td>6</td>
<td>Are the crucible &amp; the chamber electrical isolated? _______ MΩ</td>
<td>O</td>
</tr>
<tr>
<td>7</td>
<td>Press TiO$_2$ powder to tablets and weight the used amount.</td>
<td>O</td>
</tr>
<tr>
<td>8</td>
<td>Ensure that the crucible stem does not touch the chamber.</td>
<td>O</td>
</tr>
<tr>
<td>9</td>
<td>Place the tablets in the crucible and feeder.</td>
<td>O</td>
</tr>
<tr>
<td>10</td>
<td>Close the reactor</td>
<td>O</td>
</tr>
<tr>
<td>11</td>
<td>Place the torch and put the electrical isolation between the flanges and the torch and all metal connections.</td>
<td>O</td>
</tr>
<tr>
<td>12</td>
<td>Pressure test: 4 psi air (0,275 bar). Does the pressure remain constant after 5 minutes? If no, use Snoop (soap solution) and search for leaks!</td>
<td>O</td>
</tr>
</tbody>
</table>
13 Are the ground cables connected? O

14 Is the resistance between cathode & ground infinite (cables not connected)? _______ MΩ

15 Is the resistance between cathode & nozzle infinite (cables not connected)? _______ MΩ

16 Is the resistance between nozzle & ground infinite (cables not connected)? _______ MΩ

17 If the wires of the high frequency generator are connected, the resistance between cathode and ground conducts approximately 22 kΩ which means to be the resistance of the voltmeter. If the cooling water is running, the magnitude decreases to approximately 8 kΩ. Measurement cathode to ground: _______ kΩ.

18 Is the observation window covered with welding glass? O

Experimental procedure

<table>
<thead>
<tr>
<th>Number</th>
<th>Procedure</th>
<th>Check</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Make sure the exhaust (elephant trunk) is working and place it at the exhause gas exit.</td>
<td>O</td>
</tr>
<tr>
<td>2</td>
<td>Turn on the cooling water flows (reactor shell &amp; torch).</td>
<td>O</td>
</tr>
</tbody>
</table>
### Appendix D: Experiment Procedure

1. **Check for leaks.**
2. **Turn on the booster pump.**
3. **Check for leaks again.**
4. **Are the water flow indicators working?**
5. **Turn on the argon gas flows for torch & window.**
6. **Purge system with 5 slpm of argon for 1 hour.**
7. **Is the cathode covered with plastic to avoid human contact?**
8. **Plug in the control panel and high frequency power cables.**
9. **Is the High Frequency Generator switched on?**
10. **Are the cables marked as “Transferred arc anode” (red plug) and “Transferred arc cathode” (black plug) attached to the grey box named “Connection box” (corridor)? Make sure, that nothing else is connected; otherwise there will be a short circuit of 70 A!**
11. **Is the cable labelled “Transferred arc” connected to the socket on the blue remote control box (corridor)?**
12. **Turn on the main circuit breakers marked 1&5, 2&6, 3&7, 4&8 (corridor).**
13. **Increase the argon gas flow rate for the experiment: 20 slpm argon gas**
for the torch and 5 slpm for the window.

16 Set the rheostat for the power control to zero (control panel).

17 Turn on the power switch of the control panel and the high frequency power switch.

18 Turn on the switch marked “DC power supply” (control panel).

19 Release the emergency button (out position). The voltmeter on the control panel should indicate 600 V.

20 Press the auxiliary anode relay button (small red button).

21 To create a spark, push the high frequency toggle switch to the right. An arc is generated between cathode and nozzle, which is transferred to the graphite rod in the center of the crucible.

22 Increase the power by adjusting the power supply rheostat.

23 Turn on the first vacuum pump.

24 Turn on slowly the quench gas.

25 When needed, turn on the second and the third vacuum pump.

26 Start the data acquisition system (approximately one minute after the arc ignition).

27 For powder collection, set the filter from bypass to inline, the temperature in the exit tube should be almost constant which takes
Appendix D: Experiment Procedure

approximately 45 minutes.

Shut-down procedure

<table>
<thead>
<tr>
<th>Number</th>
<th>Procedure</th>
<th>Check</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bypass the filter.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Turn off power switch and simultaneously set rheostat to zero.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Push red emergency button.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Turn off quench gases (air, SiCl₄ enriched argon).</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Turn off the vacuum pumps.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Reduce argon flow of the torch &amp; window.</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Turn off control panel and high frequency power switch.</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Turn off main circuit breakers 1&amp;5, 2&amp;6, 3&amp;7, 4&amp;8.</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Turn off the booster pump.</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Argon purge and cooling water must continue until the reactor is cooled down to normal temperatures of ca. 400°C in the exit tube.</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Turn off water and argon flows.</td>
<td></td>
</tr>
<tr>
<td>Property</td>
<td>Measurement</td>
<td>Unit</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>Mass of crucible+graphite rod</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass of crucible+graphite rod+ TiO₂</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass of TiO₂ in crucible</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass of TiO₂ lump+container</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass of empty container</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass of TiO₂ in feeder</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass of new filter</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass of chamber+top+bottom</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Start time of purge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amount of purge gas argon (torch)</td>
<td></td>
<td>slpm</td>
</tr>
<tr>
<td>Amount of purge gas argon (feeder)</td>
<td></td>
<td>slpm</td>
</tr>
<tr>
<td>Amount of purge gas argon (window)</td>
<td></td>
<td>slpm</td>
</tr>
<tr>
<td>End time of purge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duration of purge</td>
<td></td>
<td>min</td>
</tr>
</tbody>
</table>
Appendix D: Experiment Procedure

Start time of experiment

Amount of purge gas experiment (torch) ________________________________ slpm

Amount of purge gas experiment (window) ________________________________ slpm

Amount of purge gas experiment (feeder) ________________________________ slpm

Starting time of data collecting

Current ________________________________ A

Voltage ________________________________ V

Amount of quench gas air ________________________________ slpm

Start time of feeding

End time of feeding

Duration of feeding

Start time of powder collection

End time of powder collection

Duration of powder collection ________________________________ min

Pressure in the reactor during experiment ________________________________ psi

End time of experiment
<table>
<thead>
<tr>
<th>Duration of experiment</th>
<th>min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of crucible at the end</td>
<td>g</td>
</tr>
<tr>
<td>Mass of chamber+top+bottom at the end</td>
<td>g</td>
</tr>
<tr>
<td>Mass of TiO2 in the feeder at the end</td>
<td>g</td>
</tr>
<tr>
<td>Mass of powder + filter</td>
<td>g</td>
</tr>
<tr>
<td>Mass of powder collected</td>
<td>g</td>
</tr>
<tr>
<td>Mass of TiO2 used in total</td>
<td>g</td>
</tr>
</tbody>
</table>