Titanium Particle Combustion

Malcolm Cairns

Masters of Engineering

Department of Mechanical Engineering

McGill University
Montreal, Quebec
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ABSTRACT

In order to increase the validity of numerical models of the detonation of heterogeneous titanium explosives, experimental results are needed. The combustion of titanium is studied using two experimental techniques. The first technique is the study of the burn time for a single particle over a wide range of initial diameters while altering the oxygen concentration. To accomplish this a new flat flame burner to study particle burn time has been designed. Luminous tracks caused by the light emitted by the combustion of the particles are analyzed and burn time is inferred. Burn time in air and in an oxygen enriched atmosphere were determined. A second experiment involves the study of large scale detonation of heterogeneous charges. The charges are filled with nitromethane and a packed bed of titanium particles. The titanium particles varied in morphology and particles size. A critical charge diameter for charge ignition (CDPI) was found for irregularly shaped particles but was not found for spherical particles.
ABRÉGÉ

Pour augmenter la validité des modèles numériques sur détonation d'explosifs hétérogènes contenant du titane, des résultats expérimentaux sont nécessaires. Le combustino de titane est étudié en utilisant deux techniques expérimentales. La première technique est l'étude du temps brûlé pour une particule sur une large gamme de diamètres initiaux en changeant la concentration d'oxygène. Pour l'accomplir un nouveau bruleur de flamme plat pour étudier la particule brûle le temps a été conçu. Les empreintes lumineuses provoquées par la lumière mise par la combustion des particules sont analysées et brûlent le temps est déduit. Brûlez le temps dans l'air et dans l'atmosphère enrichie d'un oxygène ont été déterminés. Une deuxième expérience implique l'étude de grande détonation d'élle de charges hétérogènes. Les charges sont remplies de nitrométhane et un liant emballe de particules de titane. Les particules de titane variaient dans la grandeur de particules et la morphologie. Un diamètre de charge critique pour l'ignition de charge (CDPI) a été trouvé pour les particules irrégulièrement en forme de, mais n'a pas été trouvé pour pour les particules irrégulièrement en forme de mais n'a pas été trouvé pour les particules sphériques.
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CHAPTER 1
Introduction

The combustion of metal particles is of interest due to their relatively high energy densities. They are abundant, safe to handle, can be found in a number of particle sizes, and are relatively inexpensive. Small diameter metal particles are common fuels in rocket propellants and due to their ability to burn in water are being considered for underwater propulsion [20]. Metals can also burn in a CO$_2$ environment making them a possible choice as an energy source on Mars.

High temperature metal combustion provides the spectacular lighting shows in pyrotechnics. Self-propagating high-temperature synthesis (SHS) uses a variety of metal powders when burnt produce gasless products and whose combustion front can be stabilized. The study of metal combustion is also important for safety considerations as metal fires and explosions are very dangerous and has led to the loss of life.

Metals have also been added to explosives to increase the overall energy density. The addition of metals to conventional explosives, results in a decrease in peak pressure but an increase in positive phase impulse, in effect increasing the blast strength. These enhancements in blast properties are only achieved when the metal particles are ignited promptly after the detonation of the charge.

Zhang et al [21] developed a simple method to study the combustion of a mixture of explosive and inert metals, forming a so called heterogeneous explosive. A metal
powder is saturated with nitromethane and is then detonated. Frost[5], [7] studied reactive metals such as magnesium and aluminum particles in a spherical geometry. Frost[5] also studied these heterogeneous charges in a cylindrical geometry. These experiments have since been modeled using specially developed Chinook CFD code at Martek Ltd. [18]

Titanium particles are known to have high energy densities and are considered relatively easy to ignite. The standard enthalpy change of formation of Ti to $Ti_3O_5$ is $-2459kJ/mol$, which is well above the corresponding values for the formation of common metal additive metals such as aluminum ($Al_2O_3, -1676kJ/mol$), magnesium ($MgO, -601kJ/mol$), and zirconium ($ZrO_2, -1097kJ/mol$). This is little data on the combustion of titanium particles, particularly in comparison with more widely used metals such as aluminum.

The focus of this study is to determine how titanium particles burn in air and how they react after being explosively dispersed from a cylindrical charge. First a bench top experiment was designed, and experiments were conducted to investigate the combustion of single particles of titanium with varying oxygen concentrations. These experiments were conducted at McGill University. A second set of experiments were conducted at DRDC Suffield, which studied the combustion of Ti particle clouds. These particle clouds are generated by the detonation of cylindrical heterogeneous charges, similar to those described in Frost[5].
The present report is divided into 6 chapters. This introduction is followed by a review of the pertinent literature. This is followed by a description of the experiments in chapter 3. Results are then presented and their implications discussed. An overview is given in the conclusion in chapter 6.
CHAPTER 2
Literature Review

2.1 Metal Combustion

The combustion of metals involves chemical and physical processes which occur simultaneously. Early work found that metal combustion was dependant on "1) the importance of volatility of the metal relative to the volatility of the metal oxide and 2) the relationship between the energy required to gasify the metal or metal oxide and the overall energy from the oxidation reactants" [20]. The magnitudes of these energies and the volatilization-dissociation temperature are used to classify the metal combustion process. Metal combustion mechanisms are generally classified into two groups: a) Homogeneous combustion in which combustion occurs in the gas phase when the metal is relatively volatile and b) combustion occurs by heterogeneous surface reactions and the metal is non-volatile [20]. Purely condensed phase combustion, can occur for these heterogeneous reactions. In these cases, it is possible for combustion products to coat the surface of the burning particle limiting the diffusion of oxygen to the burning surface [20].

2.1.1 Metal Combustion in Oxygen

Metal particles reacting in oxygen burn at a known temperature: the vaporization temperature of the metal oxide product [8]. Metal oxides are highly refractory and the flame temperature cannot exceed the oxide’s boiling point. "The terms vaporization-dissociation temperature and volatilization temperatures are used here
since few condensed-phase metal oxide products actually form gaseous molecules of the original metallic oxide upon gasification.[20] They generally break down into suboxides, \( \text{O}_2 \) molecules, and \( \text{O} \) species rather than their original metallic oxide.

If \( q_r \) is the heat of reaction of the metal at 298K and \( H_{T,\text{vol}}^\circ - H_{298}^\circ \) is the enthalpy required to raise the products oxide to its volatilization temperature then

\[
\Delta H_{\text{vap-dissoc}} > q_r - (H_{T,\text{vol}}^\circ - H_{298}^\circ) = \Delta H_{\text{avail}} \tag{2.1}
\]

\( \Delta H_{\text{vap-dissoc}} \) is the heat of vaporization-dissociation of the metal oxide, and \( \Delta H_{\text{avail}} \) is the heat available in the reaction.

Equation assumes there is no vaporization or decomposition between the reference temperature and the volatilization temperature. Furthermore, Equation 2.1.1 states that the heat of the reaction of the system is insufficient to completely evaporate all the oxide present. For example, for the case of Al combustion it was found that in order to melt the oxide, 140 cal/mole was needed [8]. However "The heat amounting to the difference between 400.3 kcal (enthalpy of reaction) and 140kcal must be interpreted as being used to vaporize and decompose the aluminum oxide at its boiling point" [8]. The heat of reaction is unable to raise the system's temperature above the oxide's vaporization temperature, in effect providing a flame temperature limit. The limiting flame temperature is formally considered the temperature where the enthalpy of reaction is unable to volatilize all of the condensed phase metal oxide present [8].
In 1959, Glassman [8] proposed the "Glassman Criterion": for a condensed-phase fuel droplet to burn in the vapor phase. Vapor burning metals can be determined by comparing their oxide volatization temperature ($T_{vol}$) to the metal’s boiling point ($T_{boil}$).

Table 2–1: Properties of Metals and their Oxides ([8])

<table>
<thead>
<tr>
<th>Metal</th>
<th>Oxide</th>
<th>$T_{boil}$</th>
<th>$T_{vol}$</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
<td>Al$_2$O$_3$</td>
<td>2791</td>
<td>4000</td>
</tr>
<tr>
<td>B</td>
<td>B$_2$O$_3$</td>
<td>4139</td>
<td>2340</td>
</tr>
<tr>
<td>Be</td>
<td>BeO</td>
<td>2741</td>
<td>4200</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr$_2$O$_3$</td>
<td>2952</td>
<td>3280</td>
</tr>
<tr>
<td>Fe</td>
<td>FeO</td>
<td>3133</td>
<td>3400</td>
</tr>
<tr>
<td>Hf</td>
<td>HfO$_2$</td>
<td>4876</td>
<td>5050</td>
</tr>
<tr>
<td>Li</td>
<td>Li$_2$O</td>
<td>1620</td>
<td>2710</td>
</tr>
<tr>
<td>Mg</td>
<td>MgO</td>
<td>1366</td>
<td>3430</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti$_3$O$_5$</td>
<td>3631</td>
<td>4000</td>
</tr>
<tr>
<td>Zr</td>
<td>ZrO$_2$</td>
<td>4703</td>
<td>4280</td>
</tr>
</tbody>
</table>

If the oxide-vaporization temperature is less than the boiling point of the metal oxide product ($T_{vol} < T_{boil}$) than the combustion must undergo heterogeneous surface reaction. Vapor burning metals are identified by examining their oxide’s boiling point and comparing it to the temperature where this oxide is decomposed to gas-phase molecules ($T_{vol} > T_{boil}$). According the the Glassman criterion, Ti is expected to burn in the vapor phase because its boiling point ($T_b$) is 3631K and its oxide volatization-decomposition temperature ($T_{vol}$) is 4000K (Table: 2–1). Whereas Zr has a $T_b = 4703K$ and a $T_{vol} = 4280K$ and hence will burn heterogeneously. Referring to Table: 2–1 Al, Be, Cr, Li, and Mg will also burn in the vapor phase at 1atm and in pure oxygen. B however undergo a much longer heterogeneous surface reaction.
Straightforward application of the Glassman criterion may not be valid. For example, if a metal oxide’s volatilization-dissociation temperature is within 400 K of $T_b$, such as in the cases of Ti, Hf, Fe, and Cr thermal heat losses (conductive, convective, and radiative) can change the predicted combustion mechanism [20]. A flame temperature can be below that of the volatilization temperature due to these losses [8].

2.2 Kinetic versus Diffusion modes of Combustion

Generally speaking there are two particle combustion regimes: kinetically controlled and diffusive controlled. The type of combustion regimes will have an affect on the overall burning time of the material. It is the surface temperature of the particle, which is unknown a priori, which governs oxidation rates. Hence in the case of a surface reaction, it cannot be assumed that kinetic rates are faster than those of oxygen diffusion [8]. We can assume that the rate of reaction ($j$) is dependent on the kinetic mechanism. This reaction mechanism is dependant on the concentration of the reacting species ($C''$) at its surface. Assuming a stationary particle, the reaction rate must be equal to the concentration of the combustion material available at the particle’s surface:

$$j = \beta(C - C'')$$  \hspace{1cm} (2.2)

Equation 2.2 can be equated to the reaction rate, and we obtain:

$$f(C') = \beta(C - C'')$$  \hspace{1cm} (2.3)
Where \( \beta \) is the mass-transfer coefficient, \( (C') \) is oxidizer concentration at the surface, and \( C \) is the concentration of the metal core. \( \beta \) is obtained either analytically or via experimental data. We can assume an Arrhenius reaction rate of the form:

\[
\dot{m} = ACk = ACk_0 \exp\left(\frac{-E_a}{RT}\right) \tag{2.4}
\]

where the chemical kinetic rate \( k = k_0 \exp\left(\frac{-E_a}{RT}\right) \) is solely dependent on temperature. To simplify matters, consider a first-order law for the reaction rate at the surface of the particle. The Arrhenius reaction rate is then

\[
f = kC' \tag{2.5}
\]

Equating 2.3 with our first-order reaction rate

\[
\beta(C - C') = kC \tag{2.6}
\]

and re-arranging terms gives

\[
C = C \frac{\beta k}{k + \beta} \tag{2.7}
\]

Hence, for our case the rate of reaction can be expressed as

\[
j = \frac{k \beta}{kl + \beta} C \tag{2.8}
\]

Depending on the values of \( k \) and \( \beta \), equation 2.8 determines the regime of combustion of a particle. In the kinetic regime we can assume that the oxidizer concentration at
the surface (\(C'\)) is equal to the concentration of the environment (\(C\)). Hence, in this regime, \(k \ll \beta\) and therefore

\[
 j = kC 
\]  \hspace{1cm} (2.9)

In this regime the rate limiting step is the chemical kinetics of the reaction. In contrast, when \(k \gg \beta\) the combustion is dependent on the available concentrations of oxidizer and fuel which are governed by the mass-transfer coefficient \(\beta\).

\[
 j = C\beta 
\]  \hspace{1cm} (2.10)

The mass-transfer coefficient (\(\beta\)) can be expressed in terms of the Sherwood number, the ratio of convective to diffusive mass transport:

\[
 \beta = \frac{ShD}{d} 
\]  \hspace{1cm} (2.11)

where \(D\) is mass diffusivity, \(Sh\) is the sherwood number, and \(d\) is initial particle diameter.

The particle combustion time can be approximated, and then re-arranged using 2.11

\[
 t_b \approx \frac{m}{m} \approx \frac{d^3}{m} \approx \frac{d^3}{C'\beta d^2} = \frac{d^2}{ShDC'} 
\]  \hspace{1cm} (2.12)

for the diffusive regime, where one obtains the Glassman’s [8] classical \(t_b \, d^2\). For the kinetic regime:

\[
 t_b \approx \frac{m}{m} \approx \frac{d^3}{m} \approx \frac{d^3}{C'kd^2} = \frac{d}{kC'} 
\]  \hspace{1cm} (2.13)
were a relation of \( t_b \sim d \) is obtained. These results suggest that Ti should burn with a \( d^2 \) relation.

### 2.3 Ignition

Reactive gas mixtures, liquids, or solids are known for being reactive due to their ability to undergo a fast reaction. Generally these substances are in a steady state in which there is no net change in chemical species. An equilibrium between heat generation and heat loss exists. When the rate of thermal energy generation due to chemical reaction is greater than the rate of energy dissipation, thermal ignition of a substance occurs. Thermal ignition is impossible when the energy dissipation is greater than that of the energy generation [8].

#### 2.3.1 Semenov Theory of Thermal Ignition

Semenov considered the ignition of a uniform energetic material at a uniform temperature. The basis of this theory is a competition between an Arrhenius heat release of the combusting substance (\( q_r \)) and a conductive heat loss (\( q_l \)). The heat release can be expressed as follows:

\[
\dot{q}_r = Q\rho^n V A \exp \left( \frac{-E_a}{RT} \right)
\]

(2.14)

where \( V \) is the volume, \( \rho \) is the density, \( Q \) is the thermal heat release of the substance, \( A \) is the Arrhenius pre-exponential constant, \( E_a \) is the activation energy, \( R \) is the universal gas constant, and \( T \) the temperature of the reaction. Assuming convective heat transfer, the heat loss can be written as follows:

\[
\dot{q}_l = h S (T - T_o)
\]

(2.15)
where $h$ is the heat transfer coefficient, $S$ is the surface area, and $T_o$ is the temperature of the environment.

The overall energy equation for this system is

$$c_v \left( \frac{dT}{dt} \right) = \dot{q}_r - \dot{q}_l$$

(2.16)

When the heat generation is equal to heat dissipation the reactive substance is said to be at steady state (ie $d_q \{d_t = 0$ in 2.16). At this condition $q_r = q_l$ and the system is said to be in thermal equilibrium (point A on Fig: 2–1).

Figure 2–1: Heat generation and heat loss of a reactive substance

At point $T_a$ the system is in a stable thermal equilibrium state. If the system at $T_a$ is perturbed in such a that its temperature is above that of $T_a$, the system will return back to $T_a$ due to the system’s cooling rate ($q_l$). Point B on 2–1 is a second equilibrium point, however it is unstable. If the system is perturbed in any way it will either undergo rapid cooling or thermal explosion.
At this condition, \( q_r = q_l \) and we can assume we are at the critical point of ignition. From here an ignition temperature can be determined.

### 2.4 Titanium Combustion

The study of titanium particle combustion dates back to the 1960s. Gordon [9] studied the combustion of a variety of metals, including titanium. Particles were ignited above a flat flame burner and their combustion was recorded with a particle streak camera. Particles diameters ranging from 44 to 420 \( \mu m \) were studied. Titanium was found to be easily ignited with the combustion terminating via explosion. Titanium’s burn time was found to be considerably longer than either magnesium or aluminum and the particle had an ability to dissolve large amounts of oxygen without the transition to a second phase. An empirical dependence of burn time on particle diameter was found to be

\[
\ln t_b = 1.59 \ln d - 2.56 \tag{2.17}
\]

\( t_b \) is the burn time in milliseconds and \( d \) is the initial particle diameter. Nelson performed two studies (in [16] and [17]) that examined falling Ti and Zr metal droplets of the order of hundreds of microns in diameter into pure oxygen or a mixture of oxygen and nitrogen. A particle streak camera recorded the combustion. Particles were then quenched at different stages of combustion. These quenched particles were then weighed, and examined using X-ray diffraction. Again, the termination of combustion was accompanied by the explosion of the particle. Zirconium, burning in oxygen, did not exploded. An explosion could be induced if nitrogen was used as a gaseous component or if it were dissolved into the metal prior to combustion.
Nelson proposed an explanation for the observed explosion of these particles. He explained that the burning droplets absorbed both nitrogen and oxygen while the droplet was metal rich. As the oxygen rich combustion products were being formed, nitrogen is released. When the pressure of the nitrogen exceeds the cohesive forces in the droplet, an explosion occurs.

Dolganov et al. [2] studied Ti particles combustion of an average size of 4\(\mu m\) in high speed flows of argon (80 \%) and oxygen (20\%). \(O_2\) was mixed with pre-heated argon, and the particles were then ignited in this flow. The temperature of the burning particles was estimated, via pyrometry, to be 2400-2600K. Particle combustion would end with an explosion.

Makino et al [1] studied the combustion of titanium particles (41 to 115\(\mu m\)) with different oxygen concentrations. Particles were dropped into a flat flame burner’s combustion products where they would ignite. Different mixtures of methane/oxygen/air and methane/oxygen/argon were used. A streak camera was used to capture the falling burning particles. Particle explosions were observed after the particle’s size had decreased by 30\%, which was independent of particle size or oxygen concentration.

Molodetsky et al [15] studied the combustion of large Ti particles (240 and 280 \(\mu m\)) which were formed by melting a solid wire of titanium using a micro arc. This study measured particle temperature using a three colour pyrometer. Particles, at different stages of combustion, were quenched and analyzed using spectroscopy to determine composition. Burning times for the 240 and 280 \(\mu m\) particles where found to be 240 and 300 ms respectively. Combustion always terminated with an
explosion. The particle temperature peaked at a temperature close to 2700 K then dropped and remained constant at 2100K where explosion occurs. It should be noted that this is well below the volatization temperature of either the oxide or titanium.

Examination of the quenched particles found little change in diameter due to the combustion process. The internal structure of the quenched particles found a mix of two phases, each containing a mixture of Ti, O, and N atoms. Oxygen and nitrogen were distributed uniformly throughout the particle, rather than an oxide film or oxide inclusions. Internal composition analysis did not show a measurable decrease in the bulk titanium content during the combustion. It was determined that the gas phase reactions were insignificant. Molodetsky surmised that the explosions were caused by a nitrogen release during the formation of stoichiometric $\text{Ti}_2\text{O}_3$ oxide, and solidification of the oxide occurs. Nitrogen buildup causes the oxide to crack, allowing oxygen to react with a fresh titanium layer. The temperature increase due to this fresh reaction causes gas bubbles within the particle to expand and then explode the particle.

A recently published paper by Shafirovich et al. [19] studied the combustion of individual levitation particles. The study was conducted by placing a single particle of known size into a custom made electrodynamic chamber. The electrodynamic forces stabilize the electrically charged particle at the center of the chamber, upon which it was ignited by a 60W $\text{CO}_2$ laser. The particle combustion was recorded using a high speed video camera. Images were generated from the video at known intervals. Light emitted due to the combustion was captured using a photo-multiplier. Irregular shaped titanium particles were sieved into 9 different ranges ranging from 20 to
125 $\mu m$. Upon ignition, the particle melted to form a spherical droplet. Burning time was determined by analyzing the particle’s light emission. A typical emission profile included an initial peak, a long plateau, and narrow peak at the end which corresponded to particle explosion. Burn time was measured to be the time between the initial peak and the explosion. An empirical formula for the burn time of particle range of 15 to 110 $\mu m$ was determined to be

$$t_b = 1.29 \times 10^3 d^{1.56}$$

(2.18)

where $t_b$ is the burn time in milliseconds and $d$ is the initial particle diameter in $\mu m$. His results for the burn time are around three times shorter than Gordon’s results. Shafirovich added two data points from Molodetsky to obtain the following empirical formula for burn time for particles in the range from 15-280$\mu m$

$$t_b = 3.14 \times 10^3 d^{1.85}$$

(2.19)

Equation 2.19 approaches the classical $d^2$ law for diffusion-controlled combustion proposed by Glassman [8]. This result suggests that for the size range 15 to 280 $\mu m$ the gas-phase diffusion of oxygen plays an important role in the combustion of titanium in air. Shafirovich [19] also reasoned that the increase in the power exponent from 1.56 (equation 2.18) to 1.85 (equation 2.19) may indicate that kinetics plays an important role for smaller particles.
2.5 Explosive Dispersal of Particles

Over the past 10 years much work has been done on the detonation of particle beds saturated in a detonable liquid, denoted a heterogeneous charge. Once these heterogeneous charges have been detonated, particles are rapidly accelerated outwards creating a particle cloud. Depending on a variety of factors it is possible for these particles to ignite. The experiment focused on how the addition of these particles influenced the blast wave when compared to a homogeneous explosive. Numerical models have been developed (see [18], [3]) which have the ability to track an individual particle’s path and to study the effects of the detonation on this particle. More data on the combustion of single particles and on the overall combustion of titanium clouds are needed to improve the reliability of numerical models. Inert particles (glass beads, and iron powder) and reactive powders (aluminum, magnesium, zirconium and titanium have been tested) by [6], [21], [14] and many others.

When a homogeneous explosive is detonated, a single step energy release occurs directly following its detonation. Adding solid particles to a homogeneous explosive adds a secondary energy release stage if the particles are able to ignite. This ignition introduces additional length and time scales which influence the propagation of both the detonation wave and the subsequent blast wave in air. Due to the addition of these solid particles a detonation velocity difference when compared to the homogeneous case occur due to momentum, and energy transfer and the acceleration, heating, and breaking of the particles [6].

The solid particles are launched radially outwards by the detonation of the homogeneous explosive. Already traveling at high speeds, they are further accelerated
by the drag associated with the expanding detonation products. The balance between the acceleration due to expanding products and the initial detonation changes depending on particle size and density. In some cases it is possible for particles to penetrate the blast wave. Small, low density particles rapidly accommodate to the flow of the expanding products. As a result they tend to remain close to the shock wave. If the particles do penetrate the shock wave, they will be quickly decelerated due to the quiescent ambient air. This interplay of momentum and energy has the effect of lowering the overpressure and changing the decay of the blast wave when compared to a homogeneous charge.
2.5.1 Physics behind a Cylindrical Explosion

2.5.2 Physics behind the dispersal

When packed a bed of metal particles saturated with sensitized nitromethane (9:1 ratio of nitromethane to triethylamine by weight) is detonated via a booster charge, a detonation wave travels downwards through the heterogeneous mixture. The detonation wave creates large overpressures within the packed bed of particles. The pressure gradient causes particles to be quickly accelerated radially outwards. Upon reaching the limits of the explosive charge, the detonation wave is transmitted to the air in the form of a blast wave. A reflected expansion wave travels back towards the center of the charge. The expansion wave results in an quick expansion of the detonation products of nitromethane, whose drag helps to further accelerate the particles outwards creating a particle cloud. Velocities of 1-2 km/s have been shown to occur after only a couple charge diameters [21]. Kurbangalina [11] and Lee [14],[13] were able to measure detonation velocities and the critical diameter for failure as a function of the sensitivity of the explosive and the particle diameter. A cylindrical geometry provides a fundamental configuration where the ignition of particles can be observed, without being affected by the initial booster.

Initially the particles are located in the hot detonation products of the detonation, where convective heat transfer increases the particle temperature. If the ignition threshold is reached, combustion of the particles occurs. However in many cases, the particle’s heating must compete with the cooling adiabatic expansion of the products, and in some cases the ignition temperature is not achieved. The convective heat transfer rate is governed by particle size [18]. Smaller particles have high
heat transfer rates and are more sensitive to both the heating and cooling processes. Quenching of the particles combustion may occur if the cooling rate is sufficient to overcome the reaction rate of the burning particle.

Once the particles penetrate the combustion products interface they enter the shock heated air region, which will be important for reactive particles. Very fine particles will rapidly equilibrate to the flow velocity whereas large particles will have a slower equilibrium time due to their higher inertia. Particles may even penetrate the leading blast wave, depending on the particle size and density and the charge diameter. For an intermediate range of particles their inertia will cause them to be accelerated quickly enough to a speed, where coupled with the decay of the blast wave, it is possible for the particles to catch up to and penetrate the shock front. Lanovets [12] performed numerical simulations of an explosive particle charge in a spherical geometry and found that for a range of particles sizes and densities, solid metal particles can overtake the combustion products and the primary blast wave. Zhang [21] showed that for large particle sizes (275\(\mu m\) to 950 \(\mu m\)) overtaking distance does not change significantly. When the particle diameter is reduced, drag plays a more important role. As these particles penetrate the blast wave, they are slowed down due to the drag of the air ahead of the blast wave. A reduction in particle density increases its early time acceleration which results in a reduction in overtaking distance. The overtaking distance is reduced by a factor of approximately 2.75 when steel particles (\(\rho = 7.8g^3\)) are replaced by glass particles (\(\rho = 2.7g^3\)) of the same diameter. Zhang et al[21] also showed that for a spherical geometry it is possible for particles to penetrate the blast wave. Once the particles penetrate the shock wave
they encounter a drag force which slows them down. In some cases the shock may subsequently overtake the particles that have escaped. Further studies of different particles burning in air are needed to fully understand the phenomena.

2.5.3 Dispersal of Reactive Particles

For general explosives there is a critical diameter where detonation fails to propagate. Frost et al in 2002[7] found that "the effect of adding metal particles on the critical diameter for detonation failure is the result of the interplay between the desensitizing effects of the particles (since the particles typically do not react within the explosive reaction zone, the particles act as an inert dilutants and momentum and heat losses to the particles tend to increase the failure diameter) and the sensitizing effect of hot-spot generation due to shock/particle interactions. Depending on the choice of the particles and liquid, the failure diameter of the heterogeneous explosive may be either larger or smaller than that of the liquid itself."

Frost et al [7] introduced the concept of a Critical Diameter for Particle Ignition (CDPI), referring to the charge diameter where combustion of the particle cloud occurs. The residence time of particles in the hot gases produced from the detonation of the charge must be large enough to overcome the cooling effect of the expansion of the products. If this residence time is achieved, particles will react within the cloud. In some cases, particle reaction occurred after an induction time. For these cases, the addition of the particles had little effect on the shock overpressure for the experiment. Conversely if the particles react promptly, the strength of the generated blast wave is augmented. It is believed that the blast wave is augmented only when particle ignition is prompt, as the energy release combustion of these relatively dense
particle clouds is high. The CDPI was found to be a strong function of initial particle size, and depends on particle morphology. This study defined CDPI for magnesium particles in the form of a linear border between prompt ignition and delayed or no ignition of the particle cloud for spherical charges (Fig: 2–2).

Figure 2–2: Effect of particle and charge diameter on the ignition of magnesium particles in a spherical geometry. Number of trials at given conditions shown in parenthesis. Dashed line is relation $D_{\text{charge}} = D_{\text{particle}}^{1.75}$. Plot reproduced from [7]

Magnesium was tested in cylindrical geometry. It was reported that “For 240 µm particles, particle ignition did not occur for 34 and 49 mm diameter charges (the detonation fails to propagate in a 28 mm diameter tube). For 85 µm particles, both the particle ignition and detonation failure thresholds were observed as the tube diameter was decreased progressively. For 47 mm and 25 mm diameter charges, immediate ignition of the particles was observed. For an 18 mm charge, particle ignition is delayed. When the diameter is reduced to 16 mm, particle ignition during the dispersion does not occur.”
Much work has been done on examining how the combustion of aluminum particles affects the blast wave of a heterogeneous explosion in both spherical and cylindrical geometries. Frost et al [5] found that for cylinders ranging from 9-74mm in diameter, the CDPI displays a monatomic increasing behavior for spherical aluminum particles ranging from 2 to 100 $\mu m$ with the minimum CDPI of 19 mm corresponding to 54$\mu m$ particle size. A plot summarizing the data for aluminum, steel, and glass spheres is reproduced in Fig 2–3.

Figure 2–3: Dependence of particle reactivity on charge and particle diameter. Cross: Regime 1 - no reaction; Open circle: Regime 2 - reaction at isolate spots or rings; Filled circle: Regime 3 - rapid continuous reaction. Plot reproduced from [5]
CHAPTER 3
Experimental Details

3.1 Experiments

Titanium particle reaction was examined using two experiments. The first experiment involves the study of the combustion of a single titanium particle in the region above a flat flame burner where the flame heats the particle to its ignition point. The experiment’s focus is to determine particle burn time. Experiment two involves the detonation of a cylinder of sensitized nitromethane packed with a bed of spherical titanium particles. This study involves determining the critical cylinder diameter which will induce particle ignition.

3.2 Flat Flame Burner

3.2.1 Overview

Experiment 1 of this work, using a flat flame burner, is designed to study the combustion of a single titanium particle. The burner uses a triple mixture of oxygen, air, and methane as reactants. The gases are injected separately and are then carefully mixed and ignited. A single particle is then injected into the center of the flame via an air stream. Due to the high temperature of the flame, the particle ignites then burns with the oxidizers available. A stoichiometric and a lean flame were tested to determine if oxygen concentration affects the combustion. Upon ignition the ascending particle create a particle streak which was photographed and then analyzed.
3.2.2 Burner Design

The burner consists of 5 sections: the flow control board, the burner base, the mixing chamber, the flame, and the test section. A schematic of the burner is show in Fig: 3–1. The base of the burner contains two sets of channels: fuel carrying and oxidizer carrying 3–1. These channels exit the burner base creating a series of holes, Fig: 3–2. The matrix of outlets is 7.62cm (3”) in diameter. The fuel and oxidizer channel matrices are isolated from one another. This intricate network of channels ensures that there is no mixing of the reactants within the burner base. The oxidizer channels are injected with a mixture of pure $O_2$ and 99% dry air. The fuel channels carry pure methane gas ($CH_4$). All 3 gas flows are regulated by Matheson Tri-Gas model 603 Rotameter flow meters, and are calibrated in liters per minute ($l/min$).

One of the major concerns in any burner design is the possibility of a flashback. A flashback occurs when a flame is too rich or too lean to be stabilized on the burner surface. The flame then propagates upstream into the burner. In the event of a flashback, a constant volume explosion is possible within a mixing chamber. The intricate network of channels was originally designed in order to avoid the necessity of a mixing chamber filled, avoiding pre-mixing gas for as long as possible. However, when attempting to ignite a flame above the outlets of these channels a series of flamelets was obtained rather than the desired smooth flame Fig: 3–2. A flamelet was centered in the middle of 4 channel exits, drawing the reactants and oxidizer from the surrounding channels. The series of flamelets created an uneven post flame temperature region.
To avoid these flamelets, a mixing chamber was added to the design. The fuel and oxidizer channels open into a 7.62cm diameter and 4cm tall mixing chamber filled with two types of spherical ceramic beads. The 1st bead bed, with yellow yellow with an average diameter of 2mm, is 1.91cm (3/4”) thick. As the gases leave their channels they are forced to travel through gaps in between the beads, where the gases mix. The mixed gas then travels through the 2nd set of smaller beads also 1.91cm (3/4”) thick; the beads are white with an average diameter of 0.5mm. The two types ceramic beads are shown in Fig: 3–3. The second set of beads stabilizes and equilibrates the gas flow over the burner surface. When a flame was lit above the larger beads the flame flickered wildly, which would de-stabilize the post flame temperature and air flow. To reduce this effect, the smaller beads were added on
Figure 3–2: Flame was originally lit over matrix of channels on the burner base. Flamelets rather than a flat uniform flame was obtained.

Figure 3–3: Ceramic beads, placed next to each other to show relative size top. With the addition of the smaller bed a flat flame could be generated. Fig: 3–4 shows a similar view to Fig: 3–2 with the mixing chamber added to the burner base. Although this re-design incorporated a mixing chamber within the beads, flashback
was kept to a minimum as the gaps between the beads were below the flame quenching limits for the mixture used. A 50cm long, 5cm diameter pyrex tube is positioned 1cm above the burner’s face (Fig: 3–4). The Pyrex tube ensures that there is little heat exchange between the hot products of the flame and the environment. The 1cm gap allows for the entrainment of air. Without this air entrainment, the Ti particles did not ignite.

3.2.3 Particle Injector

Titanium particles are injected into the flame by the particle injector as shown in Figs: 3–5 and 3–1. The particle injector main body is a 40mm plastic sphere, a ping pong ball, which has been fixed to the diaphragm of small audio speaker. Protruding vertically from the sphere is an 18.5cm long tube (.058" OD, .05" ID) denoted the injection tube, by which particles travel from the plastic sphere and are then injected into the flame (see Figs: 3–5 and 3–1). Air is introduced through an inlet, which is located just above the sphere’s equator.

Before beginning an experiment, titanium particles are fed inside the sphere. A function generator is set to create a step wave function whose signal is then passed through a signal amplifier. Depending on the input frequency, which ranged from 15 to 120hz, the speaker produces a low to high pitched humming. The humming is produced by the speaker’s diaphragm oscillation. This motion is transferred to the ping pong ball and the particle bed. The effect of the agitation is a bed of particles which "hop and dance" akin to popcorn popping.

An air stream is directed into the agitated particle, creating a fluidized bed, and then exits through the injection tube. At times, the air stream entrains a particle
and carries it along with it out the injection tube. The particle is then sped up to the speed of the exiting air jet, and is ejected into the flame.
The number of particles being injected at a time depends on the agitation, the air stream, particle diameter, and particles remaining inside the injector. Depending on these factors it is possible to inject any number of particles into the flame at a time. The challenge lies in injecting between 1 and 5 particles at a time into the flame.

3.2.4 Diagnostics

A particle streak imagery system was designed and built to diagnose particle burn time. As a particle burns, it emits light. If a burning particle is moving it leaves a streak as illustrated in Fig: 3–6. Particles are captured by a Canon EOS SLR camera whose exposure is varied from a setting of 8” to 0.5 seconds depending on particle size. Larger particles require a longer exposure due to their longer burn time. The aperture of the camera was set for all experiments at a setting of f/19.
With little light in the laboratory this aperture setting captures only the faint blue hue of the flame and the bright white particle streak.

![Luminous particle streak of a burning titanium particle](image)

Figure 3–6: Luminous particle streak of a burning titanium particle

The light emitted from a particle’s combustion is chopped by a chopper wheel (Fig: 3–7). The chopper wheel is a 12 inch disk with 16 evenly spaced slots and is fixed to the axle of an AC motor. The speed of rotation is determined by a reflective optical sensor, Optek model OPB794. Reflective tape is placed on the wheel; as this
tape passes the sensor a peak in reflectivity is measured. This peak is transmitted to an oscilloscope, which displays a voltage spike. The frequency of these voltage spikes gives the rotation speed of the wheel. The rotation speed was set to either 32 or 16 Hz, depending on the burn time of the particle.

Figure 3–7: Chopping Wheel

As the disk spins, the slots in the wheel let light pass through the disk periodically. For stationary objects, the chopping of the image has no effect. For moving objects the chopper blocks the camera from recording sections of its path. For the
case of a burning particle its streak is chopped into a series of dashes Fig: 3–8. Each
dashed line represents a unit of elapsed time. With 16 slots and the wheel spinning
at 32Hz, each dash line represents 1 millisecond.

Particles are analyzed by counting the number of dashes to determine particle
burn time. Particle streaks are only counted if their entire combustion history can
be traced. Before a particle ignites, it is heated to its ignition temperature. During
this heating stage, a particle emits a yellow-orange colour. The colour and intensity
of the light is significantly different once ignition occurs. After ignition, the particle’s
emission is turns to bright white. A micro-explosion marks the end of the combustion
process. Particles are only analyzed if they clearly show these three components
such as the 3 particles in Fig: 3–8. The transition from particle heating to particle
combustion is very quick, lasting between two and five milliseconds. Particles which
bounce off the Pyrex tube, which deviate from a strait path, or are far from the
center of the flame are also disregarded.

For the vast majority of the photographs taken, counting of the light dashes was
performed using the image software Image J. A particle is isolated and the original
colour image is split into its red, green, and blue components. Splitting the image
into its three colour components creates three gray scale images. In all cases the
red image was kept. The image is then converted to a binary image by selecting a
gray scale cutoff level. Gray scale pixels below this level become black and those
above become white. This process can be seen in Fig: 3–9. This cutoff level is kept
constant for the particles analyzed. Converting the images this way gives a standard
cutoff level for the particle streaks to determine the onset of ignition. If a streak’s
brightness is below the cutoff, it is converted to white and is not counted. Once in this mode, particles are counted by Image J’s counting software, and particle count burn time is calculated.

Using emission spectroscopy, particle temperatures were also tested using an Ocean Optics model USB2000 spectrometer was used. The spectroscopy was integrated over multiple particle combustion events to provide sufficient light for the spectrometer (Fig: 3–10).
Figure 3–9: Left: Unprocessed particle burning, Middle: red image, Right: greyscale applied to particle

3.2.5 Titanium Particles

The spherical titanium powders used, commercially denoted as CP-Ti particles, were obtained from Raymor Industries in Broisbriand Quebec. The particles are
formed by melting a titanium wire elevated over a specially designed cooling chamber. As the particles fall through the chamber, they solidify as spheres. The particles, as advertised, have a very high degree of sphericity as shown shown in Fig: 3–13. These CP-Ti particles eliminate inconsistencies that may be present in other particles such as morphology, size variations within a sieved range, and porosity. From the ordered particles, four ranges were sieved and studied for the burner experiment (see Table: 3–1)
3.2.6 Flames Studied

In order to determine the effect of oxygen concentration on the burn times; two flames were studied, denoted Flame A and Flame B. Flame A’s products were tailored in order for the product species to be void of $O_2$. Flame B is a lean flame, in which the air and oxygen levels in the products are increased from flame A levels. An estimation of the flame species was made using the chemical kinetics code CAE. Table 3–2 shows the results for flames A and B along with a stoichiometric flame computed at 1atm and 2223 K, the adiabatic flame temperature for methane-air.

<table>
<thead>
<tr>
<th>Species</th>
<th>Flame A</th>
<th>Flame B</th>
<th>Stoichiometric</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.12190</td>
<td>0.00335</td>
<td>0.01578</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.07422</td>
<td>0.14589</td>
<td>0.08210</td>
</tr>
<tr>
<td>H</td>
<td>0.0019</td>
<td>0.00023</td>
<td>0.00053</td>
</tr>
<tr>
<td>$H_2$</td>
<td>0.09173</td>
<td>0.00126</td>
<td>0.00673</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>0.29903</td>
<td>0.29283</td>
<td>0.18758</td>
</tr>
<tr>
<td>NO</td>
<td>0.00009</td>
<td>0.00669</td>
<td>0.00100</td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.41003</td>
<td>0.44635</td>
<td>0.70246</td>
</tr>
<tr>
<td>O</td>
<td>0.00001</td>
<td>0.00096</td>
<td>0.00011</td>
</tr>
<tr>
<td>$OH$</td>
<td>0.00102</td>
<td>0.00854</td>
<td>0.00236</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.00002</td>
<td>0.09389</td>
<td>0.00134</td>
</tr>
</tbody>
</table>
Flame A’s reactants, according to the calculations, have no excess oxygen. Flame B on the other hand has a large excess of oxygen, with a mole fraction of almost 10 times that of flame A.

Flame A is of interest as the majority of studies have used air as the oxidizing agent. According to the CAE simulation the majority of oxygen which injected into the burner reacts with the methane. It is assumed that the particles are burning in the air which is entrained by the pyrex tube, and are not reacting with the other oxidizers present in the flow (CO$_2$ and H$_2$O). The flame is hence used only as a means to heat the particles to the point of ignition. The results of the experiments with this flame are intended to be compared with those in which a particle is burnt in air.

Flame B, a lean flame, is studied in order to determine the effect of increasing the oxygen concentration on the combustion process of a titanium particle. Increasing the availability of oxygen in the burning environment effects the diffusion of oxygen to the particle. In this case, the flame not only heats up the particle to the point of ignition but also injects excess oxygen into the combustion environment.

3.2.7 Experimental Procedure

Particles are first fed into the particle injector’s sphere. All monitoring devices are turned on and all connections (electrical, gas) are checked. A fume hood is turned on. First $CH_4$ is slowly introduced into the burner. The Pyrex tube is slid up from the mixing chamber’s surface, for ease of access in igniting a $CH_4$- air flame. The methane flow is slowly increased to the desired value for the experiment. The Pyrex tube is lowered, with its bottom end resting 1 cm above the burner surface. Air is
entrained through this centimeter gap, which stabilizes into a conical flame. As the flame is now fuel-rich, the flame has an orange and yellow colour. Lighting in the lab is turned off.

Dry air is then slowly added to burner. The apex of the conical flame descends towards the burner surface as the $CH_4$ begins to react with the injected air. Once the pre-determined air level is reached, the flame is allowed to burn for 2-3 minutes. Oxygen is then slowly injected into the burner where it mixes with the air inside a mixing chamber. The apex of the cone descends even further towards the burner surface.

At this point particles can be injected into the flame. An air flow is injected into the particle injector, and the particle agitator is turned on. The air flow rate and the frequency of the agitator are manipulated to tune the injection of particles. Burn time experiments require three or fewer particles to be injected at a given time, and for temperature measurements a particle jet is required Fig: 3–10. Photographs, which are chopped, are then taken at random. During the process, photos are examined to ensure that the camera exposure is capturing the entire burn history of the particles. Large particles, which have a longer burn time, need a longer exposure time than shorter particles. A minimum of 100 photos are taken per experiment.

After the experiment the oxygen is turned off first, followed by the air and finally the methane. Once the flame has been extinguished, the gas lines for the three gases are vented separately.
3.3 Cylinder Explosive Trials

The focus of the cylindrical experiments is particle cloud combustion. A detonation wave travels though a heterogeneous mixture of titanium powder and sensitized nitromethane. Two combustion limits are classically associated with a cylindrical heterogeneous charge. The critical charge diameter for detonation failure depends on the competing effects of the explosive hot products and shocked heated air and the quenching effects of expanding flow. Above this limit, a detonation wave will propagate through the charge. In the case of the cylinders of this study, which are ignited from the top, the detonation wave will propagate from the ignition source down the length of the tube. If a charge is below this critical charge diameter, propagation will be interrupted at some point during the experiment. The second limit also occurs for these heterogeneous charges is called the critical diameter for particle ignition (CDPI). The CDPI describes a charge where the particles burn quickly after their dispersion. CDPI depends on the particle residence time in the hot gases, charge diameter, particle size, and particle morphology. The aim of the current study is to determine a CDPI for titanium powders.

3.3.1 Field Trial Facilities

Experiments were carried out at the research division of the Canadian Armed Forces base Suffield, DRDC-Suffield. The trial series was carried out at the Multi-burst facility, which is one of many locations where explosive tests are conducted on the research range. Ground zero for this trial series is on a section of a concrete pad far from any structures. Two bunkers are provided. The first is an instrumentation bunker where diagnostics, communications, and charge ignition equipment
are located. The second bunker is a mixing bunker where nitromethane, TEA (tri-ethylamine), and the metal powders are stored and where charges are prepared. A schematic of the test site is shown in Fig: 3–11.

Figure 3–11: Suffield test range setup for cylindrical charges

The facility has a number of safety regulations which must be respected and a team of technicians to aid in the experiments. The field trial officer, who runs the
safety and explosive handling and gives the final approval before an experiment may proceed. Two ammunition technicians handle the condensed explosives, in our case C4 used to initiate the charge. An ambulance is present at all trial series. There is also a number of support vehicles such as a fire truck, and bobcats loaders. Two Phantom VII video cameras using frame rates of up to 40 000 frames per second were used to record the event.

3.3.2 Charge Design

Titanium particles are packed into 122cm long Pyrex tubes of diameter ranging from 19mm to 59mm. The packed beds of particles is saturated with a mixture of nitromethane and 10% by weight TEA. The heterogeneous explosive contained 88.10.3% Ti by mass. The charges are filled by alternating between pouring particles and then the liquid mixture to ensure the absence of air gaps.

A charge booster is made from 10g of C4 tightly packed into a ball which a high voltage detonator is inserted into. This assembly is lowered into a 10cm nitromethane section. The detonator initiates the C4 ball which transmits the detonation into the nitromethane liquid section. The gap ensures that a well developed detonation wave is transmitted into the packed particle bed. Without this fully developed wave in the gap, the detonation from the booster can fail to propagate to the packed bed. The charge base is hermetically sealed to a wood base by epoxy. Due to nitromethane corrosive properties, charges must be prepared and tested quickly. As TEA is toxic, protective gloves, jumpsuit and a gas mask are required when preparing and manipulating charges.
Figure 3–12: 49mm cylindrical charge with unknown Ti content mounted on stand, prior to insertion of booster charge.
Charges are placed on a retrofitted charge stand. The charge base is placed 60cm above the ground, and is supported by a 10cm rod. The detonator and booster charge are lowered into the gap only when the charge is on the stand by a technician.

3.3.3 Titanium Powders

Two sets of powders were tested. The first set of particles was supplied by Atlantic Engineering Equipment (AEE). Three batches designated Ti-109, Ti-107, and Ti-104 were used. These powders are irregular in shape. The second set are the same powders that were used in the flat flame burner test. Again three ranges were used. Table 3–3 shows the powder size ranges as described by the producer.

<table>
<thead>
<tr>
<th>Powder Name</th>
<th>Range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEE Ti-104</td>
<td>0 - 44</td>
</tr>
<tr>
<td>AEE Ti-107</td>
<td>0 - 74</td>
</tr>
<tr>
<td>AEE Ti-109</td>
<td>0 - 149</td>
</tr>
<tr>
<td>Spherical Fine</td>
<td>40 ± 14</td>
</tr>
<tr>
<td>Spherical Medium</td>
<td>95 ± 26</td>
</tr>
<tr>
<td>Spherical Coarse</td>
<td>250 ±77</td>
</tr>
</tbody>
</table>

The main difference between the two powders is their morphology and the texture of the particle surface. Figure 3–13 shows an electron microscope image of the AEE and spherical powders. The powders in the images are of comparable size distribution and have both been magnified by 350 times.
Figure 3–13: Image of titanium powder, 350 times amplification Left: Spherical Fine Powder Right: Ti-104
CHAPTER 4
Results

4.1 Flat Flame Burner

4.1.1 Particle Distribution

Particles obtained from AP&C were delivered in three bin sizes. The particles
with then manually sieved into four particle ranges, denoted ranges A-D. A par-
ticle size distribution was determined. The distribution was obtained by measuring
particle diameter using an optical microscope. The microscope has 3 magnification
settings: 10X, 40X and 100X. A 1mm grid pattern etched onto a microscope slide is
used for calibration. Calibration was performed for each magnification. A minimum
of 200 particles were measured per particle range. Due to the high degree of spheric-
ity of the particles in these experiments, the diameters measured can be considered
accurate along any axis. In order to avoid any biases in the case of slight elongation,
particles were always measured along the horizontal axis.

Plotted in Fig: 4–1 is the raw data from the particle distribution study. Bin
sizes for the histograms were chosen in order to best represent the distribution. The
bins are plotted against the total number of particles counted.

A smooth curve fit is applied through the peaks of the bins from Fig: 4–1 points
to obtain a continuous particle distribution.
Figure 4–1: Histogram: Particle Distribution
Figure 4–2: Curve fit: Particle Distribution. Red squares represent histogram peaks.
Figure 4–3: Total particle distribution for range tested
The overlap in the particle range is clear from Fig: 4–3. The most two glaring overlaps are the of ranges A, B, and C, and the second overlap is in ranges C and D (Fig: 4–3).

Table 4–1: Particle Sieved ranged

<table>
<thead>
<tr>
<th>Range Name</th>
<th>Cohort</th>
<th>Average Particle Size (µm)</th>
<th>Standard Deviation (µm)</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0-20</td>
<td>49</td>
<td>2</td>
<td>A1</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>53</td>
<td>1</td>
<td>A2</td>
</tr>
<tr>
<td></td>
<td>40-60</td>
<td>55</td>
<td>1</td>
<td>A3</td>
</tr>
<tr>
<td></td>
<td>60-80</td>
<td>57</td>
<td>1</td>
<td>A4</td>
</tr>
<tr>
<td></td>
<td>80-100</td>
<td>59</td>
<td>1</td>
<td>A5</td>
</tr>
<tr>
<td>B</td>
<td>0-20</td>
<td>58</td>
<td>2</td>
<td>B1</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>64</td>
<td>1</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td>40-60</td>
<td>67</td>
<td>1</td>
<td>B3</td>
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<td>60-80</td>
<td>70</td>
<td>1</td>
<td>B4</td>
</tr>
<tr>
<td></td>
<td>80-100</td>
<td>75</td>
<td>2</td>
<td>B5</td>
</tr>
<tr>
<td>C</td>
<td>0-20</td>
<td>70</td>
<td>6</td>
<td>C1</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>86</td>
<td>3</td>
<td>C2</td>
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<td>40-60</td>
<td>95</td>
<td>2</td>
<td>C3</td>
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<td>60-80</td>
<td>103</td>
<td>3</td>
<td>C4</td>
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<td>80-100</td>
<td>119</td>
<td>7</td>
<td>C5</td>
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<td>0-20</td>
<td>108</td>
<td>11</td>
<td>D1</td>
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<td>20-40</td>
<td>132</td>
<td>3</td>
<td>D2</td>
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<tr>
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<td>40-60</td>
<td>142</td>
<td>3</td>
<td>D3</td>
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<td>60-80</td>
<td>154</td>
<td>5</td>
<td>D4</td>
</tr>
<tr>
<td></td>
<td>80-100</td>
<td>181</td>
<td>11</td>
<td>D5</td>
</tr>
</tbody>
</table>

Each curve in Fig: 4–2 is divided into 5 sections, or cohorts, each representing 20% of the total number of particles counted. The particle size for a given cohort is the average particle size within that cohort (Table: 4–1). The majority of the cohorts are concentrated in the range 50-110 µm. Cohorts are labeled by their size.
range (A to D) and their position within this size range (1 to 5). For example the 3rd cohort in range B is denoted B3.

The standard deviation from the average is small in ranges A and B (Table: 4–1). Ranges C and D have small deviation in the middle cohorts of the range, however the 1st and 5th cohort in both cases show large a deviation. For the majority of the cohorts, there is a 3 micron or less deviation from its corresponding average size. This small deviation from the average is equal to at most 11 percent standard deviation from the average. The standard deviation for all ranges is 3.3%. As for the overlapping of cohorts, in all cases the first cohort (denoted A1,B1,C1,or D1) in one range overlaps the last cohort in the previous range (denoted A5,B5,C5,or D5). The overlap between ranges B and C is the only case where this is untrue. In this case B4 is equal to that of C1. Although both cohorts represent a particle size of 70 $\mu$m, range B’s cohort has significantly lower deviation (6 to 1).

4.1.2 Burn time results flame A

Particles from ranges A through D were all able to ignite and burn to completion in the post flame region of flame A. Particles were counted using the software Image J as explained in the experimental details chapter. The distributions of particle burn time was plotted versus number of particles counted, similar to the particle distribution.

Fig: 4–4 shows the initial burn time count in the form of a histogram. Once again a smooth curve fit was applied through the peaks of the histogram to produce a continuous burn time curve.
Figure 4–4: Histogram: Burn time for flame A
For ranges A to D, particle burn time varied from 7 to 97 ms. The different particle ranges are plotted against the number of particles counted Fig: 4–5. The generated curves represent burn time versus particle diameter. Range A follows a perfect bell shaped distribution. The other three ranges have an overall bell shape, but are accompanied by slight local peaks.

Range A has the shortest total range of particle burn time, which is expected as this range had the shortest distribution. As particle diameter is increased, burn time increases. The burn times are plotted on a common plot in Fig: 4–6.

For each range the burn time is divided into 5 cohorts and the average burn time and standard deviation are computed and are listed in Table: 4–2. It is reasonable to assume that the 0-20th (A,B,C or D-1) cohort for particle size distribution can be matched with the 0-20th cohort (A,B,C or D-1) for burn time for the same range. Doing this for all the particle ranges will produce a burn time versus particle size plot.

The cohorts range from 12ms to 97ms for all the particles tested. To refer to the cohort, they have been labeled A thorough D and 1 to 5 (A1 to D5). To distinguish the burn time results from the size distribution, the cohort labels include a FA (for flame A) or a FB (for flame B, see below). As in the case for the particle distribution in many cases the top cohort (A,B,C or D5-FA) of one burn time range overlaps with the bottom cohort (A,B,C or D1-FA) of the next range. Other than these cases of overlap, the burn time increases as the range’s size increase.

The values given to the cohorts, the average burn time for the particular cohort, have small deviation and in most cases translate into an error of less 10 percent or
Figure 4–5: Curve fit: Burn time flame A. Red squares represent histogram peaks
Figure 4–6: Burn time data for all particles tested in flame A
Table 4–2: Particle Burn Time - Flame A

<table>
<thead>
<tr>
<th>Range Name</th>
<th>Cohort</th>
<th>Average Burn Time (µm)</th>
<th>Standard Deviation (µm)</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0-20</td>
<td>12</td>
<td>1</td>
<td>A1-FA</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>15</td>
<td>0</td>
<td>A2-FA</td>
</tr>
<tr>
<td></td>
<td>40-60</td>
<td>16</td>
<td>0</td>
<td>A3-FA</td>
</tr>
<tr>
<td></td>
<td>60-80</td>
<td>17</td>
<td>0</td>
<td>A4-FA</td>
</tr>
<tr>
<td></td>
<td>80-100</td>
<td>19</td>
<td>1</td>
<td>A5-FA</td>
</tr>
<tr>
<td>B</td>
<td>0-20</td>
<td>15</td>
<td>2</td>
<td>B1-FA</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>20</td>
<td>1</td>
<td>B2-FA</td>
</tr>
<tr>
<td></td>
<td>40-60</td>
<td>22</td>
<td>1</td>
<td>B3-FA</td>
</tr>
<tr>
<td></td>
<td>60-80</td>
<td>25</td>
<td>1</td>
<td>B4-FA</td>
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<td></td>
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<td>30</td>
<td>2</td>
<td>B5-FA</td>
</tr>
<tr>
<td>C</td>
<td>0-20</td>
<td>27</td>
<td>2</td>
<td>C1-FA</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>32</td>
<td>1</td>
<td>C2-FA</td>
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<tr>
<td></td>
<td>40-60</td>
<td>36</td>
<td>1</td>
<td>C3-FA</td>
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<td>60-80</td>
<td>41</td>
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<td>C4-FA</td>
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<td>C5-FA</td>
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<td>29</td>
<td>8</td>
<td>D1-FA</td>
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<tr>
<td></td>
<td>80-100</td>
<td>97</td>
<td>13</td>
<td>D5-FA</td>
</tr>
</tbody>
</table>

less. For the middle three cohorts, which represent 60 percent of the total range, the deviation is less than 5 percent.

4.1.3 Burn time results flame B

Flame B was specifically tailored to be oxygen rich. Originally, only flame A was to be studied to better understand the combustion of titanium particles in air. However, as a side experiment particles were tested using slight deviations in flame conditions. The conditions of flame B were settled upon due to their noticeable effect on burn time. All particles sizes were then retested using the condition of flame B.
Particles were once again counted using Image J, and a histogram was plotted in Fig: 4–7.

The procedure for recording and reducing data is identical to that of Flame A. The individual plots for burn time per particle size range are shown in Fig: 5–8. For the case of flame B, the results follow a bell shape curve. There are slight deviations from the bell curve at a local max in range B, the early region of range A has a long lead in, and range D has a long tail.

As with flame A there is considerable overlap, see Fig: 4-9. As expected, range A has the smallest burn time and range D has the longest. The most interesting feature of Fig: 4-9 is the peaks of ranges C and D has similar values. In fact range D seems to encompass the majority of range C.

Burn time ranges were once again divided into cohorts. Cohort values are listed in Table: 4–3. The average cohort values range from 11 to 64 ms, a considerable drop from the 12 to 97 ms for flame A. As with the particle distribution and with the cohorts for flame A, the 80-100 cohort (A,B,C, or D-5) overlap with the 0-20 cohort (A,B,C, or D-1) of the its neighboring particle range. The case for range D, as with flame A, has a large overlap.
Figure 4–7: Histogram: Burn time for flame B
Figure 4–8: Curve fit: Burn time flame B. Red squares represent histogram peaks
Figure 4–9: Burn time data for all particles tested in flame B
Table 4-3: Particle Burn Time - Flame B

<table>
<thead>
<tr>
<th>Range Name</th>
<th>Cohort</th>
<th>Average Burn Time (µm)</th>
<th>Standard Deviation (µm)</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0-20</td>
<td>11</td>
<td>1</td>
<td>A1-FB</td>
</tr>
<tr>
<td>A</td>
<td>20-40</td>
<td>13</td>
<td>0</td>
<td>A2-FB</td>
</tr>
<tr>
<td>A</td>
<td>40-60</td>
<td>14</td>
<td>0</td>
<td>A3-FB</td>
</tr>
<tr>
<td>A</td>
<td>60-80</td>
<td>15</td>
<td>0</td>
<td>A4-FB</td>
</tr>
<tr>
<td>A</td>
<td>80-100</td>
<td>18</td>
<td>1</td>
<td>A5-FB</td>
</tr>
<tr>
<td>B</td>
<td>0-20</td>
<td>17</td>
<td>1</td>
<td>B1-FB</td>
</tr>
<tr>
<td>B</td>
<td>20-40</td>
<td>20</td>
<td>1</td>
<td>B2-FB</td>
</tr>
<tr>
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<td>40-60</td>
<td>21</td>
<td>1</td>
<td>B3-FB</td>
</tr>
<tr>
<td>B</td>
<td>60-80</td>
<td>23</td>
<td>1</td>
<td>B4-FB</td>
</tr>
<tr>
<td>B</td>
<td>80-100</td>
<td>27</td>
<td>1</td>
<td>B5-FB</td>
</tr>
<tr>
<td>C</td>
<td>0-20</td>
<td>23</td>
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<td>C1-FB</td>
</tr>
<tr>
<td>C</td>
<td>20-40</td>
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<td>C3-FB</td>
</tr>
<tr>
<td>C</td>
<td>60-80</td>
<td>35</td>
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<td>C4-FB</td>
</tr>
<tr>
<td>C</td>
<td>80-100</td>
<td>42</td>
<td>3</td>
<td>C5-FB</td>
</tr>
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<td>80-100</td>
<td>64</td>
<td>9</td>
<td>D5-FB</td>
</tr>
</tbody>
</table>
4.2 Explosive Cylinder Trials

The focus of the cylinder experiments is on the combustion of a titanium particle cloud, and on the critical diameter for particle ignition (CPDI). Two different sets of titanium particles were tested. The difference between the sets is particle morphology. The particles obtained from APC are spherical, denoted as “spherical particles” for this report and identical to those used in the flat flame burner tests. The particles obtained from Atlantic Engineering are irregular in shape, and are denoted ”irregular particles”. The surface of the spherical particles is smooth whereas the irregular particle’s surface is uneven and rough. This can best be seen in the SEM images of the particles shown in the experimental details in chapter 2.

As mentioned in the experimental details section, the diagnostics used in the case of the cylinder experiments is high speed video imaging. Frames from the video, which range from 10,000 to 32,000 frames per second, are isolated and meshed together creating a video composite of the explosive trial. Each image within a composite is a snapshot of a single experiment at a set time interval. For the majority of composites the snapshots are taken at regular intervals. The intervals may vary per experiment as framing rates were used depending on charge and particle size.

A particle cloud is considered to be burning if it emits lights after the detonation wave and during the subsequent expansion. Four cylinder diameters (19, 25,34,49 or 59 mm) per particle type (spherical or irregular) and per range (3 ranges per particle type) were tested. Experiments were carried out over three trial series during the summers of 2006, 2007, and 2008.
### Cylinder Charge Burn Regimes

<table>
<thead>
<tr>
<th>Regime Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete and prompt reaction</td>
<td>Entire cloud reacts directly behind detonation wave without dark bands.</td>
</tr>
<tr>
<td>Small band reaction</td>
<td>Entire cloud reacts directly behind detonation wave. Many small bands are present as opposed to few large bands.</td>
</tr>
<tr>
<td>Large band reaction</td>
<td>Reaction occurs directly behind the detonation wave. Combustion occurs in large distinct bands</td>
</tr>
<tr>
<td>Delayed band</td>
<td>Bands appear only after expansion of particle cloud. Detonation travels, cloud darkens. Ignition then appears in distinct bands.</td>
</tr>
<tr>
<td>Inert Dispersal</td>
<td>Detonation propagates through entire tube, particles are expelled radially outwards but do not react.</td>
</tr>
<tr>
<td>Detonation Failure</td>
<td>Detonation does not propagate through total length of tube.</td>
</tr>
</tbody>
</table>
Six different simple burn regimes were identified and were classified according to mechanism with which the particle cloud burns; their description can be seen in table 4.2 which is followed by a video composite of each regime.

Different regimes from Table 4.2 describe different burn behaviors for the particle cloud, an example of each burn regime is provided in the following images. Fig: 4–10 shows complete and prompt cloud reaction, and Fig: 4–11 demonstrates the small band reaction regime. The differences between these two regimes is clear, with the complete regime showing no dark spots or bands, and the small band reaction regime showing many. The detonation wave, a bright white band, can be seen traveling down the tube in both cases. Note the dark region which follows the detonation wave (Fig: 4–10 frames 216, 243, 270µs and Fig: 4–11 108, 135, 216, and 242 µm). The explanation for this dark region, which has been noted in other studies involving different metals, is at present unknown. It is possible be this dark region is due the nitromethane detonation products masking the Ti combustion. After an induction period, particles begin to burn and overtake the products.

Following the dark region, the products and particles expand conically where they begin to burn. In the case of the complete and prompt reaction see (Fig: 4–10), this expanding cone is bright without the presence of any dark spots or regions for the duration of the experiment. In the small band reaction regime in Fig: 4–11 the bottom half of the cylinder reacts like that in Fig: 4–10, the top half however needs some expansion before the reaction begins. This top section’s requirement to expand before combustion begins separates these two regimes.
Figure 4–10: Complete and prompt reaction. 49mm cylinder filled with AEE Ti-109 powder.
Figure 4–11: Complete reaction with bands. 59mm cylinder filled with AEE Ti-104 powder.
The following images compare the middle regimes, where combustion occurs only in isolated regions and is delayed. A detached detonation wave can be seen in many of the frames in Fig: 4–12. After the detonation wave, the particles expand without the onset of ignition. Depending on the regime type, ignition then begins in different locations but does not engulf the entire product/particle expansion cone. In some cases, after a time, the entire cloud may burn however it is unlikely to enhance blast properties. Dark regions, where particles remain un-burnt, separate the burning regions. In the experiments shown, as the particle cloud expands so does the relative percentage of the cloud which is burning. In the cases shown here reaction of the particle begins directly after the passing of the detonation wave; this is not necessarily true for all the band reaction cases. The last two images display an inert dispersal (Fig: 4–13. In this case the detonation wave reaches the bottom of the cylinder, however the Ti particles do not react. Fig: 4–14 is an example of detonation failure.
Figure 4–12: Three band reaction. 34mm cylinder filled with AEE Ti-107 powder.
Figure 4-13: Inert Dispersal. 49mm cylinder filled with spherical coarse powder.
Figure 4–14: Detonation Failure. 49mm cylinder filled with spherical fine powder.
CHAPTER 5
Discussion

5.1 Flat Flame Burner

For each particle size range, luminous particle tracks from over 100 different particles were analyzed to determine the total particle burn time. When a histogram of the particle burn times was generated, a bell-shaped distribution resulted, which was similar in shape to that of the particle size distribution. These plots were divided into 5 cohorts, each representing 20 percent of the total number of particles counted. With the assumption that the burn time will increase with particle size, the average burn time for each cohort was associated with the average particle size for the corresponding cohort (e.g., the 20th percentile of the burn time distribution would correspond approximately to the 20th percentile of the particle size distribution, B1 compared with B1-FA). The results for particles burn time in flames A and B are shown in Fig: 5–1.

As expected, the particle burn time increases with particle diameter. The error bars plotted in Fig: 5–1 show the standard deviation from the average for both burn time and particle distribution cohorts. The scatter in the results is largest for the particles sorted into the tails of the particle size distribution, which have the largest range of particle sizes. For ranges A and B (d < 80µm), the particle burn times for the two different flames are about the same, within experimental scatter. However as the particle size increases, particle burn time decreased in the oxygen enriched
flame B. For example the largest particles tested having an average size of 180µm, the average burn times were 97 ms and 64 ms, in flames A and B, respectively.

The power law curve fits to the present data for total particles ranging from 50 to 180µm, have the following forms, with \( t_b \) in milliseconds and the initial particle diameter, \( d \), in millimeters:

\[
\begin{align*}
    t_b &= 1.04 \times 10^3 d^{1.44} \quad (5.1) \\
    t_b &= 0.342 \times 10^3 d^{1.06} \quad (5.2) \\
    t_b &= 1.29 \times 10^3 d^{1.56} \quad (5.3)
\end{align*}
\]
Equations 5.1 and 5.2 were determined from the results of the present study for flames A and B respectively. Equation 5.3 is taken from the study performed by Shafirovich [19]. Equations 5.1 and 5.2 have been re-plotted in Fig: 5–2. The curve fit from Shafirovich [19] is valid for titanium particles ranging in size from 15 – 120µm burning in air, and agrees well with the present results for flame A.

This result is not surprising since in both cases the particles are burning in air. For the case of the Shafirovich study, particles are ignited via laser and burn in air. Flame A, a specially tailored flame whose products are void of O_2, serves only to heat the titanium particles to their ignition point. The particles then burn in the entrained air above the flame. As both data sets involve air combustion, its no surprise that these two data sets match up well. The curve fits are plotted in Fig. 5–2.

A fourth curve is potted in Fig: 5–2 which includes data from the Shafirovich [19] study with the inclusion of two data points from Molodetsky [15] and which skews the results upwards. Molodetsky [15] studied the combustion of falling titanium particles of 240 and 280 µm in air. Shafirovich added these results to his own and obtained a d^2 scaling law which is common for diffusive controlled combustion regimes such as Ti.

There is a substantial effect due to the increased O_2 concentration in flame B. The additional oxygen increases the diffusion of O_2 to the particle, as there is more available O_2. With oxygen readily available at the particle surface, it appears kinetics take over, and the expected (d^1) scaling law for kinetically controlled combustion is found. The reduction of exponent in the case from flame A to flame B agrees with the
Figure 5–2: Burn time data from 5–1 for flames A and B, shown together with power law curve fits to the present data and from earlier work by Shafirovich [19]
conclusion in Shafirovich [19] that gas-phase diffusion of oxygen is the rate-limiting step in Ti combustion for large particles. If the oxygen concentration surrounding a particle is increased from that of air, the effect is a lowering in burn time.

Observing the particles at the low end of the size distribution (up to 115 \( \mu m \)) to match the Shafirovich [19] study, the results from flames A and B have little deviation from one another. The results for this range, for the case of the current study it includes ranges A to C (50 to 118\( \mu m \)), are plotted below in Fig: 5–3.

For this range of data, the empirical formulas are found to be:

\[
t_b = 1.75 \times 10^3 d^{1.63}
\]  

(5.4)
\[ t_b = 0.916 \times 10^3 d^{1.43} \] (5.5)

The case of combustion in air, flame A has an exponent similar to that of the Shafirovich study (1.63 to 1.56) [19]. When excess oxygen is added to the post flame region from flame B there is a slight decrease in particle burn time, reducing the exponential factor is to 1.43.

The largest particles studied, 115-180µm, have a significant effect of lowering the burn time of the entire range. The exponential factor drops from 1.63 to 1.44 for flame A, and from 1.43 to 1.06 for flame B due to the inclusion of the large particles. The exponent of flame A still matches closely the 1.56 of Shafirovich, however is far from the 1.85 Shafirovich/Molodetsky equation. The present study and the Shafirovich [19] data alone indicate that the burn time for Ti particles of size 15 – 180µm in air follow a \( d^{1.5} \) scaling law. Increasing the oxygen concentration has a greater effect of lowering the burn time of particle with diameter over 100 µm. This again agrees with Shafirovich [19] that gas-phase diffusion of oxygen is the rate-limiting step in Ti combustion for large particles.

As in other studies titanium particle explosions ended were observed ( see [19],[15],[9],and [1]). Combustion was considered terminated at the explosion, and burn time was defined as the time between ignition and explosion. On closer inspection, particle fragmentation occurs due to the explosion process. The fragments which are ejected from the original particle continue to burn as they move away from the explosion’s ground zero. The emission intensity of the fragments matches that of the original particle, indicating the fragments are burning Ti particles. For the
larger particle sizes (ranges C and D), the fragments are large and can be seen to burn for milliseconds after the explosion. This phenomena was observed for both flames A and B. Fig: 5–4 shows a good example of the fragmentation burning, with all three particle exhibiting the fragmentation burning. The present study found a $d^{1.5}$ scaling law, which leads to shorter burn time than the expected $d^2$. The burning fragmentations suggests that Ti particle combustion does end with the explosion and that not all the Ti has been combusted at the time of explosion. The $d^{1.5}$ is the burn time to explosion, and not the time of reaction of the all the Ti in a given particle. This burning fragments also suggest energy release, in the form of burning Ti, after the explosion event. If one were to take into account the fragment burn time, this would increase overall burn time perhaps leading to a $d^2$ relation.

Using emission spectroscopy, particle temperatures was estimated to be $3100 \pm 100^\circ C$ using the techniques of Goroshin in [10]. The spectroscopy was integrated
over multiple particle combustion events to provide sufficient light for the spectrometer. Hence, the temperature represents an average over the total particle combustion event. This temperature agrees with previous study which concluded that titanium burns in the liquid phase, as the melting point of titanium is 1650°C. Although this temperature is higher than measured in other, different, experiments, it is still below the boiling temperature of titanium (3560°K). The discrepancy with earlier results may be due to the high-temperature particle jet that was formed in order to record temperature. Within this jet, there is little heat exchange from the particle to the environment, as is the case with single particle ignition experiments. One would expect a large heat exchange only at the boundary of the particle jet. The temperature was recorded in the center of the jet, where many particles are burning at one time. It can be assumed that the center region of the jet, convective and conductive heat losses are negligible. The temperature of 3373°K is close to the adiabatic flame temperature estimated in Shafirovich [19] to be 3400°K. The difference between these two values is likely due to radiative heat losses.
5.2 Cylinder Trials

5.2.1 Spherical Powder

Tests were carried out with the three Ti particles sizes and charge inner diameters 16, 25, 34, and 49 mm. A summary of the results is shown in table 5–1.

<table>
<thead>
<tr>
<th>Powder</th>
<th>19mm</th>
<th>25mm</th>
<th>34mm</th>
<th>49mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 µm</td>
<td>Inert dispersal with bright band at the bottom</td>
<td>Large band reaction</td>
<td>Small band reaction</td>
<td>Detonation Failed</td>
</tr>
<tr>
<td>95µm</td>
<td>Not Tested</td>
<td>Inert Dispersal</td>
<td>Inert Dispersal</td>
<td>Inert Dispersal</td>
</tr>
<tr>
<td>254 µm</td>
<td>Not Tested</td>
<td>Inert Dispersal</td>
<td>Inert Dispersal</td>
<td>Inert Dispersal</td>
</tr>
</tbody>
</table>

Combustion of Ti particles during the particle dispersal process occurred for the smallest particle size (40µm), but not for the larger particles (95µm or 254µm). The 40µm powder reaction is dependent on charge diameter. The extent of particle reaction in the powder cloud increases with increasing charge diameter. Fig. 5–5 shows the particle reaction behavior for 40µm particles in charges 19, 25 and 34 mm in diameters. In each case the frame shown was taken 300µs after detonation of the charge. As the charge size increases from 19mm to 34mm, a larger proportion of the cloud reacts. Interestingly, the detonation wave failed to propagate through the tube for the 49mm case whereas propagation was observed in all other cases. The detonation traveled approximately one half of the length of the tube where it
abruptly ended. The top section of the tube expands conically as expected. Initially there is no reaction, but after 2ms reaction is observed.

Over the range of charge diameters tested, the critical Ti particle diameter for particle ignition is on the order of $65 \pm 25 \mu m$. However, in only one case (34mm id) is full reaction of the cloud observed. Note that even for the larger particles, some particle luminosity occurs immediately behind the detonation wave but then quenches. This may be the result of reactive ablation of metal from the particle surface during the early stages of particle dispersal when the relative particle velocity and the gas pressure and temperature are still very high. It may also be due to the
dark nitromethane detonation products masking the early Ti cloud burning. As the particles emerge through this dark region, their burning becomes visible.

### 5.2.2 Irregular Powder

Similar tests were carried out with three Ti irregular particle sizes. The same charge diameters were tested with one exception; a 59mm inner diameter charge was tested in the Ti-104 case.

For the irregular shaped particles, combustion was observed for all particle sizes. A summary of the combustion regimes is given below in Table 5–2.

**Table 5–2: Irregular Particle Combustion Regime**

<table>
<thead>
<tr>
<th>Powder</th>
<th>19mm</th>
<th>25mm</th>
<th>34mm</th>
<th>49mm</th>
<th>59mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-104 (&lt;44µm)</td>
<td>Inert dispersal with delayed single band</td>
<td>Large band reaction</td>
<td>Large band reaction</td>
<td>Not tested</td>
<td>Small band reaction)</td>
</tr>
<tr>
<td>Ti-107 (&lt;74µm)</td>
<td>Detonation fails to propagate</td>
<td>Large band reaction</td>
<td>Large band reaction</td>
<td>Complete and prompt reaction</td>
<td>Not Tested</td>
</tr>
<tr>
<td>Ti-109 (&lt;149µm)</td>
<td>Delayed band reaction</td>
<td>Large band reaction</td>
<td>Prompt complete reaction</td>
<td>Prompt complete reaction</td>
<td>Not Tested</td>
</tr>
</tbody>
</table>

There is a clear trend in cloud reactivity. For a given particle range, as the cylinder size increases, reaction begins as a series of delayed bands(Fig:5–6). As the cylinder diameter increases the bands ignite promptly. Generally speaking there are three bands: top, bottom, and middle band. As the cylinder diameter is further increased, these bands become more numerous until the entire cloud reacts promptly without any bands.
Figure 5–6: Particle reaction morphology 600 μs after initiation of the detonation for Ti-104. Diameters left to right: 19mm, 25mm, 34mm, 59mm.

For the 19mm charge diameter the three particle ranges (Ti-104, Ti-107, Ti-109) all have difficulty igniting. Either the detonation fails to propagate (Ti-107) or there is a delayed reaction of 1 band (Ti-104) or 3 bands (Ti-109). At 25mm the three ranges all have a delayed 2 band reaction. The residence time for the first two cylinder sizes (19 and 25mm) is not insufficient to induce prompt cloud reaction, regardless of the particle size. At 34mm, the reaction regime varies with particle sizes. The Ti-109 reacts promptly and uniformly, while Ti-104 and Ti-107 exhibit band reaction (Fig:5–7). This trend continues for the 49mm and 59mm cases. For the 49mm case, Ti-107 and Ti-109 both react promptly and completely whereas Ti-104 has a band reaction in the larger 59mm cylinder test. This result is counterintuitive, as the reaction of the particles within a cloud is expected to be a function of its relative residence time within the hot detonation products. The smaller particle will heat up to an ignition temperature quicker than the larger particles, and the cloud would have a larger proportion of particles reacting.
Figure 5–7: Particle reaction morphology 600 $\mu$s after initiation of the detonation in a 34mm cylinder. From left to right: Ti-104, Ti-107, Ti-109.

In order to match the combustion regimes in [5], two plots have been generated with similar reaction regimes that were determined for aluminum and magnesium particles. The four regimes used in previous studies were: continuous reaction, discontinuous reaction, inert dispersal, and detonation failure. The discontinuous reaction is defined as when the combustion occurs in bands (Tables 5–2 and 5–1). Complete and prompt reaction in Tables 5–2 and 5–1 is considered continuous reaction, while inert dispersal and detonation failure remain unchanged. The band reaction regimes have been included together as it has been proven in the past that only complete and prompt reaction of the particle cloud increases blast properties.

CDPI for irregular shaped titanium particles depends on particle size. Discontinuous reaction occurs for Ti-104 and Ti-107 charge diameters above 20mm. All charge diameters for Ti-109 ignited discontinuously. Continuous reaction is obtained for all charges above 40 mm, and above 30mm for Ti-109 in Table 5–2. The U shaped
particle reaction dependence trend which was observed for aluminum particles is not reproduced.

Figure 5–8: Particle reaction dependence on charge and particle diameter in glass tubes. Right: Spherical particles, Left: irregular particles. Full green squares: Continuous Reaction. Half filled blue: Discontinuous reaction. Empty red square: Inert Dispersal. X: Failed Detonation. Dashed lines indicate CPDI for irregular particles

The difference between the two particle types is clear. Reaction occurred for all particle sizes for irregularly-shaped particles, with increasing proportion of the cloud igniting with increased cylinder size. Whereas for the smallest sized spherical particles reacted. As the particle size distributions were very similar, particle morphology seems to be the driving factor in the observed increase in reactivity. Frost et al. [4] showed that the properties of the metal particles will influence the time required
to heat the particles until combustion is initiated, and the subsequent total particle combustion time. The size of a particle that can be heated to a specified temperature during the residence time of the particle within the hot combustion products will depend on the heat transfer rate and thermal diffusivity within the particle. The thermal diffusivity of the metals Ti/Zr/Al/Mg (evaluated at 298°C for comparison) are in the relative proportions of 1.0/2.0/14.3/15.2. The low thermal diffusivity of Ti implies that for a given charge diameter only very small Ti particles will have time to be heated and ignite within the expanding products in comparison with Mg and Al particles.

In a previous study by Frost et al [4], it was found that the zirconium particles were relatively easy to ignite in relation to other metals studied (aluminum, magnesium, and titanium). It was found that even large particles, on the order of 5mm, readily ignited. They surmised that the “irregular, porous morphology of the Zr particles may play an important role in the particle reactivity”. It is assumed that the pores and the irregularities in the shapes of the particles increase hot spots which induce particles to react. Ignition begins at the hot spots, and the combustion spreads to engulf the entire particle. The irregularly shaped particles are able to react more readily as the entire particle must be not heated to a reaction temperature to induce reaction, but merely a section where ignition could begin.

The irregular shaped particles have thin protrusions and pores, much like the Zr particles from [4]. Ignition of particles may occur in an isolated area of the particle without the necessity of the entire particle reaching a uniform ignition temperature, much like the Zr particles. Sustaining this combustion depends on the particle size,
and the residence time of the particles in the hot detonation products. If these requirements are met the particle burning will spread and the particle will burn to completion. If these conditions are not met, the particle will quench. The requirement for particle size and time within the detonation leads to a CDPI for the irregular shaped particles.
CHAPTER 6
Conclusion

The ignition of titanium particles has been experimentally investigated using two experiments. The first study involved the ignition of spherical titanium particles in the post flame region of a specially designed flat flame burner. The second study involved the detonation of a charge with titanium particles saturated in sensitized nitromethane.

The flat flame burner study involved launching particles into the products of a flame where their burning history can be tracked. The burner is specially designed to avoid the possibility of a flash back. A particle injector consisting of a small sphere, audio speaker, and function generator was also designed in order to inject particles into the flame. The flame is intended only to serve as a heating mechanism for the particles. Burn time for particles ranging from 50-180 \( \mu m \) were investigated within two environments, flame A and flame B.

Flame A was tailored in order for the product species to be lacking in oxygen. Hence the particles are heated and burnt in entrained air. The results for flame A match and extend the results from a study performed by Shafirovich \[19\] showing a \( d_{\text{particle}}^{1.5} \) scaling law over the range studied. This agreement also suggests that the titanium particles are burning in the \( O_2 \) in this post flame region, and not with other oxidizers present in the flow (\( CO_2, H_2, OH \) etc).
Flame B was designed to have an excess of $O_2$. However in this case the particle burns with an a residual $O_2$ concentration. For this flame condition the average burn time was reduced for each particle range. The effect of altering the oxygen has the largest effect for large particles.

In both flames, particle explosions were observed. Fragments of titanium particles were observed to burn after the explosion, suggesting that at the time of explosion there is still unreacted Ti left in the particle. The explosion was considered to end combustion of the particle. It may be that the expected $d^2$ scaling law is not observed for titanium particles as particles are not burning to completion.

Future work should include testing the effect of morphology on burn time. More detailed investigation on the affects of increased $O_2$ concentration on large particle diameters is needed. Furthermore, sampling of the post flame environment should be taken and analyzed in order to determine the exact concentration of oxygen.

The detonation of cylindrical charges investigated the burning of a cloud of titanium particles. Spherical and irregular shaped particles were tested in order to determine the effects of morphology. Charge diameter and particles size were also varied.

For the case of spherical particles reaction was only observed for the smallest titanium powder range ($40\mu m$). Reaction was also dependent on charge geometry with larger charges displaying increasing cloud reactivity. Over the range of charge diameters tested, the critical Ti particle diameter for particle ignition is on the order of $65 \pm 25\mu m$. 
The reaction for irregular particles was observed for all three size ranges tested ($< 40$, $< 74$, $< 149\mu m$). Six regimes were originally determined, and they were later reduced to 3. For all three ranges, increasing charge diameter had the effect of increasing the reactivity of the particle cloud. A CDPI was determined for the irregular particles. Irregularly-shaped particles were found to ignite more readially than the spherically-shaped particles. The non-uniform morphology of the irregular particles induces reaction in a single location where reaction then then spreads to engulf the entire particle.

The results presented here will lead to increase sensitivity in the modeling of titanium heterogeneous charges. The flat flame burner adds burn time data for the modeling of single particles within the reactive flows. The cylinder explosive tests can be used to validate these models.
References


