Effect of Oxygen Concentration on the Combustion of Titanium Particles

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1 Introduction

The study of metal particle combustion is of great interest due to the relatively high energy density of metals in comparison with hydrocarbon fuels. Metal particles are common additives in rocket propellants, high explosives, and pyrotechnics, and are being investigated for applications involving a variety of oxidizing environments (e.g., CO_2 , H_2O). For the case of titanium combustion, in addition to energetic applications, the formation of titanium dioxide has environmental applications due to the photo catalytic properties of TiO₂ [1].

Previous investigators have studied titanium particle combustion using a variety of experimental techniques, including injection into a gas flame [2], droplet formation and ignition with a pulsed micro-arc [3], and particle levitation with laser ignition [1]. In all cases, the titanium combustion process was terminated with a microexplosion of the particle. When other metals (e.g., aluminum, magnesium) were studied using similar techniques, titanium was found to ignite more easily but burn relatively slowly. The objective of the present study is to quantify the dependence of titanium particle burn time on initial diameter and oxygen concentration over a wide range of particle sizes.

Given that the boiling point of titanium (3560 K) is less than the oxide volatilization temperature (~4000 K for Ti₃O₅), Glassman's criterion suggests that titanium may burn in the vapour phase in oxygen [4]. In this diffusive-limited combustion regime, the particle burn time can be shown to be proportional to the square of the initial particle diameter ($t_b \sim d^2$). However earlier experiments have shown a more complex combustion behaviour for titanium [e.g., 1,3]. While the combustion of Ti vapour may occur during the early stage of burning, the majority of the combustion process is dominated by surface combustion during which oxygen and nitrogen are adsorbed on the droplet surface, forming a liquid Ti-O-N solution [1,3]. Shafirovich et al. [1] found that gas-phase oxygen diffusion played an important role in the combustion mechanism for Ti particles of size 100 µm and larger, whereas kinetic effects became important for smaller particles. They found that the empirical dependence of burning time on particle size was a function of particle size, and varied from $t_b = 1.29 \times 10^3 d^{1.56}$ for particles of size 15 – 110 µm, to $t_b = 3.14 \times 10^3 d^{1.85}$ for the range 15 – 280 µm, when data from [3] was included in the curve fit. With respect to particle temperature, Molodetsky et al. [3] reported a maximum temperature of 2400°C for a 240 µm Ti particle burning in air, which dropped to 1780°C just before microexplosion of the particle.

2 Experimental Procedure

The present study utilized a flat flame burner designed to eliminate the possibility of flashback. The fuel and oxidizer are introduced into a series of channels within a 75 mm dia cylindrical block. The gases exit the channels and mix within a 25 mm deep packed layer of 1 mm dia ceramic beads.

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The flame is stabilized on the surface of the beads and the Ti particles are injected into the combustion products via a small diameter ($250 \ \mu m$) ceramic tube with the tube exit placed at the flame surface. The particles are contained within a plastic sphere which is agitated with a small speaker to loft the particles. A small flow rate of air through the sphere entrains individual particles for injection into the combustion products above the burner. The particle injection rate can be controlled by varying the speaker frequency and air flow rate. The combustion products are confined and thermally isolated from the surroundings by a 30-cm long Pyrex tube placed above the burner. A 1-cm gap between the tube and the burner allows a layer of air to be entrained around the rising product gases and helps to stabilize the flame.

Particles ignite shortly after injection into the hot combustion products and the motion of the burning particles is visualized with open-shutter photography with a digital SLR camera. The particle motion is viewed through a spinning slotted disk so that the luminous particle track appears as a series of bright line segments, as shown in Fig. 1. The rotational speed of the disk is set so that each line segment corresponds to a time of about 1 ms. By counting the number of segments between the points of particle ignition and microexplosion, the total particle burn time is determined. For each particle size range and flame composition, the particle burn time for a minimum of 100 particles was determined.

Spherical Ti particles were obtained from AP&C (Advanced Particles & Coatings Inc., Montreal), and the degree of sphericity is illustrated in an SEM photograph in Fig. 1. The particles were sieved into four different size ranges. The particle size distribution for each size range was determined by measuring the diameter of at least 200 particles from a given sample with an optical microscope and had a bell-shaped distribution.

Two different gas mixtures were used with the flat flame burner: flame A was formed from a stoichiometric methane-air mixture whereas flame B had excess oxygen added to the reactant mixture. The exact oxygen concentration within the combustion products is not known precisely due to entrainment of adjacent air. However, the flame B products are estimated to have an oxygen mole fraction of 0.1, not including the entrained oxygen. Particle temperature was estimated with emission spectroscopy (integrated over multiple burning particles) using an Ocean Optics USB-2000 spectrometer, with a procedure described earlier [5].



Figure 1. Left: SEM photograph of a sample of the spherical Ti particles used. Right: open-shutter photograph of multiple luminous tracks (chopped into segments by visualization through a rotating slotted disk) from burning Ti particles, terminated by microexplosions. Flame stabilized on the flat flame burner is faintly visible at the bottom. The Pyrex tube surrounding the combustion products is not visible.

3 Results and Discussion

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. Each of these distributions was divided into 5 cohorts, each representing 20% of the total particles. With the assumption that the burn time will increase monotonically with particle size, the average burn time for each cohort was associated with the average particle size for the corresponding cohort (e.g., the 20^{th} percentile of the burn time distribution would correspond approximately to the 20^{th} percentile of the particle size distribution). The results for particles burning in flames A and B are shown in Fig. 2.



Figure 2. Average particle burn times for particles divided into four different size ranges (denoted by the different symbols), which were further divided into 5 equal-sized cohorts, as a function of particle diameter for Flame A (left) and Flame B (right).

As expected, the particle burn time increases with particle diameter. 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 the smaller two size ranges ($d < 80 \,\mu$ m), the particle burn times for the two different flames are about the same, within experimental scatter. However, as the particle size increases, the particles burn more rapidly in flame B, which had excess oxygen. For example, for the particles with an average size of 180 μ m, the average burn times were 97 ms and 64 ms, in flames A and B, respectively. It should be noted that larger particles, ranging in size from 150-325 μ m were also tested. In this case, the majority of the particles did not ignite within flame A whereas most of them did ignite in flame B.

The data from Fig. 2 have been replotted in Fig. 3, together with the empirical power law curve fits obtained by Shafirovich et al. [1]. The power law curve fits to the present data for particles ranging from $50 - 180 \,\mu$ m, have the following forms, with t_b in milliseconds and the initial particle diameter, d, in millimeters:

Flame A: $t_{\rm b} = 1.04 \times 10^3 d^{1.44}$ Flame B: $t_{\rm b} = 0.342 \times 10^3 d^{1.06}$

The curve fit from Shafirovich [1], i.e., $t_b \sim d^{1.56}$, for Ti particles ranging in size from 15 – 110 µm burning in air, agrees well with the present results for flame A, which is not surprising since in both cases the particles are exposed to air. The second curve fit shown in Fig. 3, from Shafirovich et al. [1]

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is skewed upwards due to the inclusion of two data points (for 240 and 280 μ m particles) from Molodetsky et al. [3]. So, in summary, the data in the present study as well as [1] indicate that the burn time for Ti particles of size 15 – 180 μ m in air follow a $d^{1.5}$ scaling law. When the concentration of oxygen is increased, the burn time is reduced for particles over 100 μ m, which agrees with the conclusion in [1] that gas-phase diffusion of oxygen is the rate-limiting step in Ti combustion for large particles.



Figure 3. Burn time data from Fig. 2 for flames A and B, shown together with power law curve fits to the present data and from earlier work by Shafirovich et al. [1].

Using emission spectroscopy, particle temperatures were estimated to be $3100\pm100^{\circ}$ C. 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. 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 post-flame environment which reduces the heat loss to the environment when compared to experiments conducted at room temperature which would lead to higher heat losses. In fact, the temperature of 3100° C is close to the adiabatic flame temperature estimated in [1] to be 3400 K.

References

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