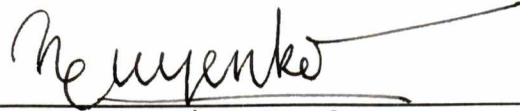


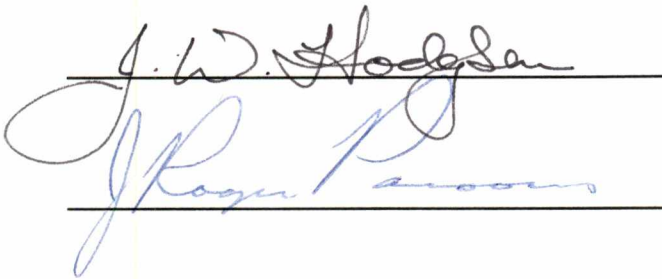
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AN EXPERIMENTAL INVESTIGATION OF THE IGNITION AND
COMBUSTION PHENOMENA OF LASER-IGNITED BORON AGGLOMERATES
IN A FLOWING OXYGEN ENVIRONMENT

A Thesis
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Master of Science
Degree
The University of Tennessee, Knoxville

Chris B. Schechter

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Abstract

An experimental investigation of the ignition and combustion phenomena of laser-ignited boron agglomerates in a flowing oxygen environment is presented. Individual agglomerates with initial diameters ranging from 350-1100 μm were supported by silicon carbide fibers and ignited by a cw CO_2 laser. A near-infrared two-color pyrometer and a broadband radiometer were used to measure the surface temperature and the radiation emitted during the combustion event. From the outputs of the pyrometer and radiometer, it was possible to determine the ignition delay time and the burning time of the boron agglomerate. High-speed motion picture photography was also used to record the phenomenological events and to correlate the instrument data.

For the agglomerate diameter range used in the study, a linear relationship was found between the square of the agglomerate diameter and the burning time, signifying the burning rate of boron agglomerates is controlled(limited) by the diffusion of oxidant to the surface. Increased oxygen flow rate was found to significantly increase the burning rate, thus significantly decrease the burning time. It was also found that the surface temperature of the agglomerate exceeded 2450K(i.e. melting point of boron) in all cases, therefore it appears that the melting of boron agglomerates does occur during combustion. In addition, from the results of the high-

speed cinematography, the existence of BO_2 (boric oxide) has been confirmed in boron agglomerate combustion. To obtain an accurate model of boron combustion, the chemical reactions involving BO_2 must be considered. In general, the techniques used to measure burning time in the present study appear more efficient than those used in previous studies.

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CHAPTER 1

INTRODUCTION

Recently, several studies pertaining to the utilization of slurry fuels in air-breathing propulsion systems have been carried out. The increased interest is due to the potential advantages of combining liquid fuels (pumpability and injectibility) with solid fuels (high volumetric energy density) to increase the performance of the system. Aluminum, boron, and magnesium are a few solid fuels under consideration due to their relatively high energy values. Table 1.1 shows two forms of heating values for various solid and hydrocarbon fuels. Boron seems to have the most potential because of its superior volumetric energy density.

When the boron slurry fuel is sprayed into the combustion chamber, the liquid component is rapidly vaporized and consumed, leaving behind micron-size boron particles that group together to form loosely-bound, porous agglomerates. The radiation and convection from the hot oxidizing environment heat-up the agglomerates to eventual ignition and full-fledged combustion. Since the liquid component is so rapidly consumed, the boron agglomerates must ignite and achieve complete combustion within a limited residence time (<100ms) in the combustor, otherwise the potential output of the system is not reached. In addition, increased erosion problems within the system can result. Thus, the efficiency of the boron slurry

Table 1.1 - Heat of Combustion for Various Fuels(Ref.11)

Fuel	Gravimetric Heating Value, cal/g	Volumetric Heating Value, cal/cm ³
JP-5	10,150	8,230
Shelldyne -H	9,860	10,000
(CH ₂) _n	10,400	9,600
Aluminum	7,420	20,000
Magnesium	5,910	10,300
Boron	13,800	32,200

fuel is highly dependent on the ignition and combustion mechanics of its boron agglomerates.

A number of studies have been carried out on the ignition and combustion mechanisms of single boron particles, using various ignition techniques, the most popular being flat-flame burner ignition[1] and laser ignition[2,3,4]. In these studies, it has been observed that the burning of single boron particles occurs in two distinct stages: an ignition stage and a full-fledged combustion stage. The full-fledged combustion stage is either controlled by the diffusion of the oxidizer to the surface of the particle(i.e. diffusion-controlled) or by the kinetics of the chemical reaction(i.e. kinetics-controlled). In the single particle studies, the "burning mechanism" was found to be diffusion-controlled.

The existence of a boron oxide(B_2O_3) layer on the surface of the solid boron hinders particle ignition, potentially causing a long ignition delay. The ignition delay time is the time from initial exposure to the ignition source to the point of rapid combustion and can be a considerable fraction(as much as 50 percent) of the total burning time of the particle. The oxide can exist in the liquid state at relatively high temperatures in the range of 750-2300K(the melting and boiling points of boron oxide at 1 atm) and diffusion of reactants through this oxide layer governs the net reaction rate. Not until a sufficient amount of this oxide is removed can rapid diffusion of oxidants occur, in turn, removing the oxide

layer. The temperature at which this occurs (2316 K) is commonly referred to as the ignition temperature.

The events occurring in the burning of the boron particles and boron agglomerates are similar in nature, but differences should be observed. The loosely-bound agglomerates are very porous, therefore their burning is strongly influenced by the diffusion of oxygen into the pores and to the surface. Thus, the reactive surface area of the agglomerates is much larger since the reaction occurs not only at the outer geometric surface area, but also in the pores. Consequently, results from single particle studies may not be directly applicable to agglomerate studies.

Many of the various experimental techniques used in past investigations have drawbacks, however. For instance, the flat-flame burner ignition technique is limited because the maximum pressure that could be safely attained is 1 atm., whereas the combustion of slurry fuels typically occurs in a very high pressure environment (>20 atm.). Another troubling aspect of previous studies is the wide variation of ignition temperatures obtained (700-2000K). The discrepancy results from the fact that the ignition temperatures have been approximated from gas temperatures and no attempts have been made to measure the surface temperature of the agglomerates.

High-speed motion picture photography has been employed previously to determine the ignition point and burning rate in terms of visually evident diameter decay of agglomerates. The

ability to measure diameters of agglomerates during combustion, from the high-speed film is under question. The procedure is also expensive and time-consuming. Also in the agglomerate studies, there has been no conclusive evidence of complete melting, which for boron occurs at 2450K.

In the present study, the ignition and combustion phenomena of boron agglomerates in a flowing oxygen environment are investigated, using newly-developed experimental techniques to determine the ignition delay time and the burning time. Boron agglomerates, supported by silicon-carbide(SiC) fibers were used in the study and the ignition of the agglomerates was obtained by using a cw CO₂ laser. A fast-response, near-infrared two-color pyrometer was used to measure the surface temperature of the agglomerate for the duration of each experiment. This would ascertain whether melting of the boron agglomerate occurs during combustion.

In the present study, the ignition point is defined as the point at which the temperature of any point on the surface the boron agglomerate, as measured by the two-color pyrometer, reaches 2316K(i.e. the boiling temperature of boron oxide). For temperatures below 2316K, the boron oxide layer is present, preventing ignition. At 2316K, the oxide layer vaporizes rapidly and the boron becomes completely cleansed of the oxide, thus allowing rapid reaction between the hot boron and the oxidant, resulting in ignition. The ignition point is determined directly from the two-color pyrometer surface

temperature measurement.

A broadband radiometer was used to measure the radiation intensity emitted by the laser-ignited boron agglomerates. From the temporal outputs of the pyrometer and radiometer, it is possible to determine the surface temperature of the agglomerate at any time, the point of ignition, the ignition delay time, and the total burning time. In the present study, these values were determined as a function of varying agglomerate diameter, with oxygen flow rate onto the agglomerate and laser power as fixed parameters.

The relationship between agglomerate size and the agglomerate burning time is important for the determination of the mechanism controlling the burning rate of boron agglomerates. The burning mechanism is said to be "diffusion-controlled" if the burning time is proportional to the square of the agglomerate diameter (" d^2 law") or "kinetics-controlled" if it is proportional to the agglomerate diameter. A brief discussion of burning mechanism theory is given in Appendix A.

The cw CO_2 laser was chosen as the ignition source for several reasons. It is a high-energy input, capable of heating rate of up to 50,000K per second, thus decreasing the ignition delay time drastically. The CO_2 laser can also be employed in future studies that require variation of ambient pressures and the molar concentrations of gases in the combustion environment, which can be performed using a combustion chamber.

The two-color pyrometer is chosen as the surface temperature measuring device because the high temperatures attained dictate the use of radiation means of temperature measurement. Typical thermocouples can only withstand temperatures up to about 2000K, even though agglomerates for the present study could be produced by depositing boron particles onto the thermocouple bead. The broadband radiometer was chosen because the beginning and end of the event can be easily determined by recording the radiation emitted. The high-speed camera, capable of up to 25,000 frames per second, is also used occasionally to record the phenomenological events of boron agglomerate combustion and to correlate the pyrometer/radiometer data to the observed phenomenological events.

The primary objective of the present study is to show that the techniques used are more efficient than techniques of past investigations. The pyrometer/radiometer configuration allows the burning time to be determined readily. The secondary objectives of the study are as follows:

1. To show that burning mechanism of boron agglomerates is diffusion-controlled.
2. To ascertain whether boron agglomerate melting (2450 K) occurs during the full-fledged combustion stage.
4. To detail the phenomenological events of boron agglomerate ignition and combustion and to provide additional

information to contribute to accurate modelling of boron combustion.

A literature survey of previous studies in this area is given in Chapter 2. A detailed discussion of the experimental apparatus and procedure is given in Chapter 3. A detailed discussion of the results of the investigation, including a description of the high-speed camera correlation, is given in Chapter 4. Finally, a statement of conclusions and suggestions of future study is given in Chapter 5.

CHAPTER 2

LITERATURE SURVEY

The following chapter presents a review of past investigations of the ignition and combustion of single boron particles and boron slurry agglomerates. It should be noted that the single boron particle studies by Macek et al. [1,2,3] in the 1970's are important in that they have laid the groundwork for many of the later studies in this area. Many of the same phenomena observed by Macek have been confirmed by subsequent research.

In an early paper, Macek and Semple [1] investigated the kinetic aspects of single boron particle combustion using the flat-flame burner ignition technique. Particles from pure, crystalline boron powder, 35-45 μm diameter, were injected into a hot oxidizing gas stream, generated by the combustion of CO or propane in oxygen, with N_2 as diluent.

In their study, two types of tests were performed. In the first, single boron particles were injected into the gas stream. The ignition times and burning times of the particles were estimated by using time-lapsed photography. In the second test, a continuous stream of particles was injected into the gas stream and the ambient gas temperature was lowered with the diluent until the particles cease to ignite.

The temperature range of hot oxidizing gases at which

ignition occurred was determined to be between 1850-2000K. The flame structure of the burning particles observed consisted of a "luminous" front very near the surface surrounded by a 300-400 μm wide symmetric, but less luminous, zone. A green envelope of up to 1 cm exists, brighter at higher gas temperatures, however Macek does not provide an explanation of the green luminosity.

They observed that the combustion of the boron particles takes place in two distinct stages, with a dark period in between, the second being the longer and brighter of the two. As the particles are first exposed to the gases, the boron oxide(B_2O_3) layer, which hinders ignition, melts and allows oxidant diffusion through the layer, increasing the reaction rate. Simultaneously, the oxide layer grows and there is a decayed reaction rate, causing the dark period. The temperature of the boron particle continues to increase and when the temperature of the particle reaches 2316K, the oxide layer vaporizes, leading to rapid diffusion of oxidants to the particle surface and an increased reaction rate. They state that the second stage of combustion is controlled by the gas-phase oxidant diffusion.

Various oxidizing gas compositions were used(i.e. O_2 , Air, CO_2), but in general, as oxygen concentration is increased, the two stages tend to merge, however they found no trend of ignition temperature with particle size or gas temperature. They also found that the presence of water vapor seemed to

promote ignition (lowers ignition temperature) and enhance burning rate. The burning rates increase with increasing temperature and are proportional to the mole fraction of O_2 . They did, however, determine that the burning time is proportional to the square of the particle diameter, thus implying the burning rate is diffusion-controlled (i.e. d^2 law).

The flat-flame ignition technique is limited in that pressures greater than 1 atmosphere are not feasible in the study, where slurry fuels are consumed in high pressure environments. In their study, the ignition point is not well-defined in the time-elapsd photographic records.

A second paper by Macek[2] presents an investigation of the combustion of boron particles at elevated pressures. A focused CO_2 laser was used as the ignition source. Crystalline boron powder with particles averaging $75\text{ }\mu\text{m}$ in diameter were used in the study. The particles were dropped through the focused laser beam, in various oxidizing atmospheres (i.e. O_2 , O_2/Ar , Air, CO_2). Pressures were varied from 1 to 35 atmospheres. Time-elapsd photography was again used to determine ignition times and burning times.

In general, their results show that as pressure increases, ignition time increases and burning time decreases, but total burning time (i.e. ignition + combustion) increases. The effect of pressure on the ignition time and burning time of boron particles is shown in Table 2.1. Macek also states that

Table 2.1 - Effect of Pressure on Ignition Time and Burning Time of Boron Particles(Ref. 2)

Pressure (atm)	No. of Particles	t_i (msec)	t_b (msec)
Combustion in O ₂ /Ar (20/80)			
1.0	19	7.3 ± 0.9	41.3 ± 2.7
7.8	23	8.4 ± 0.9	34.3 ± 2.6
21.4	28	24	28.5 ± 2.5
35.0	22	70	20.5 ± 1.7
Combustion in Air			
1.0	33	5.0 ± 1.7	50.0 ± 5.6
7.8	29	5.3 ± 1.0	40.8 ± 4.1
21.4	16	26	39.6 ± 5.8
35.0	24	71	21.6 ± 2.2
Combustion in Oxygen			
1.0	40	1.8 ± 0.2	6.8 ± 0.5

diffusion rates are expected to be invariant with pressure.

Mohan and Williams[3] investigated experimentally the ignition and combustion of laser-ignited boron particles and developed a model describing the ignition and combustion phenomena. An emphasis is placed on the ignition-hindering boron oxide(B_2O_3) coating and its removal. In the experiment, granular and amorphous boron particles ranging from 50-150 μm in diameter were held at the tip of 10 μm glass fibers in a chamber of various O_2/Ar compositions. The ignition source was a neodymium-doped glass laser. A high-speed motion picture camera(5000 fps) was employed to record the events.

During ignition of the boron particles, it was observed that the particle and its supporting fiber separate, thus no interference of the fiber with the combustion process. The "granular" boron particles were found to be relatively difficult to ignite at atmospheric conditions. It was also observed that the particles spin after detachment from the fiber, likely due to one-sided burning. Corresponding periodic intensity variations on the high-speed motion picture histories were also observed. They note that boron melting "likely" occurs(2450K), due to the small temperature increase needed from the oxide melting temperature(2316K), although the event would not be observed because the particle has moved out of view of the camera at that point.

The "amorphous" boron particles behaved noticeably different than the granular boron particles. It was observed

that the two-stage burning mechanism of the amorphous boron particles was comparable to that found in previous studies, but on a much shorter time scale. The amorphous particles have a porous, agglomerate-like structure, thus a greater reactive surface area.

A 1-D boron combustion model was formulated, based on the particle surface and oxide surface reactions that occur in the ignition and combustion mechanism of boron particles. Since combustion perpetuates itself at the hottest spot, this is an important phenomena incorporated into their model. Boron has a relatively low thermal conductivity and the rate of oxide vaporization is greatest at high-temperature locations, keeping the oxide layer thin there.

In general, the model was formulated for both the "low" and "high" temperature combustion stages. The low temperature stage model is based on the oxide coating removal and the high temperature stage is based on "droplet burning". Expressions for burning times were derived for both stages as function of oxide layer thickness, O_2 concentration, ambient temperature, etc. and when compared to the experimental burning times from Macek studies were in close agreement.

A third paper by Macek[4] presents a theoretical discussion of boron particle combustion, supported by experimental results. In this study, burning times of single boron particles were determined as functions of three variables: particle diameter, pressure, and O_2 mole fraction. The

aforementioned laser ignition technique is again employed, with particle diameters ranging from 37-124 μm . Pressures were varied from 0.17-35.0 atm and mole fractions of O_2 were varied from 0.1 to 1.0. The induction period, or ignition delay time, and the burning time were measured for various atmospheres.

It was observed that for high O_2 mole fraction and pressure, the combustion stage is relatively bright and the pre-ignition is relatively dim, indicating temperature variations. As O_2 mole fraction and pressure decrease, the two stages become almost indistinguishable, the combustion temperature decreases, and the pre-ignition temperature increases. The effect of particle diameter and pressure on the burning times of boron particles is shown in Table 2.2.

Macek concludes that if particle diameter, pressure and oxygen mole fraction are sufficiently large, then burning time is proportional to the square of the particle diameter(d^2 law). The experimental results also show that pressure(up to about 8 atm) has no effect on the burning rate.

The experimental burning times were then compared to theoretical data from the study by Mohan and Williams[3] for values at $p=1$ atm. For large d , the experimental results and the theoretical results are in close agreement, however, as d decreases, the results deviate. The theory predicts a much greater decrease in burning time with increased oxygen mole fraction than does the experiment. Macek suggests the model needs refinement.

Table 2.2 - Burning Times of Boron Particles(Ref. 4)

Pressure, atm.	Diameter, μm			
	37	54	98	124
0.50	-	-	-	139 $\pm$ 5
1.0	17.9 $\pm$ 1.5	27 $\pm$ 2	75 $\pm$ 3	121 $\pm$ 5
4.4	-	23 $\pm$ 2	-	-
7.8	11.1 $\pm$ 0.7	21 $\pm$ 1.5	64 $\pm$ 3	106 $\pm$ 4
14.6	-	-	56 $\pm$ 3	*
21.4	8.7 $\pm$ 0.9	-	-	*
28.3	6.1 $\pm$ 0.7	-	43 $\pm$ 3	*
35.0	7.7 $\pm$ 1.0	-	40 $\pm$ 10	*

* - No Ignition

A model of boron particle ignition is given by King[5], also emphasizing the generation and removal of the oxide layer. King's model is similar to Mohan and Williams[3], except that 2-D, spherical coordinates are used. He assumes that the removal of the oxide layer is both diffusion-controlled and kinetics-controlled.

Equations for the time rate-of-change for particle radius, oxide layer thickness, and the isothermal temperature of the particle were generated. The equations are functions of initial sizes and boundary conditions. These equations were then incorporated into computer code to output the following as functions of time: particle radius, oxide thickness, particle temperature, oxide mass, boron mass, oxide generation and evaporation rates, and oxide removal rate by presence of water vapor. A stability analysis was performed to determine the minimum ambient temperature for ignition.

King found that for ambient surrounding temperatures of about 2100K, ignition and self-sustained combustion occur readily. For temperatures of 2000K, there is a "degenerate" ignition whereby quasi-steady-state is obtained, but no actual ignition. For temperatures of 1900K, there was no ignition because the oxide generation rate at all times exceeds the oxide evaporation rate. The effects of total pressure and oxygen mole fraction on the ignition time is shown in Figure 2.1 and the effect of particle radius on ignition time is shown in Figure 2.2. The model agrees with Macek[1,2,3] for

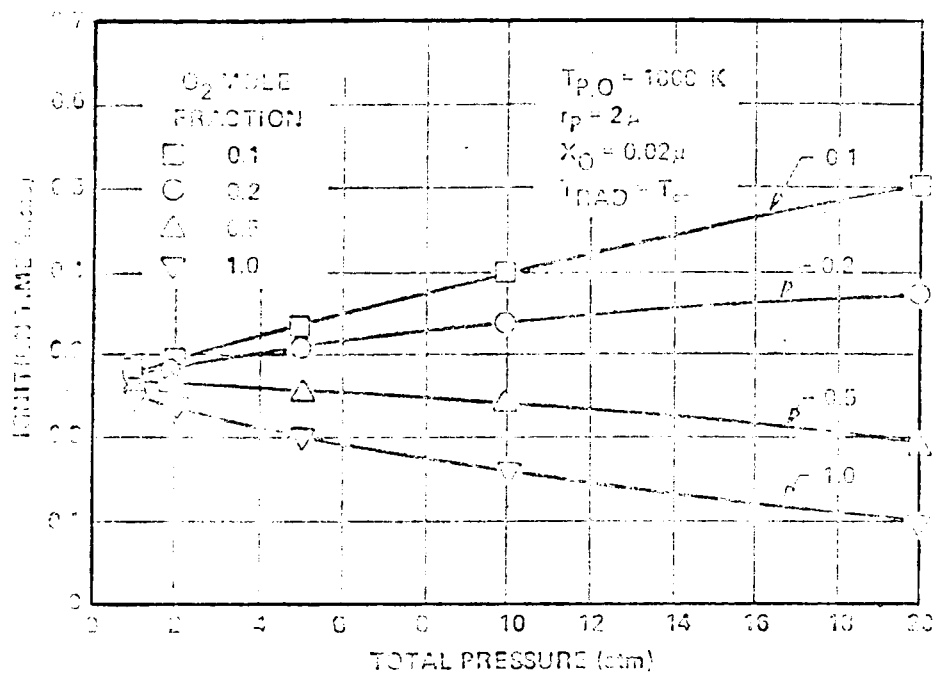


Figure 2.1 - Ignition Time Versus Total Pressure for Various Oxygen Mole Fractions at 2200K. (Ref. 5)

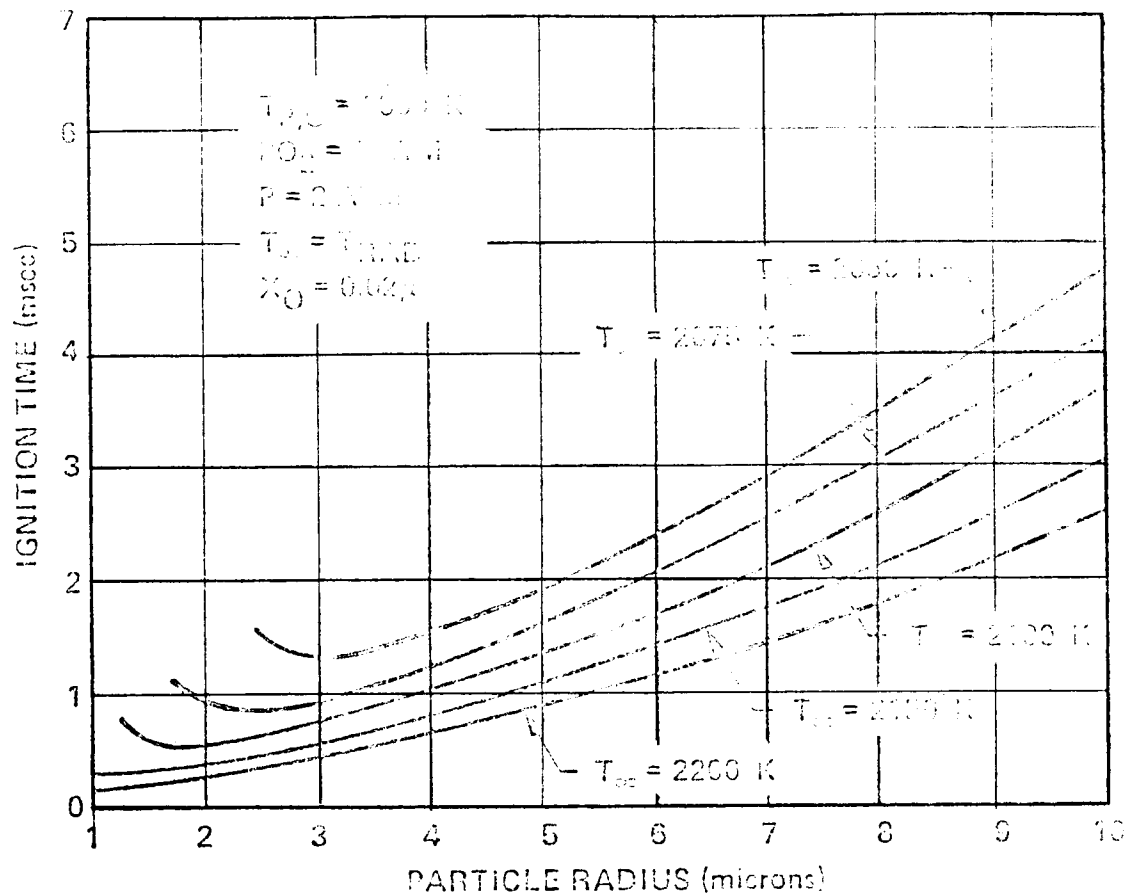


Figure 2.2 - Effect of Particle Radius on Ignition Time.
(Ref. 5)

predicted ignition times.

Shevchuk et al.[6] present a study of the ignition and combustion phenomena of loosely-bound, high porosity boron "clumps" (i.e. agglomerates). A theoretical model is developed that predicts the critical ambient temperature for the ignition of boron agglomerates in a hot oxidizing environment. Assuming evaporation of boron oxide and the heat loss due to radiation are negligible during the pre-ignition stage, the oxidant concentration to the pores of the agglomerate is the same as to the geometric surface, and there is no temperature difference along the radius of the agglomerate, they developed time rate-of-change equations for the boron oxide thickness and the agglomerate temperature. Implementing these equations, the critical ambient temperature was determined as a function of the following: agglomerate diameter, individual particle diameter, agglomerate density, and oxygen partial pressure.

The critical ambient temperature was predicted by their model to decrease with increasing agglomerate density, oxygen partial pressure, and the ratio of reactive surface area to the apparent geometric surface area. The theoretical work was followed by an experimental study using agglomerates of high porosity from 0.25-2 mm in diameter, formed at the end of 50 μm tungsten wire. An electrically-heated flowing oxidizing environment was used as the ignition source, with total pressures ranging from 0.2-1.0 atm. The temperature of the gases at the moment of ignition is assumed to be the critical

ambient temperature, however, their ignition criteria is not clear in their paper. Their results, however, indicated an agreement between their experimental and theoretical work.

A recent paper by Holl et al.[7] presents a more extensive experimental investigation of boron agglomerate ignition and combustion. Agglomerates from 175-800 μm in diameter, produced at the end of quartz probes were used in the investigation. Three samples of boron powder were used in the agglomerate production: pure amorphous, pure crystalline, and impure amorphous. The smaller diameter agglomerates(175 μm) were used in the actual ignition/burning rate study and the larger agglomerates(300-800 μm) were used for surface morphology study. A flat-flame burner was used as ignition source, as well as high-speed cinematography(500 fps) to determine the ignition and burning times as functions of oxygen and water vapor concentrations. The range of gas temperatures used in the study was 1690-1975K, at a pressure of 1 atm.

From the high-speed cinematography, two distinct ignition times were defined. The first being the time from initial exposure of the agglomerate to the hot gases, to the appearance of particle "glowing", and the second being the time from initial exposure to the beginning of "rapid diameter decay". Both ignition times were determined to decrease with increasing oxygen concentration and the burning rate was found to increase with increasing oxygen concentration and the presence of water vapor.

Using the second-stage ignition time, a relationship for burning time versus the square of the agglomerate diameter is shown in Figure 2.3. The linear relationship indicates the burning rate is dependent on the diffusion of the oxidant to the surface(i.e. diffusion-controlled). It is also suggested that the agglomerate is a molten droplet in the second stage, since 2450K(boiling point of boron) was attained in the study, but no conclusive evidence was presented.

The combustion behavior of boron/JP-10 slurry droplets was investigated by Takahashi et al.[8]. A stream of single droplets, 0.3-0.5 mm in diameter, were injected downwards into a high-temperature oxidizing gas stream(fuel-lean mixture of methane) at 1 atm, using a hypodermic needle. The adiabatic flame temperature and the mole fractions of major combustion products were calculated using available computer code.

The mole fraction of oxygen was varied from 0.07 to 0.39 and the equivalence ratio was varied from 0.3 to 0.7, all cases in low Reynold's number conditions ($Re < 2$). A stroboscopic back-lighting technique, triggered by a He-Cd laser, was used to obtain photographs for use in determining the size of the droplets. High-speed cinematography(5200 fps) was used to record the transient phenomena of combustion. The velocity of the droplet was determined anemometrically and the gas temperature along the channel was measured by silica-coated thermocouples. In addition, the boron mass fractions of the boron/JP-10 slurries used in the study were 0.05, 0.1,

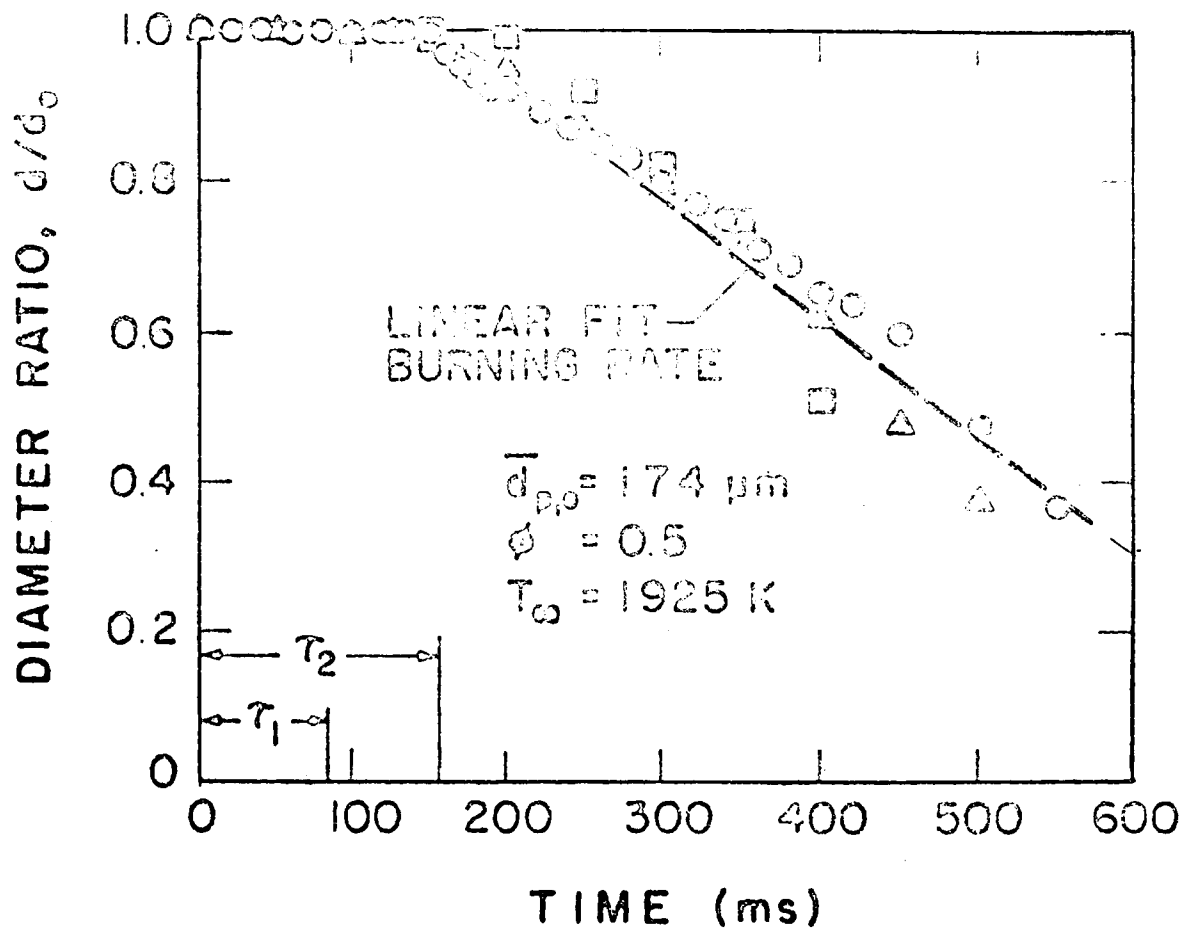


Figure 2.3 - Experimental Agglomerate Diameter Histories for Conditions of Ignition and No Ignition. Symbols Denote Different Tests. (Ref. 7)

0.2, and 0.3.

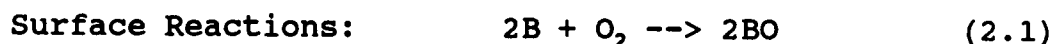
The droplets were found to ignite shortly after exposure to the hot gases(< 10 ms). An envelope diffusion flame developed shortly after ignition followed by a yellow flash(i.e. "disruption"), marking extinction. The results obtained support the d^2 law(diffusion-controlled) for an initial period, up to the point of disruption. This disruption occurred in all cases except those with the lowest boron mass fraction and those with the lowest oxygen mole fraction. The disruption was followed by a "popping"(i.e. particle ejection) and a bright green flash, attributed to excited BO_2 . A "zig-zag" trace on the high-speed cinematographs also suggests the droplet is spinning during part of combustion.

The ambient gas temperature was, in all cases, less than 1900K, matching the minimum gas temperature which Macek[1] found necessary to ignite single particles. It was determined that as oxygen mole fraction was increased, time from exposure to disruption decreased, and as the boron mass fraction was decreased, time to disruption significantly increased. Additionally, for any boron mass fraction, if the diffusion flame temperature at the point of disruption was greater than 2316K(boiling point of boron oxide), then the green emission and "popping" were observed.

An agglomeration of particles at the droplet surface, forming a rigid shell, was observed, causing the flame to move closer to the surface. This allows more heat transfer to the

interior of the droplet structure and a pressure build-up, prior to disruption. For the free JP-10/boron droplets, the experimental results show a deviation from the d^2 law sooner than the model predicts.

A theoretical study of the combustion characteristics of uncoated boron particles is presented by Makino and Law[9], in which the finite rate kinetics of both surface and gas-phase reactions are taken into consideration. The two main focuses of the study are to include the stoichiometric and thermo-kinetic parameters of the boron oxidation system, and the possibility of surface condensation of the boron oxide. The following chemical reactions are considered:



The complicated model formulated is identical to the model presented by Makino and Law[10] of the combustion of carbon, with the exception of stoichiometric differences. Various coupling functions can be identified to allow derivation of solutions for "limiting" situations. Combustion limits that define a feasibility regime for combustion were generated. The first limiting case is when the gas-phase reaction is "frozen"(i.e. the effect of the surface reaction is practically nil). When the gas-phase reaction is infinitely

fast, a "flame-sheet" limit is achieved. A "flame-attachment" limit is reached when particle combustion rate decreases below a certain level. If two of the three gas-phase reactions occur infinitely fast, the classical diffusion-limited behavior is attained.

Feasibility "regimes" with burning rate as a function of particle temperature and with particle temperature as a function of ambient temperature are presented for the various limiting behavior. A trend that the model predicts is that as particle radius and pressure increase, the feasibility regime shifts to a lower ambient temperature, because of the increase in surface reactivity. Expressions for total burning time were developed for the limiting cases (i.e. flame-sheet and flame attachment). Burning time was found to be linearly proportional to the square of the particle diameter when particle diameter is large and linearly proportional to particle diameter when particle diameter is small. In other words, the d^2 law holds for larger particles. The results of the theory are also in agreement with experimental data obtained in previous studies.

A detailed description of the experimental apparatus and procedure of the present study of the ignition and combustion phenomena of boron slurry agglomerates is presented in Chapter 3.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

The present chapter contains a detailed description of the experimental apparatus and procedure used in the ignition and combustion study of laser-ignited boron agglomerates. An overview of the experimental apparatus used in the study is given in Section 1. A description of the techniques used to produce boron agglomerates is given in Section 2. Detailed discussions of the essential instruments utilized in the study; i.e. CO₂ laser, two-color pyrometer, broadband radiometer, high-speed camera, and the data acquisition system, are presented in Sections 3 to 7. A detailed description of the experimental procedure is given in Section 8 and, finally, Section 9 discusses the methods of data analysis.

3.1 OVERVIEW OF EXPERIMENTAL METHOD

An overall schematic of the experimental apparatus is shown in Figure 3.1. A sub-millimeter boron agglomerate, supported by a Silicon-Carbide fiber, is mounted vertically in the target area. Ignition of the agglomerate is obtained by a cw CO₂ laser beam. The beam is directed onto the front of the agglomerate by a focusing system consisting of two mirrors, M₂ and M₃, a beam steering device, S, and a zinc selenide(Zn-Se)

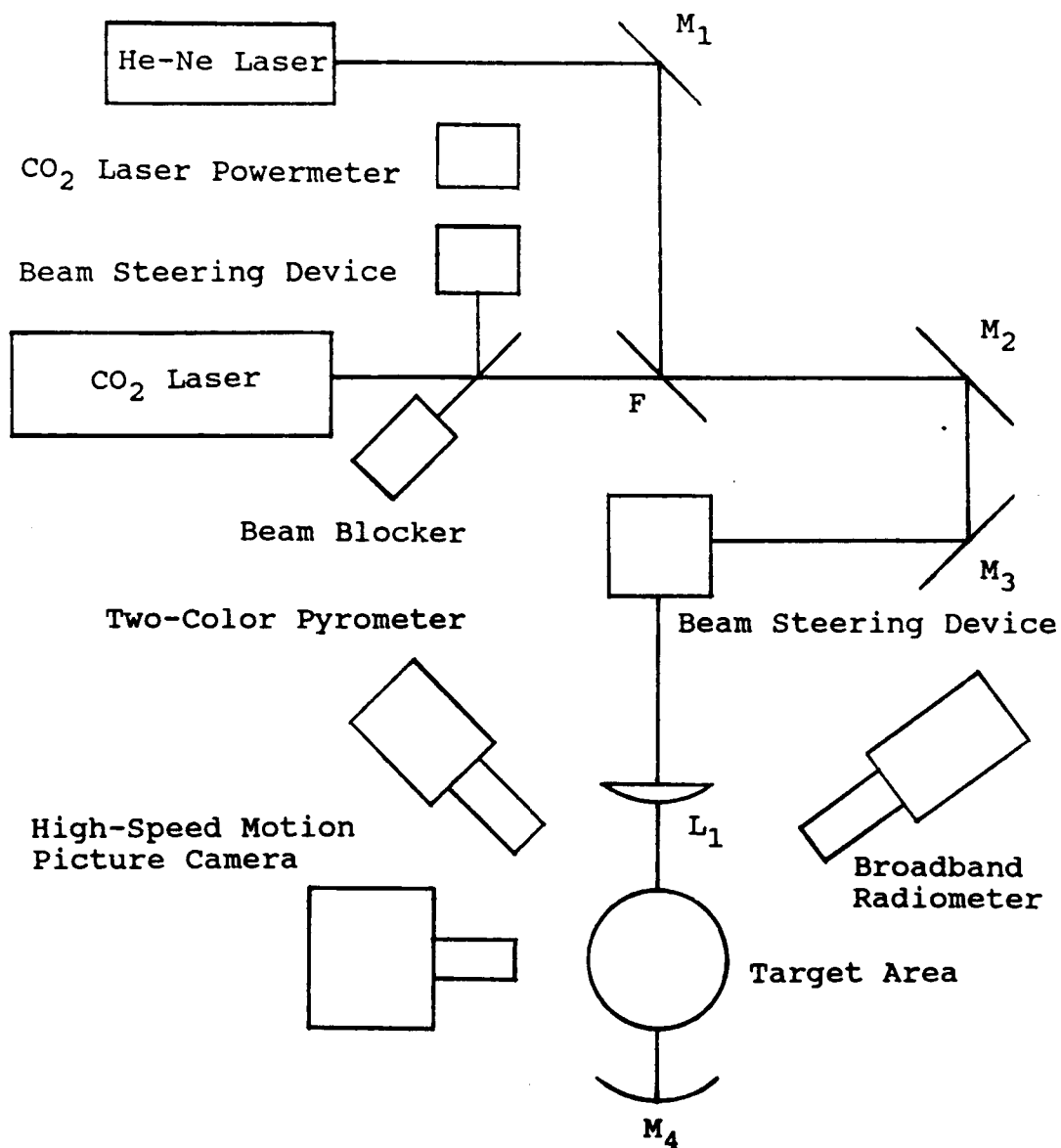


Figure 3.1 - Schematic of Experimental Apparatus

plano convex lens, L_1 , of 250 mm effective focal length.

Since the output of the CO_2 laser beam is in the infrared, the suspended agglomerate is aligned for the CO_2 laser using a helium-neon(He-Ne) laser(Aerotech LS5R, 15 mV) as a visual reference. The visible He-Ne laser beam is introduced into the laser focusing system by a mirror(M_1) and Zn-Se optical flat(F). The optical flat transmits 98% of the infrared CO_2 beam while reflecting 95% of the He-Ne beam.

By making adjustments, as the He-Ne laser beam emerges from the optical flat, it would coincide with the CO_2 laser beam. Alignment is achieved when the He-Ne laser beam illuminates the suspended boron agglomerate. A concave spherical mirror(M_2) of 300 mm radius of curvature is placed directly across from lens(L_1) to reflect the CO_2 laser beam onto the back surface of the agglomerate. In this manner, the incident radiant fluxes on the opposite sides of the agglomerate would then be approximately equal, thereby preventing localized ignition.

The CO_2 laser beam is entered into the focusing system by means of a solenoid-activated beam blocker. By energizing the solenoid, the spring-loaded arm of the beam blocker swings out of the way of the beam, creating a shutter. The duration of the "laser pulse" can be varied from 40 msec to 1.0 sec. This timer circuit interfaces with and activates the data acquisition system. A mirror is mounted on the swing arm of the beam blocker and reflects the CO_2 laser beam into the

powermeter, prior to an experiment, and the the actual laser power can be measured. The laser power is adjusted either by varying the flow rates of the gases(CO_2 , He, and N_2) into the plasma tube or by varying the applied electrical current.

The temperature measurement consists of a fast-response, two-color pyrometer that operates in the near-infrared in two spectral regions centered at 0.8 and 1.0 μm . A broadband radiometer is utilized to measure the relative radiation intensity emitted by the laser-ignited boron agglomerate in the spectral region from 0.3 to 1.1 μm .

The output signals from the two-color pyrometer and the broadband radiometer are input to the data acquisition system and allow the determination of ignition temperature, ignition delay time and total burning time of the laser-ignited boron agglomerate. A high-speed camera(Hycam, 16 mm) capable of up to 25,000 frames per second, is used occasionally in conjunction with the pyrometer and radiometer data to allow an accurate correlation of the phenomenological events during boron agglomerate ignition and combustion. Figure 3.2 shows the two-color pyrometer, broadband radiometer, and the target area of the experimental set-up used in the study of the ignition and combustion of laser-ignited boron agglomerates.

A detailed discussion of the elements essential to the study of the ignition and combustion of laser-ignited boron agglomerates is given in the following sections.

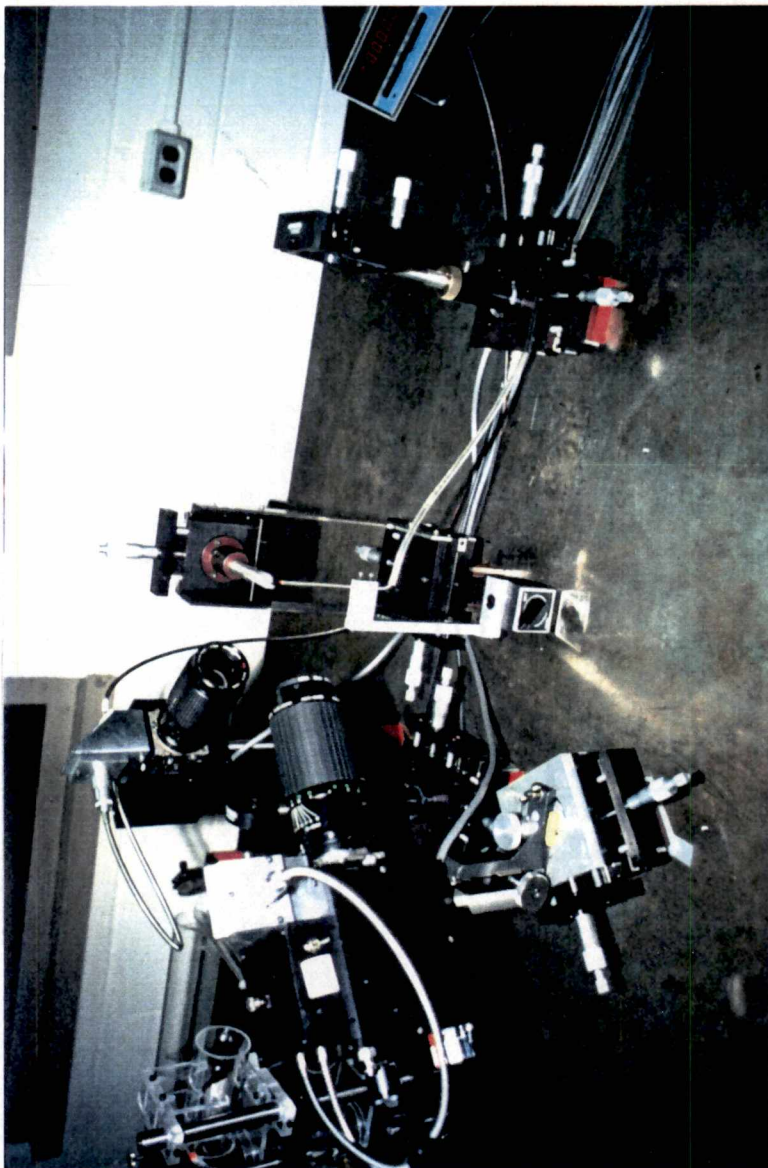
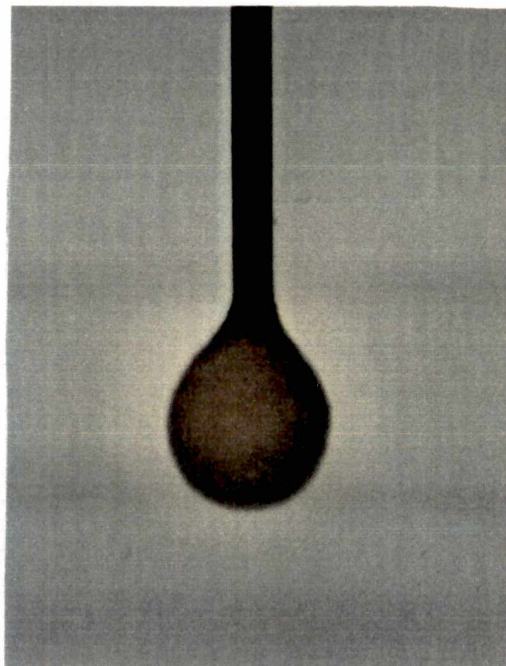


Figure 3.2 - Photograph of Two-Color Pyrometer,
Broadband Radiometer, and Target Area

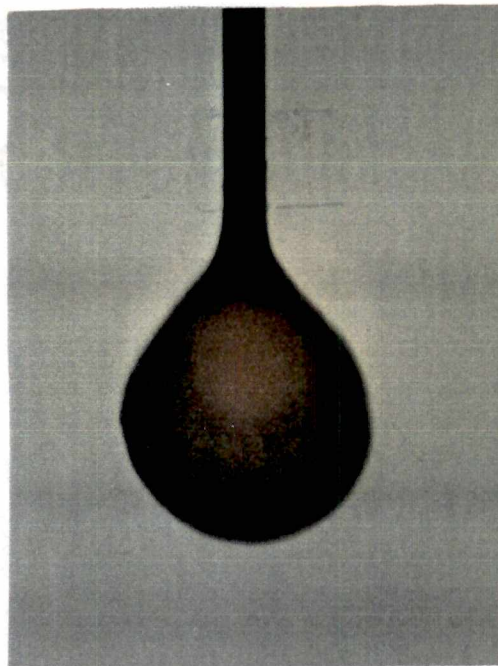
3.2 BORON AGGLOMERATE PRODUCTION TECHNIQUE

To simulate the agglomeration burning in the overall combustion process of boron slurry fuels, a technique has been developed to produce boron agglomerates at the end of silicon-carbide(SiC) fibers. Powdered(1-2 μm) amorphous boron is mixed with alcohol and deposited on the end of 150 μm SiC fiber using a hypodermic syringe. The alcohol evaporates rapidly, leaving a thin coating of solid boron powder. Additional applications of the droplet result in sufficient boron to form a nearly-spherical particle at the end of the fiber.

A comparator microscope with a micrometer stage is utilized to measure and to assure uniformity of the produced agglomerates. Figure 3.3 shows typical agglomerates used in the present study. It has been shown that nearly-spherical boron agglomerates as small as 150 μm in diameter, supported by 50 μm tungsten fibers can be produced using the present technique, however, agglomerate diameters ranging from 300-1200 μm will be utilized in the present study. It has been found that the alcohol/boron mixture ratio has little or no effect on the porosity of the final agglomerate. Several large agglomerates(e.g. 3 mm) produced with different mixture ratios were weighed and the densities were determined. All agglomerates were shown to be approximately 35% solid boron by volume.



(a)



(b)

Figure 3.3 - Photomicrographs of Two Boron Agglomerates:
(a) Diameter=660 μm , (b) Diameter=990 μm

3.3 CO₂ LASER SYSTEM

A 100 Watt cw CO₂ laser has been designed and constructed. The laser optical resonator is formed by a gold coated spherical concave copper mirror(100% reflection) of 10.0m radius of curvature and a Zn-Se flat partial reflector(35% reflection). The two mirrors are separated by approximately 2.5 m. Since the separation distance between the two mirrors is less than the radius of curvature of the concave mirror, the resonator is referred to as a "quasi-hemispherical" resonator. Power is coupled out of the laser through the Zn-Se partially-reflective flat mirror via the zero-order reflection.

A four rod structure is used to support the mirror assemblies and the laser plasma tube as shown in Figure 3.4. The laser plasma tube is constructed of pyrex and consists of an 18 mm inner bore and a 38 mm diameter water cooling jacket. There are two anodes located near the ends of the laser plasma tube and a cathode located at the midsection of the tube. One central gas inlet and two outlets are provided to ensure a uniform gas flow throughout the amplifying region. At the ends of the laser plasma tube, two rectangular Zn-Se windows are mounted at a Brewster angle of 67.4°. At this Brewster angle, the electric-field component in the plane of incidence is transmitted with no reflection. Thus, the output of the CO₂ laser in the design is linearly polarized in the vertical direction.

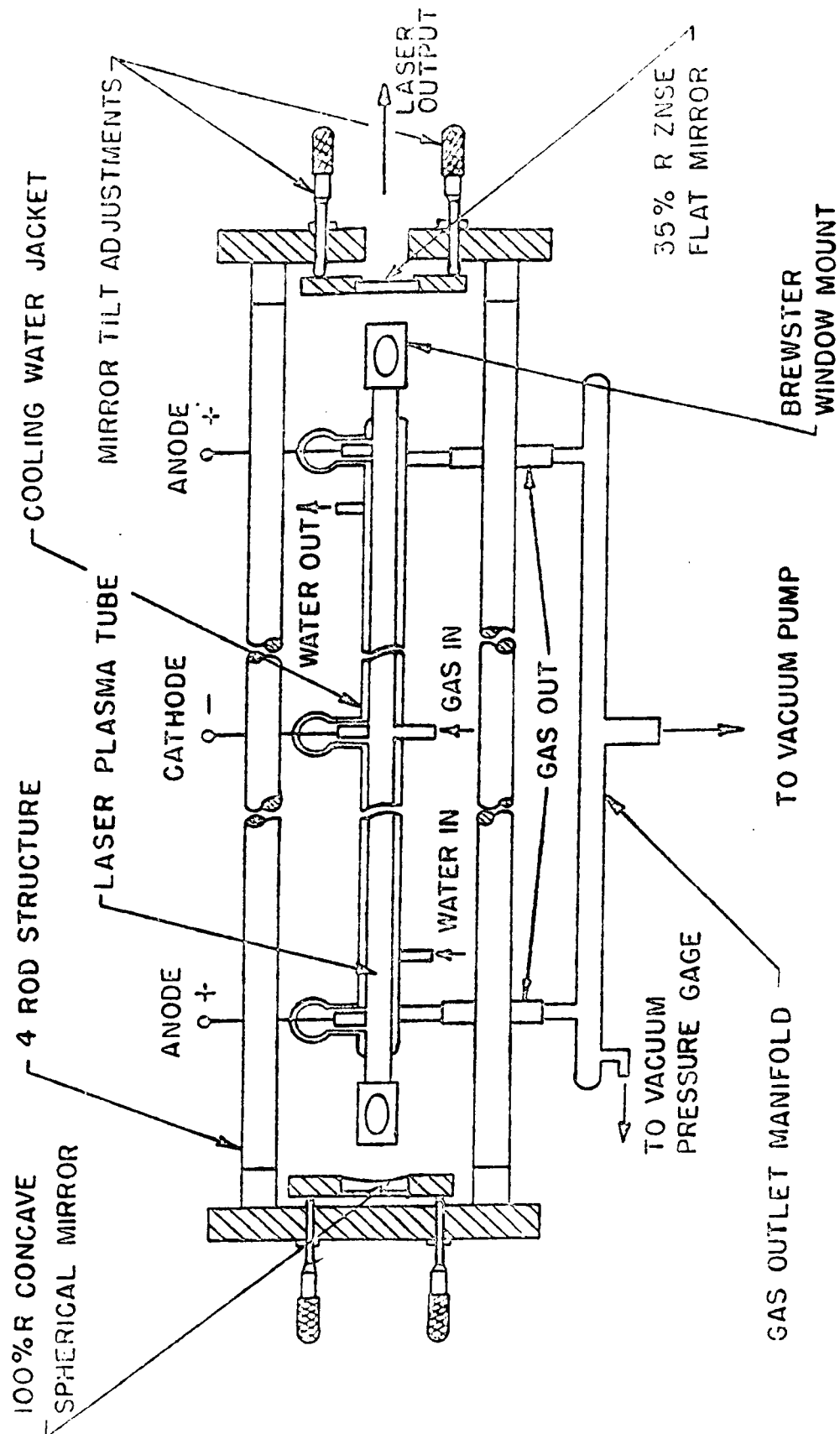


Figure 3.4 - Top View of Laser Optical Resonator, Laser Plasma Tube and Mechanical Structure of cw CO₂ Laser.

The gases are premixed in a mixing chamber and are drawn through the laser plasma tube by a vacuum pump. It has been experimentally determined that for optimum operation, a mixture of 80% He, 15%N₂, and 5% CO₂ is used. In addition, for optimum operation, a gas flow rate of 1.5 slpm and a pressure of 10 Torrs is used. The pressure of the laser plasma tube is monitored at the outlet of the tube by a vacuum gauge.

A 20 kV, 100 mA Universal Voltronics power supply is used to excite the gas mixture. The maximum power of the CO₂ laser is obtained at a discharge current of about 70 mA. For safety consideration, safety switches and relays are installed on the laboratory door to ensure the power supply will operate only when the door is closed. Fire brick material is placed in front of the laser head, when not in operation, to absorb the 10.6 μ m radiation of the CO₂ laser.

3.4 NEAR-INFRARED, TWO-COLOR PYROMETER

The present section presents a detailed discussion of the two-color pyrometer. A brief discussion of the theory behind radiation means of temperature measurement is first presented, followed by discussions of the optics and circuitry designs. A discussion of the methods used to calibrate the pyrometer, employing various correction factors is presented in Appendix B.

3.4.1 THEORY

When a sub-millimeter boron agglomerate is irradiated with the focused high-power laser beam, a heating rate in excess of 50,000K per second is achievable. This high heating rate and the size constraints dictate the use of radiation methods for the measurement of surface temperature. A fast-response, two-color pyrometer has been designed and constructed to operate in the near-infrared region at two spectral regions centered at 0.8 and 1.0 μm . It has a temperature range of 1000-4000K with time resolution of 25 μsec . The pyrometer is used to measure the spectral radiance, R , of the radiation emitted by the laser-ignited boron agglomerate. Using Wien's Law for a gray body radiating at two separate wavelengths, λ_1 and λ_2 , it can be shown that the spectral radiance ratio, R , is given by the following (See Appendix B):

$$\log R = A_1 / T + A_2 \quad (3.4.1)$$

where A_1, A_2 = pyrometer constants whose values are determined by calibrating the two-color pyrometer against a known source

T = temperature

R = spectral radiance ratio

Once the spectral radiance ratio is obtained, the surface temperature of the agglomerate can be determined.

3.4.2 OPTICAL ARRANGEMENT

A schematic diagram of the optical arrangement of the two-color pyrometer is shown in Figure 3.5. Radiation emitted by the laser-ignited boron agglomerate is focused onto the randomized common leg of a Cuda glass bifurcated fiber optic cable by a Sigma Macro Zoom lens and a swinging mirror, M. The bifurcated fiber optic cable is used to split the incident beam into two separate beams by means of two fiber optic cables, C_1 and C_2 . The cables transmit approximately 70% of the incident radiation with wavelengths between 0.3 and 1.3 μm .

The beam transmitted by the fiber optic cable C_1 is then directed onto a detector housing. The incident beam first passes through an Ealing Optics bandpass interference filter, IF_1 , with a centered wavelength on 0.8 μm , a nominal bandwidth of 80 nm and a peak transmittance of 60%. Located directly behind the interference filter is an SDC silicon photodiode detector, D_1 , operated in the photoconductive mode. The detector is red and infrared enhanced and is sensitive to light of wavelengths between 0.3 and 1.2 μm , with a response time of 5.3 nsec. At the two wavelengths of interest, the detectors have a typical spectral response of 0.5 mA/mW.

Similarly, the beam transmitted by the fiber optic cable, C_2 , passes through an interference filter, IF_2 , with a centered wavelength of 1.0 μm , a nominal bandwidth of 14 nm and a peak transmittance of 45%, onto detector D_2 . The broader bandwidth of IF_1 is purposely chosen to enhance the signal output ratio.

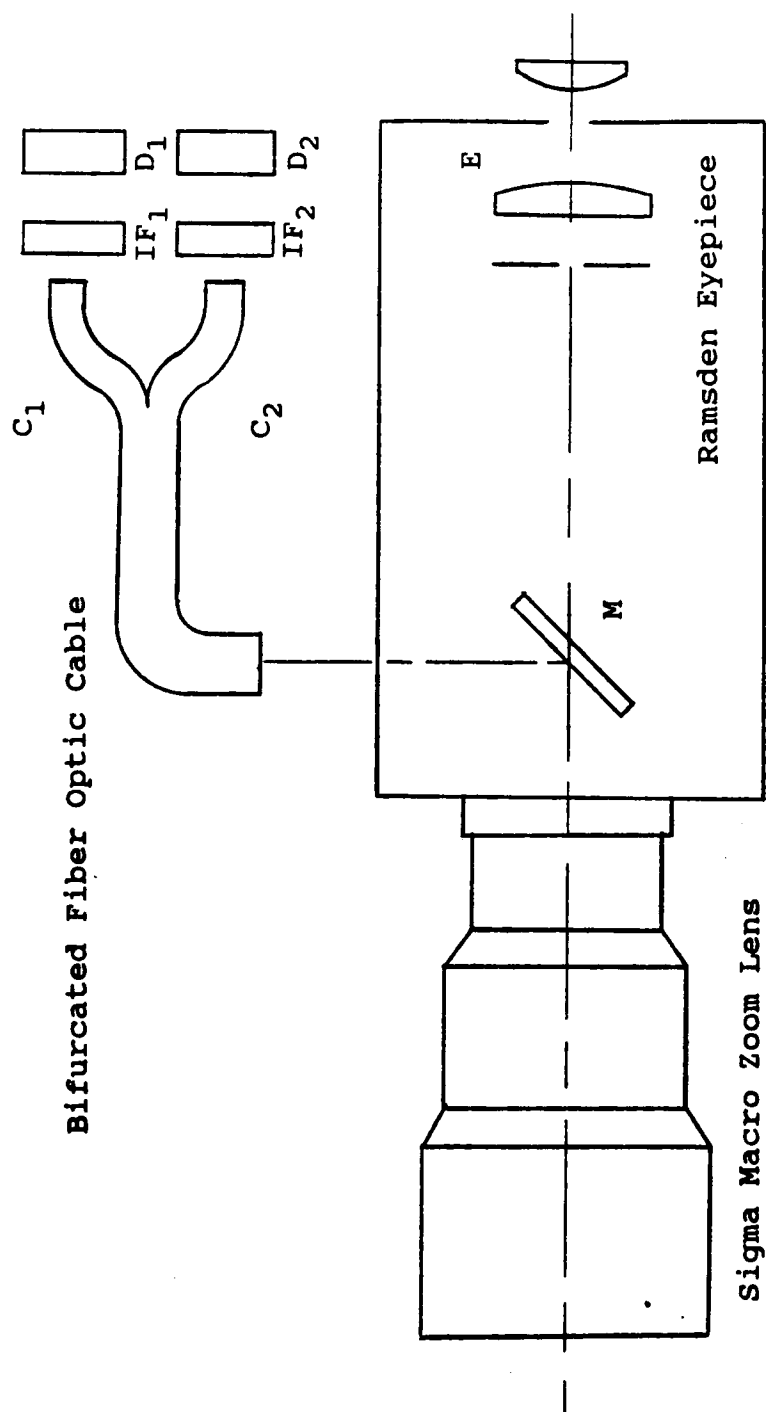


Figure 3.5 - Schematic of Optical Arrangement
of Two-Color Pyrometer

The mirror, M, when in the upward position, directs the image of the boron agglomerate formed by the macro zoom lens to the eyepiece, E. The widefield Ramsden-type eyepiece, with a magnification of 10X, allows precise alignment of the two-color pyrometer to the agglomerate.

3.5 BROADBAND RADIOMETER

A broadband radiometer is used to measure the radiation intensity emitted by the laser-ignited boron agglomerate. The radiometer is similar in design to the two-color pyrometer with the following notable exceptions:

There is a single fiber optic cable rather than a bifurcated one and there is no interference filter in the optical path. This allows the radiometer to be sensitive to a broad radiation spectrum. The radiometer output is a voltage proportional to the overall level of the emitted radiation in the target area. The lens system for the fiber optic cable is identical to that of the pyrometer.

The function of the broadband radiometer is to measure the total burning time of the laser-ignited boron agglomerates. By measuring the radiation emitted by the agglomerates, the point at which it is first exposed to the CO₂ laser beam and the end of the event can be readily determined. The radiation intensity histories will also depict important phenomenological events occurring in boron agglomerate combustion.

3.6 HIGH SPEED CAMERA

A Hycam Model K2004E-115, 16 mm high speed motion picture camera is occasionally employed in some selected test runs. A series of extension tubes, coupled with a 50 mm lens provide the capability to produce an acceptable image size on the 16 mm frame. The camera is positioned adjacent to the two-color pyrometer with its objective lens approximately 10 cm from the test particle. It is placed on an aluminum plate, which can be elevated or tilted, to allow adequate aiming. Satisfactory preliminary results have been obtained by exposing Kodak Ektachrome ISO 400 color film at 4000 frames per second through an f/2.8 aperature and 72 mm extension tube.

When the camera is employed on a test run, the system is set-up such that the shutter/beam blocker timer circuit and the data acquisition system are both triggered after approximately 25 feet of the 100 ft roll of film has been exposed. This allows the camera to obtain a nearly steady frame rate and also allows any layers of film partially exposed during the loading process to move past the shutter. A red strobe light in the camera is connected to a timer, preset at a 1 kHz frequency, to produce a timing mark on the edge of the film which allows an accurate correlation between the filmed events and the data acquired from the radiometer and pyrometer.

3.7 DATA ACQUISITION SYSTEM

The output voltage from the two-color pyrometer and the radiometer are entered into an IBM PC through a Metrabyte Dash 16 A/D converter system. The system has the capability to sample at a rate of up to 50,000 samples per second.

The system is activated by a signal from the shutter timer. When the high speed camera is utilized as mentioned, it activates the timer, thus initiating data collection. There is enough of a mechanical lag time in the shutter mechanism such that there is a short deadband at the beginning of the pyrometer and radiometer data set. This deadband, however, allows for an accurate determination of the start of the event and the ignition point.

As data is collected, a graph of the output voltages as a function of time from both the pyrometer and radiometer appears on the monitor and can be saved to the computer's hard disk if desired. The data is processed by a set of transfer equations en route to the hard disk. The radiometer data is normalized so that the saved information is actually the relative intensity of the emitted radiation as a function of time. The pyrometer data is processed by the calibration equations so that the surface temperature of the boron agglomerate is saved as a function of time. (See Appendix B).

3.8 EXPERIMENTAL PROCEDURE

Prior to performing experiments, several preliminary steps must be taken. The internal calibration of the two-color pyrometer is first checked for any drift caused by fluctuating temperatures on the electronic circuitry over a period of time. The vacuum pump for the CO₂ laser is then used to evacuate the plasma tube prior to initiating the ionizing gas flows. Water flow through the laser plasma tube cooling jacket is started prior to activating the CO₂ laser. The CO₂, N₂, and He gases are then pumped into the plasma tube. With the current of the power supply set to its maximum value(100 mA), the power supply is activated to excite the gases. The current is then reduced to about 50 mA immediately after the laser is activated.

The Zn-Se mirror at the CO₂ laser output is adjusted to produce the brightest, most uniform laser beam(i.e. a Gaussian distribution). The power of the CO₂ laser can be adjusted to the desired level by either adjusting the current of the power supply or by adjusting the CO₂ flow into the plasma tube.

The alignment of the CO₂ laser beam for the target area is then checked, using the He-Ne laser beam as a visual reference. In the current configuration (refer to Figure 3.1), as the He-Ne laser beam emerges from the optical flat(F1) and enters the focusing system, it becomes coincident with the CO₂ laser beam. By vertically mounting a piece of plastic or plexiglass material in the target area, the He-Ne laser beam

is allowed to strike the plastic. By making adjustments to mirror M1, the He-Ne laser beam can then be manipulated such that the CO₂ laser beam strikes the plastic, centered on the He-Ne beam, signifying coincidence of the CO₂ and He-Ne lasers.

After laser alignment is achieved, the probe-supported boron agglomerate can then be placed in the target area, held by a thin plexiglass clamp mounted on a micro-adjustable translator in the vertical plane. The translator is mounted on two additional translators such that precise 3-axis positioning is allowable to align the test agglomerate with the He-Ne laser beam.

The two-color pyrometer and the broadband radiometer are then aimed for the test agglomerate by sighting through the eyepiece when the mirror is in the "up" position, centering the image of the agglomerate with the crosshair graticules on the eyepiece. On subsequent test runs, alignment of the test agglomerates is achieved by simply using the initial position settings of the pyrometer and radiometer. The position of the test agglomerate is centered using the translators on the agglomerate mount. The mirrors are then moved to the "down" position to focus the image of the agglomerate to the ends of the fiber optic cables. If the high-speed camera is to be employed on the particular test run, it is connected into the circuit and its frame speed, aperture settings, aiming, film loading, etc. are set.

If necessary, the CO₂ laser power is then adjusted to the desired level by the aforementioned procedure. Upward oxygen flow onto the test agglomerate, to promote ignition, is also adjusted to the desired flow rate. Finally, the test is initiated by triggering the shutter/beam blocker manually or by starting the high-speed camera, if used in the particular test run. A superimposed plot of both surface temperature and relative intensity versus time appears on the monitor of the data acquisition system, immediately after combustion and the data can be saved to the hard disk at that time for future analysis.

3.9 DATA REDUCTION AND ANALYSIS

In this section, the methods used to analyze and reduce the experimental data are given. A discussion of correlating the pyrometer and radiometer data to the phenomenological events recorded by the high-speed photography is also presented.

The three most important parameters in the present study, such as ignition delay time, burning time and surface temperature can be determined directly from the temperature and radiation history curves of the laser-ignited boron agglomerates. As mentioned previously, the ignition point has been defined as the point at which the surface temperature of the boron agglomerate reaches 2316K (i.e. the boiling point of boron oxide). For temperatures below 2316K, ignition of the boron agglomerates cannot occur since the presence of the

boron oxide layer impedes the diffusion of reactants. At a temperature of 2316K, the oxide layer vaporizes rapidly and the boron agglomerate becomes completely cleansed of the oxide, thus allowing rapid reaction between the hot boron and the oxidizer, resulting in ignition.

From the two-color pyrometer surface temperature data, the ignition point can be determined directly. The ignition delay time is simply the time difference between the beginning of the event and the ignition point. The burning time of the laser-ignited boron agglomerate is then the time difference between the total time of the event and the ignition delay time.

Typical experimental temperature and radiation histories for laser-ignited boron agglomerates in the present study are shown in Figure 3.6. It should be noted that a relative intensity of 0.05 and a surface temperature of 1414K are the lowest values recorded by the system and are evident preceding and following the event. Since the temperature range of interest is greater than 2000K, no discrepancy will result.

The beginning of the event is considered the point at which the laser begins to irradiate the front surface of the agglomerate, corresponding to the first rise in radiation output on the radiation history. The ignition point of the boron agglomerate is the point at which any point on the surface of the agglomerate reaches 2316 K, as previously defined. The end of the event is then the point at which the

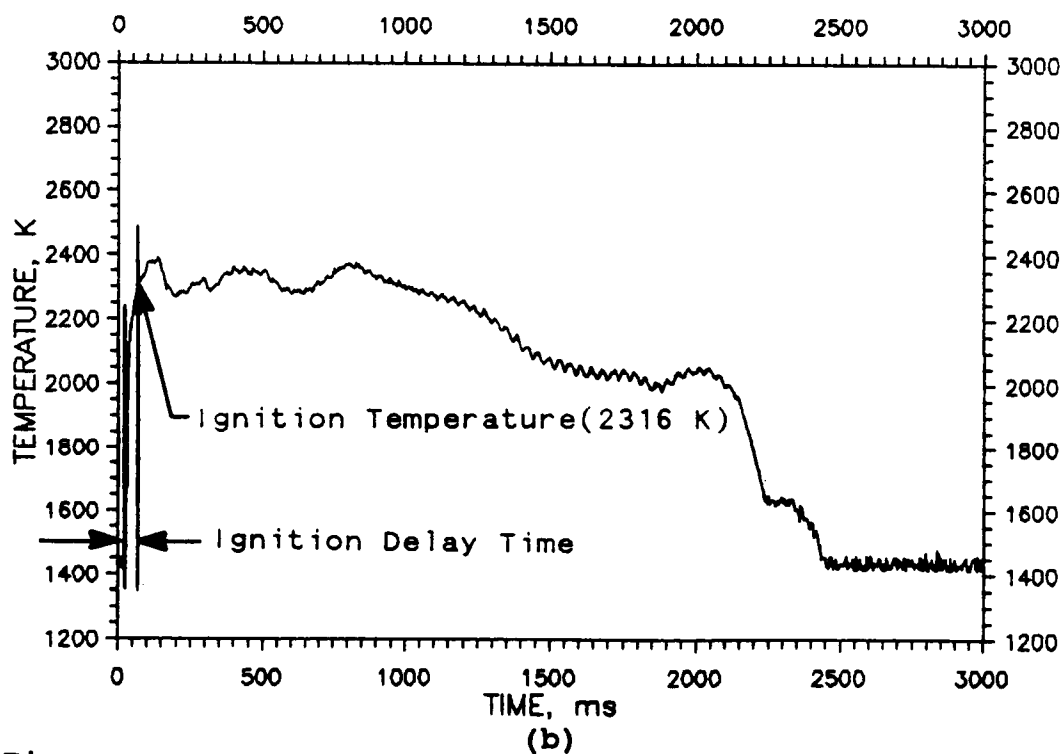
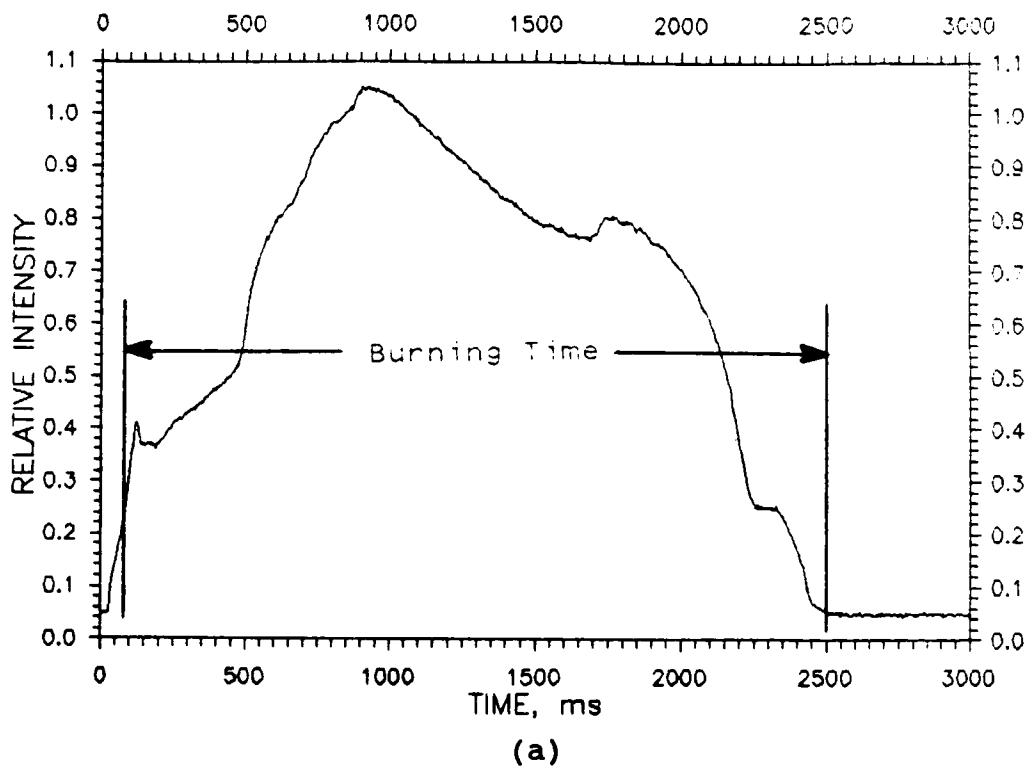


Figure 3.6 - Typical Instrument Output Curves of Laser-Ignited Boron Agglomerates: (a) Radiation History, (b) Surface Temperature History

agglomerate combustion is complete, corresponding to decay of the radiation history to the deadband value.

In the present study, several boron agglomerates will be used for data, each agglomerate diameter and its corresponding burning time are considered separate data points. Some experimental data points can be eliminated(rejected) directly from inspection(e.g. incomplete agglomerate combustion). Other experimental data points can be eliminated by using Chauvenet's criterion for statistical analysis[13]. Chauvenet's criterion basically states that a data point can be eliminated if the probability of obtaining the particular deviation from the mean(average) is less than $1/2n$, where n is the number of data points in the set. In general, if the ratio of the deviation of a particular reading to the standard deviation is "relatively" large(depending on the total number of readings), then that data point is eliminated.

The average boron agglomerate diameter and its average burning time from each set can then be used to determine the burning mechanism of boron agglomerates in flowing oxygen environment. For instance, if the relationship between the agglomerate diameter and the burning time is linear, then the burning mechanism is said to be "kinetics-controlled" (i.e. reaction kinetics control the reaction rate). On the other hand, if the relationship between the square of the agglomerate diameter and the burning time is linear, then the burning mechanism is said to be "diffusion-controlled" (i.e.

the diffusion of the oxidizer to the surface of the boron agglomerate controls the reaction rate).

The phenomenological events of the laser-ignited boron agglomerates as recorded by the high-speed cinematography can be correlated with the data from the pyrometer and radiometer. The timing marks that are visible on the processed high-speed film allow for determination of the ignition delay time and total burning time of the boron agglomerate. However, in the present study, the ignition delay time and total burning time will be determined solely by the instrument outputs.

A discussion of the results pertaining to the use of the two-color pyrometer and the broadband radiometer to measure the burning time of boron agglomerates is given in Chapter 4. In addition, a detailed description of the phenomenological events as recorded by the high-speed cinematography is presented.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

The ignition and combustion phenomena of laser-ignited boron agglomerates in a flowing oxygen environment has been studied and the experimental results are presented in the present chapter. Boron agglomerates of various diameters ranging from 350-1100 μm were produced and used in the study. A two-color pyrometer and a broadband radiometer were implemented to measure surface temperature and emitted radiation, respectively, throughout the duration of each experiment, enabling the determination of ignition delay time and burning time of each agglomerate. In addition, high-speed cinematography was used on selected runs to record the phenomenological events of boron agglomerate combustion.

A discussion of some important conditions that were apparent in the experimental investigation is provided in section 4.1. General observations from a typical experiment are presented in Section 4.2. The effects of diameter on the combustion phenomena are discussed in Section 4.3, followed by a discussion of the effects of increased oxygen flow in Section 4.4.

4.1 IMPORTANT EXPERIMENTAL CONDITIONS

In the present study, a CO₂ laser power of 23.3 Watts and an oxygen flow rate of 37.1 cc/min were used consistently for each experiment, with the exception of a few tests using a higher oxygen flow rate, discussed in Section 4.3.

The CO₂ laser beam itself is assumed to have a Gaussian distribution and the fraction of the laser power that irradiates each agglomerate can be approximated. Depending on proper mirror alignment, the amount of laser power that irradiates the agglomerate may vary from test to test, however the effects of laser power are not considered as long as the power is sufficient to achieve ignition. The duration of laser irradiation for each agglomerate size, however, has been considered. Minimum laser pulse durations were experimentally determined(trial and error) for each agglomerate diameter to successfully achieve ignition for the given laser power(i.e. 23.3 Watts). Those values are given in Table 4.1.

4.2 GENERAL OBSERVATIONS

Radiation and surface temperature histories for a typical experiment(Agglomerate Diameter = 697 μ m) are shown in Figure 4.1 and several frames from the corresponding high-speed motion picture film are shown in Figure 4.2. It should be noted that a discussion of the chemical reactions involved in boron combustion is presented in Appendix F and it is beneficial to be referred to by the reader.

Table 4.1 : Laser Durations

Agglomerate Diameter(μm)	Laser Duration(msec)
350	40
500	40
700	40
900	100
1100	300

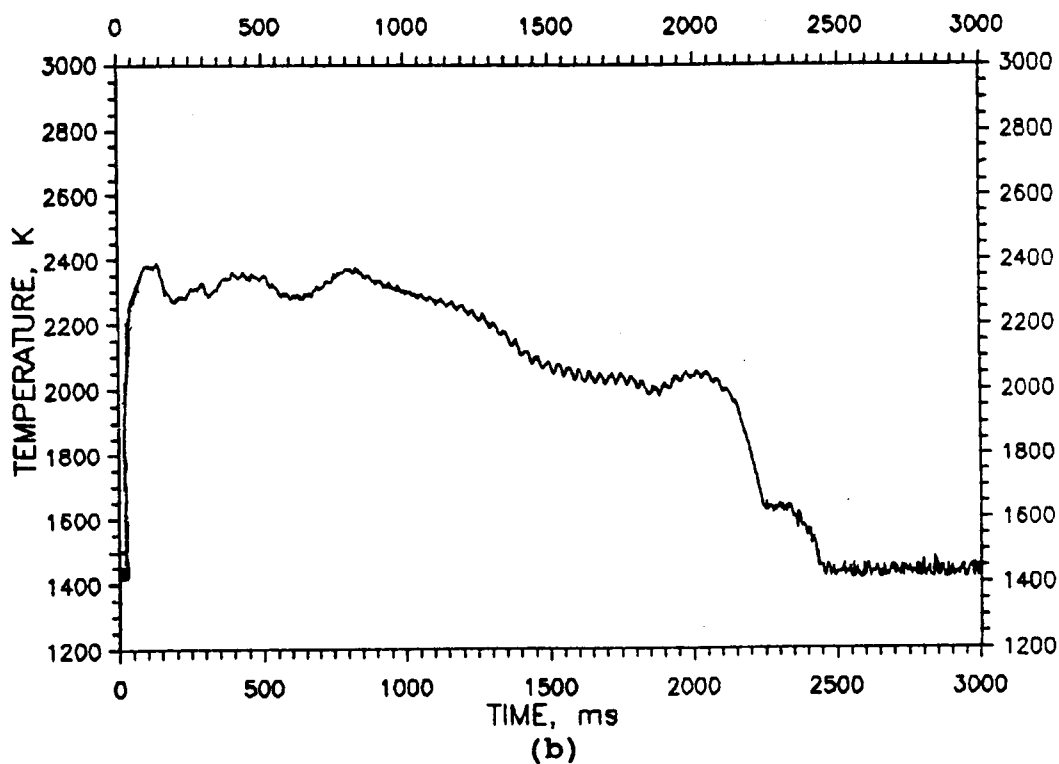
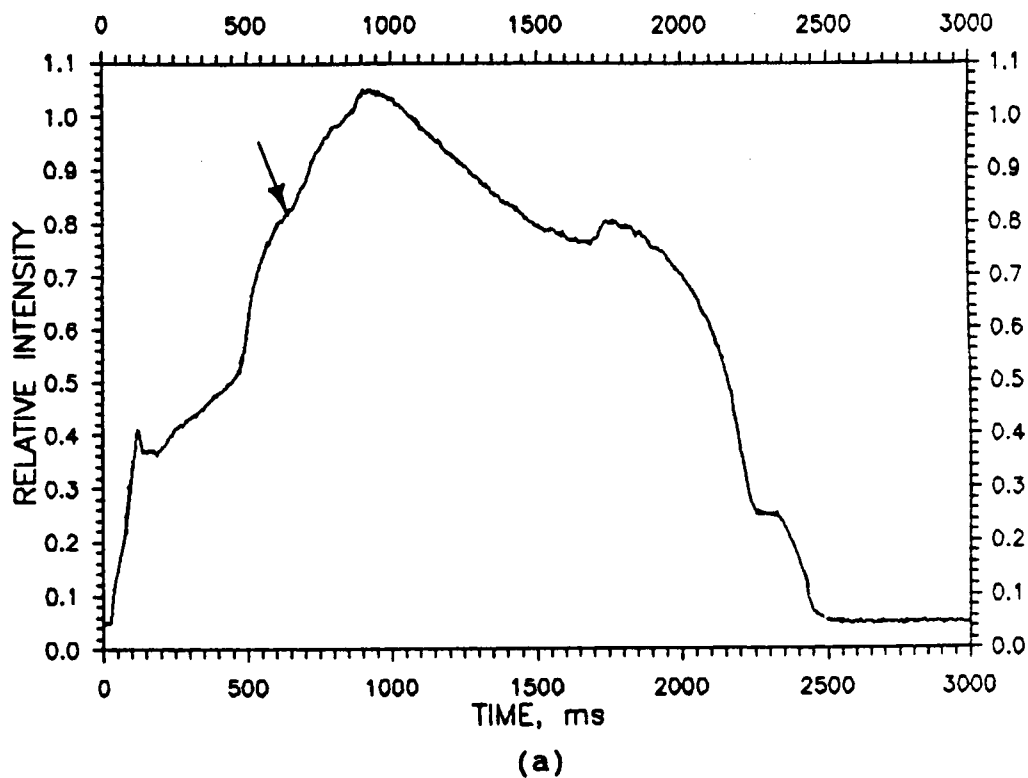


Figure 4.1 - Initial Agglomerate Diameter = 697 μm , Oxygen Flow = 37.1 cc/min: (a) Radiation History, (b) Temperature History.

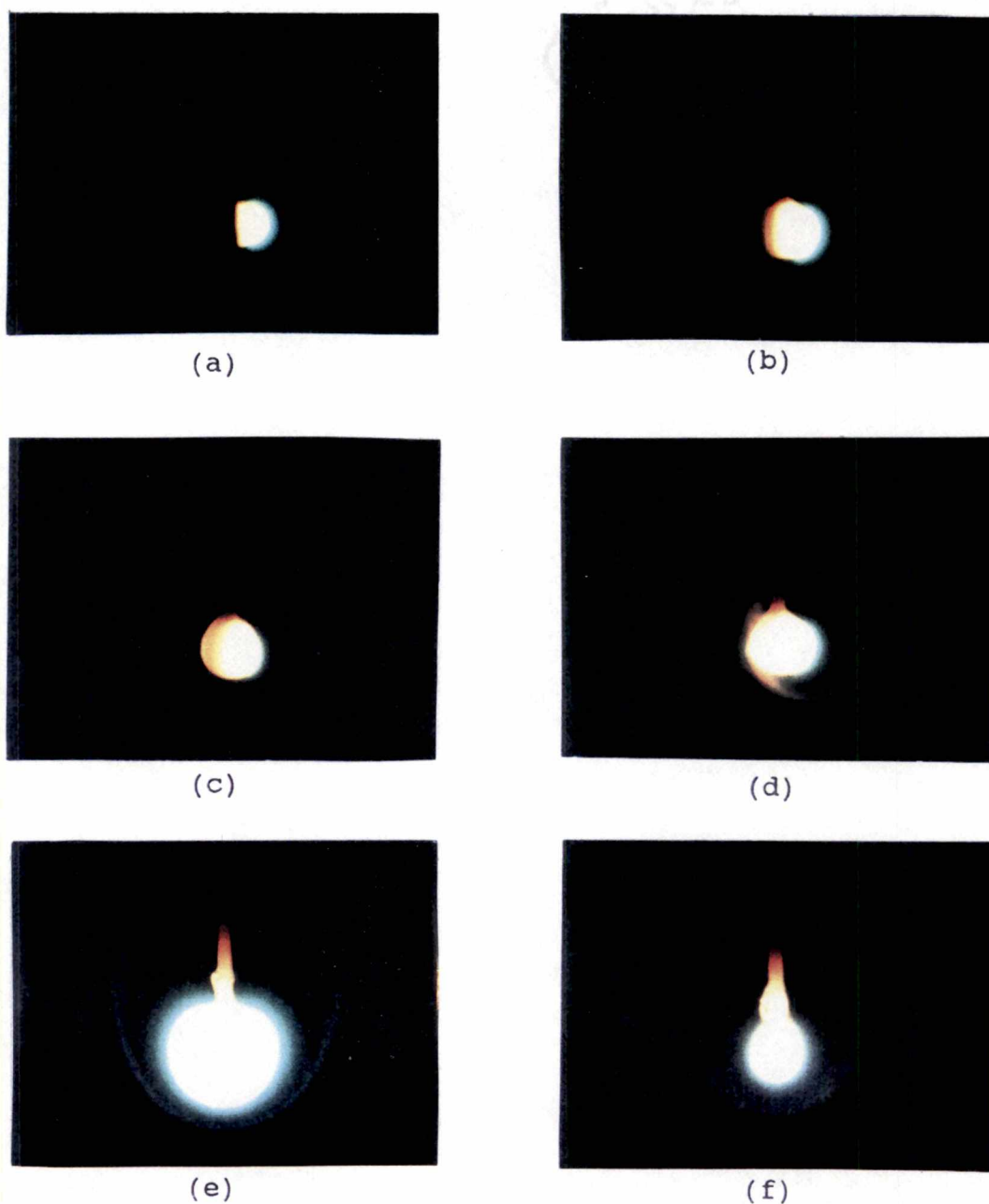


Figure 4.2 - Progressive Stages of Combustion Phenomena
Recorded by High-Speed Cinematography;
 $d_o = 697 \mu\text{m}$, Oxygen Flow = 37.1 cc/min:
(a) Time = 30 ms, (b) 110 ms, (c) 300 ms,
(d) 480 ms, (e) 600 ms, (f) 1520 ms

Almost instantaneously upon laser irradiation(2-3msec), a localized ignition point, marked by a bright "green" flame front, appears close to the surface of the agglomerate. The green emission indicates the presence of gaseous BO_2 and results from two electronic transitions in the BO_2 linear symmetric molecule[16].

From the surface temperature history(Figure 4.1b), it is observed that 2316 K(i.e. ignition temperature) is achieved approximately 30 msec after initial laser exposure, thus by definition, ignition(localized) occurs during the laser pulse(Figure 4.2a). The front then steadily grows until nearly a hemisphere of the agglomerate is encompassed by the flame front(Figure 4.2b), at which time the front begins a decay in size and intensity. This point corresponds to period immediately following the laser pulse. A corresponding decay can be seen on the radiometer(intensity) history. The flame front then diminishes steadily to the point where it is very near the surface of the agglomerate, almost indistinguishable(Figure 4.2c). Simultaneously, heat has been conducted throughout the agglomerate, observable as a bright orange "glowing" of the entire agglomerate.

The flame front near the surface of the agglomerate, transfers more heat to the agglomerate, thus aiding in the increased reaction rate and the removal of the oxide layer. As the oxide layer becomes very thin, the flame front begins to grow rapidly and there is first evidence of a brighter white

reaction zone between the green reaction zone and the agglomerate surface, likely consisting primarily of BO , due to the dominant surface reactions, and B_2O_3 , due to diffusion back to the surface of the agglomerate.

A "whitish" envelope, encompassing the green zone, appears and its boundary is distinguishable due to the fluid dynamics of the situation (Figure 4.2d). It appears to be a streamline formed by the upward oxygen flow and outward velocity of reaction products (i.e. B_2O_3), where the velocity of the product gases are equal to the oxygen flow velocity. It is most likely a "diffusion envelope", through which oxygen can only diffuse to reach the inner reactions.

The diffusion envelope is noted to rise parallel to the fiber, in the direction of oxygen flow, above the agglomerate, rather than converge to the axis of the fiber, as would be expected for boundary layer phenomena relating to laminar flow around a body. It appears that this phenomena is likely due to a combination of both the fluid dynamics (i.e. analogous to uniform flow over a point source) and forced convection effects of the O_2 flow. In turn, these effects carry the products directly upward.

A rapid propagation of the flame front and its corresponding envelope occurs and proceeds until the entire agglomerate is encompassed and symmetry of flame fronts (reaction zones) is achieved (Figure 4.2e). The point at which this occurs is marked by the arrow in Figure 4.1a. Note

that the point at which the agglomerate becomes completely encompassed by the flame front does not coincide with the absolute maximum peak of the radiation intensity history. Steady, full-fledged combustion follows and accounts for a majority(i.e. 80%) of the total event time. Since the reproduction of the 16 mm film(Figure 4.2) decreases the clarity of the images, an illustration of one particular stage of the full-fledged combustion from this particular experiment is presented in Figure 4.3. Approximate dimensions are given.

The diffusion envelope, which appears very faintly in Figure 4.2e, is approximately 3400 μm in diameter at this point. This full-fledged combustion period is marked by a steady diameter decay where the ratio of apparent green flame front diameter to agglomerate diameter remains relatively constant. It is however difficult to clearly distinguish the outline of the agglomerate. In addition, there is a steady decrease in both the radiation and surface temperature curves.

The apparent thickness of the green band is relatively constant around the circumference of the agglomerate. Also, molten boron oxide can be seen to accumulate on the SiC fiber, just above the remaining agglomerate, in the wake region outside the flame zone, where it is likely the temperature at this point is less than 2316 K(Figure 4.2f).

As the agglomerate diameter has decayed, nearing complete consumption, the diffusion envelope disappears(i.e. gas-phase reaction becomes less prominent) and the apparent diameter of

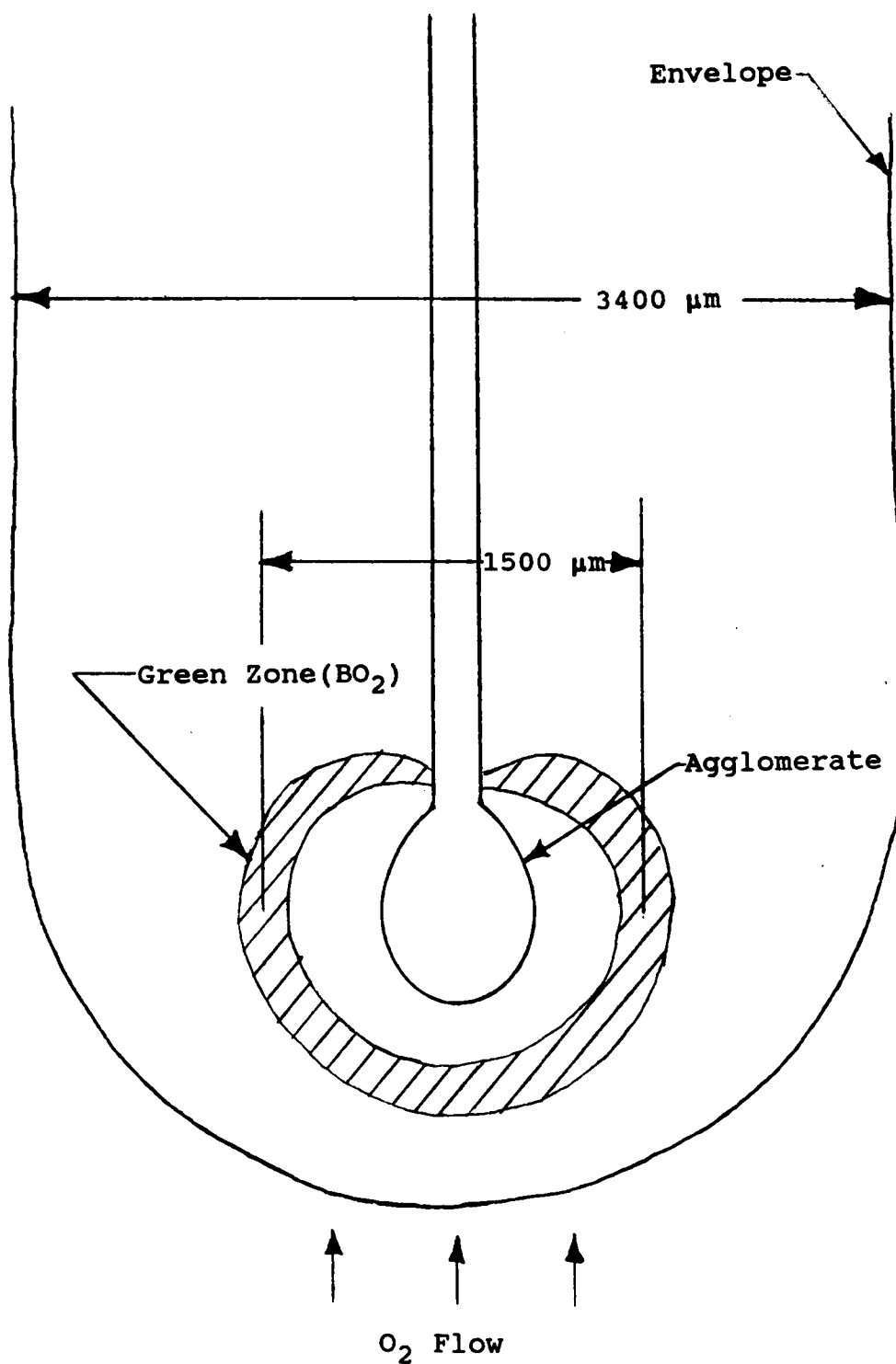


Figure 4.3 - Illustration of Steady Boron Agglomerate Combustion at 600 msec. Oxygen Flow = 37.1 cc/min, $d_o = 697\ \mu\text{m}$.

the green front shrinks drastically until the event is complete. A corresponding rapid decay of the radiation and temperature histories starts at about 1800 msec and continues until the end. After the experiment, a small amount of B_2O_3 , evident as a fine, white powder, is observed on the SiC fiber. The burning time for this particular agglomerate was determined to be 2420 ± 20 msec, from the pyrometer and radiometer histories. Note, that the ignition delay time was determined to be approximately 30 msec for this particular case, about 1% of the total burning time. Thus, the ignition delay time can be considered negligible.

4.3 DIAMETER EFFECTS

One of the main objectives of the investigation was to determine the effect of diameter on the combustion phenomena (i.e. burning time) of boron agglomerates in a flowing oxygen environment. Several boron agglomerates were produced and consumed for the following five chosen diameter variations: 350 μm , 500 μm , 700 μm , 900 μm and 1100 μm . Since the agglomerate production process is controllable to only about ± 10 μm for the smaller agglomerates and about ± 40 μm for the larger agglomerates, diameters varied slightly for each set. For the sake of discussion, the mean agglomerate diameter value of each of the five sets will be referred to, and they are as follows: 354 μm , 515 μm , 674 μm , 889 μm , and 1107 μm .

To better discuss diameter effect on the ignition and

combustion phenomena of boron agglomerates, the most "typical" radiation and temperature history found in each diameter set is used. The experimentally determined burning times for each individual agglomerate are shown in Appendix C.

The intensity/temperature histories for agglomerate diameters corresponding to 334 μm and 512 μm are shown in Figures 4.4 and 4.5, respectively and depict very similar trends. The ignition temperature(2316K) is reached at approximately 20 msec in each case. After the initial peak corresponding to the laser duration, and subsequent ignition, a decrease in intensity and a slight decrease in temperature occurs, followed by a rapid increase to a (maximum) peak, most likely occurring after the propagation of flame fronts, thus encompassing the entire agglomerate. This maximum peak occurs at a point after approximately 40% of the total event time has elapsed, in both cases.

After the peak, the radiation and temperature curves begin a decay, accompanied by an observable phenomenon referred to as "particle ejection". This phenomenon was observed for most of the 354 μm and 515 μm agglomerates used in the study. It is characterized by "spiking" of the radiation and temperature history curves. The following explanation of particle ejection is given:

Consider two spherical particles of radii, r_1 and r_2 , where

$$r_1 > r_2$$

A ratio of surface area to volume of a spherical particle is

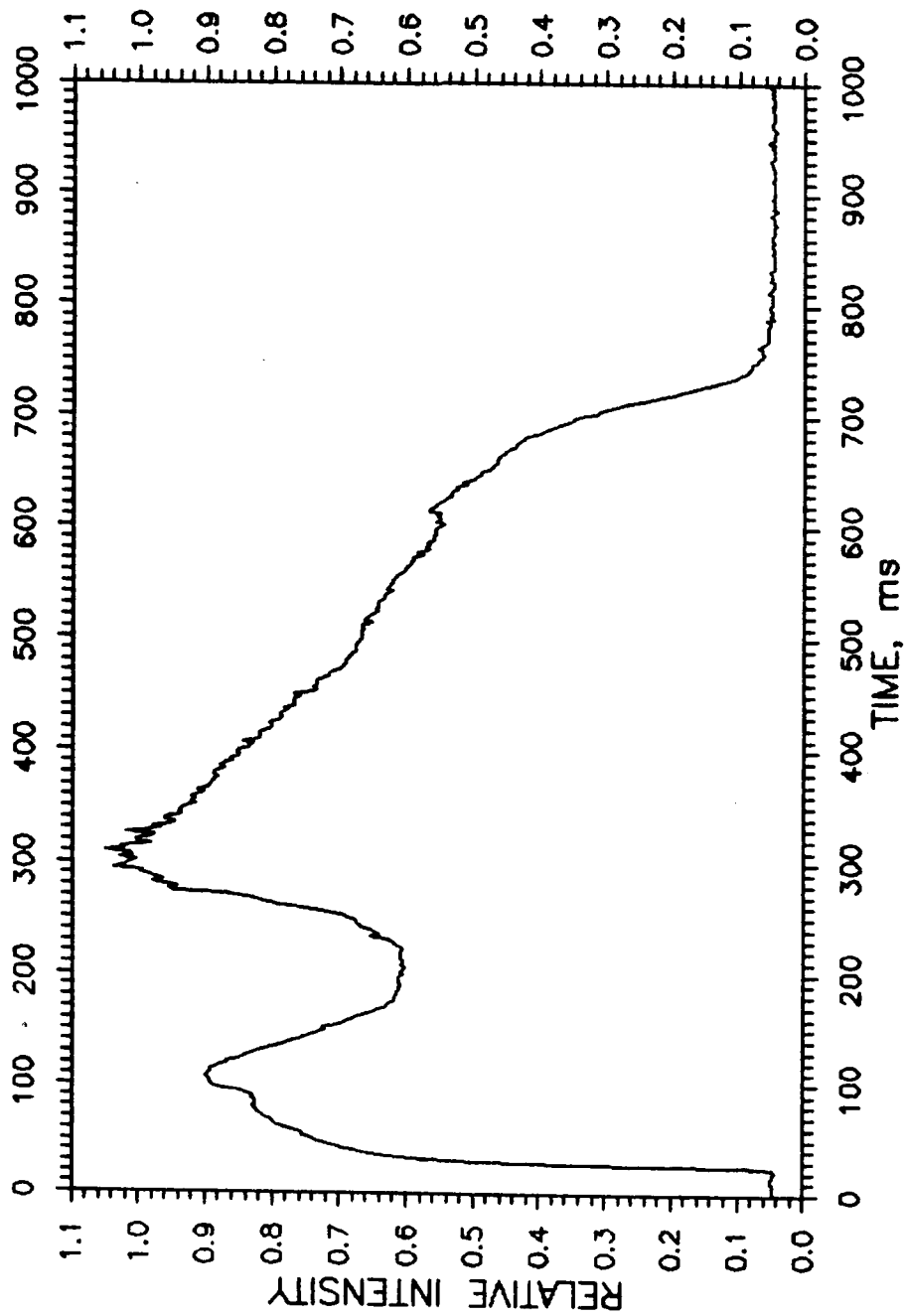


Figure 4.4(a) - Agglomerate Diameter = 334 μm :
Radiation History

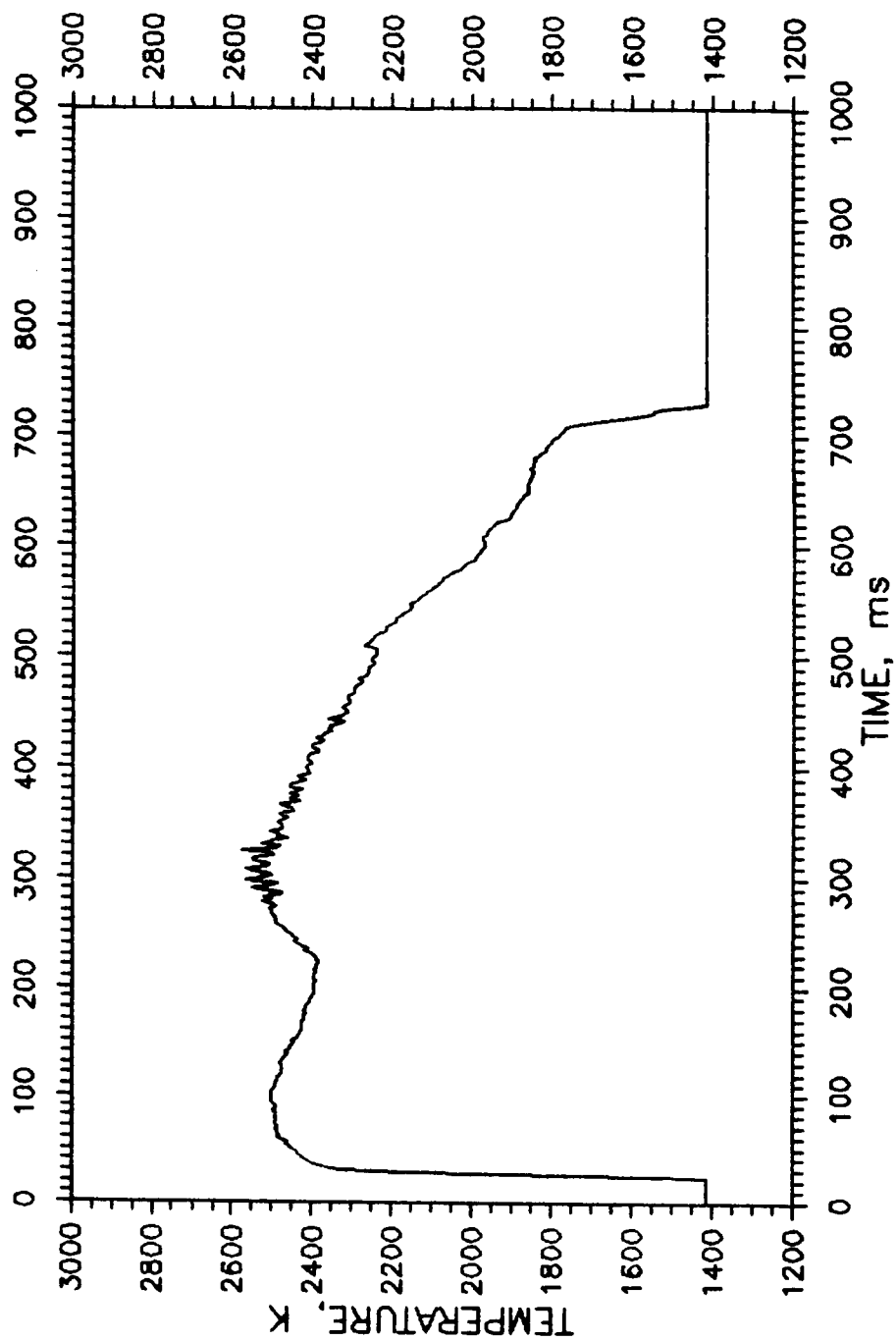


Figure 4.4(b) - Agglomerate Diameter = 334 μm :
Surface Temperature History

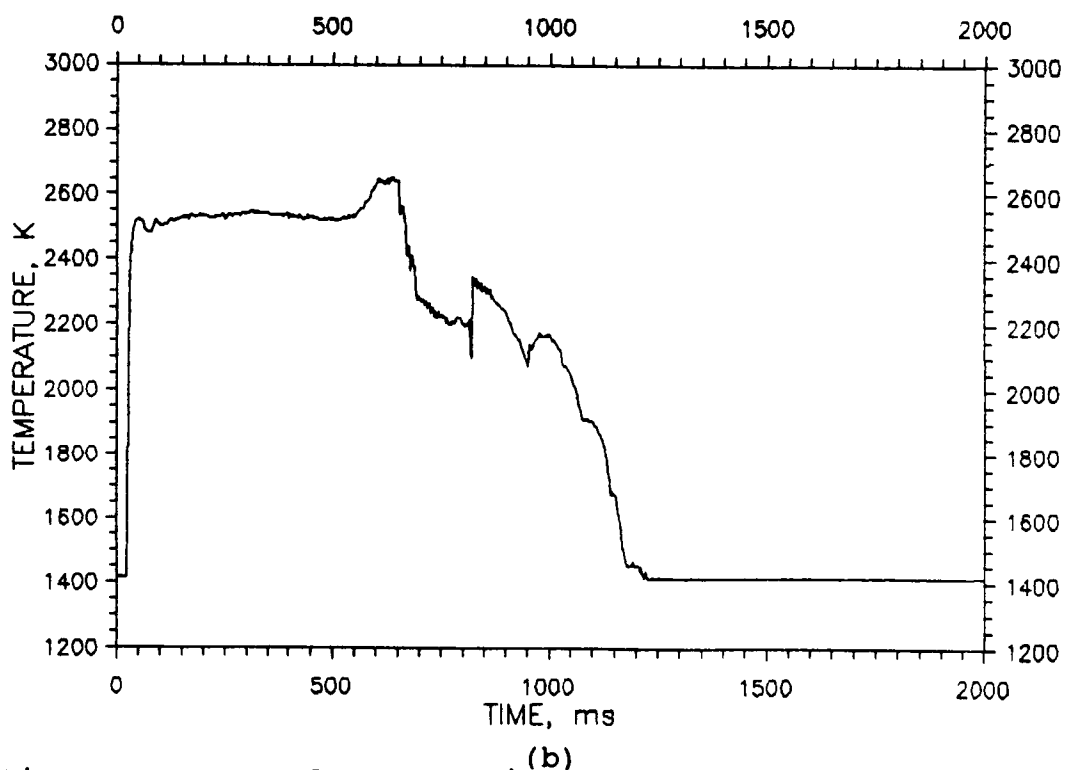
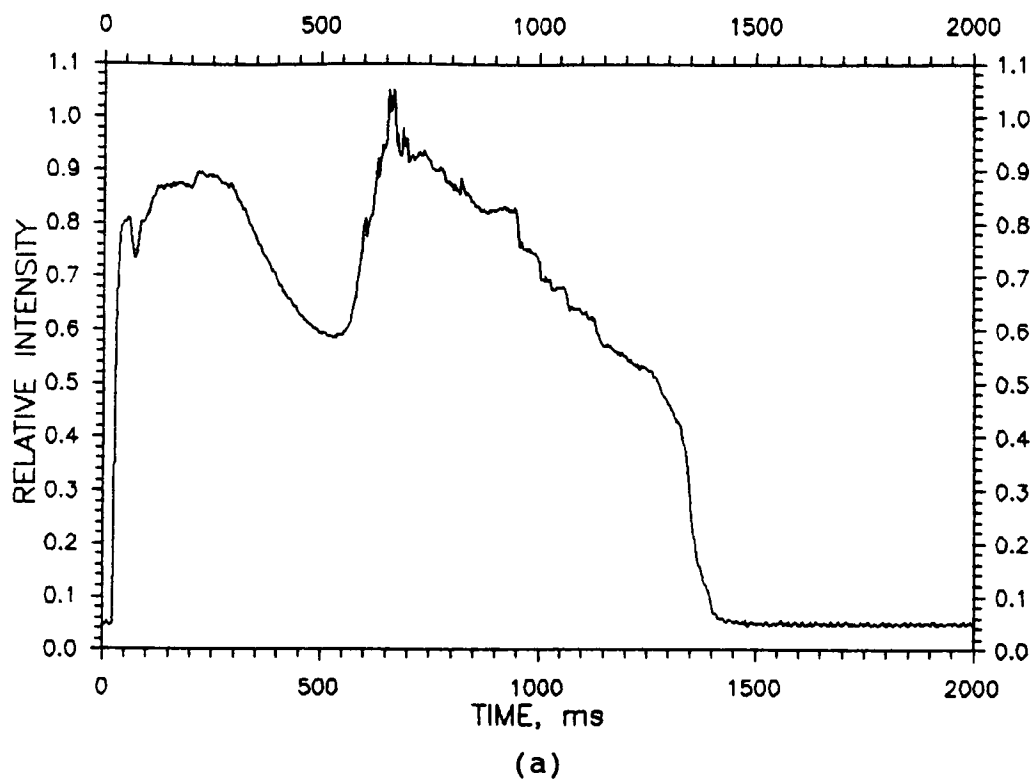


Figure 4.5 - Agglomerate Diameter = 512 μm : (a) Radiation History, (b) Surface Temperature History

$$\frac{\text{S.A.}}{\text{Vol.}} = \frac{4\pi r^2}{(4/3)\pi r^3} = \frac{3}{r}$$

Therefore for the two particular particles, $A_2/V_2 > A_1/V_1$, which shows that the smaller diameter particle has more reactive surface area per unit volume. Thus, the chemical reactions at the surface are more prominent(relative), in general, than the heat conduction into the particle for the smaller diameter particles. The apparent higher surface activity can result in a pressure build-up beneath the surface, causing the expulsion of trapped gases, which in turn expel fragments of the particle surface. It should be noted that a qualitatively similar phenomenon was observed by Takahashi et al[8] in their combustion study of boron slurry droplets.

It is likely the agglomerate is a molten droplet during the particle ejection period, due to the noted high temperatures achieved(2450K, i.e. melting temp. of boron). Since the pyrometer surface temperature measurement reaches nearly 2600K during the full-fledged combustion stage, it appears almost certain that boron melting does occur. This fact has yet to be proven in past research. The final stage of the event is marked by the gradual decay of both the radiation and surface temperature curves to the end of the event.

From the two-color pyrometer and broadband radiometer data, it is determined that the burning times are 750 msec and 1420 msec, respectively, from the "typical" histories of the two

smallest agglomerate diameters, and a maximum surface temperature of about 2600K was recorded in both cases. The ignition delay times are less than 3% of the total burning time for each case, therefore are considered negligible.

The typical radiation/temperature histories for agglomerate diameters corresponding to 685 μm and 908 μm are shown in Figures 4.6 and 4.7, respectively. The histories show a slight change in trends from the aforementioned smaller agglomerates. Ignition delay time is again small enough to be considered negligible. The initial peak of both histories, corresponding to the laser pulse, is followed by a smaller decrease in the intensity and a quicker return to the (maximum) peak value. A much smaller percentage(20%) of the total event time is consumed before full-fledged combustion is achieved.

Relatively steady, self-sustained combustion period follows, marked by a steady, but slow decrease in intensity and a steady, but slow increase in temperature over a period of time which makes up 50-60% of the total event time. This "steady" period is immediately followed by a rapid decay of both graphs, leading to the end of the event and complete combustion. The burning times are determined from the instrument histories to be approximately 2400 ± 30 msec and 3650 ± 40 msec, respectively. In addition, a maximum surface temperature reading of about 2700K was achieved during the event. Fewer fluctuations in the histories over time also indicate a seemingly steadier combustion than observed in the

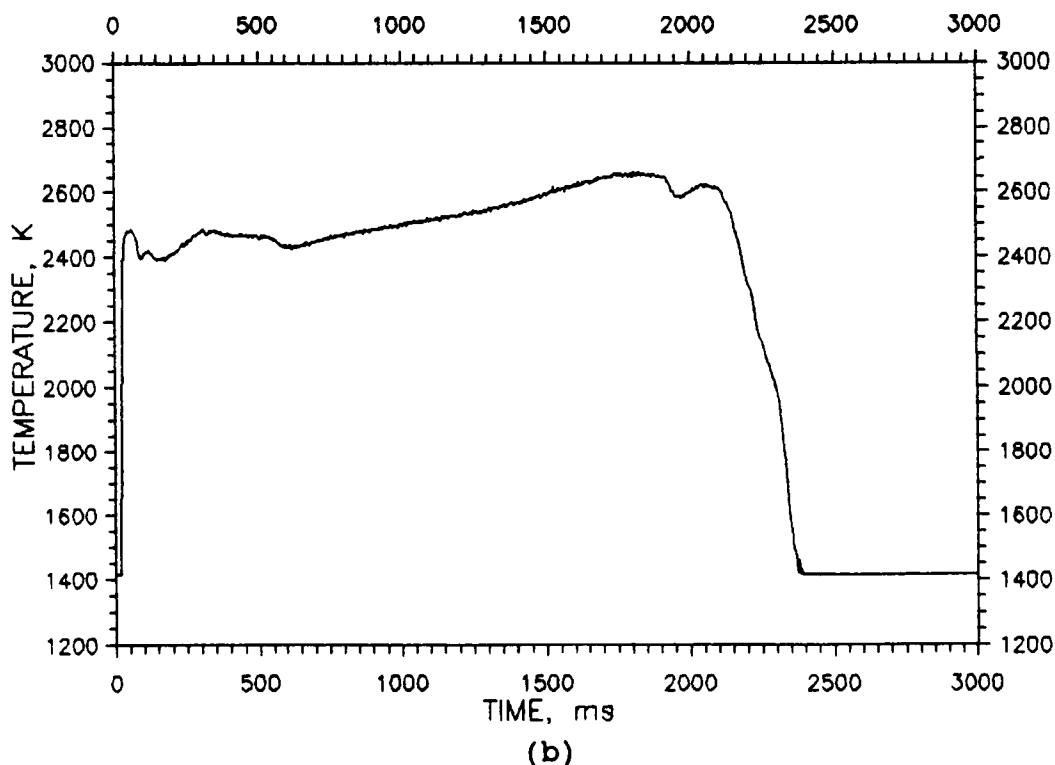
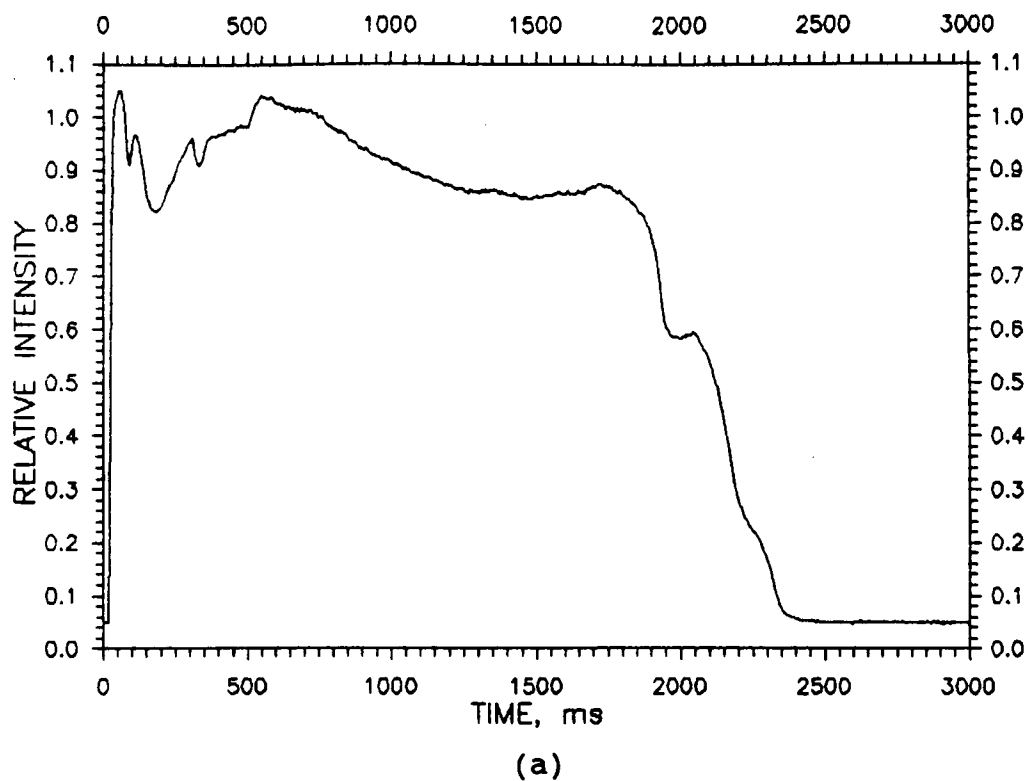


Figure 4.6 - Agglomerate Diameter = 685 μm : (a) Radiation History, (b) Surface Temperature History

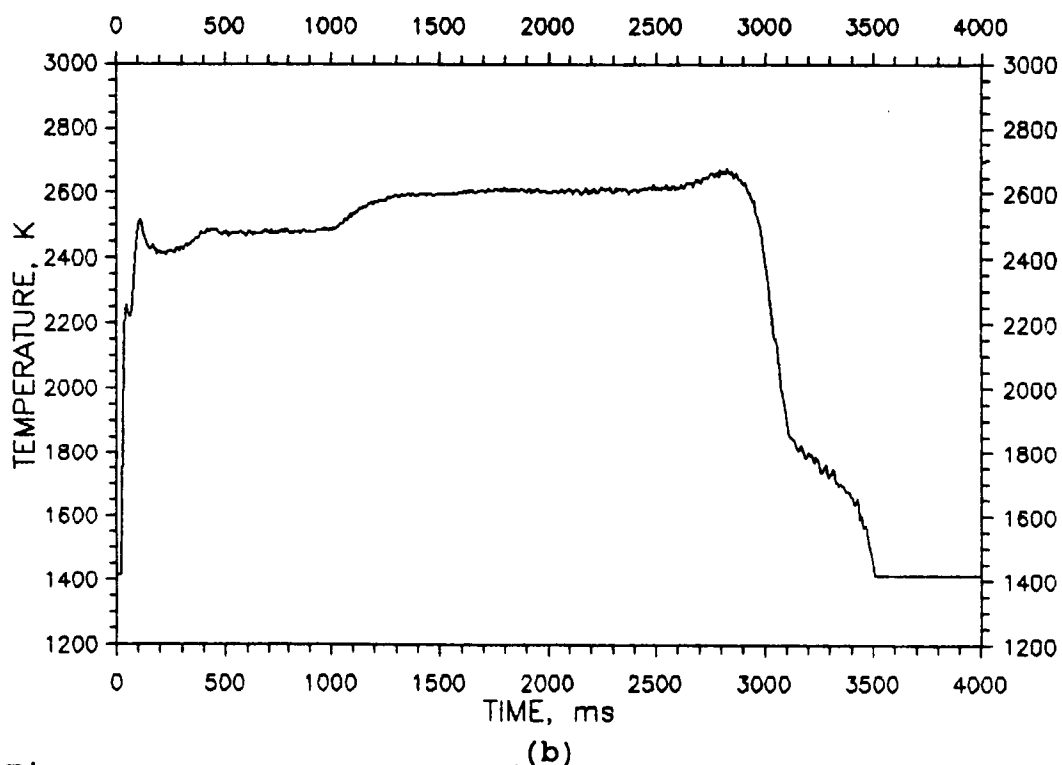
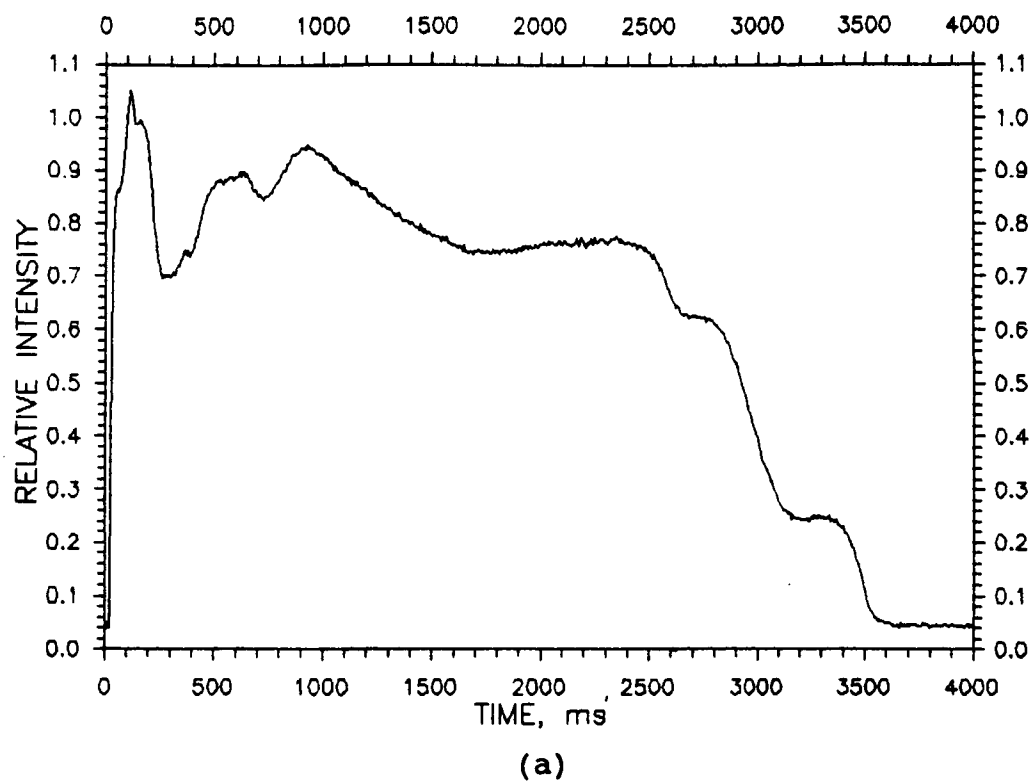


Figure 4.7 - Agglomerate Diameter = 908 μm : (a) Radiation History, (b) Surface Temperature History

smaller agglomerate cases.

The radiation/temperature histories for agglomerate diameter corresponding to $1107\text{ }\mu\text{m}$ are shown in Figure 4.8. The typical case shows very similar trends in surface temperature history graph that were seen in the previous two sets, however the radiation history is markedly different. Ignition delay time is again negligible. The temperature peaks initially, followed by a slow, steady increase through steady combustion, until a drastic decay near the end of the event. The intensity curve shows the initial peak corresponding to the laser pulse, but in this case, drops to a minimum shortly following, and remains low and relatively constant for the remainder of the event until the agglomerate is completely consumed. This implies "very steady" combustion and this period accounts for 65-75% of the total event time. The burning time for this particular case was determined to be approximately 5250 ± 50 msec and the maximum temperature achieved during the event was about 2700K, as measured directly by the two-color pyrometer. In general, it appears that increasing the agglomerate diameter results in steadier combustion.

It has been shown, the burning times for each agglomerate can be readily determined for each experiment from the two-color pyrometer and broadband radiometer data following the event. The uncertainty in determining the burning time is small in comparison to the magnitude of the total burning time itself. No calculations or processing is necessary to

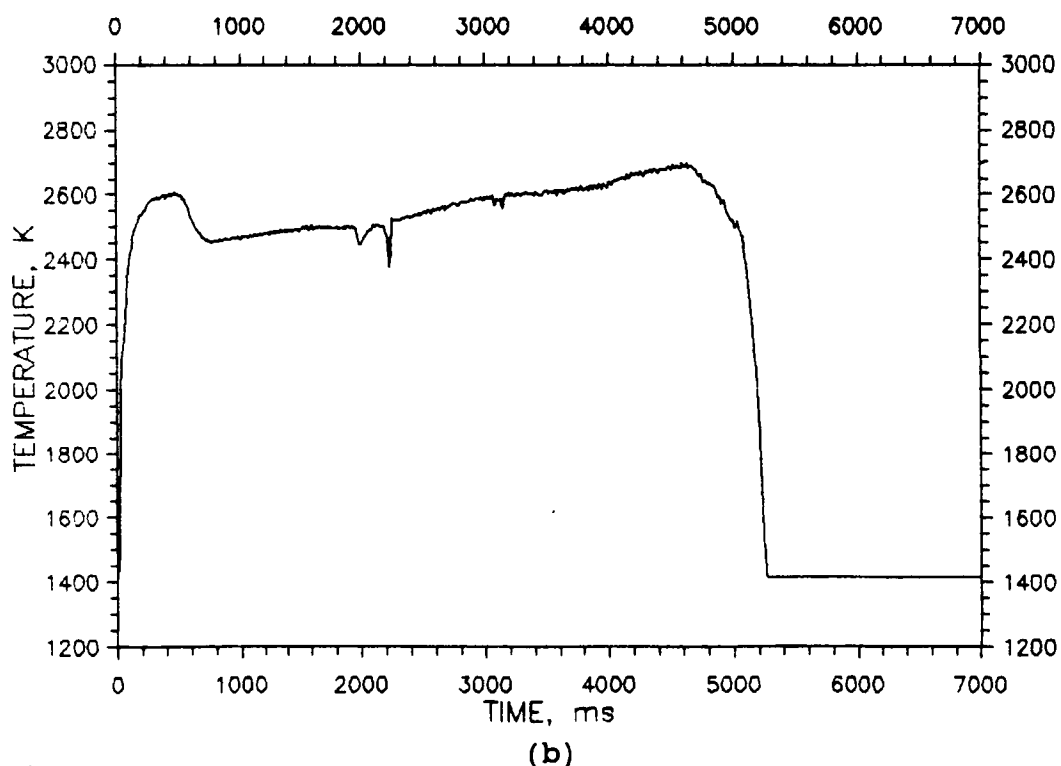
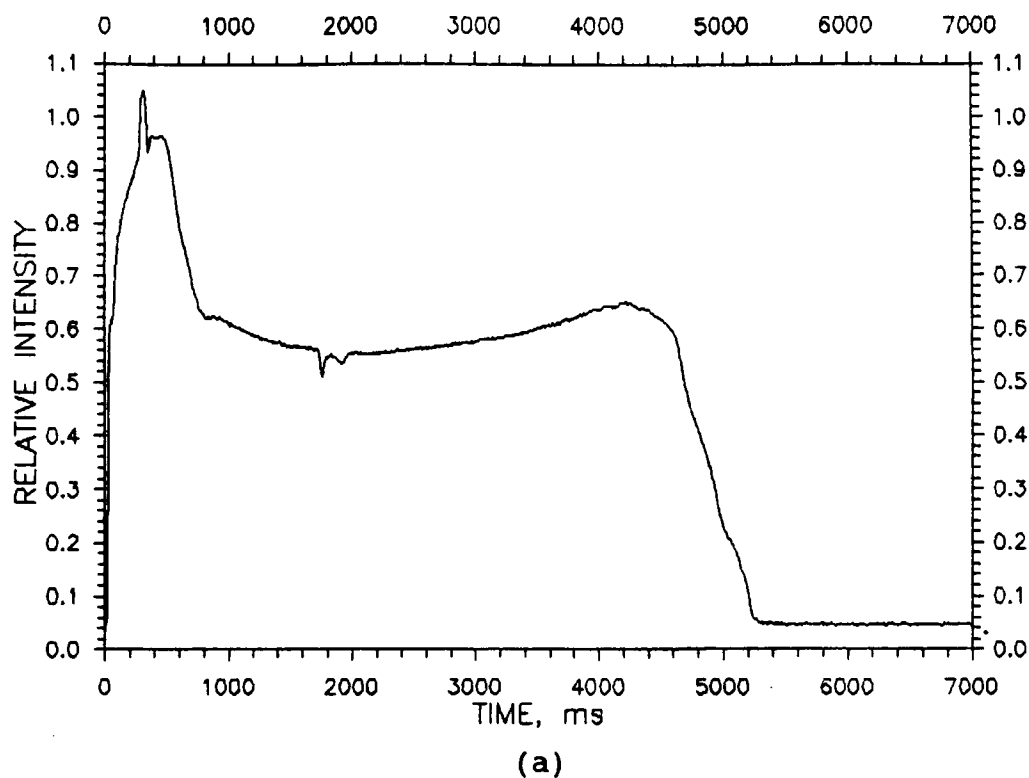


Figure 4.8 - Agglomerate Diameter = 1145 μm : (a) Radiation History, (b) Surface Temperature History

determine burning times as in previous study, for the data acquisition is instantaneous.

It is also evident in the temperature histories of each "typical" case discussed, as well as each individual case, that the temperature measured directly by the two-color pyrometer exceeds 2450K (melting point of boron) in each case, reaching nearly 2700K in some cases. Thus, it appears from the instrument data that boron melting (at surface) does occur consistently in boron agglomerate combustion.

The effects of diameter on the burning time are of primary interest in this study, to determine the burning mechanism. To summarize the findings, an average agglomerate diameter and corresponding average burning time were determined for each of the five agglomerate sets, based on the data in Appendix C. These experimentally determined average burning times are shown in Table 4.2. Figure 4.9 shows a plot of the square of agglomerate diameter vs. burning time for the each agglomerate of each diameter set consumed in the study. The linearity of the graph confirms the existence of the " d^2 law" for boron agglomerate combustion, where combustion depends on diffusion of oxidant to the surface of the agglomerate. It can thus be stated that the burning mechanism is diffusion-controlled for the range of agglomerate sizes used in the study. It is expected, from previous study [14], that agglomerates less than about 100 μm would deviate from d^2 behavior, thus exhibiting kinetics-controlled behavior, where combustion depends on the

Table 4.2 : Average Burning Times

Agglomerate Diameter(μm)	Burning Time(msec)
354	748 $\pm$ 124
515	1425 $\pm$ 125
674	2358 $\pm$ 322
889	3460 $\pm$ 650
1107	5037 $\pm$ 552

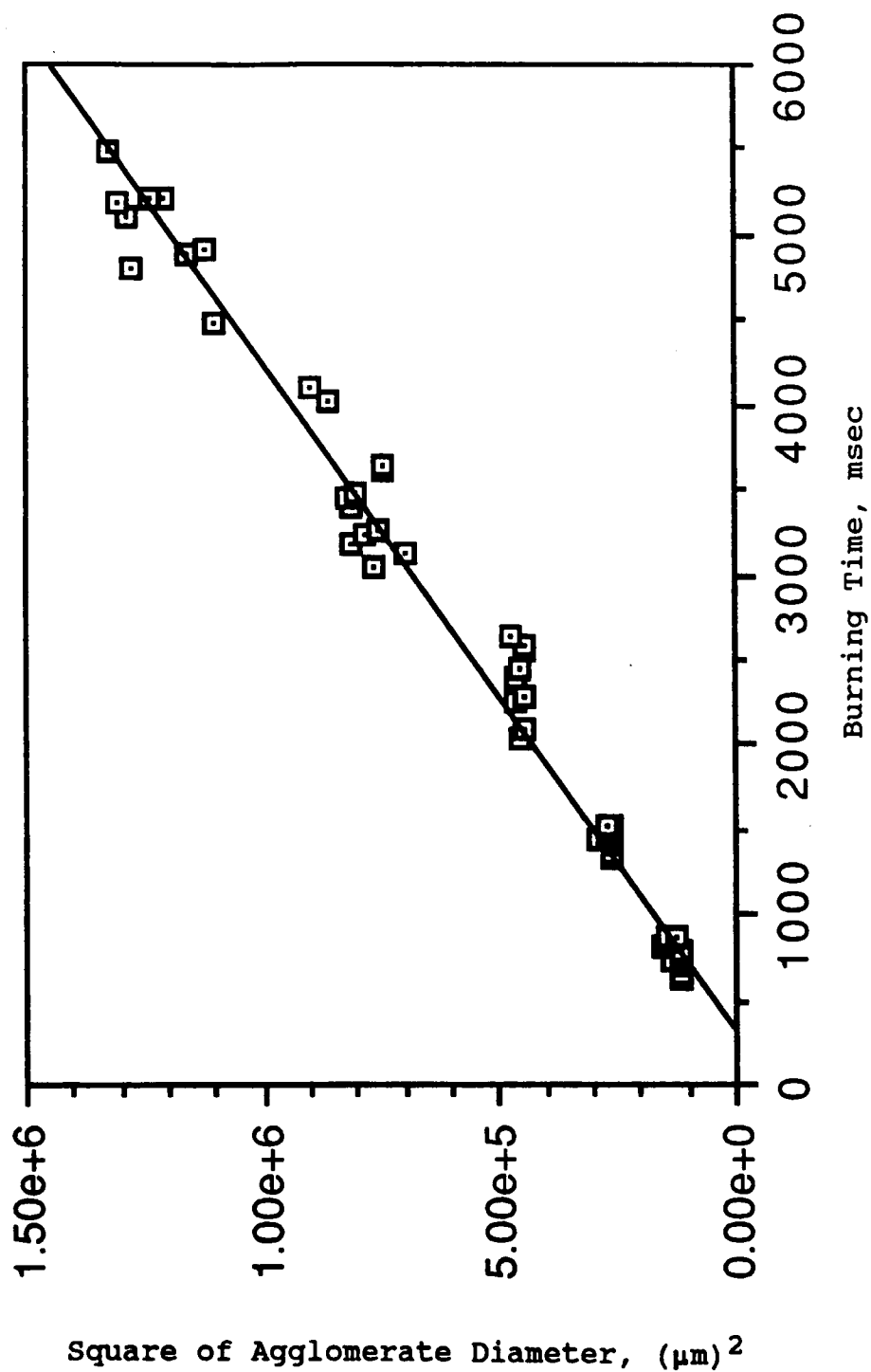


Figure 4.9 - Square of Agglomerate Diameter vs. Burning Time

reaction kinetics.

4.4 INCREASED OXYGEN EFFECTS

Although the oxygen flow rate was consistent for each experiment in the study, a few agglomerates were consumed at a higher oxygen flow rate (151.8 cc/min) and filmed with the Hycam to observe the effects of higher flow rate. The radiation and surface temperature histories are shown in Figure 4.10 and the progressive combustion stages for the higher oxygen flow rate are illustrated in Figure 4.11.

The initial stages are similar to the previous case, with an immediate appearance of the green(BO_2) front (Figure 4.11a) and rapid front growth (Figure 4.11b), however, following the laser pulse, the flame front immediately begins a rapid propagation and the entire agglomerate is completely consumed at a point much sooner (relative) than in the lower oxygen flow rate case (Figure 4.11c) discussed in Section 4.2. The concentricity of reaction zones as seen in the lower oxygen flow case is not seen in this case which is directly attributed to the higher oxygen flow rate. An illustration of the event at approximately 350 msec is shown in Figure 4.12.

The apparent outer diameter of the green reaction zone is also much larger relative to the apparent agglomerate diameter and the brighter white zone near the agglomerate surface is more prominent than in the previous case. This is due to the increased oxygen available supplying the dominant surface

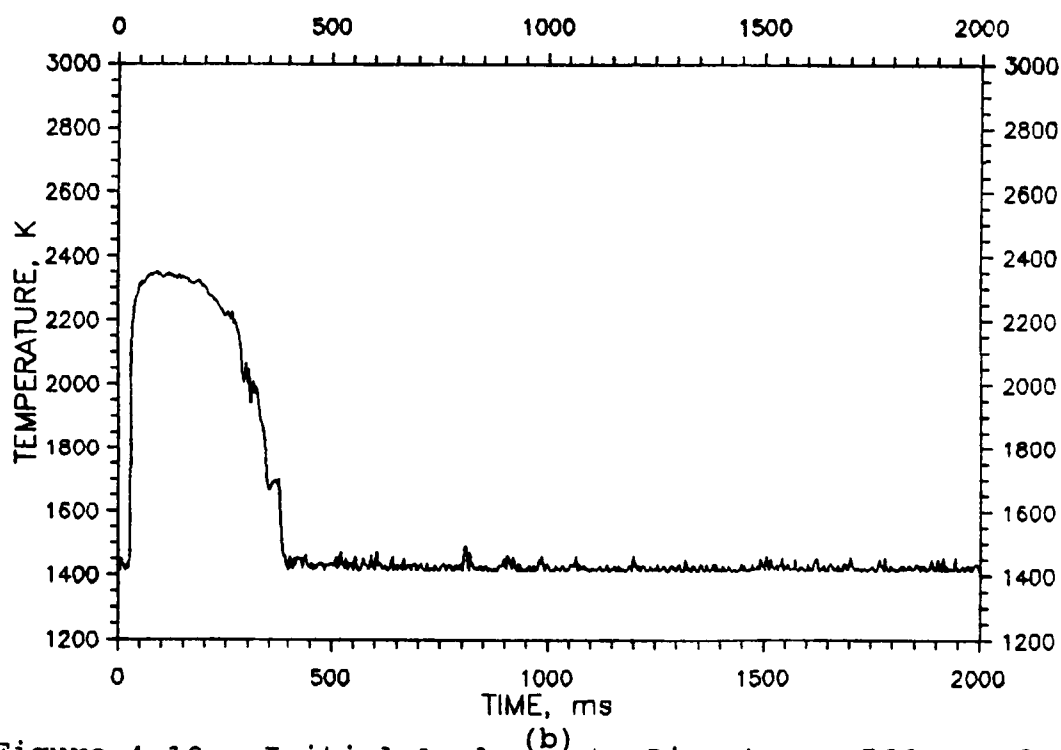
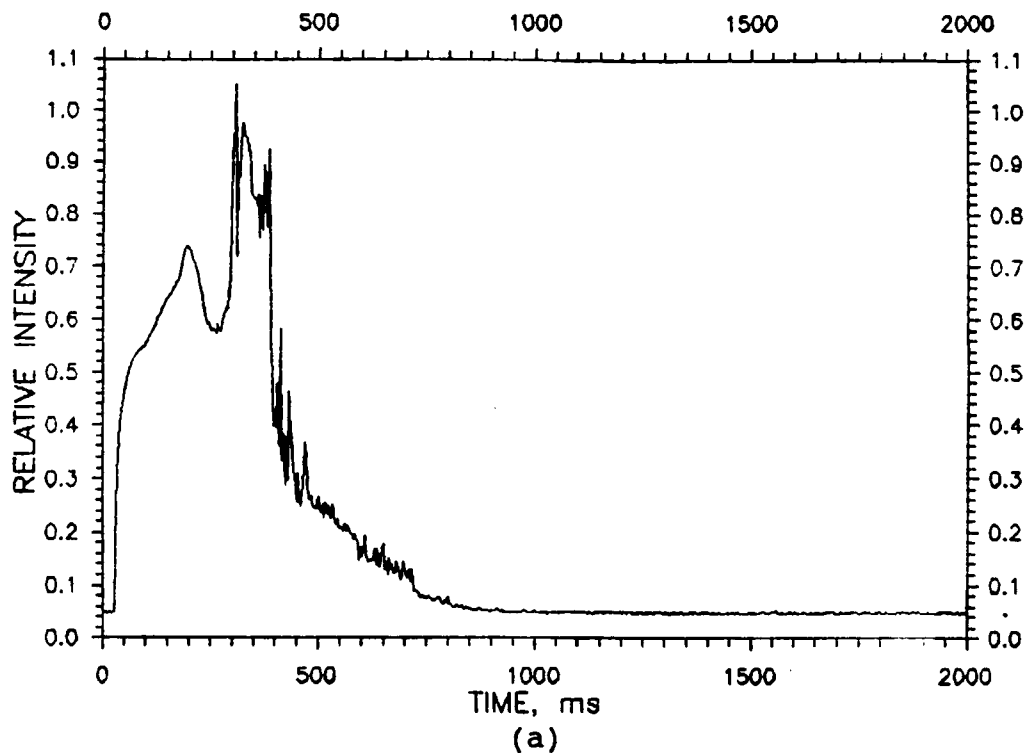


Figure 4.10 - Initial Agglomerate Diameter = 566 μm , Oxygen Flow = 151.8 cc/min: (a) Radiation History, (b) Temperature History.



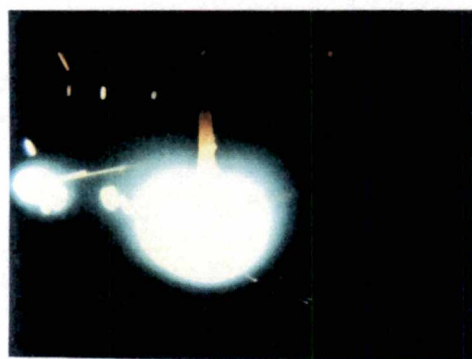
(a)



(b)



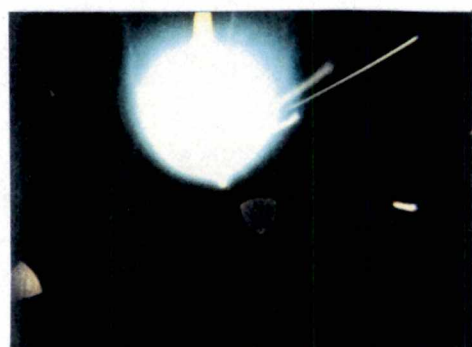
(c)



(d)



(e)



(f)

Figure 4.11 - Progressive Stages of Combustion Phenomena
Recorded by High-Speed Cinematography;
 $d_o = 566 \mu\text{m}$, Oxygen Flow = 151.8 cc/min:
(a) Time = 15 ms, (b) 30 ms, (c) 55 ms,
(d) 300 ms, (e) 510 ms, (f) 725 ms

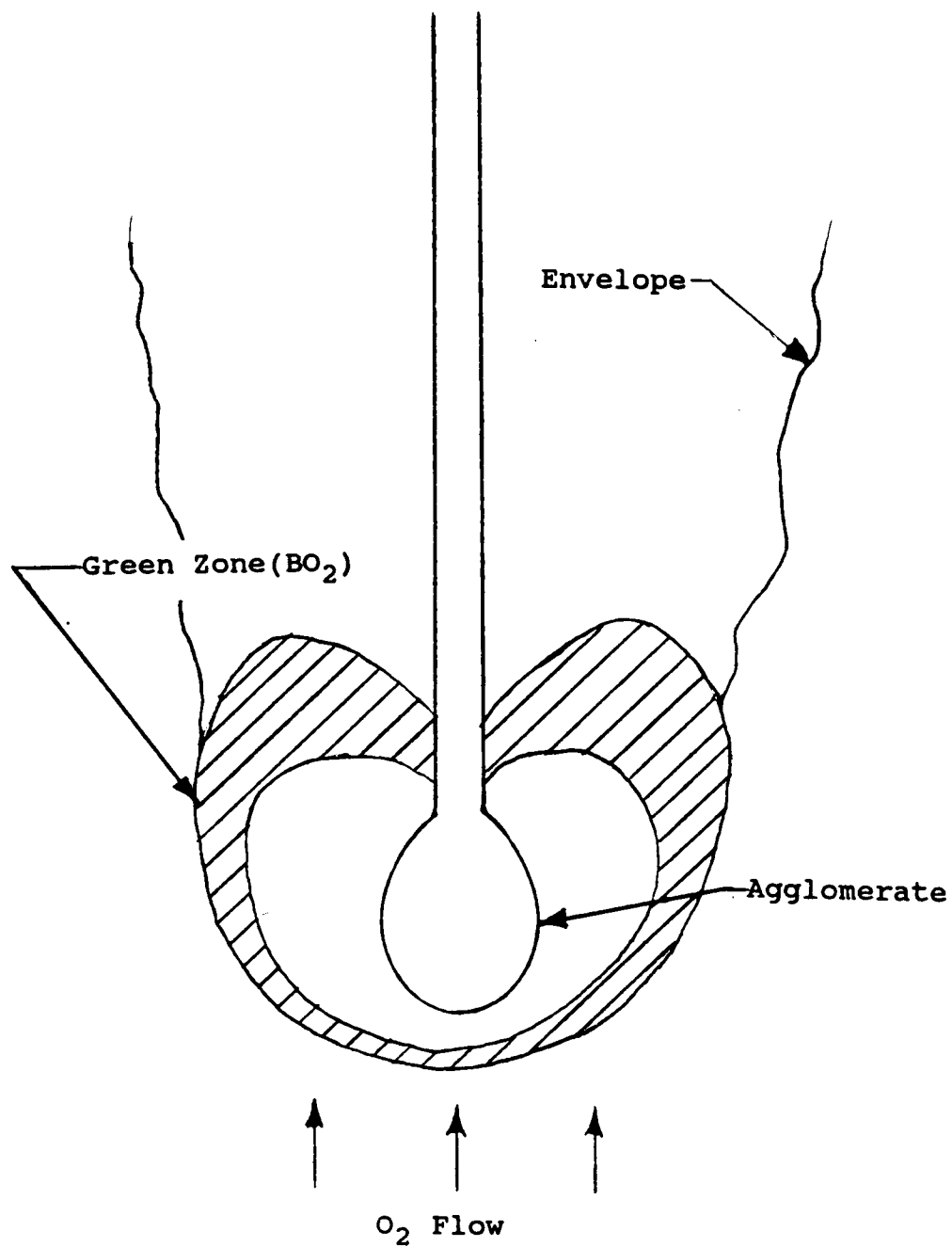


Figure 4.12 - Illustration of Transient Boron Agglomerate Combustion at 350 msec. Oxygen Flow = 151.8 cc/min, $d_o = 566 \mu\text{m}$.

reactions. The particle ejection phenomena initiates relatively early in the event and occurs more violently with the increased oxygen(Figure 4.11d). It is observed that the particles ejected exhibit the same flame structure (green zone and inner white zone) as the boron agglomerate remaining on the SiC fiber. This indicates that the particles ejected are also molten droplets, thus most likely consumed rapidly after ejection, due to their relatively small diameters.

The violent particle ejection is coincident with noticeable agglomerate swelling, indicating the agglomerate is likely a molten boron droplet for a large portion of the event. Figure 4.11e illustrates one of the many occurrences of "swelling" and flame front movement during the event. The outer diffusion envelope observed in the previous case, is periodically observed, however, for the case of higher oxygen, it appears to be forced back to the outer edge of the green reaction zone and appears very faintly in Figure 4.11e. It is observed that the apparent thickness of the green zone at the point at which the oxygen flow first comes in contact with the agglomerate (leading edge) is significantly smaller than the thickness in the wake region(trailing end) of the flow. This is due to the fact that the increased oxygen flow speeds up the reaction sequence to readily allow an increased production of BO from the surface reactions and a more rapid formation of final products(B_2O_3) at the leading edge. In other words, the fuel does not need to travel as far to find its oxidizer. Also,

since the velocity of the oxygen flow is significantly higher than in the first case, it is expected that the point at which the velocity of the product gases is equal to the oxygen velocity, would be forced, by the flow, closer to the surface of the boron droplet.

In addition, the thickness of the green reaction zone, in the wake region at the trailing end, is also noticeably larger(relative) than the in the lower oxygen flow case(See Figure 4.3). It appears from limited study that a relative oxygen deficiency in the vicinity of the burning agglomerate causes a higher BO_2 concentration or merely a "slower" transition to B_2O_3 . Above the agglomerate, in the wake region, the diffusion envelope (turbulent in this case) can be seen, with its apparent diameter no larger than the outer diameter of the green zone. Again it appears that the envelope does not converge to the axis along the fiber(Refer to Figure 4.12).

The swelling of the molten boron droplet and the violent particle ejection in this case are accompanied by coinciding movements of the reaction zones, again depicting a more unsteady, violent event than the previous case with a lower oxygen flow rate. The radiation history also depicts the more violent combustion and particle ejection, seen as "spiking"(See Figure 4.10). In this case, the molten boron droplet is observed to move up the SiC fiber in the direction of oxygen flow during the latter stages of combustion, as the fiber itself is slowly consumed and the droplet moves nearly

out of view of the Hycam, as well as the radiometer and pyrometer. Although the fields-of-view of the pyrometer and radiometer are about 2-3 mm, it is possible that some error in the determination of the total burning time is introduced.

Violent combustion, which accounts for a majority of the event(i.e. 60%), continues until the fronts decay, reactions subside and the event is complete. A significant amount of solid "white" B_2O_3 remains on the SiC fiber after agglomerate consumption, verifying an increased production of B_2O_3 from the gas-phase reaction, resulting from an increased generation rate of the surface reactions producing BO, as is discussed in Appendix D.

It should be noted that the initial diameter of the agglomerate in this case was approximately 566 μm . The burning time for this diameter agglomerate would be expected to be on the order of 1600 msec for oxygen flow rate of 37.1 cc/min, according to the experimental findings. However, a burning time of 823 msec was achieved with the higher oxygen flow rate of 151.8 cc/min. Thus, it appears that increasing oxygen flow rate onto the boron agglomerate significantly increases the burning rate, thus significantly decreases the burning time.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDY

A primary objective of the present study has been to show the advantages of using the prescribed techniques in determining the total burning time of laser-ignited boron agglomerates. Although boron combustion phenomena is of primary concern in the present study, it should be noted that the techniques are applicable to any pulverized, liquid or slurry fuels that can be investigated within the limitations of the experimental method.

The use of the CO_2 laser as the ignition source significantly reduces the ignition delay time and allows the agglomerate to burn freely without the forced-burn apparent with hot oxidizing gas environment ignition. The use of the two-color pyrometer to measure surface temperature of the boron agglomerate during combustion is important because of the high temperatures achieved. It also allows an easy and effective means of determining the ignition point of the boron agglomerate. In the study, ignition (2316 K) was achieved during the laser pulse, therefore making the ignition delay time negligible with respect to the burning time.

By measuring the relative radiation intensity emitted during the combustion event, the broadband radiometer allows for an effective determination of total burning time (i.e. start to end), from which ignition delay time and burning time

can be approximated. Utilizing the data acquisition system, these values are determined immediately following each experiment, reducing the time consumption and expenses required for calculations and processing, using previous experimental techniques. Since it was found to be difficult to clearly distinguish the surface of the agglomerate during combustion, it appears unlikely that the point of initial rapid diameter decay could be determined as in Holl's study[7].

From the temperature histories, it is noted that in every case, the melting temperature of boron(2450 K) was achieved and exceeded(up to 2650 K), therefore it appears that boron does in fact achieve complete melting, at least at the surface. This phenomenon is also confirmed by the swelling observed in the high-speed cinematography. Thus, the combustion of boron agglomerates can be modelled as that of a molten "droplet." As a result of the present study, the d^2 law was shown to prevail for boron agglomerates, for the sizes investigated in the study. It is then confirmed that the burning mechanism is "diffusion-controlled", where the burning rate and, thus, burning time is dependent on the oxygen diffusion to the surface.

Another objective of the present study has been to detail the phenomenological events of boron agglomerate combustion in an oxygen flow environment. The Hycam results are important for the development of an accurate model. The results

confirmed the existence of BO_2 as a species involved in boron combustion reactions. Takahashi[13] observed similar phenomena in his study of the combustion of boron slurry droplets and Macek[4] observed an outer "green" zone during boron particle combustion, however he did not indicate its origin. Holl et al[2], however, did not consider BO_2 as a gas-phase product in the formulation of their theoretical model. It therefore appears that accurate modeling requires inclusion of BO_2 .

Some discrepancy may be inherent in the definition of "ignition point" in the present study. The ignition point has been defined as the point at which "any" point on the agglomerate surface reaches 2316 K (boiling point of B_2O_3). It was observed in the high-speed cinematography that ignition is localized and there exists a finite, transient period from the point of localized ignition to the point at which the entire agglomerate is surrounded by the flame front. This time has been included in the total burning time. To help alleviate this in future study employing laser ignition technique, it is suggested that a beam splitter be installed in the location of mirror M_3 (See Figure 3.1) to allow equal amount of the laser power to strike on opposite sides of the suspended agglomerate, thus minimizing the time from laser exposure to the point at which steady, full-fledged combustion is attained.

Since combustors operate at high pressures (>20 atm), it is also suggested that similar experimentation be performed using

a combustion chamber, allowing pressure variation in a quiescent environment. The effects of high pressures($>> 1$ atm) and oxygen concentration on the phenomenological events of boron agglomerate combustion can be investigated and compared to the results found in the present study at 1 atm in a oxygen flowing environment.

It has subsequently been shown that decreasing the boron agglomerate diameter, increases the burning rate, thus decreasing the burning time. Therefore, minimizing the diameter of the droplets in a boron slurry spray, optimizes the efficiency of the fuel. The lifetime of the largest droplet diameter in a slurry spray dictates the minimum time the droplet should be allowed to reside in the combustor. Perhaps the "particle ejection" phenomena that was observed in the present study could be investigated further to find ways to enhance the particle ejection. Enhancing it to such a point that the entire droplet is rapidly transformed to several smaller droplets, smaller than can be achieved by controlling the slurry spray, thus leading to a decrease in overall burning time.

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APPENDICES

APPENDIX A
BURNING MECHANISM THEORY

In combustion studies, it is essential to know under what conditions the combustion rate is controlled by mass transfer or by chemical kinetics. This is important when designing liquid or slurry-fueled rockets, gas turbines, etc. Designers must understand the chemical mechanisms of the combustion, where they occur and how the operating conditions influence the combustion mechanism, to optimize efficiency. The "burning mechanisms" considered are mass transfer-controlled (i.e. "diffusion-controlled") and chemical kinetics-controlled (i.e. "kinetics-controlled").

In theory, single spherical fuel droplets or particles combust as a diffusion flame in an oxidizing environment as shown in Figure A.1. A fuel spray could then be treated as a group of individual droplets. Theoretical combustion of single particles, phenomenologically similar to the combustion of droplets, can be divided into two distinct stages. The early combustion stage is marked by an evaporation of volatile components, followed by the latter stage marked by a slower, heterogeneous combustion of an involatile residue (i.e. full-fledged combustion). The distinction of the burning mechanism applies to the full-fledged combustion stage.

Theoretically, for diffusion-controlled burning, oxygen molecules from the oxidizing environment react instantaneously at the particle surface to form a gaseous product. The following expression was derived for the reaction rate according to diffusion-controlled burning of a pulverized fuel

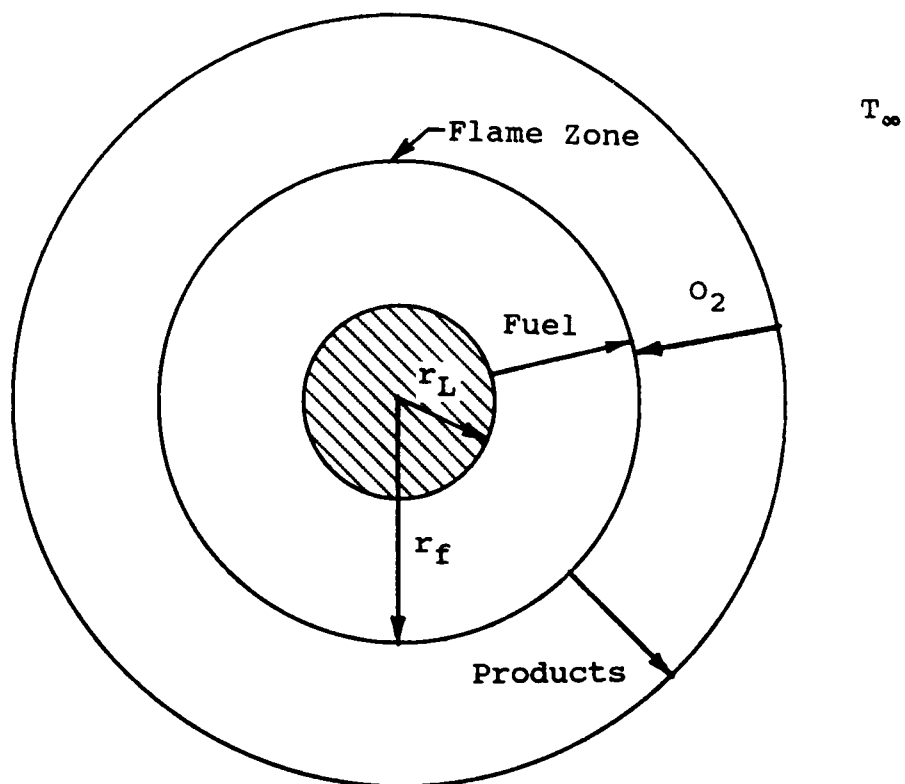


Figure A.1 - Model of Droplet Combustion

particle[14]:

$$R_p = \frac{3(D_o(f_m/d) \rho_o (T/T_o)^{0.75}}{2} \quad (A.1)$$

where ρ = gas density
 D = diffusion coefficient
 d = particle diameter
 f = oxygen mass fraction
 o = standard conditions
 T = reaction temperature

From the expression, it is noted that the reaction rate is a function of particle diameter, but not a function of pressure. An increase in particle diameter would decrease the reaction rate, thus increasing the burning time.

For kinetics-controlled burning, oxygen molecules require a finite time to react at the surface. A similar rate expression is derived for the reaction rate according to kinetics-controlled burning[14]:

$$R_k = [(2M_{O_2}P_{O_2})/(2\pi RTM_{O_2})^{0.5}] \exp(-E/RT) \quad (A.2)$$

where M = molecular weight
 P = oxygen partial pressure
 R = gas constant
 T = temperature
 E = activation energy

It is noted that the reaction rate for this case is proportional to the bulk oxygen concentration, but not proportional to particle size. An increase in pressure or an increase in temperature would increase the reaction rate, decreasing the burning time.

The overall reaction rate is a contribution of both the kinetics-controlled reaction rate and the diffusion-controlled

reaction rate and can be expressed as:

$$R_T = 1/(1/R_D + 1/R_K) \quad (A.3)$$

where R_D = diffusion-controlled
reaction rate
 R_K = kinetics-controlled
reaction rate

Therefore, if the kinetics of the chemical reaction is very high, the reaction is limited by the mass transfer rate and vice versa. From Equation A.1, if the fuel particle diameter is decreased, the rate of mass transfer at some point will become much greater than the rate of chemical reaction, thus R_K becomes rate-controlling at that point. It has been experimentally determined that kinetics-controlled burning is dominant for particles less than approximately 100 μm in diameter.

Assuming the fuel is a liquid "droplet", the mass burning rate is shown to be related to the decrease in droplet size by the following expression:

$$\dot{m} = \frac{d}{dt} \left(\frac{4}{3} \pi r^3 \rho \right) \quad (A.4)$$

where r = droplet radius
 ρ = droplet density
 m = mass of droplet

Manipulating Equation A.4 gives the following expression:

$$\frac{d}{dt} (d^2) = \frac{3 \dot{m}}{\rho \pi r} \quad (A.5)$$

where d = droplet diameter

The right-hand side of Equation A.2 is commonly referred to as the "burning rate coefficient". It has been shown experimentally that the burning time of a fuel droplet is proportional to the square of the droplet diameter[17]. This relation is commonly referred to as the " d^2 law" and is prevalent in diffusion-controlled combustion.

It should be noted that expressions derived to quantify the droplet combustion are based on the droplet "evaporation" rates, but are applicable for droplet "burning".

APPENDIX B

TWO-COLOR PYROMETER THEORY, CIRCUITRY AND CALIBRATION

B.1 THEORY OF TWO-COLOR PYROMETRY

By using Wien's Law[18], it can be shown that for a body radiating at wavelength λ and temperature T , with corresponding spectral emissivity ϵ , the current output of a silicon photodiode detector can be expressed as follows:

$$I = \tau_o(\lambda) \tau_f(\lambda) \mathfrak{R}(\lambda) \epsilon(\lambda, T) C_1 \pi^{-1} \lambda^{-5} \exp(-C_2/\lambda T) \omega A \Delta\lambda \quad (\text{B.1})$$

where τ_o $\equiv$ overall transmittance
 τ_f $\equiv$ interference filter transmittance
 $\mathfrak{R}$ $\equiv$ responsivity of photodiode
 C_1 $\equiv$ first Planck's constant
 C_2 $\equiv$ second Planck's constant
 ω $\equiv$ solid angle subtended by target
 A $\equiv$ target area

The following assumptions were made to achieve the preceding equation: $\tau_o(\lambda)$, $\tau_f(\lambda)$ and $\mathfrak{R}(\lambda)$ are constant over a narrow bandwidth $\Delta\lambda$ of the interference filter and, thus, λ is a "mean effective wavelength."

In two-color pyrometry, two wavelengths, λ_1 and λ_2 , are of interest. The ratio of the current outputs, R , of the two silicon photodiode detectors can be expressed as:

$$R = B(\lambda_2/\lambda_1)^5 \frac{\epsilon(\lambda_1, T)}{\epsilon(\lambda_2, T)} \exp[-C_2(1/\lambda_1 - 1/\lambda_2)/T] \quad (\text{B.2})$$

where $B \equiv$ pyrometer constant
 $= \frac{\tau_o(\lambda_1) \tau_f(\lambda_1) \mathfrak{R}(\lambda_1) \Delta\lambda_1}{\tau_o(\lambda_2) \tau_f(\lambda_2) \mathfrak{R}(\lambda_2) \Delta\lambda_2}$

Equation B.2 is applicable for any radiating body, however for a graybody, in which emissivity is a function of temperature alone, Equation B.2 becomes:

$$R = A(\lambda_2/\lambda_1)^5 \exp[-C_2(1/\lambda_1 - 1/\lambda_2)/T] \quad (\text{B.3})$$

B.2 ELECTRONIC CIRCUITRY

A schematic of the electronic circuitry is shown in Figure B.1. Detectors, D_1 and D_2 , operated at 15 V, with output currents proportional to incident radiation. The output of detector D_1 is I_{ref} and the output of detector D_2 is I_{in} . The detector outputs feed into an Intersil A007-8048 log amplifier. The log amplifier also operates on a 15 V source which is mounted on the underside of the pyrometer. The output voltage of the amplifier is described by the following equation:

$$V_{out} = -\log_{10}(I_{ref} / I_{in}) \quad (B.4)$$

B.3 PYROMETER CALIBRATION

The calibration of the two-color pyrometer was performed by utilizing a General Electric tungsten strip lamp and a Pyro Micro-Optical Disappearing Filament Pyrometer. A known voltage is applied to the tungsten lamp and the temperature of the tungsten filament is measured by the disappearing filament pyrometer. Corrections must be made to the obtained temperatures before their utilization. For instance, the effects of the glass(window) surrounding the tungsten filament must be taken into account. Temperature correction data for the range of temperatures from 600°C to 3000°C was obtained from the operating instructions of the disappearing filament pyrometer. This data was used and fitted to the following second-order polynomial:

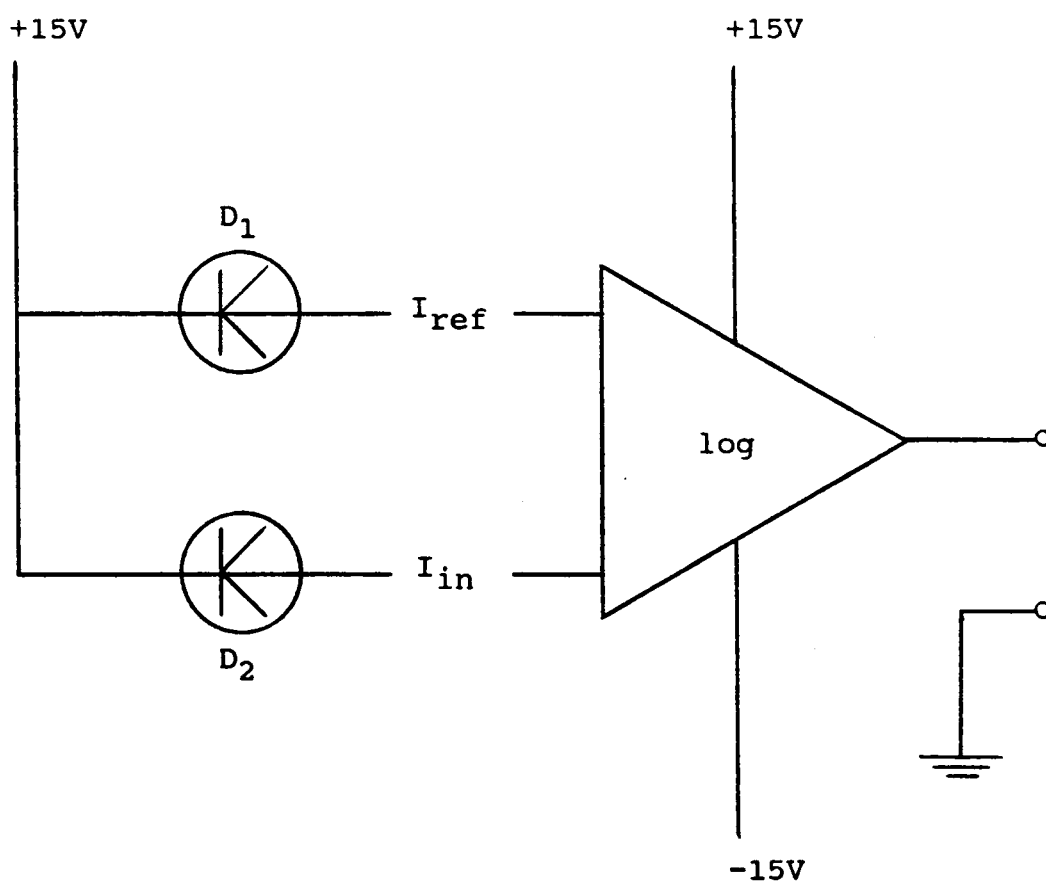


Figure B.1 - Pyrometer Electronic Circuitry

$$TWC = TO + 0.66021 + 2.119 \times 10^{-3} \times TO + 4.782 \times 10^{-6} \times (TO)^2 \quad (B.5)$$

where TO = observed temperature
 TWC = temperature with added correction

In addition to the window correction factor, the effective wavelength of light that passes through the filter of the disappearing filament pyrometer is calculated as a function of temperature. Again, using data from the disappearing filament pyrometer operation instructions, the following equation is obtained for the effective wavelength as a function of temperature:

$$\lambda = 668.8 - 7.224 \times 10^{-3} \times TO + 1.068 \times 10^{-6} \times (TO)^2 \quad (B.6)$$

where λ = effective wavelength
 TO = observed temperature

The final correction takes into account the change in emissivity as a function of temperature. The following expression is used:

$$E = 0.614 - 0.197 \times \lambda - 3.20 \times 10^{-5} \times T + 0.98 \times 10^{-5} \times \lambda \times T \quad (B.7)$$

Employing the three corrections, the actual temperature of the tungsten strip lamp is determined from the following equation:

$$1/T_a - 1/T_p = \lambda \ln(E)/C_2 \quad (B.8)$$

where T_a = actual temperature(K)
 T_p = corrected temperature obtained from pyrometer(K)
 λ = effective wavelength

E = emissivity of tungsten strip
 C_2 = Second Planck constant(micron-K)

The actual temperature of the tungsten strip is determined by entering the observed temperature and the applied voltage into a pyrometer temperature conversion computer code, which utilizes the aforementioned correction factors.

The two-color pyrometer can then be calibrated against the tungsten strip lamp. By applying various voltages to the lamp, the actual temperatures corresponding to these voltages are then determined and the output of the two-color pyrometer is determined. In addition, there is also a built-in adjustable reference calibration circuit which is used prior to an experiment to correct for any drift caused by the effect of fluctuating ambient temperatures on the photodiode circuit itself.

APPENDIX C
EXPERIMENTAL DATA

Table C.1 : Agglomerate Set 1

TEST CONDITIONS:		Laser Power = 23.2 Watts
		Oxygen Flow = 37.1 cc/min
		Laser Duration = 40 msec
Agglomerate Diameter(μm)		Burning Time(msec)
	345	640
	346	646
	346	752
	337	708
	368	732
	390	820
	382	829
	383	856
	367	732
	357	872
	339	638
	334	740
	343	764
	342	727
	337	732
	340	778
Mean	354	748

Table C.2 : Agglomerate Set 2

TEST CONDITIONS:		Laser Power = 23.2 Watts
		Oxygen Flow = 37.1 cc/min
		Laser Duration = 40 msec
Agglomerate Diameter(μm)	Burning Time(msec)	
540	1432	
512	1404	
514	1365	
509	1320	
518	1455	
512	1493	
508	1300	
512	1493	
514	1360	
517	1480	
518	1440	
519	1530	
512	1400	
509	1475	
512	1508	
509	1407	
Mean	515	1425

Table C.3 : Agglomerate Set 3

TEST CONDITIONS:		Laser Power = 23.2 Watts
		Oxygen Flow = 37.1 cc/min
		Laser Duration = 40 msec
Agglomerate Diameter(μ m)	Burning Time(msec)	
668	2282	
679	2244	
677	2450	
685	2385	
686	2620	
673	2036	
670	2543	
665	2573	
664	2087	
670	2394	
678	2323	
Mean	674	2358

Table C.4 : Agglomerate Set 4

TEST CONDITIONS:		Laser Power = 23.2 Watts
		Oxygen Flow = 37.1 cc/min
		Laser Duration = 100 msec
Agglomerate Diameter(μm)	Burning Time(msec)	
877	3030	
865	3600	
867	3270	
833	3120	
898	3480	
862	3625	
901	3175	
908	3460	
903	3406	
885	3221	
926	4027	
947	4110	
Mean	889	3460

Table C.5 : Agglomerate Set 5

TEST CONDITIONS:		Laser Power = 23.2 Watts
		Oxygen Flow = 37.1 cc/min
		Laser Duration = 300 msec
Agglomerate Diameter(μm)	Burning Time(msec)	
1050	4485	
1100	5205	
1145	5190	
1078	4900	
1129	4800	
1061	4920	
1133	5115	
1115	5224	
1153	5490	
1092	5022	
1123	5053	
Mean	1107	5037

APPENDIX D
CHEMICAL INTERPRETATION OF BORON COMBUSTION

The reactions that occur in the combustion of boron are generally agreed upon by researchers, based on enthalpy and structural factors. However, a slight variation in chemical processes will be discussed in the present section.

As mentioned earlier, for ignition of boron to occur, the boron oxide(B_2O_3) layer that exists on the surface of the boron agglomerate must first be removed to allow rapid oxygen diffusion. Once the oxide layer is removed, exposing the hot boron to the oxidizing environment, the dominant surface reactions producing BO are as follows:



The overall homogeneous gas-phase reaction is expressed as:



The production of BO_2 , which is characterized by "green" emission, occurs in an intermediate reaction and, according to Glassman[12] is of the form:



It is likely that there are several rapid intermediate reactions producing BO_2 , and one such probable reaction is given as:



A reaction is said to be probable if the sum of the Gibb's free energy of the products is less than the sum for the reactants. The reaction in Equation D.4 has been proposed in the literature[12], however the reaction in Equation D.5 is

more probable based on Gibb's free energy balance. A concentration analysis would have to be performed to accurately determine which process is dominant, which is beyond the scope of the present study.

The further reaction and/or dissociation of BO_2 are possible according to Equations D.6 and D.7, respectively:



Since BO is unstable at relative low temperatures (i.e. away from the surface), it is possible that reaction D.6 may not occur in the combustion process, however energy analysis will show that the reaction is probable. Although reaction D.7 is unlikely, based on energy analysis, and it has not been mentioned in previous work, it is still noted.

B_2O_3 is apparent at relatively low temperatures and is a known product of boron combustion. B_2O_3 may be produced by reaction D.6 or by the overall gas-phase reaction (D.3). Energy balance shows that reaction D.3 is probable, however since B_2O_3 is the primary product comprising the diffusion envelope formed by streamline between products and oxygen flow, the location is relatively far away from the surface of the boron. The temperature at this location is relatively low and since BO is relatively unstable at low temperatures, reaction D.3 may not be as significant as predicted. Some B_2O_3 likely diffuses back to the surface of the droplet to further react with boron according to reaction D.2.

For the combustion of boron agglomerates in a higher oxygen flow as discussed in Section 4.4, the increased oxygen available allows reaction D.1 to be more prominent, producing more BO. This is evident in the high-speed film history, for the apparent diameter of the white reaction zone between the green BO_2 zone and the boron surface is significantly larger relative to both the apparent boron droplet diameter and the apparent BO_2 zone diameter. This indicates the prominence of the reactions between the droplet surface and the BO_2 zone. Enhancing reaction D.1 thus allows for more production of B_2O_3 , via reaction D.3.

VITA

Christopher Brian Schechter was born in Oak Ridge, Tennessee on October 23, 1966. He lived there and attended public schools until graduation from Oak Ridge High School in June 1984. An early interest in engineering prompted his enrollment into a mechanical engineering curriculum at the University of Tennessee at Knoxville in September 1984, where he received a Bachelor of Science degree in Mechanical Engineering, with honors, in May 1989.

During his undergraduate days, he participated in the Cooperative Engineering Program and was employed by Lockheed Aeronautical Systems Company in Marietta, Georgia.

In June 1989, he started graduate school, and received a teaching assistantship in September 1989. He later received a Master of Science degree in Mechanical Engineering in December 1990.