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ABSTRACT

IMPROVING BORON FOR COMBUSTION APPLICATIONS

by

Kerri-lee Annique Chintersingh

Boron has received much attention as a potential additive to explosives and propellants due to its high theoretical gravimetric and volumetric heating values. The challenge, however, is that boron particles tend to agglomerate, have lengthy ignition delays and very low combustion rates. Prior research indicates that boron's long ignition delays are due to its inhibiting naturally occurring oxide layer, impeding the diffusion of reactants for oxidation. For combustion, current studies report that boron particles have two consecutive stages, but the actual reaction mechanism is poorly understood. Despite many years of relevant research, quantitative combustion data on micron-sized boron particles are limited and most of the proposed modifications of boron powder for its improved ignition and combustion substantially diminish the energy density of the produced composites. Such modifications affect low-temperature oxidation kinetics, and thus, aim to reduce the ignition delay rather than accelerate high-temperature reactions affecting combustion rates and efficiencies.

The objectives of this research are to achieve higher burn rates for boron powders without jeopardizing their thermochemical performance, safety and stability, and to develop an experimentally validated model adequately describing boron oxidation kinetics that can be used in practical simulations for a broad range of temperatures. The study is also aimed to close the gap in data for combustion of fine boron particles in varying oxidizing environments.

In this work, burn times as a function of particle size, ignition delays and temperatures of commercial and modified boron powders are collected from optical emissions and images of single particles burning in air, steam, and gases formed by combusting hydrocarbons. In each case, the oxidizing gas environment is described accounting for thermodynamic equilibrium and using computational fluid dynamics. Unlike previous work, the complex morphology of boron aggregates is explicitly accounted for by correcting for their fractal dimension. The fractal dimension is determined by scanning electron microscopy (SEM) image analysis by box counting and diffusion limiting cluster morphology theories. Strategies to modify boron's heterogeneous reactions by functionalizing its surface by organic solvents and using transition metals as "shuttle catalysts" are explored. It is found that washing boron with acetonitrile removes hydrated surface oxide and reduces ignition delays while preventing rapid aging and re-oxidation at ambient conditions. Doping boron with less than 5wt% transition metals (Fe or Hf) by high energy ball milling or wet synthesis, accelerates surface reaction rates leading to shorter particle burn times compared to the starting commercial powder.

A kinetic model is derived from low-temperature thermo-analytical measurements to describe the oxidation of complex aggregated boron particles accounting for their surface morphology. Comparison with particle combustion experiments shows that the same model can describe reactions at high temperatures typical of the full-fledged boron combustion, suggesting that the same heterogeneous reactions govern both ignition and combustion of boron. It is found that the morphology of as received boron powders comprising micron-sized agglomerates of finer primary particles does not always change to spherical droplets even at temperatures exceeding the boron melting point. This leads to variation in burn rates and temperatures for various particles.

IMPROVING BORON FOR COMBUSTION APPLICATIONS

by Kerri-lee Annique Chintersingh

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemical Engineering

> Otto H. York Department of Chemical and Materials Engineering

> > August 2019

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APPROVAL PAGE

IMPROVING BORON FOR COMBUSTION APPLICATIONS

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TABLE OF CONTENTS

Ch	Chapter		
1	INTRODUCTION		
	1.1	Background	1
		1.1.1 Factors affecting boron combustion	2
		1.1.2 Ignition studies	6
		1.1.3 Combustion studies	10
		1.1.4 Single particle ignition and combustion models	17
		1.1.5 Existing strategies to improve boron ignition and combustion	28
	1.2	Research Objectives	35
	1.3	Organization of Dissertation	36
2	COM ACE	IBUSTION OF BORON PARTICLES IN PRODUCTS OF AIR- TYLENE FLAME	38
	2.1	Abstract	38
	2.2	Introduction	39
	2.3	Experiments	42
		2.3.1 Experimental setup	42
		2.3.2 Particle size distributions	47
	2.4	Experimental Results	52
	2.5	Concentration and Temperature Profiles in the Air-acetylene Flame	59
		2.5.1 Modeling	59
		2.5.2 CFD results	63
	2.6	Discussion	67

Cha	apter		Page
	2.7	Conclusions	72
3	OXII WITI	DATION KINETICS AND COMBUSTION OF BORON PARTICLES H MODIFIED SURFACE	74
	3.1	Abstract	74
	3.2	Introduction	75
	3.3	Experimental Section	77
		3.3.1 Materials	77
		3.3.2 Particle combustion experiments	82
		3.3.3 Thermogravimetric experiments	84
	3.4	Results	85
	3.5	Discussion	98
	3.6	Conclusions	100
4	COM PAR	IBUSTION OF BORON AND BORON-IRON COMPOSITE TICLES IN DIFFERENT OXIDIZERS	101
	4.1	Abstract	101
	4.2	Introduction	102
	4.3	Materials	104
	4.4	Experimental Section	106
		4.4.1 Experimental setup	106
		4.4.2 Particle size distributions	109
		4.4.3 Particle emission measurements	111

Ch	apter		Page
	4.5	Adiabatic Flame Temperatures and Equilibrium Product Compositions	113
	4.6	Combustion Environments for Particles Injected in Flames	115
	4.7	Results	120
		4.7.1 Single particle emission	120
		4.7.2 Particle burn times	128
		4.7.3 Combustion temperatures	131
	4.8	Discussion	138
		4.8.1 Boron particle combustion	139
		4.8.2 Effect of doping boron with iron on combustion	143
	4.9	Conclusions	145
5	BOR IN A	ON DOPED WITH IRON: PREPARATION AND COMBUSTION IR	147
	5.1	Abstract	147
	5.2	Introduction	148
	5.3	Material Preparation and Characterization	150
		5.3.1 Material preparation	150
		5.3.2 Material characterization	152
	5.4	Combustion Setup	157
	5.5	Results	159
	5.6	Discussion	172

Ch	apter		Page
	5.7 Conclusions		
6	REA	CTIVE SHELL MODEL FOR BORON OXIDATION	180
	6.1	Abstract	180
	6.2	Introduction	181
	6.3	Technical Approach	183
	6.4	Experimental Details	188
		6.4.1 Preparation of boron powders with distinct but overlapping particle size distributions	188
		6.4.2 Powder Characterization	189
	6.5	Experimental Results	189
	6.6	Reactive Shell Thickness	192
	6.7	Spherical Primary Boron Particles in Reactive Shell	197
	6.8	Boron Oxide Thickness Limiting the Applicability of the Reactive Shell Model	198
	6.9	Conclusions	200
7	HETI COM	EROGENEOUS REACTION KINETICS FOR OXIDATION AND BUSTION OF BORON	202
	7.1	Abstract	202
	7.2	Introduction	203
	7.3	Technical Approach	207
	7.4	Materials	207
	7.5	Experiment	209

Chapter		Page	
7	.6	Boron Oxidation Kinetics	210
		7.6.1 Experimental results	210
		7.6.2 Oxidation of particles of different sizes	211
		7.6.3 Kinetic description	215
7	.7	Boron Combustion in Air	217
		7.7.1 Particle size and morphology	218
		7.7.2 Combustion times and temperatures	221
		7.7.3 Rate of full-fledged combustion	224
7	'.8	Discussion	228
7	'.9	Conclusions	231
8 E E	EFFE DOPI	CT OF PURITY, SURFACE MODIFICATION AND IRON ING ON IGNITION AND COMBUSTION OF BORON IN AIR	233
8	8.1	Abstract	233
8	8.2	Introduction	234
8	3.3	Materials	236
		8.3.1 Material preparation	236
		8.3.2 Material characterization	237
8	8.4	Experimental Details	241
8	8.5	Results	244
		8.5.1 Ignition energy	244
		8.5.2 Optical emission of individual burning particles	244

Cha	apter		Page
	8.5.3 Statistical analysis of individual emission characteristics		
		8.5.4 Boron particle combustion products from laser ignition	254
	8.6	Discussion	255
		8.6.1 Ignition energy	255
		8.6.2 Stages in boron particle combustion	256
		8.6.3 Effect of boron purity on combustion	257
		8.6.4 Effect of surface modification with acetonitrile on combustion in air	258
		8.6.5 Effect of iron doping on combustion in air	259
	8.7	Conclusions	260
9	TRA	NSITION METAL CATALYSTS FOR BORON COMBUSTION	262
	9.1	Abstract	262
	9.2	Introduction	263
	9.3	Material Preparation	265
	9.4	Material Characterization	266
	9.5	Experimental Setup	267
		9.5.1 Single particle combustion tests	267
		9.5.2 Aerosol combustion tests	270
	9.6	Results	271
		9.6.1 Powder particle morphology: effect of metal additives	271

Cha	apter			Page
		9.6.2	Single particle combustion experiments: effect of metal additives	272
		9.6.3	Combustion of aerosolized powder clouds: effect of metal additives	281
		9.6.4	Powder particle structure and morphology: effect of PCA for B-Fe	285
		9.6.5	Single particle combustion experiments: effect of PCA for B-Fe	287
		9.6.6	Combustion of aerosolized powder clouds: effect of PCA for B-Fe	290
	9.7	Discu	ssion	291
		9.7.1	Particle morphology	291
		9.7.2	Effect of metal additive on combustion of composite powders	292
		9.7.3	Effect of PCA used to prepare B-Fe composites on combustion	294
	9.8	Concl	usions	296
10	CON	CLUSI	ONS AND FUTURE WORK	297
	10.1	Concl	usions	297
	10.2	Future	e work	302
API OF 1	PEND PART	IX A CO ICLE E	ORRELATION BETWEEN INTENSITY AND DURATIONS	304
API PRI	PEND E-MIX	IX B FI ED HY	LAME CONE HEIGHT AND ANGLE FOR CFD MODEL OF DROCARBON FLAME	305
API HY	PEND	IX C C BEN DI	OMPUTATIONAL FLUID DYNMAICS MODEL FOR AIR- FFUSION FLAME	307

Chapter	Page
C.1 Model Setup and Assumptions	307
C.2 CFD Results	311
APPENDIX D PARTICLE SIZE DISTRIBUTIONS OF DOPED AND UNDOPED BORON POWDERS OBTAINED USING LOW ANGLE LASER LIGHT SCATTERING	315
APPENDIX E PARTICLE IDENTIFICATION FOR AUTOMATED SEM IMAGE PROCESSING FOR PARTICLE SIZE DISTRIBUTIONS	317
REFERENCES	319

LIST OF TABLES

Tab	Table	
2.1	Temperatures and Compositions of the Air-Acetylene Combustion Products Obtained for Different Equivalence Ratios using NASA CEA Code [1] and Used to Describe Inlet Gases in the Present CFD Model	60
2.2	Boundary Conditions Used for COMSOL Flame Modeling	63
3.1	List of Materials Prepared for Investigation	79
3.2	Summary for Temperature-Programmed Oxidation (TPO- TG) of Washed Boron Samples Aged up to 120 Days in Air at 30°C and 44% Relative Humidity	88
4.1	Temperatures and Compositions of Combustion Products/ Oxidizers Obtained Using NASA CEA Code [1] for Air- acetylene and Air- hydrogen Flames Used in Experiments	114
4.2	Measured and Calculated Combustion Temperatures for Boron and Boron- iron Composite Powders.	135
5.1	Summary of Synthesis Conditions and Resulting Compositions of the Prepared Iron-doped Boron Powders	152
5.2	D^{n} -law Fit Parameters for Boron-based Materials Laser Ignited in Air; Equation Fit: $t_{b}[ms] = aD[\mu m]^{n}$	168
5.3	Average Combustion Temperatures for Doped and Un-Doped Boron Powders Laser Ignited in Air Calculated Based on the Particle Emission Pulses Filtered at 700 and 800 nm	170
5.4	Average Combustion Temperatures for Doped and Un-Doped Boron Powders Laser Ignited in Air Calculated Based on the Emission Filtered at 700 and 800 nm (See Table 5.3) and those Based on Visible Range Emission Recorded by the 32-Channel Spectrometer; for Visible Emission	172
6.1	Specific Surface Areas for Boron Powders with Different Particle Size Distributions	191
7.1	Kinetic Parameters Reported to Describe Boron Oxidation in Air	206

LIST OF TABLES (Continued)

Tab	Table		
8.1	ICP-MS Analysis of Boron Starting Materials and Doped Samples, for Iron Content Determination	239	
8.2	Minimum Laser Energy Required for Ignition of Boron Samples in Room Temperature Air	244	
8.3	Parameters <i>a</i> and <i>n</i> for the Burn Times, <i>t</i> , vs. Particle Size, <i>D</i> , Described as $t(ms)=aD(\mu m)^n$ for Different Materials Burning in Air	251	
8.4	Average Combustion Temperatures for Different Boron Powders Inferred from Emission Signals Recorded in the Infrared and Visible Ranges	253	
9.1	Starting Powders Used for Preparation of Composite Materials	266	
9.2	D- law Trend Fit Parameters for Doped and Un- doped Boron Composites Laser Ignited in Air and Burnt in the Products of Air- acetylene and Air- hydrogen Flames	280	
9.3	Average Combustion Temperatures for Particles of Different Materials Burning in Air	281	
9.4	Estimated Combustion Efficiency and Flame Thickness for Different Materials Ignited in CVE Experiments	284	
9.5	Flame Thickness and Combustion Efficiencies of Boron- Iron Composites Milled in Varying PCAs	291	
C.1	Boundary Conditions used for COMSOL Flame Modeling Air- hydrogen Flame	311	

LIST OF FIGURES

Figu	Figure	
1.1	Gravimetric and volumetric heating values of metal additives	2
1.2	Burn times versus particle size trend for past single boron particle combustion experiments	5
1.3	Effect of gas temperature on ignition delay of boron particles	8
1.4	Single 44 μ m boron particle igniting and burning in hot gases with velocities of 1000 cm/s and temperature of 2170 K	12
1.5	Successive pictures of boron particles (5 wt%) ignition and burning in an n-decane- based fuel droplet (I) and ethanol droplet (II)	17
1.6	Comparison of ignition and combustion models presented	18
1.7	The generation mechanism of the outermost layer of the oxide layer	22
1.8	Compilation of % reduction in ignition time delays from various studies [3-8] conducted with 5-10 wt% additive to boron powders	32
1.9	(A) Boron flames as the power of the plasma discharge is changed from 0 to 78W and (B) trends of the ignition time delay versus power of the plasma discharge and ambient temperature	34
2.1	Schematic diagram of the experimental setup and photographs of air- acetylene flame at equivalence ratio 1.65 with and without particle feed	44
2.2	A typical sequence of boron particle combustion emission pulses on top of the flame emission background	45
2.3	SEM Images of amorphous SB 95 boron powder used in experiment	48
2.4	Particle size determination of boron particles with final distributions obtained from SEM image processing and low angle laser scattering	51
2.5	Boron particle combustion streaks in pre-mixed air-acetylene flame at the equivalence ratio ϕ =1.65	52
2.6	Number-based burn time distributions of amorphous boron particles injected in combustion products of air-acetylene flames at different equivalence ratios	53

FigureP		
2.7	Emission peaks amplitude number-based distribution plots for boron particle combustion in flames with different equivalence ratios	54
2.8	Effect of particle size on their burn time for boron particles injected in air-acetylene flames with different equivalence ratios	56
2.9	Integrated emission spectrum with respective Planck's curve fit for boron particle combustion in air-acetylene flame of equivalence ratio of 1.65	58
2.10	Schematic diagram of the computational domain; dimensions are in mm.	61
2.11	Experimental (circles) and calculated (lines) results for air-acetylene flame mixtures at different equivalence ratios.	65
2.12	Calculated radial temperature and selected concentration profiles plotted for different heights above the burner for flames with equivalence ratios of 0.62 and 1.65 (respective flame velocities are 60 and 100 cm/s)	67
2.13	CEA Calculations for varying boron concentrations in varying oxidizing environments	70
3.1	SEM images of as-received and processed boron powder samples	80
3.2	Particle size distributions of commercial and washed boron powders	81
3.3	Schematic diagram of the combustion experimental setup	84
3.4	Thermo-gravimetry curves of fresh and washed boron samples. Heating rate: 10 K/min	87
3.5	Points of ignition on boron particle streaks	89
3.6	Frequency distributions of ignition distances for processed and unprocessed boron powders	90
3.7	Ignition distance and ignition delay correlation to particle size for processed and un-processed boron powders	92
3.8	PMT Output signals filtered at 700 nm for different boron powders burning in the products of an air-acetylene flame	93

Figure		Page
3.9	Histograms for emission pulse amplitudes for particles of boron samples burned in hydrocarbon flame	94
3.10	Burn time distributions of processed and unprocessed amorphous boron samples in a hydrocarbon premixed air- acetylene flame	95
3.11	Burn times as a function of diameter for processed and unprocessed boron powder burnt in the combustion products of pre-mixed air- acetylene flame	96
3.12	Emission spectra for different boron samples burning in the combustion products of an air- acetylene flame	97
4.1	SEM Images of reference and milled composite materials	106
4.2	Experimental setup for feeding particles into combustion environment for capturing optical emission signals	107
4.3	Particle size distributions of commercial boron and 5 wt % iron- boron composite powders obtained from the SEM image analyses of particles	110
4.4	Adiabatic flame temperatures and main combustion products generated by boron and boron- iron composite burning in air and in the products of air- acetylene and air- hydrogen flames	115
4.5	Schematic representations of computational domains for each environment	117
4.6	Two dimensional color maps showing the distribution of temperatures and nitrogen concentrations for (left) air- acetylene and (right) air- hydrogen flames	118
4.7	Predicted and measured flame temperature along vertical axis of air- hydrogen flame (top) and predicted concentrations of the main gas species present in the environment along vertical axis for this flame (bottom)	120
4.8	Luminous streaks of boron and boron-iron composite powders burning in combustion products of an air-acetylene flame (exposure time: 8 ms)	121

Figure		Page
4.9	Luminous streaks of boron and boron-iron composite powders burning in combustion products of air-hydrogen diffusion flame (exposure time: 250 ms)	122
4.10	Luminous streaks of boron and boron-iron composite powders ignited by the CO_2 laser beam and burning in air (exposure time: 250 ms)	123
4.11	Particle streak length distribution for boron and boron-iron composite in varying combustion environments	124
4.12	PMT Output signals filtered at 700 nm for boron and boron-iron composite particles burning in combustion products of an air-acetylene flame (left), air-hydrogen flame (center), and in air (right)	125
4.13	Optical emission traces filtered at selected wavelengths for boron and boron-iron composite particles burning in air	126
4.14	Features of double-peak emission pulses produced by boron particles burning in air and recorded using a 700-nm filtered PMT	128
4.15	Burn time distributions of commercial boron and boron-iron composite particles ignited in the combustion products of an air-acetylene flame (left), air-hydrogen flame (center), and laser ignited in air (right)	130
4.16	Effect of particle size on its burn time for as received boron and boron- iron composite powders ignited in different oxidizing environments	131
4.17	Time-integrated emission spectra for boron and boron-iron composite samples laser ignited in air	133
4.18	Emission signals produced by boron particles burning in air filtered at 700 and 800 nm and corresponding time-resolved temperatures	136
4.19	Maximum temperatures measured for commercial boron burning in air using ratio of emission signals filtered at 700 and 800 nm	137
4.20	Average combustion temperatures for commercial boron and boron-iron composite powders laser ignited in air.	138
5.1	Schematic diagram of the experimental setup for doping boron with iron by thermal decomposition of iron pentacarbonyl	151

Figure		Page
5.2	SEM images and respective elemental maps of boron and iron for reference material and B-Fe samples prepared by thermal decomposition of iron penta-carbonyl	154
5.3	High magnification SEM images of boron-iron composites captured with back scattered electrons.	154
5.4	Number-based particle size distributions obtained by automated SEM image processing	157
5.5	Images of luminous streaks of boron (commercial) and boron doped with iron powder particles ignited by crossing a CO ₂ laser beam in air	160
5.6	Emission traces of single particle streaks for commercial boron and boron- iron doped samples filtered at 700 nm	161
5.7	Maximum peak intensity vs. duration for single and double peak emission pulses filtered at 700 nm for commercial boron powder	162
5.8	Emission signals recorded using a 32-channel spectrometer for commercial boron powder particles ignited by the CO ₂ laser beam and burning in room temperature air	163
5.9	Examples of time-resolved temperatures and emission pulses filtered at 641 nm for (top) commercial boron, and (bottom) doped boron samples laser ignited in air	164
5.10	Burn time distributions for commercial boron and doped boron powders (B-Fe125 and B-Fe190) laser ignited in air	165
5.11	Burn time vs. particle size correlations for commercial boron, milled boron-iron composite [9] and doped boron powders laser ignited in air	167
5.12	Combustion temperatures obtained for burning particles processing measured radiation signals filtered at 700 and 800 nm.	169
5.13	Schematic representation of reactions occurring during full-fledged combustion of boron particle proceeding in two stages considering published B-O phase diagram [10]	176
6.1	Scanning electron microscope image of typical boron particles	183

Figure		Page
6.2	Schematic representation of an oxidizing boron particle and respective concentration of oxygen	185
6.3	Size distribution of boron powders	190
6.4	TG traces for oxidized boron powders size classified in acetonitrile (A) and in water (B)	192
6.5	A subset of four size bin specific TG traces representing oxidation of size classified boron powders	193
6.6	Comparison of TG traces representing 5 μ m size bins for oxidation of fine and coarse fractions obtained by size classifying boron in acetonitrile (A-D) and in water (E-H)	195
6.7	Discrepancies between mass gains for the same 2, 5, and 10 μ m size bins for coarse and fine boron fractions separated by sonication in acetonitrile and water as a function of the assumed thickness of the reactive shell	196
6.8	Calculated primary particle size by assuming different shell thickness	198
6.9	Evolution of the oxide thickness of primary particles with temperature for different fractions of the boron powder	200
7.1	Particle size distributions of boron samples treated and size classified in acetonitrile (top) and water (bottom)	209
7.2	TG traces for boron washed in acetonitrile (top) and water (bottom) heated in an oxygen/argon flow at different rates	211
7.3	Relative masses change trends for selected particle sizes: 2.5, 5.5, 10.5 and 25 μ m, heated at 2.5 K/min	213
7.4	Relative mass of primary boron particles at different heating rates for samples washed in acetonitrile (solid lines) and water (dashed lines)	214
7.5	Apparent activation energy of oxidation of boron powder in oxygen as a function of primary particle mass, m _{PP}	216
7.6	Product of pre-exponent, k and $f(m_{PP})$ as a function of the mass change of the primary particle mass, m_{PP} for boron washed in acetonitrile	217

Figure		Page
7.7	Particle size distributions for commercial boron powder fed through laser setup	220
7.8	Burn time distribution for single boron particles laser ignited and burning in air	222
7.9	Single particle combustion temperatures determined from IR PMTs filtered at 700 and 800 nm plotted against log scale value of corresponding burn time	223
7.10	SEM Images of combustion products of commercial boron powders laser ignited in air	224
7.11	Burn times versus particle size trends for boron oxidation, assuming that particles become spherical droplets and the rate of consumption is proportional to the surface area available for reaction	226
7.12	Burn times (ms) versus particle size (µm) for boron porous aggregates in air	228
8.1	SEM Images of boron samples	238
8.2	Particle size distributions for boron samples: doped and un-doped and with varying purity	241
8.3	Characteristic images of single burning particle streaks of different boron powders laser ignited in air	245
8.4	Optical emission traces filtered at 700 nm for different boron powder particles laser ignited in air	246
8.5	641 nm emission traces and corresponding temperatures for different boron powder particles laser ignited in air	247
8.6	Characteristic double peak emission trace and summary of times for un- doped boron samples laser ignited in air	249
8.7	Burn time distributions for doped and un- doped B99, B95 and Bw samples when laser ignited in air	250
8.8	Burn time vs. particle size trends for different boron samples burning in air	251

Figure		Page
8.9	Combustion temperature distributions for single boron particles inferred from infrared emission signatures	252
8.10	SEM images of combustion products of different materials captured above laser beam in air	254
9.1	SEM Images of boron-based materials: (A) starting boron, (B) B-Fe (C) B-Co (D) B-Ni (E) B-Zr and (F) B-Hf	272
9.2	Particle size distributions for different powders passed through the feeder	273
9.3	Optical emission traces filtered at 700 nm for particles of different materials burning in different environments	274
9.4	Emission streaks of different material particles injected in the air- acetylene flame	275
9.5	Emission streaks of different material particles injected in the air- hydrogen flame	276
9.6	Emission streaks of different material particles burning in air	277
9.7	Burn time distributions for particles of different materials in different oxidizing environments	278
9.8	Burn time vs. particle size trends for different material particles burning in different oxidizing environments	279
9.9	Traces of pressure, P, and its time derivative, dP/dt, versus time for CVE experiments with different materials	282
9.10	Summary of time and pressure measurements for CVE experiments conducted with different materials	283
9.11	SEM images of iron- doped composites milled in varying PCAs	285
9.12	Particle size distributions for boron and B-Fe powders prepared using different PCAs and passed through the feeder	286
9.13	X-ray diffraction patterns for B-Fe samples milled in varying PCAs	287

Figure		Page
9.14	700 nm filtered particle emission traces for boron and B-Fe powders prepared using different PCAs and burning in air	288
9.15	Burn time distributions for boron and B-Fe powders milled using different PCAs and burning in air	289
9.16	Burn times in air vs. particle size trends for boron and B-Fe powders milled with different PCAs	290
9.17	Summary of time and pressure measurements for CVE experiments conducted with boron and B-Fe milled using different PCAs	291
A.1	Burn times vs intensity of particle emission peaks for amorphous boron in air acetylene flame	304
C.1	Schematic diagram of the computational domain; dimensions in mm	309
C.2	Calculated radial temperature and selected concentration profiles plotted for different heights above the burner for flame	313
C.3	Calculated vertical temperature and concentration profiles for different horizontal distances away from flame axis	314
D.1	Particle size distributions of boron and doped- boron materials by commercial laser scattering technique	315
E.1	SEM image of doped boron powder B-Fe125 obtained using secondary electrons for image processing with one of the particle agglomerates selected in a dashed rectangle to illustrate image processing	318

NOMENCLATURE

m _{i,0}	initial mass of particle in size bin, i
m _{i,core}	constant mass of the nonporous core,
MPP,0	initial mass of a primary particle
mi	mass of particle in size bin i
m _s , (or just m)	mass of entire sample
Шрр	mass of primary particle
hox	oxide thickness of primary particle
m'	relative mass, $(m-m_0)/m_0 = m/m_0-1$
hs	reactive shell thickness
hox	oxide thickness
Vi	combined reactive volume of all particles in size bin, i
Ni	number of particles in size bin, i
R _i	aggregate particle radius, uncorrected as measured from particle size distribution
r _i	aggregate impenetrable core radius
dm	instanteous mass gain
k	pre-exponential factor
E	apparent activation energy

R	Universal Gas constant
Т	temperature, K
f(m'pp)	progress function that describes the reaction model
D_f	fractal dimension of boron aggregates
Ν	the number of monomers in a cluster
R_g	the cluster radius of gyration
a	the monomer radius (i.e. 80 nm)
ko	pre-factor of order unity dependent on the degree of overlap
A_c	projected area of the aggregate
A_a	the projected area of the spherical primary particle
R_2	half of the major axis length of the equivalent ellipse of each aggregate
CHAPTER 1

INTRODUCTION

1.1 Background

Advances in missile propulsion systems to increase missile range capability by not carrying internal oxidizer load and allowing free stream air to provide all the oxidizer for combustion has led to the use of metal fuel additives in energetic formulations [11, 12]. This is due to the fact that metals have high energy densities, combustion enthalpies and their resulting products from oxidation can be collected and recycled using new techniques [13-15]. This makes them favorable for additives in liquid fuels, gel fuels, explosives and solid fuel propellants. As shown in Figure 1.1, boron has the highest volumetric heating value recorded for common metal energetic fuels listed [16, 17]. While beryllium has the highest gravimetric value, it is highly toxic and thus unsafe for handling. When compared to traditional metal fuels such as magnesium and aluminum, boron has a heat of combustion of 58.83 kJ/g. This value is close to two times the respective heating values for aluminum and magnesium, which are 24.79 kJ/g and 31.09 kJ/g respectively[18]. This makes the potential of boron powder addition particularly in liquid fuel ram jet systems thermodynamically attractive because boron could offer the advantage of increased range, reduced volume/ weight, higher velocities and lower time to target values for such applications [11, 19-21].



Figure 1.1 Gravimetric and volumetric heating values of common fuel additives. Source: [16].

1.1.1 Factors affecting boron combustion

Boron, however, has yet to reach its full potential in propulsion systems due to its low reaction rates during both ignition and combustion. Boron has extended ignition delays and low burn rates [5, 12, 21-29], making it currently unsuitable for most practical devices. Refs. [12, 30] suggest that this is may be due to the inhibiting naturally occurring oxide layer on the particle surface. Unlike traditional, low-melting metal fuels like aluminum or magnesium, boron has high melting and boiling points of 2350 and 4273 K, respectively [31]. Also unlike more common and refractory metal combustion products, Al₂O₃ and MgO, the melting point of boron oxide is low (723 K) [32] while its boiling point (2130 K) [32] falls within the common metal combustion temperature range of 2000 – 3000 K. As such, according to Glassman criterion, boron will not burn in the vapor phase [17]. It is believed that these properties contribute to the initial low temperature oxidation of boron

being limited to the diffusion of elemental boron or oxygen through the molten B_2O_3 shell [21]. Further oxidation and full-fledged combustion occur once the shell becomes volatilized and the clean surface of molten boron droplets heterogeneously reacts with the surrounding oxidizers at higher temperatures [25]. These two stages are currently described in the boron ignition and combustion mechanism [28]. According to [33], the first stage ends once the oxide is completely removed. During the first stage, the reaction is rate limited by diffusion of reacting species through B_2O_3 shell. During the second stage, the rate is limited by the kinetics of interaction of gas phase oxidizers with clean boron surface. However, the reaction steps are not fully understood. To further compound on its challenges, when boron reacts in moisture containing environments, the energy release is lowered due to the formation of less energetically favorable intermediates such as HOBO [30, 34], not the thermodynamically favored $B_2O_3(1)$. Boron also has the propensity to form multiple sub oxides, oxy-nitrides and nitrides dependent on the oxidizing environment [35-38], which has been so far neglected in the respective ignition and combustion models.

In an effort to tackle each of these challenges, there has been a considerable research effort to understand the effect of particle size and morphology [5, 22, 28, 29, 39], oxide layer thickness [40] and phase changes [41] on boron ignition and combustion. Several research approaches have also designed experiments tailored to exploring the role of different oxidizing environments on the rate of combustion of micron- sized boron particles, which will be discussed in Sections 1.1.2 and 1.1.3.

Similar to hydrocarbon droplets burning, existing work points to changes in the reaction mechanism for differently sized boron particles. Ref. [39] explored this effect by laser igniting pellets of 30wt% boron mixed with KNO₃. Their work suggested that ignition delays and combustion was affected by the boron particle size. Smaller particles (less than 1 μ m) had shorter delays and generated BO emissions during combustion, while larger particles (greater than 30 μ m) took a longer time to ignite and had typical black body emissions. While those results were consistent with the reported reduced ignition delay times for boron nano particles injected in an ethanol spray flame [16], they were inconsistent with findings by Ref. [33], where it was concluded that the ignition temperature for boron is not strongly dependent on particle size and is similar for both nano and micron- sized systems.

To further illustrate the effect of particle size in combustion, Figure 1.2 shows a compilation of single boron particle burn times as a function of their sizes from work conducted by Refs. [5, 26, 29, 42]. Ref. [33], recently burned boron nanoparticles in the post flame region of a flat methane flame and achieved longer burn times compared to micron sized powders investigated by Ref. [25]. Figure 1.2 shows that existing data for particles within 1- 30 µm are limited. There are also discrepancies in burn times measured for particles 1- 10 µm in size, making it difficult to observe a clear transition in reaction regimes with varying particle sizes. While differences in experimental design and identification of particle streak lengths or emissions may have contributed to the difference in burn times recorded, there is also a limitation in how the boron particle sizes are measured in different single particle experiments. In most cases, particles were treated based on their nominal sizes determined by the manufacturer or their average sizes from

sieve analysis. In reality, distributions of particle sizes for boron powders are rather broad and must be affecting significantly the results of combustion studies. As such, a statistical correlation of multiple burn times recorded with varying particle sizes measured directly from particles fed into the oxidizing environment would be better for interpreting true burn rates.



Figure 1.2 Burn times versus particle size trend for past single boron particle combustion experiments.

Source: [5, 26, 29, 42]

For particle morphological differences, Ref. [5] presented similar combustion times for crystalline and amorphous boron particles burned in a flat flame burner, indicating no significant changes in combustion. However, Refs. [43, 44] showed by laser igniting and studying different mixes of amorphous and crystalline boron particles in a thermo-analyzer, that the activation energy for oxidation and ignition time delays are lowered for amorphous materials. The study [43] also indicated changes in the emission spectra and light intensity during combustion depending on the ratio of crystalline to amorphous particles present. This was supported by lower burn rates, higher ignition temperatures and higher oxygen concentration required for ignition in micron- sized crystalline systems [22, 45-47]. Compounded by the lower cost for amorphous boron, this has led to an increased interest in amorphous boron for bulk propellant application. The fact, however, is that in most of these studies, the crystalline boron powder explored was of different purity than the amorphous form and variances observed in combustion or ignition might be affected by the presence of an impurity assisting/ impeding boron oxidation. Therefore, there is still a need to fully comprehend how the boron combustion mechanisms are affected by its purity or by presence of small contaminants in different environments. Further data on amorphous boron micron-sized particles are also needed.

1.1.2 Ignition studies

To gain a better understanding of low temperature oxidation of boron, several ignition studies have been conducted exploring the effect of oxygen concentrations or pressures, heating rates, particle size and oxidizing environments. This is primarily due to the fact that a low ignition temperature and short ignition delays are required to maximize the rate of energy release.

From the work conducted, the ignition temperatures of boron particles in oxygenated environments range from 1623 to 1950 K [25, 28, 45, 48, 49]. The actual mechanism driving ignition, however still remains debatable; depending on the oxygen concentration, gas temperatures, the size and the nature of the boron particles. Ignition temperatures were found to be dependent primarily on the presence of oxygen by Refs. [5,

33, 46]. For nanoparticles, a minimum oxygen mole fraction of 0.1 was required for ignition. The ignition temperatures measured ranged from 1578 to 1872 K. For much larger systems, Ref. [48] reported that a temperature of 1580 K was required for igniting much larger 5-8 mm lumps of boron with a minimum partial pressure ratio of oxygen to nitrogen of 0.3.

One may therefore, argue that the difference in ignition temperatures recorded are negligible between bulk powder and single particle ignition. However, work by [47, 50, 51] contradicts this reasoning and shows that in all three studies, the ignition temperatures measured (715 -800 K) for boron agglomerates are significantly lower than those reported for single particles. Work presented in Ref. [46] proved through thermo-gravimetric studies, that for particles ranged between $10-300 \,\mu\text{m}$, the ignition temperatures too ranged from 780 to 840 K. The rate of oxidation and ignition was also found to be dependent on boron particle size, heating rate and partial pressures of oxygen. The extent of the oxidation however was found to have decreased for larger particles. A similar effect was noted with the agglomerated systems, where in some cases, the samples quenched after igniting at those low temperatures [47]. These findings suggest that larger boron agglomerates exhibit a dual stage ignition mechanism and possibly only at temperatures exceeding ignition temperatures recorded in prior work (in excess of 1500 K) can full-fledged or complete boron combustion occur. Comparing different reported results also raises questions of how ignition is defined for boron in each experiment and whether or not at temperatures of 700 -800 K the oxidation reaction was self-sustained. Another possible explanation to the lower combustion efficiencies for larger sized systems is that the rate of formation of the oxide is greater than the rate of its evaporation at lower temperatures. As such, a critical

oxide thickness is reached, that impedes further combustion because of diffusion limitations [40]. However, this is yet to be proven and described quantitatively.

Ignition times on the other hand were strongly affected by gas temperature rather than oxygen concentration as shown in Figure 1.3. These findings, particularly disagree with work done by Ref [41], who prepared $100 - 200 \,\mu\text{m}$ boron filaments with tungsten or carbon cores for investigating ignition of boron in varying environments by electrical heating. The study revealed that while ignition occurred at a similar temperature range of 1773 - 1843 K, it was not dependent on the gas environment temperatures or oxygen content but instead was driven by a phase transition from α to β rhombohedral boron [41]. This would explain a constant ignition temperature found to be independent of oxidizer concentration in some cases.



Figure 1.3 Effect of gas temperature on ignition delay of boron particles.

Source: [33].

Since the impeding oxide layer has been described as the limitation for ignition [12], the objective of many ignition studies has also been to gain a better understanding of the nature of the oxide in varying environments as well as the effect of the oxide thickness on the rate of boron oxidation, if the system is truly diffusion controlled. In Ref. [52], the authors explored the diffusion permeability of the oxide film by heating a 2 mm spherical B₂O₃ particle from 600 to 1400 K in wet and dry atmospheres. They showed that the presence of water vapor improves the gasification rate of boron oxide, potentially leading to lower ignition temperatures. Similarly, it was reported that the presence of water promoted gasification of the oxide layer in a flat- flame burner [53]. Ref. [54] confirmed the positive effect of water addition for reducing ignition delay times. A comparable effect in fluorinated environments at elevated pressures of 8.5 - 34 bar using 1-3% SF₆ and 6-12% HF gases was also reported. In all cases, the additive potentially first reacts with the oxide layer, leading to further clean-surface reactions with boron. The challenge with water, however, is that it also produces unfavorable intermediates and results in lengthier burn rates during full-fledged combustion.

Refs. [40, 55, 56] further investigated the role of the surface oxide on oxidation. In varying the oxide thickness from 0 to 0.1384 μ m, Ref. [40] found that the intensity and emission spectra patterns changed during combustion, indicating a lower quantity of BO and BO₂ products formed for starting boron powders with greater oxide thickness. The extent of boron oxidation was also limited for samples with greater oxide thickness values despite having a constant oxidation onset temperature of 775°C recorded for all samples. This indicates that the oxide layer has little effect on the initial reactivity of the boron

powder and the system is kinetically controlled at low temperatures with minimal oxide thickness. This finding is supported by data from Ref. [46].

In summary, despite quite a few experimental and theoretical studies performed, boron ignition behavior remains incompletely understood. At low temperatures, oxidation may be driven by kinetics, low diffusion rates through the inhibiting oxide or polymorphic phase transformations of boron. Further studies exploring strategies of quantifying low temperature oxidation rates and considering effect of removal of well-defined modification of the natural oxide layer are required in order to improve the understanding of mechanisms of reactions involved and how ignition transitions to the second stage, full-fledged combustion for larger boron particles or agglomerates.

1.1.3 Combustion studies

In this section, we review experiments designed to capture data at high temperatures, typically above the boiling point of boron oxide (2130 K) and above melting point of boron (2350 K). For such cases, it is expected that boron particles are self-heating and reacting heterogeneously with surrounding gas phase oxidizers as molten droplets. Experiments have been conducted to observe the effect of particle size [57], surrounding oxidizer composition, oxidizer type [18, 39], temperatures and pressures [23, 58, 59] on combustion of boron particles.

Majority of the work presented use results of optical emission measurements of single burning particles. The duration of the particle streak length is useful for determining combustion times and possible flame structure. The times can be used to find the particle burn rate once the size or mass of the particle is known. The typical assumption is that the

particle proceeds into full-fledged combustion once the emission becomes visible or detected over the range of wavelengths used. A typical example of a single boron particle burning in hot gases is shown in Figure 1.4. The photograph shown is useful in determining changes in the particle emission, burning particle streak length and thickness with time. Ref. [28] has used images such as these for varying sized boron particles to determine the relationship with the ignition delay, ignition times, combustion stages and total combustion times. As shown in the image, the time corresponding to ignition delay, and the first and second combustion stages are identified by the height the particle streak first becomes visible (x_i), and the times leading up to where it changes in thickness (t₁) or before and after a period of darkness (t_2) , respectively. In more recent designs, photographs have been useful in identifying changes in color and dimensions of streaks to aid in understanding possible product formation or particle surface emission changes during combustion as well. Other optical devices with better time resolutions and lower light detection limits have also been used to capture burning particle emission data for analysis [60]. It has become common assigning the two parts of the emission trace, as shown in Figure 1.4, to ignition (or ignition delay) and full-fledged combustion stages of boron. This approach is utilized in essentially all models for boron particle combustion, as further discussed below. However, it has never been clarified why is there a period of darkness between ignition and combustion. Indeed, ignition, as discussed below is commonly associated with removal of the protective oxide film, and combustion is described as reaction of boron with clean surface. In such a scenario, the brightness of the optical emission would be expected to increase continuously, as the oxide is being removed, and as a transition to the full-fledged combustion occurs. This issue has been overlooked by most modelers and remains unresolved today.



Figure 1.4 Single 44 μ m boron particle igniting and burning in hot gases with velocities of 1000 cm/s and temperature of 2170 K.

Source: [28].

Examples of some of the first single particle combustion experiments are detailed in Refs. [5, 28, 60]. The results from these experiments have been used over the years for validation of several ignition and combustion models. In all cases, single boron particles are fed as a jet into the combustion products of a flat- flame burner with a hydrocarbon mixture. The combustion products of the flame provide the high temperature, oxidizing environment for the particles. Ref. [60], particularly designed an extensive setup to determine ignition times, combustion times and particle size history during combustion. The boron particles are loaded into a feed chamber and transported by a nitrogen stream into the product gas of a methane- oxygen- nitrogen flame mixture created by a flat flame burner. A rotating blade agitates the particles in the chamber and the feed stream is split into two; one enters the chamber and the other passes at the top. Particle feed rate is controlled by flow rates, the nitrogen flow, bypass ratio, speed of the motor and mass of boron particle loading in the chamber. One limitation to the feeder design is that for each particle size loaded, the feeding parameters have to be adjusted in order to allow a continuous stream of particles into the flame. The particle size is measured in situ using principles of laser light scattering. A 488 nm argon line laser serves as the light source to illuminate the boron particle flame, while the scattered light was detected by photomultiplier tubes positioned at different angles. Optical properties of the burning boron particles were captured from photographic images and as spectra using a polychromator backed by a silicon intensified detector and analyzer. Through their work, oxygen mole fractions and temperature regions in the flame required for sustained reaction, BO_2 emissions as product formation, ignition delays, combustion times and changes in the color and particle streak thickness, useful in understanding boron combustion in hydrocarbon environments, were identified.

Additional work by [5, 33, 42, 57, 61], all explored burn times for single boron particles either ignited by a laser or burning in the combustion products of a hydrocarbon flame. In all cases, a two stage mechanism was identified by two peaks in the emission intensity vs. time traces or photographs. The peaks were separated by a period of darkness or color change from yellow or orange to white or green [28, 60]. In most cases, BO, BO₂ emissions are observable in the second stage and the second stage is longer than the first. The burn time is calculated as the total duration of the particle emission. The burn times ranged from 10-40 ms for 34.5 μ m and 44.2 μ m particles as the surrounding temperature changed from 1800 to 2900 K. At lower temperatures of 1772-1993 K, 2-3 μ m particles burn up to 2.48 ms, while smaller, 60 nm nanoparticles had burn times of 2 ms at 1810 K. The trend from existing combustion data have been shown in Figure 1.2. As discussed in Sub-section 1.1.1., the discrepancies and limited data on single particle combustion renders difficulties in establishing a fundamental reaction mechanism for micron-sized boron combustion in varying environments.

A common limitation of such investigations, however is that the results depend on the resolution of the optical device used for measurement. In addition, to properly interpret the measurements, one may need to distinguish the emission intensity produced by the surface of burning particles from that originated from the surrounding vapor from the condensing gas phase combustion products. Such a distinction is commonly difficult to attain. In most cases, the background emission, e.g., from a flame produced by other fuels, such as hydrocarbons, should be absent or easily distinguishable from the emission generated by burning particles. The feeding system has to be designed to ensure combustion of single particles, minimizing overlap between particle emission signals and accounting for possible agglomeration of the powder particles fed. Most laboratory experiments are tailored for atmospheric pressures and for single particles, but in common applications, combustion occurs at elevated pressures and temperatures and for large masses of boron particles burning at once. Notwithstanding, optical measurements performed in laboratory experiments are useful for identifying and understanding particle emission profiles, determining product formation (gas species) and obtaining temperatures leading to improved fundamental understanding of boron combustion. Single particle experiments are also useful for model validation due to their simplicity. Despite multiple relevant reports starting from early 1960s and identifying consistently BO, BO₂ emissions for varying environments [62-65], the particle surface/combustion temperatures are missing and definite product formation at each stage of combustion is yet to be confirmed.

Recently published combustion work has focused on bulk combustion properties of boron particles in order to account for particle interactions and to simulate large scale burning environments/ processes in practical applications. For these studies, generally boron is introduced as a suspension, lump, or large group of agglomerates suspended on a tungsten wire or seeded into hydrocarbons for combustion [48, 51, 66-68]. In most cases, the combustion characteristics are measured from time resolved photographic images, bulk spectroscopic emissions, chemi-luminescence or high speed videos. Figure 1.5 shows characteristic images of combustion emission from boron nanoparticles suspended in varying hydrocarbon droplets from work done by Ref. [67]. The goal of the study was to observe the burning characteristics of fuels such as ethanol and n-decane seeded with varying particle loading of boron or iron nanoparticles for intensified combustion. The aim is that boron or iron addition promotes increased energy density, easier and faster ignition and improved combustion efficiency for liquid fuels. Each mixture (5-20 wt% boron or iron) was prepared by hand mixing and then sonicated to prevent agglomeration of the particles. For combustion studies, a droplet from the mixture was suspended on a silicon carbide fiber, heated by a heating wire in a closed chamber with quartz windows.

Qualitative data on possible product emissions and flame shape changes due to the addition of nanoparticles were collected from a high-speed video camera. As seen in Figure 1.5, particles burning were identified as bright spots surrounding the hydrocarbon flame. The images also show that boron particle combustion varies dependent on the fuel. In decane, after ignition, a steady flame from the hydrocarbon develops followed by ignition of boron particles later on. A stronger green color indicating BO emissions is visible as more particles ignite. While in ethanol, boron particles appear to be immediately transported into the flame zone and burned there. The work also reports that for higher particle loading cases, an agglomerate would form, which may or may not ignite when the flame was gone. In such cases, the products from the combustion event were also analyzed by scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (EDX) for morphology and surface composition.

While bulk combustion could potentially lead to the analysis of products collected since larger quantities of boron are used, combustion efficiencies are difficult to interpret from the data presented from the current existing studies. Additionally, data from varying studies is not easily comparable to each other and fundamental findings particularly with reaction mechanisms are harder to infer from multiple particles burning rather than single particles. As such, studies with single micron-sized boron particles are preferred. However, for such cases, experimental design and equipment should be tailored so that combustion times are not heavily dependent on optical emission data. The fractal shape and aggregation of boron particles should also be properly accounted for in such experiments.



Figure 1.5 Successive pictures of boron particles (5wt%) ignition and burning in an n-decanebased fuel droplet (I) and ethanol droplet (II).

Source: [67].

1.1.4 Single particle ignition and combustion models

In order to understand the complexities involved in the boron ignition and combustion process, several theoretical models have been developed for single boron particles in varying oxidizing environments [30]. The underlying theory for most models is that there is a diffusion-limited oxidation of boron by the inhibiting oxide layer at low temperatures, followed by clean surface boron oxidation to B_2O_3 at higher temperatures [60]. The common reaction steps involved in most models are compared in Figure 1.6 for ignition and combustion. The reactions shown summarize the main development to date for boron

ignition and combustion models. In this section, we review the main models for each oxidation stage. The figure also shows modifications to the model presented by Ref. [5] to account for vaporization and changes in the $(BO)_n$ layer by Ref. [2].



Figure 1.6 Comparison of ignition and combustion models.

Source: [2].

In most semi-empirical models presented, mass transfer of species to and away from the particle surface by natural diffusion or convection, condensed phase transport, vaporization of the oxide, radiation and convective heat losses are accounted for. Diffusion and reaction rate constants are usually estimated from low temperature oxidation studies, which may differ significantly in practical applications. Specific data enabling one to unambiguously quantify the reaction rate constants are limited or non-existent. Another major challenge is that only oxygen is considered as a species diffusing into the B_2O_3 layer or molten boron droplet at higher temperatures. Yet, recent calculations have proven that nitrogen too plays a role in dissolution in molten boron and formation of BN. Although it is not competitive at low temperatures, BN may not be easily desorbed from the boron particle surface at high temperatures [56] lowering the fraction of boron active sites available for oxidation. Reactions with less preferential oxidizers such as CO_2 in oxygenlean environments [69] have different kinetics and other products than B₂O₃, including B_4C , BN, C, and $B_{13}C_2$ are yet to be considered. Further to that, in older models presented, the potential vaporization of boron particles leading to gas phase reactions is often neglected. Generally in all cases for ease of computation, detailed chemical kinetic models [70-76] have also been ignored and there may be a need to incorporate them.

Recently, work presented by Ref. [56] addressed this need by providing an extended in- depth chemical model of an isolated spherical boron particle in a quiescent, gaseous, post combustion flame. The model was based on principles presented by Ref. [5] but primarily focused on the kinetics and possible intermediates formed at each stage. It showed findings to support that the rate controlling steps for oxide layer removal are the surface chemisorption and desorption reactions. The work was very detailed and

encompassed several hundreds of reactions unlike all other models presented. The reactions included surface reactions, surface complexes and intermediates formed at the oxide and particle interfaces. It even included boron-nitrogen chemistry, which is commendable. However, it was not suitable for use in further CFD scale up models for ramjet systems because of its cumbersome nature and the lengthy computational time required for scale up. As such, Ref. [2] simplified the model to consider only major global reactions with adjustable rates based on an arbitrary fitting parameter, *C*. This is one of the most recent models presented that accounted for B₂O₂ and B₂O₃ evaporation and (BO)_n balance on the particle surface. The major limitation is that the effect of temperature and pressure are not accurately predicted to support experimental data available.

One of the first ignition models proposed was by Ref. [12]. It was later further developed on by Refs. [21, 22, 55, 77]. The model described ignition being governed by the boron oxidation through molten boron oxide film and removal of the film due to evaporation and heterogeneous surface reaction with water vapor. The model assumed that oxygen diffused through the oxide layer to the boron- boron oxide interface and reacted with boron to produce further B_2O_3 there. Models by Refs. [78, 79] were based on this assumption. Ref. [60] also created a similar model for ignition and combustion of boron in both wet and dry environments. However, in the model, the dissolution of boron in B_2O_3 , rather than oxygen diffuse through the impeding oxide was created. The complex converts to BO_2 on the surface of the oxide- gas interface by the attack of surrounding O_2 . Ref. [5] validated the formation of the (BO)_n complex and built upon the model presented by [60], with a change in evaporation product to B_2O_2 instead of B_2O_3 . While this is the underlying

mechanism used in all subsequent models, the formation of B_2O_2 , is yet to be confirmed by experimental studies.

Yet, there is another possible mechanism to be supported experimentally. It is the model of the dissolution of oxygen in the solid boron until a solubility limit is attained. This model was presented by [80], predicting that a boron oxide is formed from the molten particle surface exhibiting strong heat release similar to other metals like aluminum, magnesium, zirconium and titanium. Just recently, a B-O phase diagram has been published supporting the possibility of changing phases of B_2O_3 liquid and boron at temperatures of interest during combustion [10], and as such, future models can now be developed considering phase changes in the oxide layer to substantiate this theory.

To date, differing theories have been long presented, with no definite conclusion on the diffusion regime for boron particles, particularly at low temperatures. The theories generally agree that the oxide plays a role, but debate whether the reaction rate is limited by oxygen [12, 21] or boron diffusing through the oxide layer [81]. Models that followed have been modified with oxygen diffusion [78, 79], boron diffusion and in some cases a bidirectional diffusion mechanism [82, 83] with both species diffusing through the layer for low- temperature oxidation.

To help elucidate the main argument of diffusion through the oxide layer, Ref. [84] developed an ignition model assuming the oxide layer was comprised of two structures: B_2O_3 layer and $(BO)_n$. The model follows a similar principle of boron oxide complex formation on the surface of boron particles. Upon further low temperature oxidation, it was proposed that a $(BO)_n$ sandwich can be created; with B_2O_3 at the outer interface of the layer

with the gas oxidizer and at the boron surface while $(BO)_n$ in the middle. A schematic diagram describing the proposed reactions at each layer is shown in Figure 1.7. As shown, the overall main reactions remain the same as those presented in Refs. [5, 60] during ignition.



Figure 1.7 The generation mechanism of the outermost layer of the oxide layer. Source:[83].

While the validity of such assumptions is limited, Ref. [5] was aimed to prove in experimental studies that boron diffuses across the molten B₂O₃ liquid for further oxidation and that boron surface particles lost their structure at elevated temperatures to become a vitreous polymer (BO)_n. The study performed investigated the microstructural evolution of crystalline and amorphous boron particles in an oxygen, argon and water environment at temperatures from 25-940°C using an environmental scanning electron microscope and XRD analysis. Findings from images taken in the varying environments show molten boron and further recrystallization in some cases, but the change in morphology does not confirm the existence of the complex. Relevant phenomena were also observed in Ref. [83] using a similar technique with a transmission electron microscope to examine boron dissolution and species diffusion at 773 K in inert-argon and oxygen environments. More recently,

Ref. [82] studied the ignition delay time for boron particles and investigated the bidirectional diffusion mechanism during low temperature oxidation with TEM slices of combustion products from wire ignition experiments. The major challenge with these systems however is that observations detailing this diffusion mechanism was not conducted in-situ and could be dependent on heating rate and the oxidizing conditions the boron system was exposed to. Furthermore, in most cases an elemental map for the oxide layer changes was not presented to validate the theory and the (BO)_n complex is assumed to exist based on changes in contrast from the images recorded, which needs to be further supported.

In the case of water-containing environments, low temperature oxidation was described as B_2O_3 reacting with water to form HOBO to eliminate the surface oxide. Further oxidation occurred with clean surface B reacting directly with water to form HOBO. A similar reaction mechanism is proposed for fluorine- containing environments [30]. However in cases where multiple oxidizers were present in an environment, Ref. [30] scaled reaction rates inversely to the number of oxidizers present, which may not valid. The fact is that multiple oxidizing molecules could be diffusing to the particle surface in parallel and the interaction of each molecule with the particle surface will differ from each other, which needs to be accounted for.

The transition from ignition to combustion occurs, once there has been sufficient energy to vaporize the naturally occurring oxide on the surface of the boron particle or the thickness of the oxide is so small, the system becomes kinetically limited (for small particles < 10 μ m) or diffusion limited (for large particles > 30 μ m) during clean surface boron oxidation. The point of transition, signifying the end of ignition in some models is not distinct or fully understood. It varies from each model presented and can be determined as a fixed oxide thickness reduction to 5% [56] or 1% [2] of the original oxide thickness. Other criteria for transition into full-fledged combustion are the beginning of the melting process where the particle mass/size falls 1% below its initial value [78] or where the particle temperature exceeds the temperature of boron melting close to 2350 K.

For full- fledge combustion models, differences in reaction mechanism theories also exist. It can be argued whether or not surface reactions are kinetically or diffusion limited. Some modelers [5] have also presented mechanisms where first BO is formed, following by further reactions involving boron sub oxides yielding B_2O_2 rather than considering formation of B_2O_3 in one step. B_2O_2 is then further oxidized into B_2O_3 at a stand- off flame during combustion. Ref. [60] is one example of such a model considering that the burning rate is limited by the diffusion of oxygen to the surface. The study also predicts that the reaction of oxygen with boron occurs on the surface and that the transition from the diffusion-controlled to the chemistry-controlled burning is dominated by the product or pressure of the oxidizing environment. Contrary to this mechanism, earlier work by Ref. [85] determined two models for a spherical immobile boron particle in oxygen at atmospheric pressures for high temperature combustion: heterogeneous surface reaction to form B₂O₃ directly and boron combustion as a gas phase flame. The model was validated by single particle results presented by Ref. [57] and assumed that the reaction occurs in the diffusion limited region. Because temperatures exceeding the boiling point of boron were calculated using this assumption, a gas-phase flame some distance away from the particle surface was later postulated, forming B₂O₃ along with other intermediates such as BO and B₂O₂. Their results, despite being in good agreement with experimental data and predicting increased combustion rates for gas phase flames, considered only thermodynamic equilibrium composition of boron vaporization products, contrary to real practical systems, which operate under non- equilibrium conditions. The scope of the model was also limited to only three possible reactions occurring at the particle surface and stand- off flame, when multiple other reactions can occur. Recently, Ref. [86] proposed a simple diffusion model with Stefan flow for 34.5 and 44.2 μ m boron particles at temperatures above 2240 K. Unlike the reactions described by Refs. [5], Ref. [86] assumes that BO and BO₂ products observed in combustion experiments are due to the decomposition of B₂O₃ in high temperature environments, rather than the pre-cursors to the formation of B₂O₂.

Beyond differences in possible reaction mechanisms proposed, the models presented in the literature are typically considering spherical boron particles with uniform temperature distribution, while in reality boron particles commonly form fractal aggregates. Ref. [47] tried to address this phenomenon at low temperatures and developed a numerical model investigating the ignition of boron agglomerates. The objective was to address the concern that oxidation of boron agglomerates at low temperatures may not result in a transition to self-sustained combustion unless a critical oxygen concentration is present. It was assumed that the evaporation of oxide was controlled by an Arrhenius expression and that local concentration and diffusion within the agglomerate would not remove the oxide film completely. Agglomerates were then modeled as equidistant layers of equally sized spherical boron particles separated by the layers of oxide with the same thickness. Each layer had uniform oxygen concentrations that were time dependent and calculated assuming molecular diffusion in porous media. Within each boron particle, the model adapted the same reactions and mechanism as proposed by Ref. [12]. The model

validity however was found to be limited to crystalline boron particles and as such requires further modification to include changes in molecular diffusion for amorphous boron structures.

To test a practical application environment with these models, work by [69] was aimed at investigating the mechanism leading to lengthier ignition times of boron in propellants. It showed that variation in boron particle size, initial oxide layer and thickness were limitations to employing their existing model proposed [83]. While their study characterized combustion products effectively through XPS, SEM, etc. in order to identify products formed and so verify the possible reaction mechanisms, there are still several challenges. These include the fact that tests were carried out with bulk boron mixed propellants in a high temperature tube furnace, having an unknown temperature profile and as such, unknown initial particle temperature. The model also did not account for condensed phase product formation and the reaction kinetics associated with these species, despite identifying other product species formed. It assumed oxygen was the main oxidizer and ignition was defined by boron oxidation due to oxygen, when there may have been other kinetics involved due to the additives present. Furthermore, the effect of agglomeration was not accounted for.

A more suitable model combining the effects of single boron particles combustion in a flow field similar to that of a ducted rocket/ ram jet, developed by CFD was conducted in Ref. [87]. It proposed the same sequence of reactions within both ignition and combustion stage as described by earlier models. The major difference is that the model was added to a commercial CFD solver and coupled with other defined combustion environments. Though the model was validated by experiments, and would be an effective tool in allowing the effects of changes in efficiencies to be estimated; possible limitations would be the lengthy computational time required to conduct simulations similar to actual systems. Model validation also needs to be conducted using actual bulk combustion experiment tests with varying oxidizers rather than single particle combustion experiments. The model is also currently limited by how well the oxidizing environment is defined.

In summary, the reality is that despite several recent advances in modeling for boron ignition and combustion because of the vast improvement in computational tools over time, models are greatly limited. Vapor phase reaction mechanisms require validations; more importantly, it remains unclear which species volatilize from surface of burning boron and participate in such reactions. Heterogeneous reaction mechanisms, involving condensed phase diffusion and formation of various intermediate condensed phases, such as boron sub oxides, boron-oxygen-nitrogen and boron-carbon-oxygen solutions are largely unexplored and require further experiments to improve upon. The challenges also include availability of data on the diffusion coefficients of O₂ and boron sub oxides in B₂O₃ at relevant temperatures, reaction kinetics [88] at low temperatures and intermediate formation and validation of data from experiments to account for particle interaction and microstructure changes during combustion. Bulk system scalability and the fact that all existing models are restricted to oxygen or water as oxidizers are further concerns. Unknown thermal histories for boron particles and surrounding gases concentrations under experimental conditions also need to be addressed, since they may affect transport properties and possibly lead to changes in the nature of the oxide phases formed at high temperatures.

From the review conducted, there is a lack of models considering hydrocarbon combustion product environments and temperatures and limited kinetic models are available. Where more detailed and descriptive models are presented, they are cumbersome and not easily integrated to be applied to CFD codes for practical systems, while semiempirical models still lack adequate detail for a thorough description of the actual boron mechanism. To add to the lengthy list of limitations, oxidation kinetics for boron is hard to obtain due to the high temperatures required. This leads to the recommendation of developing advanced diagnostic tools for in- situ, high-temperature boron chemistry or experiments tailored to combustion reactions.

1.1.5 Existing strategies to improve boron ignition and combustion

Many approaches have been employed to lower ignition temperatures, ignition delays and improve combustion rates for boron. In most cases, there are associated undesired effects, particularly losses in energy content. Modifying boron without affecting its energy content significantly is a main challenge.

Because the presence of the oxide layer is believed to be the limitation for ignition, many studies have been conducted to improve low temperature oxidation by coating boron surface. The compound selected can potentially react faster with the surrounding oxygen to produce heat in order to melt and/ or boil off the B_2O_3 layer. The approach is to add faster ignitable metals or metal alloys such as magnesium [5, 6, 46, 80, 89], lithium [90], aluminum, titanium [91, 92], polymers [8], metal oxides [7, 16, 93], metal hydrides [4], carbon [46] and fluorinated compounds [30, 61, 94-96] to the surface of boron particles.

The additive used determines the mechanism that aids boron oxidation. In some cases, it is believed that the additive disrupts the inhibiting oxide layer, creating pathways for boron oxidation. Others promote ignition by reacting with the oxide layer to produce a gas- phase product that results in a clean boron surface sooner or the additive acts as an oxygen shuttle. Ref. [97] presented work with the use of oxalic acid as a coating for boron particles, which would be reducing the B_2O_3 oxide film at low temperatures. The combustion intensity increased by 16.7%, ignition delay reduced by 42.2% and efficiencies increased by 21.5%. The additive, however, required a high temperature in order for the reaction to occur, not achieving the desired objective. 10wt% coatings of NH₄ClO₄, KNO₃, LiClO₄ and HMX were also prepared on boron samples through an extensive wet chemistry procedure [98]. The results from laser ignition combustion, FTIR, XRD and thermogravimetric analyses indicated that the surface treatment changed the naturally occurring oxide crystallinity and lowered the initial reaction temperatures and in some cases, the activation energy. HMX-coated boron particles were the most favored for combustion, yielding higher combustion temperatures and higher combustion efficiencies due to longer self-sustaining combustion times recorded. Other polymers were selected to thermally decompose to produce gas species (namely fluorine) favorable for boron oxidation [61, 95, 99] or to prevent B_2O_3 reaction with moisture [100]. The challenge with most polymers, however, is that they significantly lower the energy density of the fuel and are typically carbon-based. In oxygen starving environments, they may lower combustion efficiencies for boron or compete for oxygen to be further oxidized into carbon dioxide and water.

For some metals, it is believed that a boride formation disrupts the inhibiting oxide layer [101], creating pathways for faster ignition while in others, the metal or metal oxide is believed to act as an oxygen shuttle for boron combustion [7]. In thermite systems, particularly, Ref. [93] found that the mechanism to enhance boron ignition and combustion is dependent on the oxygen vacancy concentration and metal- oxygen bond energies for the corresponding oxides. Smaller bond energies and higher oxygen vacancies lead to lower ignition temperatures and higher combustion reactivity. Work reported in Ref. [7] showed that 5wt% of Bi₂O₃, Fe₂O₃ and SnO₂ were sufficient to lower ignition temperature of boron particles. For metals, Ref. [3] showed that a comparable weight percentage of titanium and Mg- Al alloys in 33wt% boron- based propellants with HTPB also resulted in shortened ignition delays and prolonged self- sustained combustion. Magnesium increased combustion intensity, but aluminum metal was unfavorable. The samples were prepared at 0.2 MPa and laser ignited for 1s in a custom-designed combustor. Magnalium was also studied as a potential ignition source for boron in ducted rocket systems by Ref. [102]. Lowered ignition time delays and increased combustion efficiencies were recorded from measurements using an electronic furnace and connected pipe ducted rocket, supporting earlier findings. While these results are encouraging and the use of metals could assist boron ignition by providing heat through low temperature oxidation and aiding in boiling off the inhibiting oxide layer, more data on interaction of boron with different oxides or metal additives is required. A more quantitative approach to the reaction mechanism with oxygen shuttles also needs to be considered.

From past studies, the higher the quantity of the additive, the lower the ignition temperatures and delays and the greater the combustion intensity. To help in illustrating this effect, ignition times from various studies using 5-10 wt% additives were selected to create the summary of the reduction in ignition delays for boron particles shown in Figure 1.8. For each case, the recorded ignition time or ignition delay measured for the modified material is compared to the ignition time for the boron reference material in that same study. The difference is denoted as the percentage reduction in ignition delay recorded for each additive used. A positive value indicates that the additive has a lower ignition delay, a favorable result; while a negative value indicates a longer ignition delay recorded for the modified sample compared to boron in that same study. The figure shows that research thus far has been able to improve ignition delays by typically 30%. In some cases such as the magnalium alloy, titanium and GAP-coated polymer additives, ignition times/ temperatures can be reduced by 60%. Particularly in the study by [5] where approximately 4.57% of magnesium was coated on to boron particles (indicated by 1st black bar on the left), ignition times were slightly longer for the modified sample compared to boron. However, as the amount of magnesium increases to 5% addition to a boron- based propellant mix [3] and 10% hand-mixed with boron powders [6] ignition times were reduced by 18.30% and 27.47% respectively (see second and third black bars from the left). Furthermore, in work done by Ref. [103], where the role of boron carbide as a potential additive for improving amorphous boron oxidation characteristics was explored; they found that 60 wt.% boron samples were most favorable for lower ignition thresholds. More boron- rich samples were unaffected. From the review conducted, in most cases around 10

wt% of the respective additive is required for observable changes in ignition, which affects the energy density of the material.



Figure 1.8 Compilation of % reduction in ignition time delays from various studies [3-8] conducted with 5-10 wt% additive to boron powders.

Approaches for enhancing boron have also been exploited, which do not require appreciable amounts of additives. One such approach is downsizing boron particles. Due to limiting surface reaction kinetics, downsizing boron is expected to improve burn rates because of increased reaction surface area for nano-sized systems without an energetic penalty from an additive. However, Ref. [33] has shown that nano-sized boron particles in a hydrocarbon environment have similar burn times as micron sized systems. An explanation provided to this observation is that there is substantial oxide layer present for nanoparticles, compared to available metal for oxidation, similar to aluminum. As such, researchers have explored the use of surface functionalization by some ligand, organic chemical or energetic polymer to improve stability of the metal, without growing an unfavorable oxide layer [104]. Another form of surface functionalization was recorded by Ref. [105]. Micron- sized boron particles were treated by hydrocarbon solvents using ultrasonication. It was found that acetonitrile dissolves the inhibiting oxide layer for improved ignition. Another solvent, methanol was tested by Ref. [106, 107] to eliminate B_2O_3 coatings from the B₄C powder surface with success, but it also changed the microstructure of the system and its mechanical properties. The feasibility of other energetic surface treatments or the impact of this treatment presented by [105] on high temperature combustion is not clear and is yet to be presented.

In some cases, the environment of the boron particles is altered by introduction of halogens [30], pressures, water [62] and recently plasma [64] to enhance boron ignition and combustion. Particularly, plasma is believed to assist combustion by generating a high concentration of oxygen free radicals, the starting reactant for oxidation. In work done by Ref. [65], a multi- diffusion flat flame burner fueled by methane and equipped with a needle like plasma exciter and high frequency high voltage power supply is used to investigate the effect of plasma on boron combustion. The boron particles are held in a vibrating ethanol suspension. The suspension is atomized, dried to form an aerosol and fed by nitrogen into the center of combustion products of the methane flame. The tungsten needle electrodes are positioned at the exit of the particle feeding nozzle to form the needle-like arc discharge plasma. Using a laser phase Doppler anemometer for particle sizes, broad band spectrometer and digital single reflex (DSLR) camera, the different stages of boron oxidation were identified. The boron ignition delay was reduced from 3.06 ms to 0.77 ms [65], which indicates that plasma accelerates boron combustion. A model was developed

by Ref. [64] in order to understand whether or not the improvement was driven by alterations in the reaction kinetic path or thermal effects of the plasma itself. Figure 1.9. shows the effect of plasma enhancement of boron sub- micron particles combustion in a hydrocarbon environment as results from the work conducted by Ref. [65]. As shown in the images, the intensity from boron particles burning at low temperatures (around 1500 K) in the hydrocarbon flame images increase with increased supply power to the plasma electrodes. The figure also shows the reduction in boron ignition delay as the power increases for the plasma generated. The challenge with changing the environment, however is that in practical applications, this might not be achievable within current propellant design constraints to lower costs and weights.



Figure 1.9 (A) Boron flames as the power of the plasma discharge is changed from 0 to 78W and (B) trends of the ignition time delay versus power of the plasma discharge and ambient temperature.

Source: [65].

In summary, boron has great thermodynamic potential but its oxidation mechanism, though extensively studied remains poorly understood and is rather complex due to its oxide layer and limited combustion data. Further investigations on micron sized boron particles are required to bridge the gap for data required to validate models, while accounting for boron agglomeration, purity and changes to surface oxide thickness. Also, limitations to current models need to be addressed to provide a simple mechanistic approach for boron full- fledge combustion. Finally, there are several strategies presented to improve boron, each limited to improve ignition or could potentially affect the energy density of the material. As such, there is a motivation to resolve these challenges and limitations identified, so that the energetic potential of boron can be fully utilized in combustion applications.

1.2 Research Objectives

In order to adequately address the challenges associated with boron powder combustion for its intended use as a fuel additive in explosives and propellants, further research is required. The focus of this work therefore is twofold and can be broken into the following objectives:

- 1. To modify boron particles for improved ignition and combustion, while maintaining safety, ease of handling, stability and thermochemical properties.
- 2. Improve the understanding of reaction mechanism of boron including both ignition and full-fledged combustion in different environments, so that rate controlling steps are identified and can be manipulated to improve the overall combustion rates. The kinetic model developed should be simple and easily integrated in design codes to test the feasibility of boron (modified and un-modified) fuels in varying propulsion systems.

The proposed effort will include strategies in investigating varying techniques to modify boron particles to achieve higher burn rates and shorter ignition delays; preparing and testing performance of new boron-based materials; creating and executing oxidation rate studies and combustion (both single particle and bulk) experiments, and finally developing a kinetic model suitable to describe single boron particle combustion in air.

The study should address the following outstanding scientific questions:

- 1. What is the rate limiting step in full-fledged high temperature combustion of single boron particles?
- 2. Is the reaction mechanism the same in different oxidizing environments?
- 3. What is the proposed change in combustion reaction mechanism due to the modification of boron particles by surface treatment and doping?
- 4. How is the rate of combustion affected by each type of modification to boron?
- 5. What is a suitable metal dopant and which preparation technique is most suitable for large scale applications?
- 6. Does the preparation technique of the material affect high temperature reactions?

1.3 Organization of the Dissertation

This report will present material divided into ten chapters. Chapter 1 is an introductory chapter into the existing technology and competing research for boron to date. This serves as a background to the proposed work. Chapter 2 investigates single boron particle combustion in a hydrocarbon environment with varying oxidizer type and concentration. The primary focus of this chapter is to establish combustion temperatures for single
micron-sized boron particles and to identify burn trends for a range of boron particle sizes. It also describes a new approach to directly account for the sizes of boron particle aggregates fed into the combustion environment. Findings from a computational fluid dynamics model of the flame not seeded with particles is also presented in order to describe the oxidizing environment of the boron particles. Chapter 3 describes the first approach in improving boron ignition and combustion by removal of the inhibiting oxide layer by dissolution with acetonitrile and further hydrocarbon treatment. Changes in oxidation rates, ignition delays and combustion times are compared for modified materials and the stability of the samples are tested in air for up to a period of 120 days. Chapters 4, 5, 8 and 9 presents work on modifying boron by introducing small dopants using different preparation techniques. The combustion characteristics of the doped boron powders in different environments are presented and discussed. A further qualitative description of the two stage mechanism in high temperature oxidation is presented. Chapter 4 also details the findings of a CFD model of the hydrogen-air flame environment. A detailed description of the model is provided in the appendices. Since the focus is to improve surface kinetics for boron, in Chapters 6 and 7 the gap in kinetic data available for boron surface reactions is addressed. The model developed accounts for the cumbersome morphology of boron aggregates and proves that kinetic parameters for low temperature boron oxidation reactions with negligible oxide thickness are applicable for high temperature combustion. Finally, in Chapter 10, conclusions and recommendations for future work are presented.

CHAPTER 2

COMBUSTION OF BORON PARTICLES IN PRODUCTS OF AIR-ACETYLENE FLAME¹

2.1 Abstract

Boron is an attractive fuel for propellants and explosives because of its high volumetric and gravimetric energy density. However, despite multiple previous studies, burn times and combustion temperatures of fine boron particles in well-characterized environments are not well known. The aim of this work was to characterize the combustion of boron particles injected into air-acetylene flames and to determine their burn times and combustion temperatures as a function of their size. The experiments used 95% pure commercial boron powder with particles in the range of 0.4-30 µm. Premixed acetyleneair flames with varying equivalence ratios (0.62 and 1.65) were produced. Boron powder was injected axially into the flame combustion products with a nitrogen jet. The particle size distributions were determined using powder that exited from the injector and captured directly on to microscope slides. Agglomerated particles fed into the flame were observed directly and accounted for in the particle size distributions. Powders were analyzed using scanning electron microscopy (SEM) and particle sizes were corrected accounting for the fractal dimensions of the observed agglomerates. The measured burn times were correlated with the obtained particle size distributions to recover the effect of particle size on its burn

¹ The findings presented for this chapter have been published in the peer- review journal, Combustion and Flame under the reference listing:

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time. The environment in which the particles burned was characterized in detail using computational fluid dynamics. Results indicated that for micron-sized amorphous boron particles, their time, t_b , in ms, can be described as a function of the particle diameter, d, in μ m, as $t_b \approx 4.73 \cdot d^{0.75}$. Average combustion temperatures exceed 2600 K in a pre-mixed hydrocarbon flame environment and show no significant correlation with particle size or burn times.

2.2 Introduction

Metals are used in propellants and explosives due to their high oxidation enthalpies, high combustion temperatures, and low molecular weight products. Particularly, there has been interest in the use of boron due to its high volumetric and gravimetric heating values [40]compared to other metal fuels like magnesium and aluminum [16, 108]. However, it is difficult to recover the full energy of boron oxidation in practical combustion applications. This has been attributed to its delayed ignition caused by its protective oxide coating [30, 58, 78] and long combustion times [5, 28, 29, 33, 57, 60, 109, 110]. Research further suggests that during boron combustion, heterogeneous surface reactions occur at relatively low combustion temperatures [25] because of its high boiling point. Formation of relatively stable intermediates and less thermodynamically favorable products, such as HOBO is widely considered as another limitation for boron combustion in hydrogen containing environments [33]. Polymorphic phase transitions [111], crystallinity, particle size and surface morphology of boron particles have also been reported to impact both its ignition and combustion [43].

Despite an extensive and sustained effort to understand boron combustion, majority of the published work focused on quantifying its ignition delay and oxidation kinetics [5, 40, 46, 54, 58, 88, 112]. There are limited published data on the combustion times of fine boron particles and no record of the measured boron combustion temperatures.

From the data available, correlations between the size, d, and burn times, t, for coarse crystalline [28, 29, 57] and more recently nano-sized boron particles [33] have been presented in the form of common $t \sim d^n$ trends (power law, with the exponent, n). No similar correlations are available for the most common, and more affordable micron-sized amorphous boron powders. Published experimental results and respective power law trends proposed for fine boron particles are inconsistent between one another. For example, burn times for 7 and $10-\mu m$, 99% pure boron particles were reported to be 1.5 and 2.2 ms, respectively, for the powders injected into combustion products of methane/oxygen/nitrogen flames [60]. These results are in agreement with an experimental trend and respective power law, with n=1.35 implied by earlier studies with much coarser particles [28, 29, 57]. Conversely, burn times for smaller, 2.5 and 3 µm particles (93 % pure amorphous and 99.5% pure crystalline, respectively), also injected into a hydrocarbon fuel flame, were reported to be longer, 4.1 and 4.6 ms, respectively [5]. Even shorter burn times of 0.24–0.42 ms and 0.2-1 ms were recorded for 7.2 µm and 20 µm boron particles, respectively ignited by a reflected shock wave at high pressures [54, 112]. In both Refs. [5] and [60] flat flames using methane as a fuel were used, and thus, the experimental conditions are expected to be comparable to each other. Although boron powders with different purities and crystallinities were used in different studies, it was reported that the effect of boron crystal structure on its combustion is negligible [5]. However, crystallinity was reported to affect ignition of boron, [46]. More recent experiments with still finer 0.674 µm 99% pure amorphous boron particles [33] suggest burn times greater than 2 ms, also in disagreement with the trends implied by previous experiments [28, 29, 57, 60]. One possible reason for such discrepancies maybe that in all previous studies, a specific size was assigned to a powder sample used in the experiments. However, all such powders contained particles of different sizes, and the measured burn times could have been biased to specific subsets of particles, depending on how the particles were injected in the flame and how the combustion time was measured in each case. Particles could also have been agglomerated, which would affect the measured burn times substantially. Another possible reason for the discrepancy in the measured particle burn times is that different indicators were used to identify combustion in different studies. In Ref. [5], the burn times were determined from the lengths of the photographed particle streaks. In Ref. [33], durations of pulses recorded by filtered photo-sensors were used. In Ref. [60] scattered light from a 489 nm line argon- ion laser was recorded at two angles by two photomultipliers (PMTs). The intensity of the scattered light decreased as the particles burned out. The distance over which the intensity of the light scattering signal decayed and particle velocity were used to infer particle burn times.

Thus, careful measurements are still needed to address specifically the effect of boron particle size on its burn time and take into account possible agglomeration of boron particles. As noted above, measurements of temperatures of the burning boron particles are also currently lacking. The objective of the present study is to clarify the existing discrepancies and obtain the missing data characterizing combustion of fine boron particles in well-defined oxidizing gas environments.

2.3 Experiments

2.3.1 Experimental setup

Aerosolized particles were fed axially into a premixed annular air-acetylene flame. The experimental setup is shown schematically in Figure 2.1. It has been described in detail elsewhere [113-115]. The mixed gases were fed through a 50-mm long, 19.13-mm diameter tube that was tapered to form a 5.16-mm nozzle of the burner. Flames with two equivalence ratios ($\varphi = 1.65$ and 0.62) were created by varying the acetylene flow rate between 0.64 and 0.24 L/min and maintaining the air flow at 4.72 L/min. All flow rates were measured using individual rotameters. Acetylene was used to minimize soot production and readily achieve high flame temperatures in a broad range of the air/acetylene equivalence ratios. As for the other hydrocarbon fuel gases, combustion products mostly comprised CO₂, CO and H₂O, which served as main oxidizers for boron particles, similarly to previous experiments [5, 33, 60].

Vertical temperature profiles of the flame were measured by inserting a 0.51-mm diameter, 50.8-mm long alumina rod into the flame and collecting its emission spectrum using a StellarNet Inc., Black Comet UV-VIS-NIR Blue Wave (BW16) spectrometer. The flame emission without the rod was recorded as the baseline signal. Assuming that the emissivity of alumina did not depend on wavelength, the respective temperatures were obtained from the spectra. The measured temperature profiles were compared to those predicted by a computational fluid dynamics (CFD) model, as discussed below.

For gas velocity measurements, particle image velocimetry was used, similarly to earlier work [22]. In this case, 99% pure titanium particles by Alfa Aesar (-325 mesh; less than 44 μ m) were fed into the products of the air-acetylene flame. The titanium particles were chosen based on their bright emission streaks readily visible despite the background flame emission. A chopper disk attached to a motor was installed in front of the camera. Images of the dashed streaks were captured using a SONY DSC-H50 camera at a shutter speed of 1/4 s.

Boron particles were injected in the air-acetylene flames through a brass tube with 2.39 mm internal diameter, placed axially at the center of the burner's nozzle. Approximately 0.1 g of the SB-95 amorphous boron powder, nominally 95-97% pure by SB Boron, was loaded onto a custom-built powder screw feeder and fed into the burner using nitrogen as a carrier gas. The nitrogen flow rate was 0.94 L/min and the powder mass feed rate was 0.27 mg/min. The particle feed rate and flow conditions were selected based on preliminary experiments to minimize overlapping emission peaks from particles burning simultaneously. The number density of the particles seeding the gas flow can be evaluated considering that the number average fractal corrected particle size is 2.8 µm, leading to the average particle mass of about $2.7 \cdot 10^{-2}$ µg. Accounting for the gas flow rate, one obtains the concentration of about 10^5 particles/cm³, or on average distance between particles of about 455.7 µm. This distance is much greater than the particle size suggesting that the particle interactions, e.g., leading to agglomeration or sintering of particles fed into the flame are negligible. Boron burned in the combustion products of air and acetylene; the surrounding air was mixed in the combustion products providing an additional oxidizer at greater distances from the burner.



Figure 2.1 Schematic diagram of the experimental setup and photographs of air- acetylene flame at equivalence ratio 1.65 with and without particle feed.

Optical emission pulses produced by boron particles burning in the flame were recorded using two Hamamatsu R3896-03 Photomultiplier Tubes (PMTs) equipped with 700 and 800 nm interference filters. The light to the PMTs was fed using a bifurcated fiber optics bundle, with its optical inlet positioned approximately 5 cm above the top of the burner and 17 cm away from the burner. The height of the field of view was 25 cm, while the streaks were typically originating at the height of 2 cm and ended no higher than approximately 13 cm above the burner. The voltages feeding each PMT were selected in preliminary experiments. The voltages were adjusted to avoid saturating the PMTs when recording the strongest particle emission pulses. Figure 2.2 shows characteristic examples of the boron emission signals recorded by the 700 nm filtered PMT. There is a background emission from the flame and multiple pulses from individual burning particles. The pulses

have characteristic shapes with double peaks. Interestingly, similar double peaks were reported for boron combustion in Ref.[33], although optical measurements were performed there at 546 nm, emphasizing emission of gasified boron sub-oxides. Some of the pulses recorded in the present experiments overlap with each other. Such overlapping pulses were removed from the data processing.



Figure 2.2 A typical sequence of boron particle combustion emission pulses on top of the flame emission background.

Recorded particle emission signals were processed using a custom MATLAB code [113] to determine particle burn times and the combustion temperatures. Data were collected at a rate of 100,000 samples per second using a 16-bit PCI-6123 National Instruments data acquisition board and LabView software for a total of 8 seconds for each run. A total of 80 runs were processed to analyze over 800 well-separated individual particle peaks. The 700 nm wavelength signal was selected for burn time analysis because it had the greatest signal to noise ratio. For initial processing, the baseline was identified

as an average signal value without any particle peaks calculated for a range of 1,000 points. The duration of the individual emission pulses were interpreted as particle burn times. The time was obtained when the signal amplitude exceeded the noise level by more than 10% of its maximum value. Thus, particle emission peaks were clearly distinguished from the flame background emission; the same peak duration assessment was used earlier, in Ref. [113]. Statistical distribution of the obtained particle burn times was correlated with the measured particle size distribution (see below). It was assumed that larger particles burn longer to obtain the correlation.

In addition, time- and particle- averaged boron particle temperature was determined from the time-integrated optical emission spectra from multiple particle streaks. The StellarNet BW16 spectrometer was positioned 5 cm above and 23 cm away from the burner tip. Emission spectra were recorded with an integration time of one second. A total of 1500 spectra were collected for each experimental configuration. The data were processed to filter out peaks of the boron combustion products (480-680 nm) and emission from contamination by sodium (589 nm) and potassium (740 nm- 810 nm). Effect of wavelength on emissivity was neglected, so that the remaining spectra were used to obtain the temperature by fitting them with the Planck's formula, where the temperature served as an adjustable parameter. A study by Millot et al., [116] confirms that the emissivity of boron is not affected by the wavelength. Boron was also reported to behave as a gray emitter above 0.65 nm in Ref. [117]. Hence, treating boron as a gray body emitter here is well justified.

2.3.2 Particle size distributions

To account for possible agglomeration of boron particles fed into the burner, the particle size distributions were obtained for the powder that passed the entire feeding system. The powder was fed with all gas flow rates set up as in a combustion experiment; however, the air-acetylene flame was not ignited. The powder exiting from the burner was collected for fifteen seconds on an aluminum surface positioned 4 cm above the burner. The collection surface was charged to 1 kV relative to the burner to enhance collection of fine particles electrophoretically.

The particle sizes were determined by image processing of electron micrographs. Collected powders were examined using a LEO 1530 Field Emission scanning electron microscope (SEM). Several images at different magnifications were recorded. For each magnification, the images were processed to identify particles and measure their sizes using ImageJ, a freely available software package. A characteristic image is shown in Figure 2.3. Individual particles are close to or smaller than 2 μ m; most particles are agglomerated, as is typical for boron powders.

Determining particle size distributions by image processing presents two main challenges. First: particles are agglomerates of much smaller primary particles as clearly visible in Figure 2.3. To obtain equivalent particle sizes that can meaningfully be correlated with burn times, individual agglomerates were treated as fractal objects that can be described by a fractal dimension of less than 3. Equation 2.1 was used to compute the diameter d_{corr} of the sphere that has the same volume as the observed agglomerate with the apparent diameter d_e [118]:

$$\boldsymbol{d}_{corr} = \left(\frac{\boldsymbol{d}_{e}}{\boldsymbol{d}_{ref}}\right)^{D_{t/3}} \times \boldsymbol{d}_{ref}$$
(2.1)

This formalism requires identifying the primary particle size d_{ref} , which was determined to be 0.7 µm as the smallest particle observed in high-magnification images. The fractal dimension, D_f , was determined using the box counting technique available in MATLAB[119]. For boron powder, it was found that the fractal dimension D_f =1.8.



Figure 2.3 SEM Images of amorphous SB 95 boron powder used in experiment.

(A) An overview image taken with back scattered electrons and (B) is an image taken with secondary electrons, showing several circled particles for which sizes were measured.

The second challenge is that only a narrow dynamic range of particle sizes that can be captured at any given magnification, which is a common limitation for obtaining the particle size distribution relying on SEM images. For usual broad particle size distributions, a large particle can occupy most of the image while smaller particles may not be well resolved. To address this issue, images of each powder sample were collected at several magnifications. First, a low magnification, 1,000x was selected to obtain images clearly showing the coarsest particles in the powder. The magnification was increased to 5000x, and a set of new images was obtained covering the same area of the powder-coated surface as in one of the low-magnification images. This step was repeated once again, with magnification increased to 20,000x, with multiple images covering the area of one of the 5,000x images. With this third magnification, the finest, submicron sized particles present in the sample could be clearly resolved, so no further increase in magnification was necessary. A total of 22 images were acquired for processing.

For all acquired images, apparent particle dimensions along the longest and shortest axes were measured. The equivalent diameter was estimated as the average of the two obtained lengths. A histogram characterizing size distribution for each magnification was thus obtained as shown in Figure 2.4. The three histograms were then merged into a single size distribution covering the entire range of particle sizes using the following procedure.

Initially the histograms for 20,000x and 5,000x magnifications were combined. A size bin present in both histograms and representing a particle size well-resolved in both sets of images was selected. As shown in Figure 2.4, this size bin is 1.44 μ m. It was assumed that particles less than 1.44 μ m were best resolved at the higher magnification images, and thus the part of the histogram obtained at 20,000x and showing particles smaller than 1.44 μ m was accepted. The histogram at 5,000x was then renormalized so that the number of particles in the 1.44 μ m bin was equal to that of the histogram obtained at 20,000x. Respectively, numbers of particles in all bins with greater sizes were increased accordingly.

The same processing was repeated merging the combined 20,000x and 5,000x histogram with the histogram taken at 1000x. In that case, the overlapping size bin was 5.2 μ m. Note that different bin sizes were considered for this processing as possible overlapping size bins. It was observed that any of three (3) closely positioned bin sizes, all of which were well resolved in both sets of images, could be selected for merging two histograms generating the same result. The final particle size distribution obtained by combining all three individual histograms and corrected for agglomeration is shown in Figure 2.4.

For reference, the particle size distribution was also determined using low angle laser scattering. The powder was suspended in hexane and analyzed using a Beckman-Coulter LS20 Enhanced Particle Analyzer. A drop of surfactant was added to prevent coalescence of particles. Ultra-sonication was applied. It is interesting that the fractal dimension corrected histogram obtained from SEM images is not very different from that obtained by low-angle laser light scattering. A greater fraction of larger particles observed in the SEM images was diminished due to fractal dimension correction, suggesting that such particles are mostly agglomerates.



Figure 2.4 Particle size determination of boron particles with final distributions obtained from SEM image processing and low angle laser scattering.

The fractal dimension corrected particle size distribution obtained from the SEM image processing was correlated with the experimental distribution of the particle emission durations. As noted above, that correlation was used to determine the effect of particle size on its burn time.

2.4. Experimental Results

Figure 2.5 shows a typical image of luminous streaks produced by burning boron particles. The streaks were observed within a relatively well-defined region of ca. 4-mm diameter and 13-cm height above the nozzle. Burning boron particles were bright red/yellow upon ignition and then green, as the particle ascended the flame. The green colored emission is typical for boron oxide, expected to form as a product of boron combustion [60]. The streaks typically originated above the brightest region of the flame, most likely as a result of an ignition delay of the heated boron particles.



Figure 2.5 Boron particle combustion streaks in pre-mixed air-acetylene flame at the equivalence ratio ϕ =1.65.

The burn times (or emission durations) obtained from individual particle emission pulses measured by the filtered PMTs were sorted into logarithmic bins. The number frequency distributions were plotted as histograms shown in Figure 2.6 for flames with both equivalence ratios. The number average burn time for the leaner flame (ϕ =0.62) was 6.13 ms while the more fuel rich flame (ϕ = 1.65) had an average burn time of 8.7 ms.



Figure 2.6 Number-based burn time distributions of amorphous boron particles injected in combustion products of air-acetylene flames at different equivalence ratios.

For analysis, the amplitude, *A*, was used selected as the highest point of each particle emission peak. The present experiment assumes that in each experiment larger particles or agglomerates burn longer; they also are expected to produce greater emission intensities. Indeed, the pulse amplitudes, *A* could be correlated with burn times, t_b , using a power law relationship with ($A \approx t_b^x$) where the exponent value, *x* was 0.99 and 0.67 and the goodness of fit, R^2 was 0.33 and 0.22 for flame equivalence ratios 1.65 and 0.62 respectively. Respective correlations are shown in the appendices.

The statistical distribution of the pulse amplitudes representing combustion of boron particles in air-acetylene flames with different equivalence ratios are shown in Figure 2.7. The pulse amplitudes are somewhat stronger for the flame with ϕ =1.65 compared to that with ϕ =0.62. This may be indicative of a greater boron combustion temperature obtained in the flame with a higher equivalence ratio, as indeed confirmed by the temperature measurements discussed below.



Figure 2.7 Emission peaks amplitude number-based distribution plots for boron particle combustion in flames with different equivalence ratios.

Correlation of the boron particle burn times with their size distributions yielded the trends, which describe the effect of particle size on its burn time shown in Figure 2.8. It was observed that the flame equivalence ratio has a weak effect on the particle burn time. For both flames, the trends can be reasonably well described by a power law with the exponent of 0.75, i.e., the burn time, t_b , in ms, is a function of the particle diameter, d, in μ m, as $t_b \approx 4.73 \cdot d^{0.75}$, although the best fit suggests exponents of 0.73 and 0.78 for the flames with ϕ =0.62 and 1.65, respectively.

The results from these experiments are compared in Figure 2.8 with previously published data. In all experiments, boron particles of different sizes were fed into the combustion products of hydrocarbon flames. The data from the most recent report for boron nano-particles by Young et al., [33] fit with the present results very well. The burn times reported by Yeh and Kuo [5] for the particles in the same size range as in this work are somewhat shorter than those implied by the present measurements. Because particle size distributions were unaccounted for in Ref. [5], it is likely that the measurements were biased by finer particles, and thus the burn times are shorter than expected for the volume or surface area based average particle sizes, commonly used as single size references for powders. Additionally, the discrepancy may be due to the technique used to detect particle burn times using images of the incandescent particles. The dynamic range of brightness captured by photography is relatively narrow, so that the streaks could have represented only fractions of burn times, for which the emission was the brightest. The burn times for the largest particles studied by Macek et al., [28, 29, 57] follow a D^{1.35} law. Aside from

data points for the finest particles used in the early experiments, the trend line implied by the Macek's measurements can be reasonably reconciled with the present measurement. However, the data points reported by Li and Williams for finer particles [25, 60] appear to be outliers, when compared to other measurements. This discrepancy may be due a systematic error of the measurements relying on the light scattered by burning particles. It was assumed that particle size is decreasing as they burn out, causing reduction in the intensity of the light scattering signal. However, if particles are burning heterogeneously producing condensed phase products or intermediates mixed with or dissolved in the molten boron, the particle size may not decrease during combustion. In that case, the reduction in the intensity of the light-scattering signal does not represent the beginning of the full-fledged combustion.



Figure 2.8 Effect of particle size on their burn time for boron particles injected in air-acetylene flames with different equivalence ratios.

Unfortunately, individual emission pulses recorded using filtered PMT signals could not be usefully processed to obtain accurate temperature traces for individual particles. The issue preventing processing the filtered emission traces was that the background flame emission shifted the filtered PMT signals and that shift could not be properly accounted for using the calibration of the PMTs obtained using a tungsten filament heated to different temperatures. Although the intensity ratios from individual emission pulses did not yield the appropriate temperature, they could be compared to one another qualitatively, for pulses of different duration and thus representing particles of different sizes. No effect of pulse duration on the intensity ratio was detected, suggesting that particles of all sizes burned at the same temperatures. This result was obtained for experiments with both air-acetylene flames used.

The actual temperature measurements were limited to those obtained from integrated flame emission spectra. Such temperatures are more representative of the maximum rather than average combustion temperatures observed in the experiments. Examples of a typical boron emission spectrum and its respective temperature fit are shown in Figure 2.9. Characteristic pattern of molecular emission produced by gasified boron oxides is visible; this emission comes from the vapor phase flame. For processing, the peaks produced by boron oxide emission and those by common impurities, such as K and Na were removed from the spectrum. The remaining portion of the spectrum, representing thermal emission from the surface of heated particles is shown as a bold line in Figure 2.9. This portion of the curve was used to fit a Planck's curve using temperature as an adjustable parameter. These integrated spectra yielded average temperature values of 2630 ± 240 K

and 2870 ± 370 K for particles in flames with the equivalence ratios $\phi = 0.62$ and 1.65, respectively. The difference in these temperatures is consistent with the observed difference in the amplitudes noted for the boron particle emission peaks recorded for flames with different equivalence ratios (cf. Figure 2.7).

Greater flame temperatures are surprisingly associated with longer burn times for boron in the flame with ϕ =1.65. As further discussed below, this may be explained considering different oxidizers available in different oxidizing environments, and respectively different structures of flames formed around burning particles.



Figure 2.9 Integrated emission spectrum with respective Planck's curve fit for boron particle combustion in air-acetylene flame of equivalence ratio of 1.65.

Note: The bold portion of the experimental spectrum was used to obtain the fit.

2.5 Concentration and Temperature Profiles in the Air-acetylene Flame

Present experiments characterize boron particle combustion in reaction products of an airacetylene flame. In this section, the environment to which boron particles were exposed to is characterized using a Computational Fluid Dynamics (CFD) simulation of a premixed hydrocarbon flame. The model described mixing of combustion products of the airacetylene flame with a stationary surrounding air accounting for an auxiliary central nitrogen jet. The simulation was solved using COMSOL Multiphysics software version 5.0.

2.5.1 Modeling

The model considered only mixing between hot combustion products of the air-acetylene flame, nitrogen gas (particle carrier jet), and surrounding air. No chemical reactions were considered; instead, both temperature and composition of the combustion products were described based on preliminary thermodynamic equilibrium calculations using NASA CEA code [1]. The model did not account for presence of condensed particles. It was assumed that both air and acetylene were preheated to approximately 450 K. This was based on the thermocouple-measured temperature of the burner nozzle. The nozzle and tubing used to feed the gases were pre-heated by the flame during the experiment. In calculations, pre-heating fuel and oxidizer caused somewhat higher than usual adiabatic flame temperatures.

The configuration represented in the model is shown in Figure 2.10. The flame was assumed to form a ring surrounding the central tube feeding the particle laden nitrogen flow. The flame was assumed cylindrically symmetric; thus, a 2-D model was considered.

To simplify analysis, only four most abundant combustion products were accounted for, as shown in Table 2.1, for each air-acetylene flame equivalence ratio.

It was assumed that the combustion products at the adiabatic flame temperature were injected in air from a cone, similar to a Bunsen flame. Note that the cone shown in Figure 2.10 is different from that shown in the photos in Figure 2.5 or inset in Figure 2.1. The photos capture the overall image of the flame surrounding the central tube through which the powder is fed; the flame appearance is further deformed by the central nitrogen flow carrying the particles. The cone shown in Figure 2.10 represents a cross-section of a premixed, ring-like flame produced by air and acetylene flow from the feeding system. It is smaller than the bright cone visible in the photos. The cone dimensions were determined by the mass flowrates of the combustion products, and adjusting the flame burning velocity. Burning velocity was selected to be in the range of 20-140 cm/s, reported for air-acetylene flames[120] with varying equivalence ratios. The burning velocity was treated as an adjustable parameter; it affected the flow configuration and the obtained temperature and velocity profiles.

Table 2.1 Temperatures and Compositions of the Air-acetylene Combustion Products Obtained for Different Equivalence Ratios using NASA CEA Code [1] and Used to Describe Inlet Gases in the Present CFD model

Equivalence Ratio	1.65	0.62	Used as inlet gas
Adiabatic Flame Temperature (K)	2629	2144	composition
Species	Mole fractions		
N ₂	0.65	0.76	Yes
СО	0.18	1.5×10^{-3}	Yes
H_2O	0.07	0.05	Yes
CO ₂	0.05	0.10	Yes
H ₂	0.04	1.4×10^{-4}	No
O_2	3.6×10 ⁻⁴	0.08	No



Figure 2.10 Schematic diagram of the computational domain; dimensions are in mm.

The height of the cone, h_{cone} , cone angle, α , and velocity vectors, V_z and V_r were calculated based on the flame speed and the unburned gas velocities, u_u of the reactants following the steps outlined in the appendices. Thermal expansion and the effect of gravity were also accounted for. Radiation was neglected.

The model coupled calculated heat and mass transport. It accounted for changes in properties as temperature and concentration of the species varied throughout the domain. Following related earlier work for jets and flames [121, 122], the turbulence effects were modeled using Reynolds averaged Navier-Stokes k- ω shear stress transport turbulence approach. It was assumed that the species transport and all heat transfer were by convection throughout the fluid. The simulation was done under steady state conditions. In all simulations, the convergence was achieved when residuals stabilized at values below 10⁻⁴

for each segregated group of independent variables; a similar criterion was used recently describing an H_2/O_2 flame [123].

The surrounding air was assumed to be at room temperature; the central flow (pure nitrogen) and unburned air-acetylene mixtures were assumed to be preheated to 450 K, as explained above. At the boundary, representing the Bunsen flame cone, the air-acetylene flow was converted into the respective combustion products at the adiabatic flame temperature. A summary of the boundary conditions used for each flame mixture is shown in Table 2.2.

The mesh was developed based on a COMSOL Multiphysics defined physicscontrolled mesh. The smallest, less than 10- μ m, elements were located near the tip of the flame cone. The largest, 0.3-mm elements were considered away from the flame, at the open boundaries. The mesh was refined based on results of preliminary calculations with varied configurations to ensure the independence of the final results on small changes in the mesh element dimensions.

Boundary Condition	Physics		
	Turbulent k-ω Transport	Heat Transfer in Fluids	Transport of Dilute Species
Axial Symmetry	-	-	-
Carrier Gas Inlet	5.39 ms ⁻¹	450 K	$C_{N2} = 0.042 \text{ molm}^{-3}$
Combustion Products Inlet* ϕ =0.13	V_z =7.92 ms ⁻¹ V_r =9.73 ms ⁻¹	2144 K	$\begin{array}{l} C_{O2} = 4.4 \times 10^{-4} \ molm^{-3} \\ C_{CO2} = 5.7 \times 10^{-4} \ molm^{-3} \\ C_{H2O} = 2.8 \times 10^{-4} \ molm^{-3} \\ C_{N2} = 4.4 \times 10^{-3} \ molm^{-3} \end{array}$
φ=0.34	V_z =10.55 ms ⁻¹ V_r =6.81 ms ⁻¹	2629 K	$C_{CO2} = 2.6 \times 10^{-4} \text{ molm}^{-3}$ $C_{CO} = 9.6 \times 10^{-4} \text{ molm}^{-3}$ $C_{H2O} = 3.7 \times 10^{-4} \text{ molm}^{-3}$ $C_{N2} = 3.5 \times 10^{-3} \text{ molm}^{-3}$
Open Boundary- Surrounding Air	Normal Stress =0	298.15 K	$C_{CO2} = 1.3 \times 10^{-5} \text{ molm}^{-3}$ $C_{O2} = 8.7 \times 10^{-3} \text{ molm}^{-3}$ $C_{CO} = 0 \text{ molm}^{-3}$ $C_{H2O} = 1.3 \times 10^{-5} \text{ molm}^{-3}$ $C_{N2} = 3.2 \times 10^{-2} \text{ molm}^{-3}$
Walls	Wall functions	Thermal insulation	No flux

 Table 2.2 Boundary Conditions used for COMSOL Flame Modeling

Note: Conditions listed in table are for a flame speed of 100 cm/s.

2.5.2 CFD results

Following an earlier approach [123], the temperature and velocity profiles predicted by the CFD calculations were compared to those obtained experimentally. Results are shown in Figure 2.11. Velocities of 60 and 100 cm/s were used for equivalence ratios of 0.65 and 1.65, respectively, based on the minimum discrepancy between the respective predicted and measured vertical temperature and velocity profiles. These velocities are higher than expected for laminar air-acetylene flames at the above equivalence ratios, most likely suggesting the effect of turbulent mixing on the reaction.

Vertical concentration profiles of the major oxidizing species, CO₂ and H₂O, are shown in Figure 2.11 along the flame's axis and at a radial distance of 4 mm. This distance was selected to illustrate where substantial mixing of the combustion products with surrounding air occurred.

For both equivalence ratios considered, the model predicts that the combustion products are cooling steadily from the adiabatic flame temperature as the height increases. Conversely, experimental data show an increase in the temperature at the heights of up to 2 cm; the effect is stronger for ϕ =1.65. This effect is most likely due to the air-acetylene reaction continuing above the assumed flame front location. It is likely that this effect is also responsible for a substantial discrepancy between calculated and measured temperature profiles for ϕ =1.65, as seen in Figure 2.11. The agreement between calculations and experiment is adequate for the flame with ϕ =0.62.

The calculated velocity profiles agree well with the experimental results for both flames at relatively low heights. Note that a recirculation is predicted to occur near the boundary in the model, explaining a sharp minimum in the calculated gas velocities. At heights above 6 cm for ϕ =0.62 and 4 cm for ϕ =1.65, the experimental velocities become higher than calculated, most likely due to natural convection affecting velocities of the burning titanium particles, used specifically for this measurement and heated above the surrounding gas temperature.

According to the model, the concentrations of the combustion products at the center of the flame (r=0) remain nearly constant across the domain considered. At a radial distance r=4 mm, the concentrations of the major combustion products, serving as oxidizers for boron, are reduced substantially because of mixing with the surrounding air. Substantial differences in the oxidizing environment composition are predicted for the two flames, with greater concentrations of CO₂ and lower concentration of H₂O observed for the flame at ϕ =0.62 as compared to the case of ϕ =1.65.



Figure 2.11 Experimental (circles) and calculated (lines) results for air-acetylene flame mixtures at different equivalence ratios.

Note: Flame velocity is assumed to be 60 and 100 cm/s for ϕ =0.62 and 1.65, respectively.

Calculated radial profiles for the temperature and concentration at different heights are shown in Figure 2.12. For both equivalence ratios, the high-temperature zone near the flame's axis becomes less well defined at greater heights. However, the gas compositions near the flame's axis remain mostly defined by the air-acetylene combustion products for both equivalence ratios. Concentration profiles for nitrogen are shown for both flames as indicators of mixing the air-acetylene combustion products with surrounding air. An increase in the nitrogen concentration effectively coincides with the decrease in concentrations of CO₂, H₂O, and other species introduced in the model as the air-acetylene combustion products. While the degree of mixing certainly increases at greater heights, the area near the flame's axis with a radius of about 2.5 mm is largely filled with the air-acetylene flame combustion products. Based on the observed locations of streaks produced by burning boron particles, combustion mostly occurred in that central zone of the flame, so that the major boron oxidizers were carbon dioxide, water, and carbon monoxide rather than oxygen from surrounding air.



Figure 2.12 Calculated radial temperature and selected concentration profiles plotted for different heights above the burner for flames with equivalence ratios of 0.62 and 1.65.

Note: The respective flame velocities are 60 and 100 cm/s.

2.6 Discussion

The concentration profiles predicted by the CFD simulation shown in Figures 2.11 and 2.12 suggest that the gas compositions at the center of the flame, where boron particles were injected, were defined by the air-acetylene combustion products, with only minor effect of the surrounding air. The concentrations of gas species around the flame axis did not change substantially within the distances from the burner where most boron particles burned, indicating that particles burned in oxygen depleted environments.

To discuss differences in the observed temperatures and burn times for different flame conditions, it is therefore useful to consider adiabatic flame temperatures and products of boron combustion in each of the oxidizing environments calculated using CEA code [1]. Neglecting changes in the gas compositions as a function of the distance from the burner, the gas mixtures shown in the abbreviated format in Table 2.1 were treated as respective oxidizing environments. In each case, boron concentration varied. Predicted temperatures, main boron combustion products, and main oxidizing species are shown in Figure 2.13. The horizontal axis in Figure 2.13 can be considered as proportional to the inverse distance from the particle surface. The temperatures and compositions obtained for the boron-rich conditions are most representative of those expected to occur near the burning boron particle surface.

For the flame at ϕ =1.65, the calculated temperatures are generally lower than for the flame at ϕ =0.62, indicating a discrepancy with the experimental results. It is also observed that the maximum temperature is predicted to occur closer to the particle surface for the oxidizing conditions corresponding to ϕ =0.62. Thus, the size of the vapor-phase flame for ϕ =1.65 is expected to be greater, implying smaller gradients of temperature and concentration between the particle surface and the flame.

For the case of ϕ =0.62, the calculated and measured flame temperatures are reasonably close to each other. Thus, equilibrium calculations are also expected to represent the reaction products reasonably well. The flame temperature is high due to formation of B₂O₃ and boron sub-oxides. Because adiabatic flame temperatures expected for the thermodynamic equilibrium are attained, the reaction kinetics must be sufficiently rapid. It can be concluded that in this case, the heat and mass transfer processes control the burn rate of boron particles rather than reaction kinetics.

For the flame with ϕ =1.65, the experimental temperatures close to 2870 ± 370 K exceed the predicted values. The products expected to form in the latter case in equilibrium include substantial amounts of B₄C, which reduces the reaction enthalpy compared to that expected from boron oxidation. It may be possible to explain the experimental flame temperature exceeding the adiabatic flame temperature for ϕ =1.65, if, at least at some point during particle combustion the combustion products differ from those predicted by the CEA calculations. For example, the products may include greater concentrations of B₂O₃ and lower amounts of B₄C than expected in equilibrium. This could occur if the rate of formation of B₄C is relatively low. Because the present temperature measurement obtained from time-integrated spectra was biased to the maximum flame temperature, a decrease in the temperature caused by the B₄C formation might not have been detected.

In all cases, the combustion temperatures of boron particles are substantially lower than the boron boiling point of 4275 K, suggesting the importance of surface reactions. At the same time, optically detected emission produced by the gasified boron sub-oxides indicates that the vapor phase oxidation may not be negligible.

Measurements showed slightly longer burn times for the flame with ϕ =1.65. One of the reasons may be a difference in the oxidizing species present, as represented in Table 2.2. The flame with ϕ =0.62 produces a higher concentration of CO₂ and a measurable fraction of molecular O₂, both highly effective oxidizers. The difference in burn times may also be explained by the lower temperature and concentration gradients (greater distance from flame to particle surface) leading to lower rates of heat and mass transfer between the flame and boron particle. Formation of un-oxidized products as a result of heterogeneous reactions could have also extended somewhat the overall reaction time. In particular, high concentrations of B₄C occur close to the particle surface (or at boron-rich conditions). Deposition of B₄C on the surface of boron could partially block its surface, reducing the burn rate. Additionally, despite having higher concentrations of water and carbon monoxide as potential oxidizers, the flame had lower carbon dioxide concentrations, which is the most thermodynamically favorable oxidizing species present.



Figure 2.13 CEA Calculations for varying boron concentrations in varying oxidizing environments.

Boron combustion is commonly considered to occur in two stages [25, 28, 29, 57, 60]. The first stage is proposed to include removal of the initial oxide layer, and thus be accompanied by a relatively slow heterogeneous reaction. The second stage, or so called full-fledged combustion, involves vapor-phase reactions occurring when the clean boron surface is exposed to an oxidizing environment. With this model in mind, the first of two or more emission peaks observed in earlier experiments, [54, 112], where boron powders were ignited in a shock wave, were attributed to the removal of the oxide layer. It was proposed that the subsequent peaks were caused by various combustion reactions. However, the experiments were performed with particles of different sizes, which could have ignited with different delays. This could readily explain observed complex emission pulse structures. In the present experiments, the emission patterns can be readily distinguished from the particle emission streaks and pulses, as shown in Figure 2.2. Qualitatively, these emission patterns are similar to those reported in Ref. [33]. However, the conventional two-stage scenario outlined above cannot describe such two-peak patterns adequately. Indeed, the emission intensity produced by the first peak in the particle emission pulse is often stronger than the second. There is also a minimum in the emission intensity between the peaks. This behavior is inconsistent with that expected from the process involving removal of an oxide film. When the oxide film is present, the reaction is expected to be slow, and produce only a relatively low-intensity emission. As the oxide is being removed, the particle temperature is expected to rise gradually. The emission should not decay, but only increase when the particle transitions to the full-fledged reaction mode. Upon ignition, a sharp increase in the emission intensity may be expected based on a reported jump in emissivity of boron surface once it ignites [117]. It is proposed that the

traditional first stage involving a slow heterogeneous reaction and removal of the natural oxide occurs in the present experiments without being detected optically. The streaks become bright and clearly distinguishable from the flame emission after the oxide flame was removed, and when the emissivity of boron surface increases sharply. Therefore, observed two-peak emission pulses represent "full-fledged" combustion, which thus includes more than one stage itself. Possible explanations of the double peak structures of the emission pulses could involve formation of intermediate condensed phases experiencing phase transformations, changing reactivity and emissivity of the burning particles. The intermediates could be solutions of oxygen or nitrogen in boron or suboxides, such as B₆O [37, 38], or metastable BO, BN and BON phases [35, 36]. Formation of similar solutions or intermediate phases occurs in combustion of many metals; it was reported to affect combustion of various metal particles [111, 124]. The present results are inadequate for detailed interpretations of the nature of stages of the full-fledged combustion; however, such stages were clearly detected and further work considering respective governing reactions is desired.

2.7 Conclusions

An experimental methodology is developed enabling one to measure particle size distribution of fine boron particles and account for it explicitly while interpreting particle combustion experiments. High-temperature, or full-fledged combustion of micron-sized boron particles in the combustion products of pre-mixed hydrocarbon flames occurs in two stages. For each stage, a peak in the particle emission is observed. Burn times as a function of the particle size are reasonably well described by a power law with the exponent of 0.75,
when the oxidizing environments are produced by combustion of air-acetylene mixtures with equivalence ratios of 0.62 and 1.65. Burn times are slightly shorter in the combustion products of more fuel lean flames, containing greater concentrations of CO₂ as an oxidizer; although the measured boron flame temperature for this case is slightly lower. The boron combustion temperature measured for the more fuel-lean air-acetylene flames, 2630 ± 240 K, is consistent with that predicted by the respective thermodynamic equilibrium calculations. For the more fuel-rich case, the experimental temperature is 2870 ± 370 K, which exceeds the adiabatic flame temperature for the thermodynamically equilibrated system. The temperature increases for the fuel-rich conditions, suggesting that the reaction in this case shifts closer to the particle surface. For both air-acetylene flames, no effect of particle size on the burning temperature is detected.

CHAPTER 3

OXIDATION KINETICS AND COMBUSTION OF BORON PARTICLES WITH MODIFIED SURFACE²

3.1 Abstract

This work is aimed to modify a commercial 95% pure boron powder to improve its ignition. The powder is processed using acetonitrile to dissolve the oxidized and hydrated surface layers. The washed powder re-oxidizes and agglomerates readily, which can be prevented by additionally washing it in toluene and other liquid hydrocarbons, prior to exposing it to an oxidizing atmosphere. The presence and removal of the hydrated oxide layer and oxidation of boron powders are studied using thermo-gravimetry. The processed powders are shown to retain the active boron present in the starting material and maintain their reactivity after extended exposure to an oxidizing environment. The powders are also injected in a pre-mixed air-acetylene flame and their ignition and combustion are studied based on their optical emission. Flame temperature is measured using optical emission spectroscopy. Powder particles washed in acetonitrile, toluene and hexane exhibit substantially shorter ignition delays compared to the starting commercial boron particles. Full-fledged combustion is unaffected by this processing: both, burn times and flame temperatures are nearly identical for commercial and modified powder particles.

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3.2 Introduction

Boron is an attractive material for metal combustion applications, such as explosives [125] and solid fuel additives for rocket propellants [112], because of its high gravimetric and volumetric heats of oxidation [126]. However, boron's long ignition delays [33, 127] and extended combustion times [5, 29] present major challenges for its practical use.

There have been considerable experimental and theoretical efforts [29, 40, 41, 43, 46, 56, 88, 128] to understand and characterize the oxidation kinetics and combustion mechanism of boron. Specific focus was on long ignition delays [5, 58]. It has been generally agreed that a natural surface layer of oxide (B₂O₃) or hydroxide (approximately 0.5 nm [129]) inhibits boron oxidation and therefore delays ignition [112], which leads to reduced bulk burn rates.

An accelerated removal of the boron oxide layer is expected to lead to shorter ignition delays, motivating multiple relevant efforts, e.g., see review [24]. Different studies considered addition of coating agents [99], metals [6], metal anhydrides or oxides [7, 16, 18, 40, 130, 131], rare-earth metal catalysts [16], polymers and fluorinated compounds [94, 95, 112].

Experiments [16] showed that for boron nanoparticles ball milled with ceria (20 wt%) ignition delays were reduced by almost a factor of 6. This was based on chemiluminescence measurements at a wavelength of 546 nm for particles fed in the combustion products of an ethanol flame in a customized combustor. Unfortunately, including 20 wt% of an oxide substantially reduces the energy density of an energetic composition.

The effects of metal hydrides (Ca, Li, Ti and Zr) on the ignition and combustion of 99% boron particles in a CO_2 laser were studied in Ref. [131]. Results indicated that the lithium hydride blended with a mass ratio of 10:1 in favor of boron, reduced ignition delays from 140 ms to as low as 90 ms. However, lithium hydride is difficult to handle and incompatible with processes involved with preparation of energetic formulations.

Adding fluorinated compounds or working with fluorine-containing gaseous oxidizers was shown to improve boron combustion and reduce ignition delay times, which was associated with alternate reaction pathways [112]. Practical introduction of fluorine in the reactive material may be difficult. Ignition of mixed polytetrafluoroethylene (PTFE)/boron systems was considered in Ref. [94]. It was concluded that for thermodynamically attractive, boron-rich compositions, adding PTFE was ineffective for promoting ignition.

Ignition of mixed boron and magnesium powders was analyzed in Refs. [6, 89]. Selective ignition of magnesium occurred independently of the composition; it remained unclear whether ignition of magnesium was effective in igniting boron. Another approach to modifying ignition behavior of boron was proposed in Ref. [132], where the boron surface was coated with a carbide layer. The coating was formed by prolonged exposure of boron particles to hydrocarbons at elevated temperatures. However, X-ray photoelectron spectroscopy showed that the surface layer was substantially oxidized, and that the carbide surface layer was unfavorable for rapid ignition and heat release of the sample.

Generally, a challenge with most boron additives or coatings is that they reduce the overall material energy density. Significant kinetic effects accelerating removal of the boron oxide are observed with substantial amounts of such added components, and thus, materials with significantly reduced heats of combustion. The objective of this effort is to reduce boron particle ignition delays without imposing an energetic penalty associated with most additives. The approach here is to dissolve the natural boron oxide or boric acid layer from the particle surface while preventing the powder from rapid re-oxidation.

3.3 Experimental Section

3.3.1 Materials

Commonly, boron powders are coated with a surface layer of boron oxide, B₂O₃, which readily converts into boric acid, B(OH)₃, in humid environments [133]. Reported data on solubility of boron oxide are scarce, while boric acid can be dissolved in many solvents, most easily in water and ethanol [134]. However, most effective solvents contain oxygen and thus may oxidize the exposed boron surface. To avoid such oxidation, an oxygen-free polar solvent, acetonitrile, was considered in this work. No literature data on solubility of boron oxide or boric acid in acetonitrile were found. Therefore, solubility of boron oxide in acetonitrile was investigated preliminarily. Alfa Aesar acetonitrile 99.5% was used. A 2.5-g batch of 99.98% commercial boron oxide by Alfa Aesar was placed in a beaker with 30 mL of acetonitrile at room temperature and agitated by a magnetic stirrer for 10 min. The suspension was allowed to settle for 1 hour. The clear liquid was siphoned from the top and centrifuged. The weight of the solid precipitated from the obtained clear solution

was then determined. The solubility of boron oxide in acetonitrile was found to be 30 g/L. The precipitate obtained in room air with about 70% humidity had characteristic crystal structure of boric acid. Similar experiments with Alfa Aesar 95% n-hexanes and ChemPUR® commercial grade toluene showed that less than 0.1 g/L of solid could be recovered. These preliminary experiments guided preparation of modified boron samples, as discussed below.

All boron samples used in experiments are described in Table 3.1. Sample A, an amorphous boron powder, 95 wt% pure from SB Boron was used as both the reference and starting material. Sample E, a crystalline boron powder with 99 wt% purity, by Alfa Aesar was used as an additional reference material. Samples B, C, and D were obtained starting with sample A and using washing cycles aimed to remove or minimize the thickness of the natural boron oxide or boric acid layer. 10 grams of the starting powder were loaded into a 50 mL steel vial of a SPEX Certiprep 8000 series shaker mill with 30 mL of acetonitrile. The mixture was shaken for 30 minutes with no milling media. The sample was allowed to settle, and the acetonitrile was siphoned off without exposing the washed boron to air. To rinse the washed boron, fresh acetonitrile was added, and the sample was vigorously stirred using Scientific Industries Inc. Vortex Genie X4674 shaker. Using an LW Scientific Ultra 8F-1 centrifuge, the acetonitrile solution was then separated from the boron powder and siphoned off. This cycle was repeated three times. After the third cycle, toluene was added, and the material was rinsed with toluene five more times. Some samples were additionally rinsed three times with hexane. After preparation, samples remained stored in the solvent used in their respective last washing cycle. Table 3.1 lists different materials prepared and compared in this study.

Sample ID	Starting material	Washing cycles		
		In acetonitrile, 3	In toluene, 5	In hexane, 3
А	95% pure boron	No	No	No
В	95% pure boron	Yes	No	No
С	95% pure boron	Yes	Yes	No
D	95% pure boron	Yes	Yes	Yes
E	99% pure boron	No	No	No

 Table 3.1 List of Materials Prepared for Investigation

The prepared samples were characterized using laser scattering, optical and scanning electron microscopic (SEM) techniques. Images of the prepared samples A, B, C, and D obtained using a LEO 1530 field emission SEM are shown in Figure 3.1. Sample B washed in acetonitrile only consists of strongly agglomerated particles. There are large crystalline formations consistent with precipitates of oxides remaining after rinsing with acetonitrile only. This is indicative of incomplete removal of the solvent, and this material was therefore, not used in further experiments. Particle shapes and agglomerate morphologies observed for as received boron, sample A, and both samples C and D, finally processed using toluene and hexane, respectively are essentially the same. Note, however, that the sizes of agglomerates in samples C and D are somewhat greater than those in sample A.



Figure 3.1 SEM images of as received and processed boron powder samples.

Particle sizes were analyzed for samples A, C, and D, using SEM images of particles fed into the burner used in the combustion experiments (see below). The powder exiting from the burner was collected for fifteen seconds on a 1-kV charged aluminum surface positioned 4 cm above the burner to enhance collection of fine particles electrophoretically. SEM image processing enabled one to account for agglomeration and fractal dimension [135] of the actual particles fed into the flame. Images were collected at different magnifications. For each magnification, the images were processed to identify particles and to measure their sizes using ImageJ, a freely available software package by the National Institute of Health. The size distributions were then constructed using all recorded images. The equivalent particle diameters were measured and corrected by the

agglomerate fractal dimension (FD), determined using the box counting method [136]. The FD value was approximately 1.8 for all materials. For additional details describing how particle size distributions are obtained from SEM image processing see Ref. [135]. The resulting particle size distributions are shown in Figure 3.2. Preparing the samples to account for agglomeration shifts the distributions towards larger sizes. It is also observed that washed samples C and D are somewhat more agglomerated compared to the commercial powder A. This is consistent with qualitative observation made while examining the obtained SEM images shown in Figure 3.1. These size distributions were correlated with the measured burn times and ignition delays.



Figure 3.2 Particle size distributions of commercial and washed boron powders.

3.3.2 Particle combustion experiments

Aerosolized particles were injected in an air-acetylene flame. Particle emission streaks were photographed. The locations where streaks were observed to originate were treated as locations where particles ignited; thus, ignition delays were obtained accounting for the injected particle velocities calculated for the experimental flow conditions. Particle burn times and temperatures were obtained from the optical emission measurements. Both, burn times and ignition delays were correlated with the measured particle size distributions.

The experimental setup is shown schematically in Figure 3.3; it has been described in detail elsewhere [43, 113, 115]. The particles entered the flame through a brass tube with 2.39 mm internal diameter, placed axially at the center of the burner's nozzle. Pre-mixed air and acetylene gases were fed through a 50-mm long, 19.13-mm inner diameter tube that was tapered to form a 5.16-mm nozzle of the burner. The acetylene and air flow rates were 0.64 L/min and 4.72 L/min, respectively, creating a flame with an equivalence ratio of 1.65. Approximately 0.1 g of powder was loaded onto a custom-built powder screw feeder and fed into the burner using nitrogen as a carrier gas. The nitrogen flow rate was 0.94 L/min and the powder mass feed rate was ca. 0.27 mg/min. All flow rates were measured using individual rotameters.

Particle emission traces were recorded using two Hamamatsu R3896-03 Photomultiplier Tubes (PMTs) equipped with 700 and 800-nm interference filters. The light to the PMTs was fed using a bifurcated fiber optics bundle, with its optical inlet positioned approximately 5 cm above the top of the burner and 17 cm away from the burner. The height of the field of view was 25 cm, while the streaks were typically originating at the height of 2 cm and ended no higher than approximately 13 cm above the burner.

Recorded particle emission signals were processed using a custom MATLAB code [113] to determine particle burn times and the combustion temperatures. Data were collected at a rate of 100,000 samples per second using a 16-bit PCI-6123 National Instruments data acquisition board and LabView software for a total of 8 seconds for each run. A total of 60 runs were processed to obtain and analyze more than 300 well-separated individual particle emission peaks for each powder sample. The 700 nm wavelength signal was selected for burn time analysis because it had the greatest signal to noise ratio. For initial processing, the baseline was identified as an average signal value without any particle peaks recorded for 10 ms (or 1,000 data points.) The durations of the individual emission pulses were interpreted as particle burn times. The pulse durations were obtained when the signal amplitude for each pulse exceeded the noise level by more than 10% of its maximum value.

Particle combustion temperatures were determined from the time-integrated optical emission spectra from multiple particle streaks. A StellarNet BW16 spectrometer was positioned 5 cm above and 23 cm away from the burner tip. Emission spectra were recorded with an integration time of 1 s. For each sample, 1500 spectra were collected. The data were processed to filter out peaks of the boron combustion products (480-680 nm) and emission from contaminations by sodium (589 nm) and potassium (740 nm- 810 nm). Effect of wavelength on emissivity was neglected, so that the remaining spectra were used to obtain the temperature by fitting them with Planck's formula, where the temperature served as an adjustable parameter.



Figure 3.3 Schematic diagram of the combustion experimental setup.

3.3.3 Thermogravimetric experiments

Thermogravimetry was used to investigate oxidation kinetics, which is expected to govern particle ignition. Samples were heated up to 1100 °C in oxygen using a TA Instruments model Q5000IR thermo-gravimetric analyzer. Sample masses ranging from 2 to 7 mg were loaded into the instrument in an alumina crucible. The samples were prepared in different solvents. To prevent uncontrolled oxidation of samples removed from the solvent, samples were loaded as suspensions. For consistency, as received commercial boron (sample A) was also loaded under hexane.

Prior to each experiment, both the balance and furnace were purged with 20 mL/min and 50 mL/min of argon respectively at 30 °C for at least 60 min, during which the solvent evaporated, and a stable mass reading was recorded. The reading corresponded to the mass of the initial dry sample.

During the oxidation measurements, the furnace gas was switched to oxygen at 20 mL/min. The temperature was first increased and held at 40 °C for 60 minutes before heating at 10 K/min for all powders. The weight changes for the boron samples in an oxidizing environment were recorded and depicted in Figure 3.4.

To explore the effect of aging, dried powders were placed in an oven at 30° C. The powders were kept in an air-filled sealed glass vessel together with an open container with a saturated potassium carbonate (K₂CO₃) solution in order to keep the relative humidity constant at 44%. Aged samples were analyzed using TG measurements after 7, 14 and 120 days.

3.4. Results

Thermogravimetric (TG) measurements show two major mass changes occurring during heating: (1) mass loss occurring in the temperature range of approximately 100 - 400 °C and (2) mass gain at higher temperatures. TG traces for all samples are shown in Figure 3.4. The traces are offset vertically for clarity. The inset shows magnified portions of the TG traces focusing on the low-temperature mass loss.

The low-temperature mass loss is most significant for the commercial 95% pure boron, sample A. It exceeds 5%, which is the manufacturer-specified level of impurities in this material. The mass occurs in two apparent steps: the first, sharper step occurs in near 100 °C and the second step occurs in a broader temperature range up to 400 °C. This correlates well with reported temperature ranges for decomposition of boric acid and magnesium hydroxide [137], respectively. Thus, the mass loss represents dehydration of the natural hydroxide surface layer. The magnitude of the mass loss implies that the oxide layer is rather thick for a 95% pure boron. This also means that a large fraction of the powder is unavailable for oxidation, which could lead to long ignition delays. The mass loss is the smallest for the high-purity, 99% crystalline boron, sample E. Interestingly, the mass gain signifying oxidation of boron begins for this material at a lower temperature than for all other samples. However, using such powders in practical energetic formulations is impractical because of their high cost and instability for storage in oxidizing environments.

The low-temperature mass loss is reduced substantially for all washed powders, samples B, C, and D. The difference between washed powders in terms of the magnitude of the low-temperature mass loss is insignificant; repeated measurements show the reproducibility of the low-temperature mass loss step within 2.6–3.6% of the total mass change. The mass gain signifying oxidation of boron occurs similarly for all samples A, B, C, and D. Small differences in the magnitude of the mass gain step are likely caused by irregularities of sintering oxidizing samples at elevated temperatures and thus are not important.



Figure 3.4 Thermo-gravimetry curves of fresh and washed boron samples. Heating rate: 10 K/min.

Effect of aging on the magnitude of both low-temperature mass loss and mass gain measured in the TG tests is illustrated in Table 3.2. The experiments were performed with sample D rinsed in toluene and hexane. Exposure of this material to air at 30 °C and controlled humidity did not result in appreciable changes in its oxidation behavior. In fact, the low-temperature mass loss is somewhat reduced and following mass gain are slightly increased for the samples aged for 7, 14, and 120 days. Therefore, no signs of oxidation during aging were detected. The negligible change observed may have been a result of the relatively low (44%) humidity used in the aging experiments. In hindsight, this exposure may have further dehydrated the boron oxide layer.

Samples	Low-temperature mass loss (%)	Final mass gain (%)
D: rinsed in toluene and hexane	3.51	127.3
Aged sample 7 days	1.86	129.6
Aged sample 14 days	1.99	130.3
Aged sample 120 days	0.78	135.1

 Table 3.2 Summary for Temperature-programmed Oxidation (TPO- TG) of Washed Boron

 Samples Aged up to 120 Days in Air at 30°C and 44% Relative Humidity

Images of luminous streaks of burning boron particle were processed to identify the locations where particles ignited. The images were captured using a SONY DSC-H50 digital camera with exposure time of 1/125 s (8 ms), aperture of 2.875 and focal length of 5 mm. A characteristic photograph with ignition points labeled for clarity is shown in Figure 3.5. The ignition was assumed to occur at the onset of each single particle streak; the distance from that point to the burner was measured. These measurements are summarized for three powders in Figure 3.6. For commercial boron, multiple particles were observed to ignite relatively far from the burner. Fewer such particles were observed for both washed boron samples. The average distances for the samples A, C and D are 35, 28, and 21 mm respectively. Thus, despite their larger agglomerate sizes (Figure 3.2), washed and modified boron particles ignite closer to the burner than as received, commercial boron. The ignition distances are the shortest for the powder D, rinsed in hexane.



Figure 3.5 Points of ignition on boron particle streaks.



Figure 3.6 Frequency distributions of ignition distances for processed and unprocessed boron powders.

(A) Commercial boron, (C) washed boron modified with toluene and (D) washed boron modified with toluene and hexane.

The distances at which ignition occurs were recast into particle ignition delays. The flow field above the air-acetylene flame was described using a numerical model, taking into account the flame temperature and composition of the reaction products [135]. Particles were assumed to be carried by the gas; the average gas velocity was used to estimate the time delays corresponding to the distances at which the ignition was observed. Preliminary calculations showed that the slip was negligible for all particle sizes used in experiments. Finally, it was assumed that larger particles ignited further away from the burner, and thus the particle size distributions obtained by the SEM image processing and shown in Figure 3.2 were correlated with the distribution of ignition distances shown in Figure 3.6. For each particle size an ignition distance was identified, which was recast into the ignition delay specific for this particle size. Ignition delays for different size particles for all three powders are shown in Figure 3.7. These results may be affected by irregularities in the measured statistical distributions, present for both particle sizes and ignition locations. Thus, only the general trends implied by the data shown in Figure 3.7 may be significant. Ignition delays are substantially reduced for both modified powders compared to the commercial 95% pure boron. The effect is particularly strong for finer particles, less than $6 \,\mu m$. The shortest ignition delays are observed for the powder washed in hexane, sample D. For larger agglomerates, the difference in ignition delays is diminished. Even longer ignition delays are observed for the coarsest particles rinsed in toluene as compared to commercial boron. Looking back at the data shown in Figure 3.6 suggests that these longer delays are due to single streaks detected for sample C far away from the burner. Thus, the longer ignition delays shown for large particles of sample C in Figure 3.7 were not obtained based on the statistically significant experimental data.



Figure 3.7 Ignition distance and ignition delay correlation to particle size for processed and unprocessed boron powders.

(A) Un-processed boron, (C) processed boron rinsed in toluene and (D) processed boron rinsed in toluene and hexane.

Combustion of different powders was also characterized based on optical emission measurements. Typical emission traces produced by multiple burning particles of different powders injected in the air-acetylene flame are shown in Figure 3.8. Pulses produced by burning particles appear on top of a somewhat noisy background signal produced by the flame emission. For sample A, most particle pulses had characteristic two-peak shapes, as shown in the inset. However, for samples C and D, most pulses had only one well-resolved peak. There were more overlapping pulses for samples C and, especially, D, suggesting more agglomerated particles fed into the burner. Overlapping pulses were excluded from the analysis focused on identifying the burn times of different boron particles.



Figure 3.8 PMT Output signals filtered at 700 nm for different boron powders burning in the products of an air-acetylene flame.

The pulse durations were determined from the emission peaks and correlated with particle sizes. For the correlation of the respective statistical distributions of pulse durations and particle sizes to be meaningful, it is important to establish that emission pulses were recorded for particles of all sizes. The amplitudes of the recorded emission pulses are also expected to scale with the particle sizes. Thus, if the smallest emission pulses are noticeably greater than the detection limit, defined by the emission baseline produced by the air-acetylene flame, it is likely that pulses produced by all particles are reliably detected. The frequency distributions of the emission pulse amplitudes measured in the present experiments are shown in Figure 3.9 for samples A, C, and D. For each case, the baseline level of the emission signal is shown, with a band indicating noise in the flame emission.

In all cases, the smallest pulses are reliably greater than the baseline emission, suggesting that pulses from all particles were detected.



Figure 3.9 Histograms for emission pulse amplitudes for particles of boron samples burned in hydrocarbon flame.

Note: The baseline band shows typical ranges of signals produced by the hydrocarbon flame emission.

The burn times (or emission durations) obtained from individual particle emission pulses were sorted into logarithmic bins. The number frequency distributions were plotted as histograms shown in Figure 3.10. The burn times are very similar to one another for different boron powders.



Figure 3.10 Burn time distributions of processed and unprocessed amorphous boron samples in a hydrocarbon premixed air- acetylene flame

Correlation of the boron particle burn times with their size distributions yielded the trends, which describe the effect of particle size on its burn time shown in Figure 3.11. The plots for processed powders are shifted to larger sized particles, reflecting the differences in their respective particle size distributions. The trends for the processed boron powders overlap with that for the starting, as received commercial boron. This suggests that the effect of washing and surface modification on full-fledged boron combustion is negligible. The burn time, t_b , in ms, as a function of the particle diameter, d, in µm, is reasonably well described as $t_b \approx 4.68 \cdot d^{0.74}$ for all powders.



Figure 3.11 Burn times as a function of diameter for processed and unprocessed boron powder burnt in the combustion products of pre-mixed air- acetylene flame.

Examples of typical time-integrated emission spectra produced by different burning powders are shown in Figure 3.12. The molecular peaks of BO are clearly visible for all powders. In addition, common impurity peaks by K and Na are observed. These peaks were removed manually to fit the remaining spectra with the emission given by Planck's Law while treating temperature as an adjustable parameter. The fits are also shown in Figure 3.12. These integrated spectra yielded average temperature values of 2630 ± 370 K, 2750 ± 170 K and 2960 ± 460 K for samples A, C and D, respectively. The differences between average temperatures are within the experimental error bars for all materials. Individual, time-dependent particle temperatures could not be recovered from the recorded emission traces filtered at different wavelengths (700 and 800 nm) because of a non-gray background emission produced by the air-acetylene flame. Although the temperature could not be obtained, the time-dependent intensity ratios for pulses with different durations (and thus produced by particles of different sizes) were compared to one another. No effect of particle size on the intensity ratio was observed for any material. Thus, the same material particles of all sizes burned at approximately the same temperatures.



Figure 3.12 Emission spectra for different boron samples burning in the combustion products of an air- acetylene flame.

3.5 Discussion

The low-temperature mass loss exceeding 5 % observed for the 95% pure boron powder suggests that commercial boron contains hydroxides as products of aging in humid environments. It is likely that the composition of the surface layer also includes impurities, most likely magnesium, which can also produce hydroxide that is unstable at elevated temperatures. Washing the powder in acetonitrile reduces the mass loss by approximately 50 %, as shown in Figure 3.4. The mass loss is not eliminated, suggesting that only a fraction of the surface layer is dissolved. The mass loss occurs at about the same temperature for all powders, suggesting that the nature of the reaction causing it has not changed. It is likely that in all cases the mass loss is due to decomposing hydrated oxides. Some such layers are captured between agglomerated particles and maybe difficult to dissolve. Using ultra-sonication or other de-agglomeration methods may thus be beneficial to produce a cleaner boron powder.

Removal of the acetonitrile-oxide solution by decanting is inefficient, leading to remaining boron oxide after drying cementing powder particles together. This is evident by the characteristic crystallites (Figure 3.1B). The solution can be effectively removed by replacing the solvent with toluene, and ultimately hexane. These solvents are less polar than acetonitrile and do not bind as strongly to the boron particle surface. Consequently, particle-particle contacts become energetically more favorable in toluene or hexane, leading to the formation of larger but loose agglomerates. These agglomerates appear to be slightly smaller in hexane than in toluene. Overall, however, the morphology of the powder is preserved (Figure 3.1) as well as its oxidation behavior (Figure 3.4). Therefore, the washed and surface-modified powders, which do not include any additional material

components, are as energetically attractive as commercial boron. It is also important that such materials are stable in the oxidizing environment near the room temperature, as shown in Table 3.2. Thus, such modified powders are expected to be easy to adopt as components of energetic formulations.

Shorter distances at which the washed powder particles ignite (Figure 3.6) and respectively shorter ignition delays (Figure 3.7) clearly indicate that the partial removal of the hydrated oxide layer from boron surface accelerates its ignition. This is consistent with the generally accepted understanding of the mechanism of the first stage of boron combustion, involving removal of the oxide layer from the particle surface [22, 56]. The reaction that follows, so-called full-fledged combustion, which is detected here by optical emission of the burning particles, is not affected by the initial processing. Both reaction rates and flame temperatures are nearly the same for "as received" and washed powders. This suggests that the un-oxidized or "active" boron is not changed by the present processing. Washing in acetonitrile and rinsing with toluene or hexane neither impede nor accelerate the full-fledged combustion.

Note finally that the temperatures of the particles prior to their ignition were estimated considering their heating in a gas flow of the air-acetylene flame products. Calculations performed for particles of different sizes assumed particles to remain chemically inert before they ignited. It was predicted that most particles reached and followed the gas temperature before they were flown to locations, where ignition was observed experimentally. Thus, no characteristic ignition temperature could be determined. This, once again, supports the idea that the full-fledged combustion begins when the oxide layer becomes sufficiently thin, and when accelerated rate of oxidation leads to a sharp increase in the particle temperature and its respective emission signal. This can occur at different temperatures, depending on the thickness of the initial oxide layer and on the rate of particle heating.

3.6 Conclusions

Hydrated oxide layers can be readily removed from surface of boron powders by washing them in acetonitrile. Effective removal of the solvent can be achieved by rinsing with toluene. Additional exposure to other hydrocarbon liquids, such as hexane, does not change powders chemically, but may affect agglomeration of boron particles.

Powder particles washed in acetonitrile and rinsed with toluene and hexane and injected in an air-acetylene flame exhibit substantially shorter ignition delays compared to the starting commercial boron particles. Full-fledged combustion is unaffected by the present processing: both burn times and flame temperatures are nearly identical for the commercial and washed/functionalized powder particles.

CHAPTER 4

COMBUSTION OF BORON AND BORON-IRON COMPOSITE PARTICLES IN DIFFERENT OXIDIZERS³

4.1 Abstract

Mechanical milling was used to prepare a composite powder containing 5 wt. % of iron in boron. Iron, expected to behave as a catalyst of boron oxidation, was present in the form of nano-sized particles on the agglomerates of primary boron particles. Powders of both the prepared material and as-received boron were burned in different oxidizing environments. The powders were injected in the combustion products of air-acetylene and hydrogen-oxygen flames to expose them respectively to a mixture of CO_2 , CO and to steam as oxidizers. In addition, the powders were fed through a laser beam to be ignited and burned in air. Particle size distributions were obtained for the powders passed through the feeder. Time-resolved optical emission of particles burning in all environments was recorded using photomultipliers filtered at 700 and 800 nm. Additionally, temporally and spectrally resolved emission traces were obtained using a 32-channel spectrometer recording emission in the range of wavelengths of 373-641 nm. The durations of the recorded emission pulses were interpreted as burn times. Statistical distributions of particle burn times and sizes were correlated with each other to obtain the effect of particle size on its burn time. Flame temperatures were measured assuming the radiation source behaving

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as a gray body. Burning boron particles commonly produced double-peak emission pulses, whereas single-peak pulses were produced by the composite boron-iron particles. Both peaks observed in boron particle combustion were assigned to the full-fledged high-temperature reactions unlike the assignment suggested in the earlier research linking the first emission peak with the removal of the boron oxide layer. The emission intensity for the boron-iron composite particles was weaker than that for boron, which is likely explained by the effect of iron favoring condensed oxidation and suppressing formation of the vapor-phase combustion products, such as boron sub-oxides. In air, the burn times of boron-iron composite particles were substantially shorter than those of boron. In air-hydrogen flame, boron-iron composites burned slightly faster than boron, while in the air-acetylene flame, there was no clear difference in the burn times for the two materials. The flame temperatures were very similar for the two materials in all oxidizers.

4.2 Introduction

There has been considerable interest in mechanisms of boron ignition and combustion because of its high gravimetric [21] and volumetric energy densities [40]. The high heat of oxidation makes boron attractive as a fuel additive in explosives and propellants [21, 33, 138]. However, the full thermodynamic potential of boron is rarely achieved because of its long combustion times [60] and ignition delays [5, 25]. Furthermore, combustion of boron in hydrogen-containing environments forms energetically unfavorable intermediates (namely HOBO), reducing the rate of heat release [28, 33].

Previous work has sought to mitigate these challenges combining boron with other metals [63], fluorinated compounds [30, 61], carbides [103, 110], oxides [16, 97, 98, 139] and metal hydrides [4]. These additives were incorporated by milling, coating, etc. While shorter burn times and reduced ignition delays were reported, in each case more than 10% of the additive was used, reducing the overall energy density of the reactive material.

Recently, ignition delays of boron powders were reduced by treating commercial, 95% pure boron with acetonitrile and other hydrocarbons [140, 141]. It was found that such a treatment removes, at least partially, the hydrated oxide layer forming on boron stored in air. The treatment further passivates the surface of boron from extensive oxidation, resulting in a stable boron powder, which has shorter ignition delays than the starting commercial boron. However, combustion times and temperatures remained unaffected. The measured flame temperatures were around 2800 K, suggesting that boron was far from its boiling point (ca. 4200 K). Therefore, the so-called full-fledged combustion is rate limited by heterogeneous processes on the surface of burning particles. Accelerating the kinetics of such surface reaction holds promise of achieving shorter boron burn times. Establishing the feasibility of this approach is the goal of the present study. In order to increase the rate of this heterogeneous combustion, the present work considers boron doped with a catalytic additive. The additive, iron, is selected to remain in the condensed phase at relatively high boron combustion temperatures. Iron is readily oxidized heterogeneously and exists in multiple oxidation states. It can serve as an oxide donor and can be readily reduced reacting with boron. This provides a potential kinetic pathway assisting the boron oxidation: the direct heterogeneous reaction of boron with gaseous oxidizers (CO, CO₂, O₂, H₂O) may be replaced with a heterogeneous oxidation of iron dopant reacting with gases, followed by the redox reaction of boron and the iron oxide in the condensed state. This modified reaction mechanism may also suppress formation of HOBO gas, while favoring formation of condensed boron oxide, preferred thermodynamically. Because iron would be continuously oxidized and reduced during combustion, only a small amount is expected to be needed, negligible in terms of reducing the volumetric and gravimetric heats of oxidation of the doped compared to the pure boron.

The present experiments were aimed to prepare such iron- doped boron powders and determine whether a small amount of iron added to boron particles can indeed accelerate the particle burn rates. Combustion of the prepared material is characterized in different oxidizing environments (in H_2O , a mixture of CO_2 , CO, and H_2O , and in air). Burn times of boron particles are found as a function of their sizes; combustion temperatures are also reported. The results are compared for as received commercial boron and the powder doped with iron.

4.3 Materials

A powder of 95% pure boron from SB Boron was used as both the reference in the combustion tests and starting material for preparation of boron-iron composite. The second starting material was 99% pure iron from Fisher. A composite powder with 5 wt% iron was prepared by room temperature milling starting elemental boron and iron powders in a SPEX Certiprep 8000 series shaker mill. Each 50-mL flat-ended hardened steel milling vial was loaded with 4.75 grams of boron and 0.25 grams of iron. 2 mL of n-hexanes solvent (95%, by Alfa Aesar) was also added to the vial as a process control agent (PCA).

The vials were sealed inside an argon-filled glovebox to create an inert environment during milling. 10 mm (3/8") diameter steel balls were used as the milling media. The sample was milled for two hours with a ball to powder mass ratio of 5. The milling vials were additionally cooled by room temperature air jets introduced in the mill during the experiment. After milling, the sample was recovered in an argon environment and stored under hexane.

The prepared material was characterized using scanning electron microscopy (SEM). Characteristic images of the prepared sample (B-Fe) and the reference material (B) obtained using a LEO 1530 field emission SEM are shown in Figure 4.1. The image of the composite material is obtained using backscattered electrons to highlight compositional contrast between boron and iron. Secondary electrons were used to image pure boron particles, to see better their surface morphology. The milled material has nanometer- sized iron particles, appearing as bright inclusions, mixed with the boron fractal agglomerates. Each agglomerate examined under SEM contained iron particles. The shapes of boron agglomerates appear to be similar to each other for the starting material and for the material milled with iron.



Figure 4.1 SEM Images of reference and milled composite materials.

Note: Secondary electrons on left and backscattered electrons on right.

4.4 Experimental Section

4.4.1 Experimental setup

Aerosolized particles were injected into three different combustion environments: products of air-acetylene and hydrogen-oxygen flames and in air (using laser ignition in the latter case). The emission streaks produced by burning particles were photographed; time resolved emission traces were recorded using filtered photomultipliers. Combustion times and temperatures were obtained from optical emission traces of individual incandescent particles. Duration of particle streaks were interpreted as their burn times. The statistical distributions of the measured burn times were correlated with the respective particle size distributions, assuming that smaller particles had shorter burn times and vice versa. Thus, the effect of particle size on its burn time was quantified.

The settings for each type of experiment were described in detail in previous studies, where different material powders combusted in the same oxidizing environments [114, 123, 142]. In all cases, a custom-designed screw feeder was used; however, the

powder feed rate was reduced for the laser ignition experiments performed in air compared to that used with air-hydrogen and air-acetylene flames. Figure 4.2 shows a schematic diagram of the experimental setup. For each combustion experiment, approximately 0.1 g of powder was loaded in the screw feeder. The screw was rotated using a gear reduction motor powered by a DC voltage. Using a carrier gas, nitrogen or air, the particles are lifted from the thread of the screw and fed into a carrier tube. Adjusting the DC voltage and the carrier gas flow rate enables one to adjust the powder feed rate. For the experiments with flames, the 2.39 mm internal diameter brass carrier tube was inserted axially into the burner tube feeding fuel and oxidizer gases. For the laser-ignition experiments in air, the end of the carrier tube is placed just under the focal point of the laser beam.



Figure 4.2 Experimental setup for feeding particles into combustion environment for capturing optical emission signals.

For experiments using hydrocarbon combustion products, pre-mixed air and acetylene gases were fed through a 50 mm long, 19.13 mm diameter tube that was tapered to form a 5.16 mm diameter nozzle. The acetylene and air flow rates were 0.64 and 4.72 L/min respectively, resulting in a flame with the equivalence ratio of 1.62. This condition was selected to obtain the flame, which remains stable when particles are introduced axially with a nitrogen jet. The carrier gas was nitrogen at a flow rate of 0.94 L/min. The powder mass feed rate was approximately 0.27 mg/min. Further details of the air-acetylene flame setup are described in Ref. [114, 123, 142].

For experiments using steam as the primary oxidizer, particles were fed in the products of an air- hydrogen diffusion flame. Three coaxial tubes were used: the central tube, 2.39 mm diameter, served to feed particles using nitrogen as a carrier gas. The nitrogen flow rate was 0.94 L/min. A larger 40-mm long, 5.25-mm internal diameter tube was used to feed hydrogen at 0.33 L/min. This was surrounded by a 47.55-mm internal diameter tube in which oxygen was supplied at 0.71 L/min. Oxygen mixed with surrounding air was further mixed with the hydrogen forming a diffusion flame surrounding the centrally injected particles. This minimized direct exposure of particles to oxygen. Details of the setup are provided elsewhere [123].

For the experiments in air, particles were fed with air as a carrier gas through a 10 cm long, 2.39 mm inner diameter tube into the focal area of the laser beam. The flow rate of the carrier gas was 0.60 L/min. The particles exited the brass tube and crossed the laser beam at approximately 2 mm above the nozzle. A Synrad Evolution 125 sealed CO_2 laser was used to ignite the particles. The beam was focused to ca. 250 μ m diameter using a
ZnSe lens. The laser was operated at 30% of its maximum power (i.e., at 37.5 W) in order to ignite metal particles crossing the beam with a velocity of approximately 3 m/s. Ignited particles continued to move vertically upwards and combusted in the surrounding air. Ref. [143] further describes the laser setup.

4.4.2 Particle size distributions

In order to correlate burn times recorded optically with the particle sizes, the particle size distributions of the materials were measured. To account for possible particle agglomeration or size classification occurring in the powder feeder, the particles were captured for the size measurements directly above the feeder's nozzle operated at the same conditions as in the combustion tests. However, there was no flame or laser beam to ignite the particles being collected. The technique has been described in Ref. [140, 142]. Although the same powder feeder was used in all experiments, it was operated at different gas flowrates, which could affect the final particle size distributions. The powder exiting the burner nozzle was collected for fifteen seconds on a 1-kV charged aluminum stub positioned 40 mm away from the nozzle. The electric charge enhanced the effectiveness of particle collection due to electrophoretic effect. For the laser ignition experiments, the collection surface was positioned approximately 25.4 mm away from the nozzle.

Multiple SEM images of the collected particles were obtained at different magnifications to include the entire range of particle sizes. For each magnification, the images were processed to measure particle sizes using ImageJ, a freely available software by National Institute of Health[144]. For each particle, the equivalent particle diameter was determined and corrected by the fractal dimension (FD=1.8), which was determined using

the box counting method. The details of image processing and combining the particle size distributions using images taken at different magnifications are available elsewhere [142]. The results are shown in Figure 4.3. The distributions for as received boron and the boroniron composite are comparable to each other. It was also observed that the distribution of particles fed to the laser beam shifts to smaller sizes, likely due to a reduced carrier gas flow rate.



Figure 4.3 Particle size distributions of commercial boron and 5 wt.% iron- boron composite powders obtained from the SEM image analyses.

Note: Distribution for particles fed into the burner is shown on the left and for particles fed into the laser beam on the right.

4.4.3 Particle emission measurements

Images of luminous streaks of the burning particles were captured using a SONY DSC-H50 digital camera with an aperture of 2.875 and focal length of 5 mm. The lengths of the particle streaks were determined using ImageJ software. The particle streaks measured were selected so that the starting and ending points were clearly distinguished from background and did not overlap with the streaks of nearby particles.

Two Hamamatsu R3896-03 photomultiplier tubes (PMTs) with 700 and 800 nm interference filters were used to record the time-resolved particle emission traces. The light to the PMTs was fed through a bifurcated optics bundle with its optical inlet positioned 5 cm above and 17 cm away from the burner. The height of the field of view was 25 cm. Particle streaks were detected from the range of heights of ca. 2 -13 cm above the burner tip. In the laser ignition experiments, the fiber optics bundle inlet was positioned at the same height as the nozzle tip and 16.5 cm away from it. Burning particle streaks were detected up to 5 cm above the nozzle in this case.

A 16-bit PCI-6123 National Instruments data acquisition system coupled with LabView software was used to acquire data at a rate of 100,000 samples per second for a total of 8 seconds per run. For each sample in each environment, at least 100 runs were processed to finally select a minimum of 800 of individual particle peaks. Because of minor inconsistencies in the particle feed rate, some of the collected data sets included many overlapping particle peaks, which were dismissed; some sets did not contain welldistinguished particle emission traces. Recorded particle emission signals were processed using a custom MATLAB code [114, 123] to determine the particle burn times and combustion temperatures. The emission traces filtered at 700 nm were consistently selected for burn time analysis. The baseline of the peaks was determined as the average signal value recorded for 10 ms (minimum) without any particle peaks. Combustion temperatures were determined from the calibrated ratio of intensities of the emissions from both PMTs fitted to a Planck's curve. The calibration used a tungsten lamp as an emission source and a NIST traceable StellarNet BW16 spectrometer collecting the emission spectra simultaneously with the filtered PMTs.

A 32 Channel Hamamatsu H11460-01 (A10766-007-02) compact spectrometer was used to obtain emission pulses optically for the emission ranging from 373.4 to 641 nm. This enabled time resolved spectroscopy of the individual emission pulses. The instrument was positioned 16.5 cm away from the nozzle tip for the laser and 4 cm above and 14 cm away from the burner tip in the case of the hydrocarbon and hydrogen flames. Emission pulses were recorded using multiple 16-bit PCI-National Instruments data acquisition boards and LabView software. Data was collected at a rate of 100,000 samples per second for a total of 3 s per run. A total of 50 runs were obtained for each sample in each combustion environment.

Particle combustion temperatures were also determined from time-integrated optical emission spectra from multiple particle streaks ignited by the laser and burning in air. A StellarNet BW16 spectrometer was used to record emissions within 184 nm to 848 nm. The instrument was positioned 9 cm away from the tip of the nozzle at the same height of the exit point. For each sample, emission spectra were recorded with an integration time of 1 s and over 1000 spectra were collected. Peaks of boron combustion products (480-680 nm) and emissions of contaminations by sodium (589 nm) and potassium (740-810 nm) were filtered out from the data collected [140, 142]. Planck's formula was applied to the remaining spectra to determine the temperature. The effect of wavelength on emissivity was neglected.

4.5 Adiabatic Flame Temperatures and Equilibrium Product Compositions

Thermodynamic equilibrium calculations were conducted using NASA CEA code [1] to characterize the gaseous combustion products of air- acetylene and air- hydrogen flames, in which the particles were injected. Using these predicted gas compositions as the oxidizing environment for boron, the adiabatic flame temperatures and corresponding combustion products generated by boron and boron- iron composites injected in these environments were also calculated. The changes in temperature and composition of the oxidizing environment as a result of mixing the flame products with surrounding air were predicted by computational fluid dynamics model, as discussed in the next section.

For experiments, involving boron particles ignited by the laser beam in air, the starting temperature was 298 K and air was the only oxidizer considered. For particles injected in the flames, the temperatures and compositions of the oxidizing gases obtained from thermodynamic calculations are listed in Table 4.1. Particles were assumed to be initially at room temperature, in equilibrium with the carrier gas. The effect of pre- heating the carrier gas and particles up to 450 K (the temperature measured at the burner tip by the thermocouple for air- acetylene flame) was accounted for previously [142]; this correction

of the initial temperature did not lead to significant changes in the calculated flame temperatures or product species and it was neglected here. The conditions shown in Table 4.1 were used to estimate the adiabatic flame temperatures and product makeup produced by burning boron and composite B- Fe particles.

Environment	Air- Acetylene	Hydrogen- Oxygen/ Air
	φ=1.65	φ=1
Temperature (K)	2629	2409
Species	Mole Fractions	
N_2	0.65	0.63
СО	0.18	7.0×10^{-5}
H_2O	0.07	0.32
CO_2	0.05	1.9x10 ⁻⁴
H2	0.04	0.02
O2	3.6x10 ⁻⁴	3.8x10 ⁻³

Table 4.1 Temperatures and Compositions of Combustion Products/ Oxidizers Obtained using NASA CEA code [1] for Air-acetylene and Air-hydrogen Flames used in Experiments

The plots shown in Figure 4.4 are the adiabatic temperatures and concentrations of the main combustion products for boron combustion in air and in the environments described in Table 4.1 at varying equivalence ratios. To vary the equivalence ratio, the amount of boron was changed in the calculations, while the composition of the oxidizing environment was unchanged. The temperature plots were expected to illustrate the effect of added iron on the combustion; this effect is negligible because of the small mass of iron included, corresponding to the materials used in the present experiments. To avoid clutter, product species are only shown for the calculation involving pure boron; the results are essentially the same for the material with 5% iron added to the fuel.

In both air- acetylene and air- hydrogen flames, HOBO dominates the combustion products for the fuel- lean conditions. For all flames, in fuel- rich cases, BN becomes a dominant combustion product. The predicted adiabatic flame temperatures are only slightly changing as a function of the equivalence ratio for both air- acetylene and air- hydrogen flames. For air, the temperature increases sharply as the flame moves from fuel-lean to stoichiometric conditions, and then remains nearly unchanged in the fuel- rich domain.



Figure 4.4 Adiabatic flame temperatures and main combustion products generated by boron and boron- iron composite burning in air and in the products of air- acetylene and air- hydrogen flames.

4.6 Combustion Environments for Particles Injected in Flames

For both experimental configurations involving injecting particles in pre-mixed airacetylene and diffusion air- hydrogen flames, the gas compositions and temperatures in the region where particles burned were predicted using a computational fluid dynamics (CFD) model using COMSOL Multiphysics software. The computations were validated comparing predicted and measured temperature profiles above the flames. To measure the temperatures, a thin ceramic filament was placed at different heights above the burner. The optical emission from the filament was captured using a spectrometer, and the respective color temperature was determined assuming that the filament emitted as a gray body.

The computational domains representing experimental configurations are shown in Figure 4.5. In both cases, cylindrically symmetric configurations were considered in which particles were assumed to move vertically up along the axis. The dimensions of the domains were selected to describe the environments at the heights above the burner, where burning particle streaks were observed experimentally. Details of the calculations and validation measurements for the pre-mixed air-acetylene flame are provided in Ref. [142]. Briefly, the flame was assumed to form a ring surrounding the central tube feeding the particle-laden flow. A symmetric flame cone was introduced as a boundary condition in the model. Combustion products described in Table 4.1 at the adiabatic flame temperature were introduced into the system from the flame cone. A nitrogen flow was introduced separately. The computational domain was filled with air and had open boundaries at room temperature and atmospheric pressure. The CFD model established the steady state flow field, which determined the gas composition and temperature at the axis, where the particles burned. The flame height was adjusted to ensure the match of the computed and measured vertical temperature profiles.

Calculations for the diffusion air- hydrogen flame also considered a flame front surrounding the axis of symmetry. The flame was only formed at the outer boundary of the hydrogen flow, where hydrogen could be mixed with surrounding air. As in the previous case, the flame location served as a boundary condition, at which the flame products described in Table 4.1 were introduced into the system. The flow rate of the flame products was determined based on the experimental flow rate of hydrogen.



Figure 4.5 Schematic representations of computational domains for each environment.

Two-dimensional maps for the temperature and nitrogen concentration for both flames are shown in Figure 4.6. A relatively small amount of nitrogen form the particleladen jet, only visible in the insets in Figure 4.6, is quickly diluted with the combustion products for both flames. Most of the nitrogen reaching burning particles comes from the surrounding air; therefore, the nitrogen maps are useful indicators of how quickly air mixes with the flame combustion products. Qualitatively, nitrogen concentration changes proportionally to that of the surrounding oxygen. Assuming that the particles burn close to

Note: Dimensions are in mm. Additional details for the air- hydrogen flame including an oxygen flow are shown in appendices.

the axis of the considered cylindrical domain, it can be concluded from the nitrogen concentration maps that the particles remain primarily exposed to the respective flame combustion products rather than ambient air, especially early after ignition. Additional details describing species and temperatures, including comparison with experimental temperatures for the air- acetylene flame are available elsewhere [142].



Figure 4.6 Two-dimensional color maps showing the distribution of temperatures and nitrogen concentrations for air- acetylene (left) and air- hydrogen (right) flames.

Note: Insets show close-ups of the flame regions.

For air-hydrogen flame, the calculated vertical concentration profiles for the main gas species as well as temperature profile and the measured temperatures are shown in Figure 4.7. Maximum predicted temperatures for each height are plotted for this comparison with the experimental data. The calculated and measured temperatures match well up to about 4 cm above the burner tip. Above that height, the measured temperature is substantially lower than the predicted one. Most likely, this discrepancy is caused by small asymmetry in the experimental system, which accelerates the mixing of ambient air with the rising combustion products of the air-hydrogen flame. The reduced experimental temperature at heights above 4 cm suggests that the gas environment at those heights is likely to be significantly affected by surrounding air. Based on the CFD predictions, oxygen already becomes a dominant oxidizer above 4 cm; thus the effect of oxygen at greater heights is expected to be even stronger than expected based on the profiles shown in Figure 4.7.



Figure 4.7 Predicted and measured flame temperature along vertical axis of air-hydrogen flame (top) and predicted concentrations of the main gas species present in the environment along vertical axis for this flame (bottom).

4.7 Results

4.7.1 Single particle emission

Photographs of multiple burning particle streaks are shown for the as received boron and the prepared boron-iron composite powders ignited in different environments (see Figures 4.8-4.10). In the combustion products of the air-acetylene jet flame, particles were observed to burn within 4-13 cm above the burner tip (Figure 4.8). The luminous streaks originated above the bright flame region. The corresponding particle velocities ranged from 5 to 15 m/s at the center of the jet [142]; higher particle velocities were observed further away from the burner tip. For as-received boron, the particle streaks often comprised two bright regions, as seen in Figure 4.8. A color change was observed from red/orange to yellow/green, for the first and second bright regions, respectively. Only one bright region

was observed for the composite B-Fe powders; it was commonly located somewhat further away from the burner than the first bright region observed for as received boron. A difference in the total lengths of the streaks for the composite material and as received boron noted in Figure 4.8 does not represent a consistent trend, as further discussed below. Individual particle emission streaks for both materials appeared to have a bright haze surrounding the streaks, indicative of a vapor-phase flame around burning particles.



Figure 4.8 Luminous streaks of boron and boron-iron composite powders burning in combustion products of an air-acetylene flame (exposure time: 8 ms).

For the air-hydrogen flame, as observed in Figure 4.9, most particle streaks started within the flame region. The velocities of particles measured 60-70 mm above the burner tip are around 4 m/s [123]. Most streaks were about 2 cm long for both materials. The luminous halo around particle streaks was substantially weaker for this oxidizing environment as compared to the combustion products of the air-acetylene flame.



Figure 4.9 Luminous streaks of boron and boron-iron composite powders burning in combustion products of air-hydrogen diffusion flame (exposure time: 250 ms).

For the laser-ignited particles burning in air, the particle streaks were significantly shorter than in the combustion products of either flame (Figure 4.10). Particle streaks in air were generally yellow or white with little or no green color observed. This is consistent with the boron streak color reported earlier [25, 60, 145]. For as received boron, particle streaks appear substantially brighter than for the iron-containing composite. Boron streaks gradually became thinner at greater distances from the ignition source, whereas the width of B-Fe particle streaks did not seem to change. Average particle velocity in this experiment was around 3-4 m/s [143].



Figure 4.10 Luminous streaks of boron and boron-iron composite powders ignited by the CO₂ laser beam and burning in air (exposure time: 250 ms).

The lengths of particle streaks were measured systematically for the images taken in different environments; the resulting distributions are shown in Figure 4.11. In combustion products of the air-acetylene flame, the particle streaks ranged from 0.2 to 6.4 cm in length, with average particle streak lengths of 1.9 and 2.7 cm for boron and boroniron composite respectively. Because the exposure time for this set of images, 8 ms, was comparable to the particle burn time (see below), the result might distort the distribution, reducing the number of longer streaks. However, this error is unlikely to affect a qualitative observation showing that the streaks for boron-iron composite were somewhat longer than for boron. The exposure time of 250 ms used for other environments substantially exceeded the particle burn times and thus ensured capture of streaks of all lengths. In the products of air-hydrogen flame, the average streak lengths were close to 2 cm for both materials. It appears that the histograms are slightly truncated at the shorter streak side, suggesting that there might have been additional shorter streaks, which could not be properly identified from the images taken. This effect is very significant for the streak length distributions measured for the particles burning in air. For both materials, the measured distributions peak at the shortest detectable streak length, suggesting that a significant number of shortest particle streaks remained unaccounted for. The average lengths implied by the obtained distributions were 0.5 and 0.4 cm for boron and boron-iron respectively, supporting at least qualitatively, the observation from Figure 4.10, that in air boron particle streaks are longer than those of boron-iron composite particles.



Figure 4.11 Particle streak length distribution for boron and boron-iron composite in varying combustion environments.

Time resolved optical emission measurements obtained from PMTs filtered at nearinfrared wavelengths (700 and 800 nm) and from the 32-channel spectrometer in the visible range of wavelengths (383-641 nm) showed characteristic two-peak pulses produced by most commercial boron powder particles burning in all three environments. However, burning iron-containing composite particles always produced a single peak.

The emission peaks recorded by the 700-nm filtered PMT in all three environments are shown in Figure 4.12. For these emission signals, the first of the two peaks observed in the boron particle emission pulse is stronger than the second one, consistently with earlier measurements [143, 145]. The first peak exhibits a sharp rise followed by a minimum. The second peak has a lower intensity and longer duration. The peaks of burning boron-iron composite particles were nearly symmetrical, with comparable signal rise and fall durations.





Selected emission traces produced by particles burning in air and captured in the visible wavelengths range by the 32-channel spectrometer are shown in Figure 4.13. As in Figure 4.12, for as-received boron most particle pulses had characteristic double peak shape. However, unlike Figure 4.12, the first peak was lower in intensity compared to the second one. Only a single peak was consistently observed for the boron-iron composite powder. The amplitude of the emission signal for the boron-iron composite was substantially lower than that for as-received boron. For both materials, it was observed that the intensity of the emission increased for longer wavelengths.



Figure 4.13 Optical emission traces filtered at selected wavelengths for boron and boron-iron composite particles burning in air.

The double-peak emission pulses observed for the as received boron burning in air were further processed to clarify the characteristic times of the first and second peaks. Signals recorded by the 700-nm filtered PMT were used. Among all recorded pulses, approximately 10% were selected for this processing as containing double peaks with distinct features. Figure 4.14 shows a typical emission signal, characteristic times identified (note the logarithmic time scale), and the results summarizing these times for multiple peaks. The analysis was performed using a MATLAB code, which selected the double peaks based on the number of maxima and minima identified in the derivative of the signal intensity. The results in Figure 4.14 are shown as a correlation between the characteristic times (horizontal axis) with the total particle burn time (vertical axis). Thus, open red triangles show the diagonal in the plot. For smaller particles with shorter total burn times, the durations of first peak and time to second peak increases as the total burn times become longer. However, for particles with burn times exceeding 15 ms, the duration of the first peak, t_{d1}, becomes nearly constant. The duration of the 1st peak is typically within 3 ms; it is usually shorter than the second peak in the same particle emission trace. The duration of the 2^{nd} peak appears to largely determine the total duration of the emission pulse. The maximum emission signal for the second peak occurs soon after the end of the first peak.



Figure 4.14 Features of double-peak emission pulses produced by boron particles burning in air and recorded using a 700-nm filtered PMT.

(A) An emission pulse with characteristic times labeled. (B) The total particle burn time vs. characteristic times identified in emission pulses.

4.7.2 Particle burn times

Using a custom MATLAB code, the total durations of the emission peaks were determined for each experiment; they were interpreted as the burn times of individual particles. As always for metal particles, the total burn times represent duration of multiple reactions, which may occur in parallel or serially during particle combustion. The structure of the emission peaks shown in Figures 4.12-4.14 illustrate how such events affect optical signals for the particles studied here. Nevertheless, total burn times are conventionally used to describe combustion of metal particles and are considered to be inversely proportional to their integral burn rates. Following this convention, the analysis of the total burn times for individual particles was performed here. All measured burn times were sorted into logarithmic bins and the number frequency distributions were plotted as histograms shown in Figure 4.15. Results from preliminary particle velocity calculations conducted using number-average streak lengths from Figure 4.11 and number-average burn times (see Figure 4.15) yielded results that were within the range of velocities measured and modeled previously in Refs. [123],[142], and [145].

For the air-acetylene flame, burn time distributions were very similar to each other for both boron and boron-iron composite powders. The histograms were relatively narrow, with the most common burn times close to 10 ms for both materials. For the oxygenhydrogen flame, the histograms were broader, including more short emission pulses. The distribution of burn times for the B-Fe composite powder was shifted towards shorter times, suggesting that the composite particles burned faster than as received boron. Relatively broad histograms were also observed for laser-ignited particles burning in air. In this case, there was a significant shift to shorter burn times for the composite particles.



Figure 4.15 Burn time distributions of commercial boron and boron-iron composite particles ignited in the combustion products of an air-acetylene flame (left), air-hydrogen flame (center), and laser ignited in air (right).

The correlations of the particle burn time distributions with their size distributions yielded the trends shown in Figure 4.16. In all cases, the data for the burn times, *t*, were fitted as $t=a \cdot D^n$, where *D* is particle diameter and *a* and *n* are respectively the pre-exponent and exponent of the empirical power law. In the combustion products of an air-acetylene flame, the exponents are 0.66 and 0.78 for the boron-iron composite and commercial boron, respectively. There is no significant difference between the burn times for the two materials ignited in that environment, where CO₂, H₂O and CO are the main oxidizers. For combustion in the air-hydrogen flame, the exponents describing the effect of particle size on its burn time increase to 1.26 and 1.6 for boron and boron-iron composite, respectively. In this case, coarser particles of both materials have essentially the same burn times; however, the finer B-Fe particles burn noticeably faster than boron particles of the same sizes. Finally, for the particles ignited in air, the exponents were still greater: 2.56 and 2.38

for the commercial boron and B-Fe composite, respectively. For all particle sizes, the B-Fe composite particles had substantially shorter burn times compared to as received boron.



Figure 4.16 Effect of particle size on its burn time for as received boron and boron-iron composite powders ignited in different oxidizing environments.

4.7.3 Combustion temperatures

Different optical measurements were used to recover both integrated and time-dependent combustion temperature for both as received boron and boron-iron composite. In all optical temperature measurements, the emission was not spatially resolved and came from both surface of the burning particle and from the surrounding stand-off flame and/or condensing combustion products. Thus, interpretations of these measurements are not straightforward. The results are biased towards the temperature of the brightest emitter. Emissivity of a particle surface is expected to be greater than that of the partially transparent flame. In addition, the very high boiling point of boron (4273 K) makes it most likely that the particle surface was the hottest emitter, so that the measurement was indeed biased towards the particle surface temperature. An additional difficulty is that the emissivity can change substantially between pure and oxidized boron. The data on such changes are not available, and thus such changes are neglected.

Time integrated emission spectra for boron and boron-iron composite powders burning in air, obtained using the StellarNet BW16 spectrometer, are shown in Figure 4.17. For each spectrum, BO emission patterns are distinctly observed. The traces were filtered as previously described [140, 142] to neglect the BO emission and contaminants in the powder, prior to fitting Planck's equation to determine the temperatures. The experimental spectra are shown in Figure 4.17 along with their respective Planck's curve fits. The temperature is just slightly lower for the B-Fe composite compared to the as received boron.



Figure 4.17 Time-integrated emission spectra for boron and boron-iron composite samples laser ignited in air.

Emission traces collected at each wavelength from the 32-channel spectrometer, such as shown in Figure 4.13, were processed to obtain time resolved temperatures for individual particles burning in all environments. Temperatures were determined by fitting spectra with Planck's curve, assuming that the burning particles were gray bodies. For experiments in air-acetylene flame, substantial flame emission contributed to the signal as a background for the particle emission. That background led to significant experimental errors making it impossible to determine particle temperatures using individual PMTs filtered at 700 and 800 nm [146]. In this work, the temperatures were calculated as shown in Table 4.2 processing the available measurements for all environments. The error bars

specified in the table represent standard deviations for the measured values. For each individual particle pulse, an average temperature was obtained. For two-peak pulses, average temperatures were obtained for each component peak. Thus, for as received boron, both individual peak temperatures and overall average temperatures are shown, accounting separately for the observed two-peak and single peak pulses, respectively. For the double-peak pulses, the first and second listed temperatures represent the first and second peaks, respectively. The obtained temperatures are unrealistically high for the particles burning in the products of air-acetylene flame. It is likely that as in the previous work [146], the background flame emission caused these measurements to be in error.

Adiabatic flame temperatures obtained using NASA CEA code [1] are also shown in Table 4.2. In calculations, the equivalence ratio was varied for each environment; shown are the maximum obtained temperatures and respective equivalence ratios. Note that in agreement with Figure 4.4, adding 5 wt% of iron to boron did not change the calculated temperatures appreciably. In calculations, the highest adiabatic flame temperatures are close to one another for all environments. In all cases, the high temperatures occur for the fuel-rich mixtures, when substantial formation of BN is predicted in equilibrium.

For air-acetylene flames, the experimental values substantially exceed the calculated temperatures. As noted above, this discrepancy is most likely due to an experimental error caused by the hydrocarbon flame emission overlapping with the emission of burning particles. For air-hydrogen flames, the measured temperatures are close to or lower than the calculated ones, suggesting that the combustion products predicted by the equilibrium calculations are likely to be formed in experiments. For air, the measured temperatures are somewhat higher than predicted. In this case, no additional

emission affected the measurements and thus the experimental result is more reliable than in other cases. To interpret the high experimental temperatures, it may be suggested that the formation of boron nitride is suppressed kinetically, so that the products shift towards the more exothermic formation of B_2O_3 . Additional equilibrium calculations were performed considering boron burning in air while prohibiting formation of BN. In this case, the temperature peaks around the equivalence ratio of 1, exceeding 4100 K. Thus, kinetic suppression of BN formation in air can indeed lead to higher flame temperatures than predicted by equilibrium calculations accounting for all possible products.

Environment	Measured Temperatures, K			Calculated	At
	B Double Peak	Single Peak	B-Fe Single Peak	max. adiabatic flame temperatures, K	equivalence ratios
Air-C ₂ H ₂	4790 <u>+</u> 670	4200 <u>+</u> 870	4250 <u>+</u> 440	2729	2.16
flame	4820 <u>+</u> 350				
Air-H ₂ flame	2380±160	2300 ± 400	2850 <u>+</u> 490	2755	4.65
	2840 <u>+</u> 460				
Air (ignited by	3230 <u>+</u> 300	3350 <u>+</u> 300	3530 <u>±</u> 190	2749	2.35
laser)	3950 ± 270				

 Table 4.2 Measured and Calculated Combustion Temperatures for Boron and Boron-iron Composite Powders.

Note: The measurements used emission recorded by 32-channel spectrometer (383-641 nm).

Combustion temperatures of both powders burning in air were also measured using the optical emission data recorded by the PMTs equipped with infrared filters (700 and 800 nm). Examples of recorded emission pulses and corresponding temperatures are shown in Figure 4.18. Two examples are selected, illustrating that the temperature measured for the first peak can be higher or lower than that measured for the second peak. A statistically significant sample of emission pulses (more than 150) was used to measure the temperatures corresponding to the first and second peaks. The results are shown in Figure 4.19 where the maximum temperatures for each peak are plotted against the corresponding burn time. For one of the times, the filled symbol representing the second peak temperature is missing; the result was an outlier showing an unrealistically high temperature. Although there is a substantial scatter in the measured temperatures, the overall trend appears to agree with that shown in Table 4.2. Both peaks suggest a high-temperature, full-fledged combustion. Further to this observation, the temperatures of both peaks seem to be directly proportional to particle burn times, implying that larger particles have higher first and second peak temperatures.



Figure 4.18 Emission signals produced by boron particles burning in air filtered at 700 and 800 nm and corresponding time-resolved temperatures.

Note: Both signals show double peak emission pulses. The first peak temperature can be either lower (top trace) or higher (bottom trace) than the second peak temperature.



Figure 4.19 Maximum temperatures measured for commercial boron burning in air using ratio of emission signals filtered at 700 and 800 nm

Note: The data is separated for the first and second peaks of the double peak emission pulses. The temperatures are correlated to the corresponding particle burn times.

To compare the temperature of boron combustion with that of boron-iron composite particles, which produced emission pulses with single peaks, average temperature values were obtained for both materials. In both cases, the temperatures were averaged over a portion of each emission pulse while the signal intensity exceeded 50% of its maximum value for that pulse. The obtained distributions of such temperatures for both materials are shown in Figure 4.20. For reference, boiling temperature for B₂O₃ and melting and boiling temperatures for B are shown by vertical dashed lines. The data scatter is significant for both materials, although it appears to be greater for as received boron, probably, because of the multiple pulses with double peaks. The number average values imply that for both B and B-Fe particles burning in air combustion temperatures are close to approximately 2400 K. These temperatures are substantially lower than shown in Table 4.2 and Figure 4.19 because they do not represent the maximum flame temperatures, but rather the temperatures averaged over a significant portion of the particle burn times.



Figure 4.20 Average combustion temperatures for commercial boron and boron-iron composite powders laser ignited in air.

Note: Data were collected using PMTs filtered at 700 and 800 nm and averaged over the portions of the signal exceeding 50% of the maximum for each emission pulse.

4.8 Discussion

This study reports experimental characterization of combustion of a commercial boron powder and boron doped with iron; the results primarily use optical emission measurements. Optical emission of burning metal particles is affected by several factors. The emission signal is stronger when particles are of greater size, when they are heated to higher temperatures, and when there are additional emitters, such as smoke particles, formed in the standoff flame. Additionally, the emission signal is affected by spectral emissivity of burning particles, which is defined by the particle composition. The emissivity may also be affected by the particle size, especially, when that size is comparable to the emission wavelength, as is the case for smoke particles generating visible light. These effects should be accounted for while interpreting the present results. The following discussion includes two main parts. First, results characterizing combustion of the commercial boron powder are considered. Then, combustion of the as received boron is compared to that of the composite material, in which boron was doped with iron.

4.8.1 Boron particle combustion

One of the distinct features of boron combustion is the two-staged reaction, observed from optical emission of burning particles [5, 21, 60]. The original interpretation of the two-stage emission pattern suggests that it is associated with two reaction steps. In the first step, boron oxidation is rate limited by the evaporation of a protective boron oxide coating while oxygen diffuses through the oxide. The second, so called, full-fledged combustion step involves a high-temperature heterogeneous reaction between boron and oxidizing species. More recently, the double peak emission pulses were observed for boron particles burning in both air and combustion products of a hydrocarbon flame [142, 145], in agreement with the present results. The double peak emission pulses were also common in air-hydrogen flame. A closer examination of the double-peak emission patterns suggests that they are inconsistent with the reaction model involving removal of B₂O₃ layer during the first stage of combustion identified from the particle optical emission. The particles are highly luminous during that stage (see Figures 4.12-4.14 and 4.18, presenting time-resolved

emission traces at different wavelengths and in different environments); the temperature in both air and air-acetylene flame combustion products exceeds substantially the boiling point of B_2O_3 (see Table 4.2, Figure 4.19). It is, therefore, reasonable to suggest that both first and second peaks observed in the double peak emission pulses for boron represent parts of high-temperature, and thus full-fledged reaction. The reaction limited by the removal of initial B_2O_3 layer from the boron surface must have occurred when the particles were less incandescent and thus remained invisible to the optical sensors used in experiments.

In all cases, the maximum temperatures detected in boron combustion experiments remained below the boron boiling point, suggesting that the surface reaction was important for boron particles burning in all environments considered. The reaction rate is likely governed by the kinetics of such surface reactions. The effect of heterogeneous kinetics may explain a discrepancy between the adiabatic flame temperatures predicted to occur in thermodynamic equilibrium and those measured in air (Table 4.2). The calculated adiabatic flame temperature is suppressed by the formation of boron nitride (see Figure 4.4). Higher experimental temperatures suggest that boron nitride is not generated as predicted in the equilibrium, and the reaction is likely shifted towards formation of gaseous boron oxides, accompanied by a greater heat release; this reaction scenario is in agreement with the equilibrium calculation, in which BN is removed from the products. In air-hydrogen flame, the experimental boron flame temperature is lower than the adiabatic flame temperature. Condensed products such as boron nitride and iron oxide (Fe₃O₄) are predicted to form by the equilibrium calculation in extremely fuel rich cases, which may account for lower temperatures recorded. The reduced experimental temperature can also be simply associated with a relatively low rate of reaction in steam, so that the heat losses become substantial.

Although the present measurements extend the experimental description of boron particle combustion, the mechanism of the observed two-stage combustion pattern remains unclear. The maximum temperature during the first combustion stage appears to be slightly lower than that during the second one, while the relation of emission intensities produced by burning particles at different stages is wavelength dependent. In air, for the shorter, visible light wavelengths, as shown in Figure 4.13, the emission during the first stage is weaker despite the observation in Figure 4.10 suggesting that the early part of the visible emission streak appears broader. For infrared emission, the first peak becomes stronger than the second one (Figs. 4.12, 4.14, 4.18). An explanation for this can be offered assuming that the emission comes from both burning particle surface and from smoke generated in the vapor-phase flame. The amount, make-up, and dimensions of the smoke particles can be different during the two reaction stages. For example, smoke particles with dimensions of several hundreds of nanometers could be more luminous at the wavelengths exceeding their size, and thus appear brighter in the infrared emission traces compared to those acquired in the visible wavelength range. Thus, a more significant generation of smoke during the first stage combustion would make the first peak appear stronger when using the 700 and 800-nm filtered traces even though the temperature during this reaction stage was lower than during the second stage combustion.

The smoke could be produced by condensation of gaseous BO, BO₂, B₂O₂, and HOBO species formed at the particle surface. Formation of gaseous products as a result of heterogeneous reaction usually competes with the formation of condensed phase products

and metal-gas solutions in burning particles [111, 124]. The latter types of reactions, altering the compositions of burning particles are commonly responsible for multi-stage reaction patterns, similar to that observed here. It is thus reasonable to suggest that burning boron particles dissolve oxygen and, possibly, nitrogen. In addition, in the presence of CO and CO₂, formation of molten oxy-carbides is also possible. As new phases form in burning particles, the rate of their heterogeneous surface oxidation diminishes, leading to the end of the first combustion stage. The particles cool off, experiencing a phase change. For example, excess of nitrogen can be released generating fresh surface and prompting beginning of the second stage combustion. In steam, metastable borane phases can form in the first stage, which then convert to boron oxides as the reaction continues.

The above hypothetical scenario describes combustion of boron particles qualitatively; however, a more detailed, quantitative description is required for practical applications. It is likely that additional experimental work is needed to support development of a quantitative combustion model. Although the proposed combustion process is rather complex, a simplified description of the bulk particle burn rate is given in Figure 4.16. It is interesting that the exponent in the *d*-power law describing the effect of particle size on its burn time increases from ca. 0.7 to 1.5 and to 2.5 for boron combustion in air-acetylene products, in air-hydrogen products, and in air, respectively. It is tempting to state that the presence of oxidizers other than oxygen makes the heterogeneous reactions more likely, shifting the combustion regime from that controlled by gas diffusion of oxidizer to the particle in air to that controlled by the surface kinetics in air-acetylene flame. However, as discussed above, the combustion is more complex and is unlikely to be well interpreted accounting for a single process controlling the burn rate. To account properly

for the relationship between durations of different combustion stages shown in Figure 4.14, one should consider the heat and mass transfer models for the burning particles, which occur in the transition regime, while the significance of molecular and convective contributions changes for particles of different sizes. Respectively, the significance of the vapor-phase flame zone can be affected. For example, larger particles could have a standoff flame, from which the heat is effectively removed by the convective heat transfer, leading to a shorter time between the first emission peak and the end of that peak, as seen in Figure 4.14. At the same time, an accelerated convective mass transfer of the oxidizer to that flame zone for larger particles can support for them a faster reaction, leading to the higher measured flame temperatures, as seen in Figure 4.19. For smaller particles, the standoff flame approaches the particle surface and the effect of surface reactions becomes more significant. Such surface reactions may be affected by the formation of boron-oxygen solution rather than stoichiometric boron oxide. The heat released upon formation of the solution is lower than the heat of oxidation, diminishing, temporarily, the exothermicity of the reaction. An additional heat release is then expected when the solution transforms into the stoichiometric oxide. This could occur when the particle cools down, making the solution metastable. This additional heat release may explain an increase in brightness and temperature of the burning particles during the second stage of their combustion.

4.8.2 Effect of doping boron with iron on combustion

It was observed that the intensity of optical emission produced by boron-iron composites was consistently lower than that of the reference as received boron particles. However, there was no detectable reduction in the measured flame temperatures. This can be interpreted suggesting that the role of vapor-phase reactions was diminished in the boroniron composites. Thus, there were fewer incandescent smoke particles, making the overall emission weaker. The above suggestion is also consistent with the observation of the nearly constant streak width for the B-Fe particles, while the streak widths change for boron, suggesting changes in the rate of generation of smoke particles in the stand-off flame.

It is interesting that the two-stage emission pattern observed commonly for boron was not observed for the composite particles. If the qualitative mechanism proposed above and including formation of intermediate condensed phase compounds (solutions) in the burning boron is valid, the present observations suggest that presence of iron suppresses formation of such intermediate condensed phases. Because the two-stage combustion scenario includes the period when the first stage ends, accompanied with the particle cooling off, elimination of such a period can lead to the overall acceleration of the particle burn rate. Indeed, shorter burn times were observed in this work for the B-Fe particles in air and air-hydrogen flame. The burn time reduction was most significant for air, for which the effect of nitrogen on combustion of boron is expected to be most important. To explain this, it can be assumed that boron reacts heterogeneously with both oxygen and nitrogen with the comparable reaction rates. However, when iron is present, its reaction with oxygen is preferred. This reaction is followed up with the reduction of the produced iron oxide by boron, while formation of boron nitrides or boron-nitrogen solutions occurs at a lower rate than it does in absence of iron. Similarly, the effect of added iron can accelerate combustion of boron in steam, in which preferential oxidation of iron (and then reduction of iron oxide) occurs faster than formation of metastable boranes.
No reduction in the burn times was observed in air-acetylene flame, in which carbon-containing oxidizing species were present. The change in burn time was relatively minor for the air-hydrogen flame. Because comparisons involve experiments in the same oxidizing environments and because there is no significant change in the measured particle temperatures, the lack of reduction in the burn times suggests that heterogeneous reactions of iron with carbon-containing oxidizers (CO and CO₂) and with H₂O do not occur faster than the reactions of these oxidizers with pure boron. However, when the oxidizer is oxygen, the heterogeneous iron oxidation occurs faster than that of boron, so that its catalytic effect is significant. Future work is desired to elucidate the mechanisms of such catalytic effects and, possibly, identify other dopants suitable for accelerating boron combustion.

4.9 Conclusions

A commercial boron powder was mechanically milled with iron (5 wt. %) to produce composite particles containing nano-sized iron inclusions embedded in boron agglomerates. The boron agglomerates contain nano-sized boron primary particles, which did not change noticeably as a result of milling.

Both as received boron and composite boron-iron powders were burned in combustion products of air-acetylene and air-hydrogen flames and in air. For boron, optical emission pulses produced by burning particles commonly contained two peaks. The temperatures measured for both peaks were sufficiently high for a full-fledged combustion. The measured flame temperatures were higher than the calculated adiabatic flame temperature of boron combustion in air; this discrepancy may be explained by kinetic suppression of formation of BN and shifting combustion products towards B₂O₃.

The burning boron-iron composite particles produced single-peak emission pulses in all oxidizers. The overall emission intensity produced by the composite material was lower than that for boron, which is most likely explained by the suppressed vapor phase reactions. The flame temperatures measured for boron-iron composite powders were close to those measured for boron in the same oxidizing environments. The burn times for the boron-iron composite particles were the same as for boron in air-acetylene flames. In air, the burn times for boron-iron composite particles were markedly reduced compared to boron. A slight reduction in the combustion times for the composite material burning in the air-hydrogen flame was also observed.

The effect of particle size on its burn time was characterized for all materials and environments. The bulk effect could be expressed assuming that the burn time is proportional to the particle diameter in the power, n. The exponent, n, was increased from ca. 0.7 to 1.5 and to 2.5 for both boron and boron-iron composite particle combustion in air-acetylene products, in air-hydrogen flame products, and in air, respectively.

CHAPTER 5

BORON DOPED WITH IRON: PREPARATION AND COMBUSTION IN AIR⁴

5.1 Abstract

Combustion-relevant effects of iron as an additive to boron powders were examined. 95% pure boron powder was doped with iron by thermal decomposition of iron pentacarbonyl. Iron concentration was determined using inductively coupled plasma-mass spectrometry. Two doped boron samples with 1.6 and 3.1 wt% Fe were compared to commercial boron powder for physical morphology and combustion characteristics. No significant morphological differences between the doped and un-doped samples were detected by scanning electron microscopy. Elemental maps confirmed uniform distribution of iron in the coated powders. For combustion studies, individual particles of different powders were ignited in air by passing through a CO_2 laser beam. Burn times and combustion temperatures were determined from optical emissions of burning particles. Doped boron samples have shorter burn times than particles of the un-doped commercial boron powder with the same size. The effect of doping boron with iron on burn times appears to be greater for larger particles. Combustion temperatures depend on the iron content. Lower iron concentrations showed temperatures near 3100 K, comparable to uncoated commercial boron. At higher Fe concentrations, the temperatures decreased to about 2500 K. A reaction

⁴ The findings presented for this chapter have been published in the peer- review journal, Combustion and Flame under the reference listing:

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mechanism is proposed explaining qualitatively a two-stage reaction pattern observed for the full-fledged combustion of boron; the approach uses a recently published binary B-O phase diagram. This combustion reactions are altered when boron is doped with iron, which is proposed to serve as a catalyst for boron oxidation.

5.2 Introduction

Boron has been extensively studied as a potential metal fuel additive for propellants, explosives, and pyrotechnics due to its high gravimetric and volumetric heating values [21]. The challenge, however, is that boron has long ignition delays [40] and combustion times [142, 143]. In hydrogen-containing environments, it also tends to form an undesirable metastable intermediate HOBO reducing both heat release and combustion temperature.

Additives, including aluminum [147], magnesium [5, 6, 23, 80], lithium [90], titanium [92, 148], oxides of bismuth, iron, and tin , ceria [16] and others, were explored to accelerate oxidation, reduce ignition delays and improve combustion rates of boron. In most cases, the selective oxidation of the metal additive or the intermetallic or redox reaction with the additive were expected to precede the full-fledged combustion of boron, leading to lower ignition temperatures. Additionally, the formation of a boride was speculated to lead to a discontinuous B_2O_3 layer helping further boron oxidation [147, 149]. In different studies, the additives were incorporated by milling, direct synthesis, sintering, wet chemistry, blending or other common powder technology techniques. While results have shown improvements in boron reactivity, commonly over 10 wt% of a metal or oxide were added to boron, reducing the overall energy density of the modified fuel. Recently, 5

wt% of iron was added to boron by mechanical milling [9]. Iron nanoparticles were embedded in agglomerates of boron forming a composite material. The addition of iron resulted in shorter burn times for composite particles compared to boron in air and steam, but not in products of a hydrocarbon flame. Emission pulses of burning composite boroniron particles had one peak, unlike typical two-peak pulses produced by burning boron particles. Thus, both the mechanism and rate of boron combustion were affected. It remained, however, unclear whether the observed effect was, at least partially, due to milling and respective change in morphology of the burning powder.

This work continues exploring iron as an additive potentially improving boron combustion while avoiding altering structure and morphology of the fuel particles. It was further of interest to consider whether smaller concentrations (on the order of 1 wt%) of iron could affect boron combustion. Boron powders were doped with iron through thermal decomposition of iron pentacarbonyl in dodecane at 125 - 190 °C. Because boron particles were not mechanically deformed or heated to or near the boron melting point, the powder particle morphology was preserved. The characteristics of the doped boron powder and experiments on its combustion in air are presented and discussed. Using air as an oxidizer was motivated by potential applications of boron in solid fuel ramjets [150, 151].

5.3 Material Preparation and Characterization

5.3.1 Material preparation

The steps for thermal decomposition of iron pentacarbonyl on boron particles suspended in a solvent were similar to those used elsewhere [152]. A schematic diagram of the coating setup is shown in Figure 5.1. The reaction was carried out in a 250 mL glass round bottom flask fitted with rubber stoppers. The entire setup was assembled and operated in an argonfilled glovebox. The procedure followed closely a modified wet chemistry iron deposition [153, 154]. A commercial boron (95% purity) by SB Boron was used as the starting material. Two iron-doped samples were prepared. To prepare the first doped boron sample, 4.75 g of boron powder was loaded in the vessel with 80 mL of dodecane by Fluka Chemicals (90-95% purity), a 25-mm Teflon®-coated magnetic stirrer and 0.5 mL of CE-2000 surfactant by Lambent Technologies. The vessel was flushed with argon at a rate of 154 mL/min. The exhaust was bubbled through 400 mL of 0.1M potassium hydroxide solution in order to trap decomposition products from the iron pentacarbonyl reaction. The reaction mixture was stirred under argon flow and heated at an approximate rate of 3 °C/min to 110 °C. The temperature was held constant for an hour to deoxygenate the solution and to remove any moisture from the powder sample. The temperature was then increased to 190°C and 1.5 mL of iron pentacarbonyl (99.99% purity, Sigma Aldrich) was slowly introduced into the reaction flask by injecting it with a glass syringe through a septum. The vessel was then held at 190°C for 2 hours to allow the decomposition to occur. Finally, the suspension was cooled to room temperature and the powder was collected via vacuum filtration with a 55 mm diameter Whatman 1003-055, grade 3 cellulose filter (pore size 6 µm). It was then washed and stored under hexane in an inert environment.

When iron pentacarbonyl was introduced in the solution at 190 °C, splashing occurred and a noticeable amount of Fe precipitated on the walls of the reaction flask. To avoid this, the second doped boron sample with a similar starting boron-iron pentacarbonyl ratio was prepared using less boron (3.17 g). Iron pentacarbonyl (1 mL) was introduced at a lower temperature of 125 °C after outgassing the solvent and before heating the mixture to the decomposition temperature of 190 °C.

Synthesis conditions and measured iron retained in the two recovered samples are summarized in Table 5.1. The samples prepared are referred to as B-Fe190 and B-Fe125 indicating the temperatures at which iron pentacarbonyl was introduced in the reaction batch.



Figure 5.1 Schematic diagram of the experimental setup for doping boron with iron by thermal decomposition of iron pentacarbonyl.

Sample	Temperature of IPC injection, °C	mass of Boron, g	volume of Fe(CO)5, mL	Target Fe mass fraction	measured Fe mass fraction*
Boron	-	-	-	0	0.30 %
B-Fe125	125	3.17	1.0	5 %	1.65 %
B-Fe190	190	4.75	1.5	5 %	3.07 %

Table 5.1 Summary of Synthesis Conditions and Resulting Compositions of the Prepared Irondoped Boron Powders

Note: Data retrieved from ICP-MS analysis, see below.

5.3.2 Material characterization

The products from the thermal decomposition reaction were examined using a LEO 1530 field emission Scanning Electron Microscope (SEM). Compositional analysis was conducted using Energy Dispersive Spectroscopy (EDS). Characteristic images of the prepared samples and starting boron powder as a reference material are shown in Figure 5.2. The images were taken using backscattered electrons, in order to distinguish iron from the boron aggregates. In all cases, the shapes of boron primary particles and fractal aggregates appear to be similar to each other for the starting powder and boron doped with iron.

Figure 5.2 also shows elemental maps of boron and iron for all the samples below their respective images. EDS analysis confirmed little or no iron present in the starting material. For prepared samples, however, uniform presence of iron was detected in both cases. Because the processing used here did not involve high temperature or extensive mechanical deformation of the boron powders, the original powder particle morphology remained intact. Iron could only be deposited as a surface coating; it could also cover particle surfaces inside the pores in boron agglomerates or be partially accumulated in such pores. Note for the B-Fe 190 sample, despite no clearly distinguished particles or iron, EDS confirms that iron concentration is highest where boron concentration is also high, indicating that iron has coated boron aggregates rather uniformly. Other elements detected in all three samples were oxygen, magnesium, silicon and potassium; all are expected contaminants in the starting material which was 95% pure. Elemental magnesium maps were also obtained; although not shown here for brevity, qualitatively they were similar to iron maps, correlating with elemental boron.

A closer look at the particle surface and morphology is shown for the coated materials in Figure 5.3. The higher magnification images show that for B-Fe125 sample, no individual iron particles could be distinguished at micron-scale. This observation combined with the elemental maps, showing iron correlating with boron suggest a continuous distribution of nano-scale iron on the surface of the boron aggregates. Conversely, for B-Fe190 sample, in some cases micron-sized aggregates of nano-iron particles were observed; one such aggregate is shown in Figure 5.3. Iron particles appear as bright strands, mixed with the coarser boron fractal aggregates. Although distinct iron particles are observed, iron is also noted to be present elsewhere in the sample, based on respective elemental mapping of images similar to those shown in Figure 5.3.



Figure 5.2 SEM images and respective elemental maps of boron and iron for reference material and B-Fe samples prepared by thermal decomposition of iron penta-carbonyl.



Figure 5.3 High magnification SEM images of boron-iron composites captured with back scattered electrons.

Note: The image for B-Fe190 sample is centered on an iron aggregate.

A further quantitative analysis of the samples' compositions was conducted using an Agilent 7900 series inductively coupled plasma–mass spectrometry (ICP-MS) instrument fitted with micro-mist concentric nebulizer. In preparation for the analysis, 0.5 g of each sample dried in room temperature air, was digested using diluted nitric acid (12% by volume). 34 μ L aliquots of each digested sample were further diluted and added to an internal standard that comprised 10 μ g/ml of Bi, Ge, In, Li₆, Sc, Tb, and Y. The results of this analysis were normalized by the amount of Fe measured in a pure iron sample analyzed for reference and are shown in Table 5.1 above. Some amount of iron was detected in the commercial boron sample. More iron was retained in the powder where iron pentacarbonyl was introduced at 190 °C vs. 125 °C.

Particle size distributions obtained by common low-angle laser light scattering technique were measured and are presented in the supplementary materials. In order to correct for possible powder particle size classification in the combustion experiments, while determining the effect of particle size on burn times, both particle size distributions and burn times were obtained using the same experimental setup. The laser-ignited combustion experiment, described further in Section 5.4, includes a feeding mechanism, which delivers individual aerosolized particles into the laser beam. For particle size measurements, the laser was turned off and the aerosol fed by this mechanism was deposited on aluminum stubs covered with an adhesive conductive carbon tape and placed directly where the focal spot of the laser beam would be located. Thus, samples of powders were prepared for SEM to generate particle size distributions using image analysis. The measured particle size distribution described the same fraction of the powder that was employed in the combustion tests accounting directly for any possible size classification of

the powder passed through the feeding mechanism. This approach follows previous work, e.g., [123, 143].

Collected powder samples were imaged at varying magnifications; images were analyzed using ImageJ software [144]. For image processing, particles were previously identified manually [9, 142], assuming each boron aggregate burns as a single particle. The process of identifying particles to yield a similar result was automated here in order to process multiple images in a shorter time and with a better accuracy. Details are given in the Appendix E.

The obtained particle size distributions for each material are shown in Figure 5.4. The distributions are measured by automated processing. The particle sizes range from 0.2 to 20 μ m for all materials, with a slightly higher fraction of finer particles observed for the starting material, commercial boron. For doped materials, the distributions appear to be very similar to each other, with most of the particles having the size of 1-1.5 μ m, similar to the starting powder. Lognormal distribution fits were found for each measured particle size distribution as shown in Figure 5.4. The mean value of the log normal fits for all distributions were found to be close to 1.2 μ m.



Figure 5.4 Number-based particle size distributions obtained by automated SEM image processing.

(A) As received boron powder; (B) B-Fe190 sample; (C) B-Fe125 sample. Dashed lines show lognormal distribution fits for the experimental data.

5.4 Combustion Setup

For combustion studies, 0.1 g of each sample was loaded onto a customized screw feeder connected to a motor operated by a 2V power supply. The particles, forming an aerosol were lifted from the threads of the stainless-steel screw by an air flow and transported through a 10 cm long, 2.39 mm inner diameter brass tube into the laser beam. The air flowrate was set at 0.6 L/min. The particles were fed at a rate of 0.11 mg/min into the Synrad Evolution 125 sealed CO₂ laser beam focused by a ZnSe lens to 250 µm diameter. The laser beam was positioned approximately 2 mm above the nozzle. The laser was operated at 37.5 W (30% of its maximum power) to ignite the particles moving at a velocity of 3 m/s across the beam. Once ignited, particles continued traveling vertically and burning in the surrounding room air. Details of the setup are described elsewhere [9, 143]. Emission

produced by the luminous streaks of burning particles was recorded and analyzed to obtain the particle combustion times and temperatures.

A Sony DSC-H50 digital camera with an exposure time of 250 ms and focal length of 50-60 mm was used to capture images of burning particles to identify visible differences among samples during combustion. The camera was located 20 cm away from the nozzle tip. Typical captured images are shown in Figure 5.5.

Optical emissions of single burning particles were captured using two Hamamatsu R3896-03 photomultiplier tubes (PMTs) filtered at wavelengths of 700 and 800 nm. These wavelengths were selected to not overlap with either visible or infrared molecular emission bands of BO, BO₂, and B₂O₃ [155]. The PMTs were connected to a bifurcated fiber optic cable positioned 3 cm above and 16.5 cm away from the nozzle. The total field of view measured for a minimum of 10% of the maximum signal intensity was approximately 12 cm, while particle streaks were typically within 5 cm above the nozzle. Data were collected using a 16-bit PCI-6123 National Instruments data acquisition board and LabView software for a total of 8 seconds for each run. The sampling rate was 100,000 samples per second. For each material investigated, at least 50 runs were processed to select a minimum of 800 emission pulses produced by individual burning particles. A pulse was identified when the signal exceeded the baseline level by more than 10%. Further down selection of pulses based on the signal to noise ratio was used for temperature measurements as discussed below.

A custom MATLAB code [113, 114, 123] was used to determine particle burn times and combustion temperatures. Burn times were determined from pulses found in the emission signal filtered at 700 nm, which generally had a higher signal to noise ratio than the 800 nm-filtered signal. The baseline for each emission signal was the average voltage value recorded for at least 10 ms without any particle streaks. Peaks selected were further processed for combustion temperatures based on the calibrated ratio of intensities of the emissions from both PMTs fitted to a Planck's curve, assuming a black body emitter.

Time resolved spectra of individual particle emission pulses were obtained using a 32 channel Hamamatsu H11460-01 (A10766-007-02) compact spectrometer for emission ranging 373.4 nm to 641 nm. Emission pulses were captured simultaneously by all 32 channels using a HIOKI MR8827 32 channel fully- isolated memory High Speed Hi-corder oscilloscope. Data were collected at a rate of 500,000 samples per second for a total of 1s for B-Fe125 powder. For all other powders, the sampling rate was 200,000 samples per second while the total signal acquisition time remained at 1s. The spectrometer was positioned 16.5 cm away, at the same height as the nozzle tip. For each sample, pulses produced by burning particles were analyzed for consistent features and combustion temperatures.

5.5 Results

Figure 5.5 shows images of multiple burning particle streaks for boron and boron doped with iron powders laser-ignited in air. All samples typically had white or bright yellow streaks and, in some cases, a bright green emission was observed from the B-Fe125 sample. Commercial boron generally had longer, brighter streaks than the boron-iron particles. These streaks also featured changes in thickness and particle trajectory at greater distances

from the laser beam, unlike the doped boron materials. B-Fe125 produced the shortest streaks.



Figure 5.5 Images of luminous streaks of boron (commercial) and boron doped with iron powder particles ignited by crossing a CO₂ laser beam in air.

Typical emission pulses recorded by the 700 nm filtered PMT are shown in Figure 5.6 for all three samples. The pulses shown have different intensity scales. The time scale is the same for commercial boron and B-Fe190; it is different for B-Fe125. Double peak features as shown were common in longer duration pulses, while only one peak could be resolved in short pulses. The intensity of emission for the burning doped particles is lower than the commercial powder by almost a factor of 3. For the commercial boron powder, over 10% of all counted individual burning particle pulses exhibited a two-peak structure shown in Figure 5.7, consistent with observations by [9, 26, 142, 143, 156]. The first peak is typically stronger and sharper than the second one; the duration of the second peak primarily affects the entire registered burn time. Less than 4% of the pulses analyzed for B-Fe190 particles were observed to have double peak. For such pulses, as shown in Figure 5.6, the second peak was stronger than the first, unlike for commercial boron, for which

the first peak was typically stronger. Over 50% of the double peak pulses from the B-Fe190 sample had burn times greater than 5 ms. Pulses recorded with shorter burn times of the same material appear as single peaks. For the B-Fe125 sample, only less than 0.5% of pulses had a two-peak structure. The pulse shown in Figure 5.6 for B-Fe125 is typical and was interpreted as a single peak pulse because a small feature that might be considered a short first peak (between 0.5 and 0.6 ms) was comparable to the noise-caused changes in the recorded traces.



Figure 5.6 Emission traces of single particle streaks for commercial boron and boron- iron doped samples filtered at 700 nm.

Pulses obtained from the reference powder particles laser ignited in air are presented in a plot of the maximum peak intensity against the burn time in Figure 5.7. Filled symbols show pulses with double peaks, while open symbols show single peak pulses. The results indicate that generally, shorter pulses had lower intensities and no resolvable double peak features. This finding suggests that boron particles burning with lower intensities and shorter durations may have produced double peak pulses, which were not clearly resolved by the present optical measurements.



Figure 5.7 Maximum peak intensity vs. duration for single and double peak emission pulses filtered at 700 nm for commercial boron powder.

An example of time-resolved emission pulse of a boron single particle captured at multiple wavelengths is presented in Figure 5.8. The plot shows the emission traces filtered over the range of 391- 641nm for a single boron particle laser ignited and burning in room temperature air. The intensity appears to be increasing with wavelength, with the highest emission recorded at 641 nm. A similar double peak feature as seen in the Figure 5.6

becomes dominant at 400 nm. At lower wavelengths, the intensity of the particle emission during the 2nd stage may be too weak to be resolved at the current settings. The 1st peak, however is always detected with a sharp rise across all channels.



Figure 5.8 Emission signals recorded using a 32-channel spectrometer for commercial boron powder particles ignited by the CO_2 laser beam and burning in room temperature air.

A closer look at each emission pulse filtered at the wavelength with the strongest emission, 641 nm, is shown in Figure 5.9 for all three powder samples. The corresponding temperature traces calculated for the respective emission traces are also shown. In all cases, double peaks were observed for longer emission pulses. However, for B-Fe125 sample, over 70% of the pulses analyzed had single peaks with a sharp rise and long tail. For B-Fe190, when double peak pulses were observed, similar to emission patterns filtered at 700 nm; a higher intensity was recorded for the second peak.



Figure 5.9 Examples of time-resolved temperatures and emission pulses filtered at 641 nm for commercial boron (top), and doped boron samples laser ignited in air.

Using a customized MATLAB code, multiple pulses identified from the 700-nm filtered signal were processed to obtain the particle burn times. The results of processing for more than 800 pulses for each sample are shown as distributions in Figure 5.10. As for particle size distributions, lognormal distribution functions were used to fit all measured burn time histograms; the lognormal fits are also shown in Figure 5.10. The commercial powder appears to have a broader distribution with burn times ranging from 0.2 to 30 ms. The iron-doped samples have shorter burn times ranging from 0.2 to 10 ms; respective distributions are shifted to the left compared to the commercial boron. The number-average burn times are ca. 3 ms for commercial boron and 1 ms for both doped boron

powders. Between doped samples, the distribution appears to have less variance for the B-Fe125, indicating that most particles of that material consistently burned with shorter times.



Figure 5.10 Burn time distributions for commercial boron and doped boron powders (B-Fe125 and B-Fe190) laser ignited in air.

Statistical correlations of the particle size distribution of boron powders (commercial, doped and milled) and their respective burn time distributions are shown in Figure 5.11. The particle size distributions used in each case were obtained by automated SEM image processing as described earlier. The correlation assumes that smaller particles have shorter burn times and larger particles have longer burn times. To obtain the correlation, log normal distribution fits were used instead of raw experimental data. The correlation was found using the cumulative frequency distributions of the fits to observe the general trend for each material. Use of lognormal fits led to the correlation relying

primarily on the distribution peaks rather than emphasizing the effect of burn times and/or particle sizes measured at the tails of the experimental histograms. Thus, the correlations always produced straight lines in the log-log plots of burn time vs. particle size, instead of a more complex trend that may be obtained when comparing the experimental histograms directly. Given the uncertainty of the present measurements, accounting for such more complex trends may not be supported or reasonable.

For comparison, data for milled iron-boron composite from Ref. [9] are also added to the plot. In Ref. [9], the particle size analysis was performed manually; here, the same set of images was used and the automated image processing was applied, as for the other samples in the present study. The resulting particle size distribution for the milled powder obtained here was very similar to that reported in Ref. [9]; however, finer particles were detected and thus the trend shown in Figure 5.11 for that powder is slightly different from that reported earlier. Consistently with the previous report [9], the milled sample has shorter particle burn times than the same particles of commercial boron. The doped samples prepared also have shorter burn times than the same sized commercial boron particles for all particles greater than 0.4 μ m, which clearly represents the vast majority of the powder particles for all materials. In comparison to the milled sample, particles doped at a lower temperature (B-Fe125) have shorter burn times for particles with diameters exceeding 4 µm despite having lower iron dosages. This suggests that even as low as 1.6 wt% addition of iron is sufficient to shorten burn times in air for micron-sized boron particles. Interestingly, the amount of iron detected in B-Fe125 and B-Fe190 samples (Table 5.1) does not scale with the apparent improvement in the burn rate, which is greater for B-Fe125, with smaller amount of iron.

The apparent effect of particle size on burn time diminishes for the boron powders doped with iron but not for the milled powder. This observation is supported by Table 5.2 presenting power law fits for the data in Figure 5.11. For commercial boron and milled powder, the exponent, *n* of the power law $t_b=aD^n$ (where time *t* is in ms and diameter *D* is in µm) is close to or even greater than 1. The exponent *n* is less than 1 for both iron-doped powders prepared here. The exponent values recorded are slightly lower than those reported earlier [9], when using manually determined size distribution, and are slightly higher than those reported for boron combustion in products of a hydrocarbon flame [142]. The exponent value determined for the B-Fe125 sample is lowest among all other samples tested; interestingly, among all iron-added samples, this material contains the lowest concentration of iron.



Figure 5.11 Burn time vs. particle size correlations for commercial boron, milled boron-iron composite [9] and doped boron powders laser ignited in air.

Samples	Exponent, n	Pre-exponent, a
Boron, commercial	0.98	0.95
B-Fe milled	1.29	0.23
B-Fe190	0.82	0.86
B-Fe125	0.56	0.70

Table 5.2 D-law fit parameters for Boron-based Materials Laser Ignited in Air; Equation fit: $t_b[ms] = aD[\mu m]^n$

Combustion temperatures obtained from processing the intensity ratios of the infrared emission signals filtered at 700 and 800 nm are shown in Figure 5.12. For reference, vertical dashed lines show the melting point of boron as well as boiling points of boron, boron oxide, and iron. The temperatures were determined for pulses where the signal to noise ratio was greater than 3 for both filtered emission signals for commercial boron and B-Fe190. For the B-Fe125 sample, the emission pulses were generally weaker, and the combustion temperatures are shown in Figure 5.13 only for pulses with the signal to noise ratio greater than 6. Thus, the result is biased towards particles generating stronger emission pulses. Considering the pulses with the signal to noise ratio of 3 for B-Fe125 yields a histogram similar to that shown in Figure 5.13, but with a tail extended towards higher temperatures. These very high temperatures associated with weaker emission pulses were assumed to be due to slight shifts in the signal baseline affecting significantly the ratio of relatively weak filtered emission pulses; such temperatures were disregarded. It is likely that further correction of temperature measurements is needed, which would further reduce the number of pulses implying unrealistically high temperatures. However, because no clear guidance was available to identify the signals leading to erroneous temperatures, no such further correction was performed. The temperatures for each emission pulse were taken as averages for the signal recorded while its amplitude was greater than 50 % of the

corresponding maximum peak value. For commercial boron, such average temperatures range from 1500 to 5000 K, with most values around 2000 - 3000 K. For doped B-Fe190 sample, the temperatures are slightly lower, with most particle combustion pulses characterized by the temperatures between 2200 and 2500 K. The temperatures for B-Fe125 are slightly higher than for B-Fe190 and commercial boron, with most particle pulses yielding ca. 2800 - 3000 K.



Figure 5.12 Combustion temperatures obtained for burning particles processing measured radiation signals filtered at 700 and 800 nm.

Note: For each particle pulse, the temperature is averaged for the signal exceeding 50% of its peak.

Table 5.3 compares the average temperatures for various samples obtained from their emission pulses filtered at 700 and 800 nm. For all pulses, the temperatures are averaged for signals exceeding 50% of their peak intensity. In the first column, the averages account for all pulses, for which the signal to noise ratio for both filtered traces exceeded 3. In the second column, only the pulses with the signal to noise ratio greater than 6 were accounted for. In addition, only the pulse average temperatures with standard deviations less than 1000 K were considered. Thus, the second column is biased to stronger pulses, which show a relatively steady temperature during particle combustion.

For commercial boron, the average temperature increases when only pulses with greater signal to noise ratio are considered. This suggests that stronger pulses imply somewhat higher temperatures for boron. There is effectively no change in the average temperature for B-Fe190 no matter what fraction of the recorded emission pulses is considered. For B-Fe125, the average temperature decreases when pulses with greater signal to noise ratio are considered, this is consistent with the previously mentioned observation that high temperature "tail" appears in the distribution when weaker pulses are accounted for. As noted above, this effect is considered to be superficial.

Table :	5.3 Av	verage	Comb	oustion	Temp	peratur	es for	Doped	and	Un-dope	d Boron	Powders	Laser
Ignited	in Air	Calcu	lated E	Based of	on the	Particl	le Emis	ssion Pu	llses	Filtered a	it 700 an	d 800 nm	

Samples	Average Combustion Temperatures (K)					
	Signal/noise ratio >3	Signal/noise ratio >6; STD <1000 K				
Boron, commercial	2900±650	3300±590				
B-Fe190	2500±470	2500 ± 320				
B-Fe125	4000 <u>±</u> 560	3100±520				

Note: For each pulse, the temperature is averaged for the portion of the signal exceeding 50% of its peak value.

Average values for both temperatures obtained processing filtered 700 and 800 nm signals are compared to those obtained from processing the UV-VIS range emissions from the 32-channel spectrometer in Table 5.4. Here, for the temperatures based on the emission filtered at 700 and 800 nm, only the peaks with signal to noise ratio greater than 6 were accounted for, and only the average temperatures with standard deviation less than 1000 K were taken. Because of the relatively high noise for the pulses obtained from the 32-channel spectrometer, the average combustion temperatures for each pulse were calculated only when the intensity of the signal was greater than 90% of the maximum pulse intensity. The temperatures inferred by the infrared emission taken as average when the signal exceeds 50% of the peak value (third column in Table 5.3) and 90% of the peak value (second column in Table 5.4), are nearly the same for all materials. The temperatures implied by the visible emission obtained from the 32-channel spectrometer traces are slightly higher for both doped samples; most likely this effect is superficial and is caused by molecular BO emission affecting the spectral emissivity of the burning particles.

Results shown in Tables 5.3 and 5.4 can be compared to the maximum adiabatic flame temperatures predicted by NASA CEA code for boron-air flames. This maximum temperature occurs at the equivalence ratio of 2.4 and is 2748 K. Calculations also show that temperatures as high as 4000 K are feasible if formation of boron nitride is suppressed in air. This could be a kinetic effect influencing the experimental temperatures. Further studies would be necessary to verify this possibility, however.

Table 5.4 Average combustion temperatures for doped and un-doped boron powders laser ignited in air calculated based on the emission filtered at 700 and 800 nm (see Table 5.3) and those based on visible range emission recorded by the 32-channel spectrometer.

Material	Average Combustion Temperature	(K)
	Infrared Range PMTs	32 Channel spectrometer
Boron, commercial	3300±590	3000±300
B-Fe190	2500±320	3400±190
B-Fe125	3100 <u>+</u> 520	3600 <u>+</u> 400

Note: For visible emission, for each pulse, the temperature is averaged when the signal exceeds 90% of its peak value

5.6 Discussion

The present study addressed the feasibility of using iron pentacarbonyl to dope boron powder with iron to enhance its combustion. The technique used, thermal decomposition of iron pentacarbonyl is a one pot reaction reported to form monodispersed 4 nm Fe particles with a 2.5 nm Fe₃O₄ layer in the presence of a hydrocarbon solvent in an inert environment [154]. This technique was also applied to coat Nd-Fe-B powders with a sub micro-meter to micrometer layer of neutral iron with 25-33% efficiency [152]. In this work, SEM images and EDS analysis confirmed that coatings of iron was achieved on both doped boron samples prepared. The amount of iron recovered was 32 % and 60 % of the expected amounts (cf. Table 5.1) for the B-Fe125 and B-Fe190 materials, respectively. Possible discrepancies in the amount of iron recovered could be dependent on the decomposition temperature, time available for the decomposition reaction, the boron oxide surface functionalization, the type and volume of surfactant used [157], and the volume of dodecane used to wet the boron particles' surfaces. Further optimization of the coating of boron powders with iron is thus possible in the future if such iron-doped powders become of interest for practical energetic formulations.

Consistent with previous work, in which boron was doped with iron by mechanical milling [9], burn times recorded for micron-sized doped boron powders (B-Fe125 and B-Fe190) are shorter than for the starting commercial boron powder (Figures 5.10, 5.11). The findings, therefore, support that iron addition favors combustion whether it has been incorporated by milling or coating. In this present work, as little as 1.65 wt% iron coated was found to be effective in accelerating combustion and leading to slightly higher flame temperatures.

Prior to discussing the effect of iron on boron combustion, it may be useful to consider the mechanism of the two-staged reaction observed for burning boron particles. The present analysis (Figure 5.7) suggests that the two-staged behavior is common, but may be difficult to resolve optically for weaker or shorter emission pulses. The two-staged emission pattern for boron is well recognized; the first and second stages were respectively assigned to ignition and full-fledged combustion earlier [5, 22, 27, 33, 127, 158]. However, more recent work [9, 159] as well as present measurements suggest that the temperature measured from the burning particle emission is high for both observed stages. Furthermore, a decay in the emission intensity observed by the end of the first stage reaction is inconsistent with it representing the ignition process, expected to lead to increasingly greater particle emission as it transitions to full-fledged combustion. An alternative interpretation of the two-stage emission pattern produced by burning boron particles can be proposed considering qualitatively similar two-stage emission patterns produced by burning particles of other metals [111]. For example, for Zr and Ti, the first combustion

stage is associated with formation of a liquid metal-gas solution with both oxygen and nitrogen dissolved in the burning metal droplet. The solution becomes supersaturated in the second reaction stage, when the droplet temperature decreases; this is accompanied by a phase change leading to release of dissolved nitrogen and continuing reaction of metal oxidation. Relevant phase diagrams were published only recently for both B-O and B-N [160] binary systems, although no ternary B-O-N diagram is available. According to the binary phase diagrams, at the combustion temperatures, boron readily forms liquid solutions with both oxygen and nitrogen. In the boron-oxygen system, liquid solution exists in the entire $B-B_2O_3$ range of oxygen concentrations. The boiling or saturation temperature decreases with increased oxygen concentration; it is 4200 K for pure boron, and it decreases to 2130 K when liquid solution becomes B₂O₃. Thus, it is expected that the burning particle temperature may be high initially and is decreasing during combustion, while the concentration of dissolved oxygen increases. Conversely, B-N phase diagram suggests that dissolution of nitrogen in molten boron does not affect its saturation temperature in the temperature range observed here. At a concentration of dissolved nitrogen exceeding ca. 5% and at temperatures between 2415 and 3246 K, solid BN may be forming.

With the above background, the following simplified qualitative mechanism of the two-staged boron combustion may be proposed. It is illustrated in Figure 5.13, making use of the recently published B-O phase diagram [10]. In this simplified discussion, the role of nitrogen is neglected, and boron is considered as only reacting with oxygen. The full-fledged combustion considered here involves molten boron with no surface oxide layer. According to the phase diagram, interaction with oxygen yields a liquid B-O solution. It is, therefore, natural to suggest that such a solution is formed in the burning particle. The

temperature of the particle can increase up to the boiling point of boron; however, that maximum saturation temperature decays rapidly as the concentration of dissolved oxygen increases. A first dashed line with an arrow shows a possible temperature-concentration history of the burning particle in stage one. The reaction is primarily on the particle surface, absorbing oxygen. Because of the temperature increase, the emission of burning particle increases until it reaches the saturation temperature. Further combustion will be accompanied by the temperature decrease, as shown schematically by the second dashed line. Respectively, the radiation intensity is expected to decrease. However, when the particle is at its saturation temperature (with its temperature-concentration trajectory sliding to the right along the phase diagram boundary, as shown in Figure 5.13), a significant amount of vapor may be generated. This vapor generation may lead to an increased emission intensity, and thus a second peak observed in the emission pulses (Figures 5.5, 5.6, and 5.9). This part of combustion may be referred to as stage 2. The combustion ends when the composition of the burning particle is approaching the stoichiometric B₂O₃. The rate of heat release diminishes and particle quenches.

Not reflected in Figure 5.13, but heterogeneous reaction most likely occurs simultaneously with both oxygen and nitrogen. Nitrogen can dissolve in boron in greater concentrations than oxygen; however, oxygen is thermodynamically preferred. Thus, it is expected that at some point, nitrogen may be released and replaced with oxygen. Such nitrogen release may cause a change in the particle trajectory, as seen in Figure 5.5.



Figure 5.13 Schematic representation of reactions occurring during full-fledged combustion of boron particle proceeding in two stages considering published B-O phase diagram [10].

The effect of iron on boron combustion can now be interpreted assuming that the reaction of gaseous oxygen occurs faster with iron than with boron. It is further proposed that once oxidized, iron is readily reduced by boron, which is preferred thermodynamically. The rate of boron oxidation reacting with oxidized iron is assumed to be much higher than that of boron reacting with gaseous oxygen. This leads to shorter burn times for the doped particles (Figure 5.11). Further, the product of this reaction occurring completely in the condensed phase may be closer to stoichiometric B_2O_3 rather than boron-rich B-O solution produced when boron reacts with gaseous oxidizer. Respectively, the temperature of the burning particle will be lower when a solution with greater oxygen concentration is formed, which is consistent with the present temperature measurements using signals filtered at 700 and 800 nm (see Tables 5.3 and 5.4 and Figure 5.12). Rapid formation of a solution

approaching B_2O_3 in composition cuts short the first combustion stage (involving nearly pure boron droplet) and leads to a rapid transition to the second stage, when the burning molten droplet is at its saturation temperature. Once again, this is consistent with the experimental observations.

The above mechanism can qualitatively explain the differences observed here between combustion of B-Fe125 and B-Fe190 samples. Because in the iron-doped materials, the reaction of boron with oxygen occurs at the interface of boron/oxidized iron, the reaction pathways, products and rates would be affected by the morphology and structure of that interface. In both milled composite material [9] and B-Fe190, there are distinct iron particles present in the powder (e.g., Figure 5.3). Such particles, when oxidized, can form distinct inclusions of oxidized iron in the boron droplet. The reaction between boron and such iron oxide phase is expected to readily yield a phase close to B_2O_3 with a relatively low boiling point. Conversely, B-Fe125 does not have distinct iron particles, so that upon heating, iron may be present in the form of individual ions dissolved in boron. When exposed to an oxidizing gas, such iron ions may attract oxygen, while there will be no distinct oxide phase formed before such oxygen bound to iron is reattached to boron. It thus may be more likely that a more boron-rich liquid solution with oxygen will form at the initial combustion stages rather than inclusions of a phase close to B_2O_3 . This distinction in the reaction mechanism may explain a shift to higher temperature observed for combustion of B-Fe125 particles (Figure 5.12, Tables 5.3 and 5.4). Note also that higher temperatures for B-Fe125 are observed despite a reduced overall emission signal intensity compared to the commercial boron. This apparent discrepancy can be explained considering that a relatively bright stand-off flame may be formed around burning boron

particles, producing volatile boron sub-oxides as a result of surface reaction with gaseous oxidizer. Such a stand-off flame is less likely to form around burning particles of B-Fe125, which preferentially form liquid boron-oxygen solution while boron oxidation no longer occurs at the particle surface but via reduction of the surface generated iron-oxygen complexes.

5.7 Conclusions

Iron was doped onto 95% pure commercial boron powder by thermal decomposition of iron pentacarbonyl in a dodecane/surfactant mixture in argon environment. The technique produced particles containing iron coated on the surface of the boron particle aggregates. Samples with iron concentrations of 1.65 and 3.07 wt-% were prepared depending on the specific process parameters. At higher concentrations, iron particles aggregated affecting the homogeneity and distribution of iron on the boron surface. Iron-doped boron powders were found to burn faster than starting commercial boron, even though the particle sizes and morphologies were largely unaffected by the presence of iron. The two-stage combustion pattern, typical for boron, is less prevalent for the iron-doped powders. The flame temperatures for the sample with 3.07 wt-% iron were slightly lower than for the starting boron powder; conversely the flame temperatures for the sample with 1.65 wt-% iron were noticeably higher.

A mechanism for the two-staged full-fledged combustion of boron particles is proposed based on the present and previously published results and employing a recently published binary B-O phase diagram. In the first stage, the boron-rich boron-oxygen solution is formed, and its temperature increases up to the saturation point. The second stage begins when the solution becomes saturated. The particle temperature decreases as the concentration of dissolved oxygen increases. At the same time, a vapor-phase reaction zone is formed during the second combustion stage. Combustion ends when the composition of a burning particle becomes close to that of B_2O_3 .

It is proposed that iron improves the rate of boron combustion by selectively reacting with surrounding gaseous oxygen and then being readily reduced by boron. Thus, a surface reaction of boron with gaseous oxidizer is replaced by the faster surface oxidation of iron and its rapid reduction occurring in the volume of burning particles. The reaction between boron and oxidized iron complexes occurs in condensed phase and may rapidly form products approaching in composition to the stoichiometric B₂O₃, thus accelerating greatly transition to the second stage combustion.

CHAPTER 6

REACTIVE SHELL MODEL FOR BORON OXIDATION⁵

6.1 Abstract

An approach suitable for quantitative description of oxidation of porous powders with complex particle morphology is developed and applied for a 95% pure boron powder. It is shown that boron particles, which are agglomerates of nano-sized, partially fused primary particles, can be represented as spheres with reactive porous shells and impenetrable cores. The oxidation of such powders is assumed to occur volumetrically within the reactive shells. The reactive shell thickness is obtained from simple experiments with the actual powders. To determine the thickness, thermo-gravimetric measurements are performed and processed for powders with different but overlapping particle size distributions. The processing uses measured powder particle size distributions to assign fractions of the powder mass gain to individual particle size bins. Selection of the appropriate initial reactive shell thickness makes it possible to ensure that particles of the same size present in samples with different size distributions oxidize in the same way. The specific powder studied here was successfully described with a reactive shell thickness of about 1.28 μ m. Surface area measurements can be used to interpret the reactive shell as comprising packed spherical primary particles. For the powder used here the radius of such primary particles

⁵ The findings presented for this chapter have been published in the peer- review journal, Journal of Physical Chemistry C under the reference listing:

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is 80 nm. The proposed reactive shell model is shown to be valid as long as the thickness of boron oxide grown on the primary particles does not exceed 15 nm. The approach is useful for describing reactions leading to ignition of porous powders, and of powders consisting of irregular aggregates in particular. It is also expected to be applicable to describe corrosion, catalyst aging, and other phenomena involving surface reactions for such powders.

6.2 Introduction

Due to its high gravimetric and volumetric energy density [21], boron is attractive as a fuel for propellants [98, 161, 162], explosives [163], and pyrotechnics [164]. However, relatively low reaction rates impede its use in many energetic formulations [17, 165]. In order to modify boron to achieve higher reaction rates, its ignition and combustion mechanisms must be understood and described quantitatively. It is generally agreed that boron ignition is governed by a heterogeneous oxidation, which is rate limited by transport of the reacting species through the surface layer of oxide, B₂O₃. Many models describing these heterogeneous reactions were proposed, e.g., [5, 12, 25, 166-169], which focused on identifying the reaction mechanism. Specifically, it was debated diffusion of which species, boron or oxygen, limits the rate of reaction and whether dissolution of boron in boron oxide affects the ensuing transport phenomena controlling the reaction rate. All models described in the literature to date treat boron particles as spheres. This approach is commonly used for heterogeneous reactions of powders. However, like many other materials, real boron powders have a complex morphology. Typically, boron particles with sizes in the range of 1-50 µm comprise multiple agglomerated and partially fused nano-sized particles

independently of its synthesis method [170]. Thus, a reaction kinetic model obtained for a spherical geometry will fail describing the heat release for a real igniting boron particle.

The rate of relatively low-temperature exothermic reactions important for boron ignition is readily measured for a bulk powder sample using thermal analysis. In particular, a thermo-gravimetric (TG) experiment can quantify rather accurately the amount of oxide formed in a powder sample during controlled heating. However, interpreting such measurements is difficult because particles with different sizes and shapes may react at different rates. Recently, in order to quantify oxidation rates for aluminum and magnesium powders, an approach of interpreting TG measurements was proposed that explicitly accounts for particle size distributions [171-173]. In that approach, the bulk mass gain measured by TG for oxidation of spherical powders was distributed among particles of different sizes. Each particle size bin was assigned a mass gain proportional to the fraction of its surface area relative to the bulk powder. This surface-weighted interpretation of TG and of similar thermo-analytical measurements for powders with different particle size distributions led to the development of oxidation models that are capable of detailed description of the growing surface oxide shell. However, while attractive, this approach cannot be used for boron, which does not contain spherical particles. It is also not suitable for other porous powders, or powders with irregular particle shapes in general.

This work is aimed to develop a simplified model describing oxidation of boron quantitatively while accounting for both the particle size distribution and the complex morphology of boron powders. This model, in combination with thermo-analytical measurements would be expected to recover kinetics of heterogeneous boron oxidation, necessary for modeling ignition and, possibly, combustion. It is further expected that the

182

proposed model is suitable for quantifying rates of a broader range of heterogeneous reactions for porous powders.

6.3 Technical Approach

Typical boron particles are shown in Figure 6.1. This is a commercial, nominally 95% pure boron powder by SB Boron. Submicron particles, that can be referred to as primary particles, are agglomerated or fused together and form micron-sized particles. Clearly, describing this powder as spheres with diameters matching the dimensions of the agglomerates will underestimate the available reactive surface participating in heterogeneous oxidation.



Figure 6.1 Scanning electron microscope image of typical boron particles.

Instead, such agglomerates may be seen as porous particles, in which case the oxygen concentration, and thus, the reaction rate will decrease with the depth of penetration into the particle. This is schematically illustrated in Figure 6.2(A). Details of the oxygen concentration depend on actual porosity, which is likely to be lower towards the center of the particle [170], on diffusion rates, and on oxygen removal rates determined by the oxide formation. It is not practical to develop a detailed model balancing these processes for the ranges of complex particle morphologies seen in powders (cf. Figure 6.1). Instead, a simplified and pragmatic model, as shown in Figure 6.2(B), is proposed that approximates the variation of available oxygen as well as surface area as a porous shell and impenetrable core. For such a simplified model, the oxygen concentration is treated as constant in the porous shell and is reduced to zero in the core. In other words, the reaction in the porous shell is considered as occurring volumetrically while no reaction occurs in the impenetrable core. Validation of this model effectively determines that oxidation in a porous reactive shell of a certain thickness describes the reaction adequately. The validated model thus describes summarily many physical phenomena and characteristics, e.g., effect of oxygen concentration gradient within the particle, effect of non-spherical particle shape, effect of specific morphology of primary particles, etc., which have similar effects and are difficult to distinguish. The model shown in Figure 6.2(B) may represent a useful generic simplification for particles that have open porosity volumetrically, e.g., comprising agglomerated but not fused primary particles. It may also be useful to describe particles that consist of fused primary particles, for which open porosity is limited to a surface layer of some thickness. This work offers an approach for validation of this model using a simple TG experiment.



Figure 6.2 Schematic representation of an oxidizing boron particle and respective concentration of oxygen.

(A) As a porous sphere (B) as an impenetrable spherical core with a porous reactive shell.

Here, the approach schematically illustrated in Figure 6.2(B), is validated for oxidation of boron. Considering that elemental boron has been shown to have a characteristically porous morphology [170], it is expected that this approach will be generally useful.

Modifying the methodology introduced in our previous work for spherical particles [171-173], the mass gain measured in a TG experiment with a bulk powder is distributed among different particle size bins. Each size bin consists of particles with the structure represented in Figure 6.2(B); each particle is assumed to oxidize at a rate proportional to the volume of its porous shell. Below, this shell will be referred to as reactive shell. Clearly, this model can only be valid for initial stages of oxidation as long as morphology and porosity of the shell are not compromised by growth of new oxide. Such oxidation is

typically important for describing ignition, when the powder particles are heated rapidly so that the thick oxide film does not have the time to grow. Alternatively, oxidation involving thin oxide layers is important for slow reactions occurring at low temperatures, such as aging. In a TG experiment, however, as oxidation progresses, eventually porosity becomes clogged with liquid oxide, the overall oxidation rate decreases, and the geometry shown in Figure 6.2(B) no longer applies. Particle morphology may also change while it is oxidized.

To establish whether this proposed model can describe oxidation of boron, two different powders of the same material with different but overlapping particle size distributions are used. The thickness of the reactive shell is assumed to be initially the same for all particles. For each powder, an experimental particle size distribution is used to obtain the total volume of all reactive shells in a size bin. Size-bin specific TG curves are obtained by partitioning the TG curve of the bulk powder over the size bins in proportion to the fraction of the shell volume of that bin relative to the total reactive shell volume for the entire powder. If the model adequately describes oxidation, then the TG curves for a bin of the same size, but coming from different powders, should coincide. To achieve this match of the size-bin specific TG traces, the initial reactive shell thickness was used as an adjustable parameter. For a given particle size distribution, a larger assumed initial reactive shell thickness shifts the reactive volume distribution (and thus, the assigned fraction of the measured mass gain) among size bins to fine particle sizes and vice versa. Consider a TG experiment where the mass changes in time. The measured mass increment *dm* is distributed among particle size bins so that for size bin, *i*:

$$dm_i = dm \cdot \frac{V_i}{V}$$
(6.1)

where V_i is the combined reactive volume of all particles in size bin *i*, and $V = \sum_i V_i$ is the combined reactive volume of all size bins. The reactive volume for a size bin is initially calculated from the size distribution as:

$$V_i = N_i \cdot \frac{4}{3} \pi \left[R_i^3 - r_i^3 \right] \tag{6.2}$$

where N_i is the number of particles in size bin *i*, and R_i and r_i are the radii of the entire particle and its impenetrable core, respectively. The outer radius, R_i , corresponds to the size of the experimentally measured size distribution. The inner radius is calculated from the thickness of the reactive shell, h_s , as $r_i = R_i - h_s$. In the general case, the outer radius and the reactive volume may change as oxidation progresses. In particular, the reactive volume is expected to change as any porosity in the shell fills with forming oxide. However, as long as there is any porosity left, the change of the ratio of the reactive volume of one size bin to the total reactive volume of the entire powder is expected to be small and therefore, has been neglected from here on in the present work.

Equation (6.1) is then integrated to obtain $m_i(t)$ curves for individual size bins. The objective of this is to find whether there is an initial reactive shell thickness, for which size-specific TG traces for size bins present in different powders coincide.

A more detailed description is possible accounting for the measured specific surface of boron powders, e.g., using Brunauer–Emmett–Teller (BET) method. Consistently with the simplified model shown in Figure 6.2(B), it may be assumed that the reactive shell consists of uniformly sized, spherical primary particles. The radii of such particles can be obtained using the same measured particle size distribution once the initial shell thickness is determined from the TG processing. The assumption here is that the same surface that is accessible for oxidation is also available for nitrogen absorption in a BET experiment.

6.4 Experimental Details

6.4.1 Preparation of boron powders with distinct but overlapping particle size distributions

TG experiments were performed with 95% pure boron powder by SB Boron Corp. Asreceived boron is referred to as $B_{received}$. This powder was size classified to obtain distinct powders with different but overlapping particle size distributions. To size classify the powder, it was suspended in a fluid and agitated ultrasonically, similar to the procedure described recently to obtain washed boron powders [141]. Two fluids, water and acetonitrile (99.5%, by Alfa Aesar) were used. Coarse and fine fractions were obtained for each fluid; respectively four different powder fractions were obtained.

In each experiment, 8 g of as-received boron were suspended in 175 mL of fluid (water or acetonitrile). A titanium horn of an ultrasonic agitator (Branson 902R) was submerged into the suspension and operated at 75% of maximum power for 3 min. After the horn was removed, some powder had settled while the fluid above remained cloudy. The cloudy portion of the fluid was decanted and discarded. It mostly contained dissolved boric acid and oxide. Additional 175 mL of the fluid was then poured in, and the sonication was repeated for 3 more minutes. After this second sonication, the powder from the suspension settled into two distinct layers. The obtained top and bottom powder layers, containing finer and coarser size fractions, respectively, were recovered. The fluid was removed using vacuum filtration. Powders were then dried at ca. 50 °C in a vacuum oven (National Appliance Company, Model 5831) for 2 h.

6.4.2 Powder characterization

Particle size distributions were measured for all materials by low-angle laser light scattering, employing a Malvern 3000 Mastersizer using water as the powder suspending fluid. Powder specific surface areas were measured using a Quantachrome NOVA3000a High Speed Gas Sorption Analyzer. The degassing condition was set to 3 h at 200 °C. TG measurements were carried out using a Netzsch STA 409 PC analyzer with argon and oxygen flown at 80 and 20 mL·min⁻¹, respectively. Initial sample mass was maintained at 3.25 ± 0.1 mg. Flat TG plates made of alumina were used. Experiments used a heating rate of 5 °C·min⁻¹; the temperature range was 25 - 900 °C. Each experiment was run at least twice to ensure reproducibility.

6.5 Experimental Results

Measured particle size distributions for as received and size classified powders are shown in Figure 6.3. The as-received powder has a bimodal particle size distribution, making it particularly challenging to process its respective TG or other thermo-analytical measurements. Conversely, for both powders sonicated in water and acetonitrile, the particle size distributions have clearly identifiable single modes. One exception is noted for the fine fraction recovered from acetonitrile, where a small additional peak is noted for very fine particle sizes. Still, desired distinct but overlapping particle size distributions for the same material are obtained for further processing, as seen in Figures 6.3(B) and (C).



Figure 6.3 Size distribution of boron powders.

(A) As received and size classified by sonication in acetonitrile (B) and in water (C).

Results of BET specific surface area measurements for size classified powder fractions are presented in Table 6.1. As in Figure 6.3, individual fractions obtained in water and acetonitrile are respectively denoted using subscripts ACN and H₂O. For each powder, fine and coarse fractions represent respectively powders recovered from the top and bottom layers obtained after the sonicated suspension settled. Fine fractions have consistently greater measured surface areas compared to the coarse fractions.

Table 6.1 Specific Surface Areas for Boron Powders with Different Particle Size Distributions

Sample	B _{ACN} fine	B _{ACN} coarse	B _{H2O} fine	B_{H2O} coarse
Specific Area m ² /g	16.79±0.004	7.79±0.003	11.76±0.010	7.64±0.003

The results of TG measurements are shown in Figures 6.4(A) and 6.4(B) for the powders size classified in acetonitrile and in water, respectively. Insets show corresponding differential TG (DTG) traces. Because all powders used in these experiments were effectively washed, either in water or acetonitrile, there was no well resolved initial mass loss typically observed when commercial boron powders are heated, releasing moisture. Both TG and DTG traces suggest that detectable mass gain and thus oxidation start at about 400 °C. As expected, fine fractions for both water and acetonitrile size classified powders oxidize at lower temperatures and faster than respective coarse fractions. As temperatures increase to ca. 700 °C, there is a transition and the reaction rate increases, possibly caused by the accumulation and redistribution of molten B_2O_3 sufficient to alter the initial powder morphology. Additionally, evaporative losses of B_2O_3 at elevated temperatures are not quantified and can make it progressively more difficult to interpret the TG traces at higher temperatures.



Figure 6.4 TG traces for oxidized boron powders size classified in acetonitrile (A) and in water (B).

Note: Insets show respective DTG traces. The heating rate is 5 °C/min.

6.6 Reactive Shell Thickness

Using Equations (6.1) and (6.2), the measured TG traces shown in Figure 6.4 were distributed among particle size bins using the measured particle size distributions shown in Figure 6.3. Thus, for each particle size bin, an individual TG trace was recovered for each powder. Selected samples of such particle-bin selected TG traces are illustrated in Figure 6.5. For the case shown in Figure 6.5, the initial reactive shell thickness was assumed to be 1 μ m. Thus, particles with diameter less than 2 μ m were treated as completely porous, whereas coarser particles contained impenetrable cores. Diameters of such cores were 2 μ m smaller than the diameters of the respective particle size bins. TG traces for the particle size bins of 1, 5, 10, and 15 μ m for fine and coarse fractions for the powder size classified using sonication in acetonitrile are shown in Figures 6.5 (C) and 6.5 (B); similar traces for the powder classified in water are shown in Figures 6.5 (C) and 6.5 (D). As expected, TG traces representing finer size bins exhibit faster mass gain. It is also

apparent from Figure 6.5 that, at least if the entire temperature range is considered, the TG traces representing the same size bin gain mass differently for different powders. Further analysis explores whether this discrepancy can be eliminated by varying the initial reactive shell thickness.



Figure 6.5 A subset of four size-bin specific TG traces representing oxidation of size classified boron powders.

(A) and (B): fine and coarse fractions obtained by sonication in acetonitrile; (C) and (D): fine and coarse fractions obtained by sonication in water. All TG traces shown were obtained distributing the experimental TG traces among size bins using Equations (6.1) and (6.2) and assuming a 1- μ m thick reactive shell.

The experimental results from Figure 6.4 were processed by varying the reactive shell thickness; respective size-bin specific TG traces were compared to each other. Such a comparison is illustrated in Figure 6.6. For this illustration, a 5- μ m size bin is selected. For this size bin, TG traces obtained processing experiments for all four powders are

shown. Comparisons between coarse and fine fractions are done separately for the powders size classified in acetonitrile and in water. That distinction was maintained to account for possible surface modifications for boron treated in different solvents, which could alter its oxidation behavior. The comparisons of the TG traces for the 5- μ m size bin are only shown for the temperature range of 400 – 700 °C. Higher temperatures, for which oxidation traces were expected to be affected by changes in the particle morphology were not considered.

The top set of traces in Figure 6.6 shows comparison of the 5- μ m size bin TG traces for the fine and coarse fractions obtained by sonicating the as-received boron in acetonitrile. The bottom set represents the fractions obtained by sonicating the as-received boron in water. Each plot is labeled with its respective assumed value of the initial reactive shell thickness, h_s . It is apparent that for the smaller thickness, obtained TG traces for the coarse fractions gain mass faster; conversely, at greater assumed shell thickness, the mass gain becomes faster for the fine fraction. This trend is observed for both sets of size classified powders. Thus, an intermediate shell thickness, which appears to be similar for both sets of powders (between 1 and 1.5 μ m), matches the size-bin specific TG traces for different size fractions of the size classified boron powder.



Figure 6.6 Comparison of TG traces representing 5- μ m size bins for oxidation of fine and coarse fractions obtained by size classifying boron in acetonitrile (a – d) and in water (e – h).

The comparisons graphically illustrated in Figure 6.6 for one size bin were performed systematically for all overlapping particle size bins in the range of 2 – 10 μ m. The results of this comparison are presented in Figure 6.7 for the size bins of 2, 5, and 10 μ m. Shown are the error values δ_i calculated for each size bin *i*, as:

$$\delta_{i} = \sqrt{\frac{\int \left[\left(\frac{m_{i}}{m_{i,o}} \right)^{\text{fine}} - \left(\frac{m_{i}}{m_{i,o}} \right)^{\text{coarse}} \right]^{2} dT}{\int dT}}$$
(6.3)

where *T* is temperature and m_i and m_{i0} are respectively masses of the same size bins *i* and starting masses for these bins taken, as shown by superscripts in Equation (6.3), for the fine and coarse powder fractions. The deviations δ_i were calculated in the temperature range of 400 - 700 °C.

Each plot corresponds to a specific assumed reactive shell thickness: 0.5 μ m (A and E), 1.0 μ m (B and F), 1.5 μ m (C and G), and 2.0 μ m (D and H).

These values assess the overall discrepancy between the size-bin specific TG traces for different powder fractions. The discrepancies clearly are smallest for all size bins for a reactive shell thickness of around 1.28 μ m as marked in Figure 6.7. From these calculations, the thickness values of 1.25 and 1.3 μ m are obtained for the powders sonicated in acetonitrile and water, respectively. Combining the two, a reactive shell thickness of about 1.28 μ m gives a consistent description of boron powder oxidation using the model presented schematically in Figure 6.2(B) regardless of particle size distribution.



Figure 6.7 Discrepancies between mass gains for the same 2, 5, and $10 \,\mu\text{m}$ size bins for coarse and fine boron fractions separated by sonication in acetonitrile and water as a function of the assumed thickness of the reactive shell.

6.7 Spherical Primary Boron Particles in Reactive Shell

As shown in SEM images in Figure 6.1, boron particles can be considered as composed of fine primary particles. Consistent with the model shown in Figure 6.2(B), it can be assumed that the reactive shell consists of spherical primary particles. Using its thickness determined above, the size of these particles can be calculated from the BET measurements shown in Table 6.1 and using particle size distributions shown in Figure 6.3. This calculation may be considered useful if the same primary particle size is calculated for different classified boron powder fractions. It is further of interest to consider how sensitive this calculation is for selecting the appropriate reactive shell thickness. Results of respective calculations are shown in Figure 6.8. Each trend line represents a fraction of boron size classified by sonication in either acetonitrile or water. The vertical dashed line shows the selected reactive shell thickness obtained from analysis finally illustrated in Figure 6.7. A relatively narrow range of primary particle radius is thus identified, shown by horizontal dashed lines and centered near 80 nm. Interestingly, ca. 80 nm primary particles can be readily seen in SEM images, such as shown in Figure 6.1. It is further significant that the trend lines representing different powder fractions in Figure 6.8 nearly merge exactly around the selected reactive shell thicknesses identified by the previous analysis (Figure 6.7). This could be seen as an additional validation for the proposed boron particle representation as an impenetrable core surrounded by a reactive porous shell for the purpose of describing heterogeneous oxidation.



Figure 6.8 Calculated primary particle size by assuming different shell thickness.

6.8 Boron Oxide Thickness Limiting the Applicability of the Reactive Shell Model

Considering the size of the primary particle, e.g., 80 nm, implied by calculations shown in Figure 6.8, it becomes possible to assess at what thickness of the boron oxide layer the measured TG traces can no longer be described by the proposed reactive shell model.

Taking the thickness of the surface oxide layer as $h_{ox} = r_{PP} - r_B$, i.e. the difference between the outer primary particle radius r_{PP} , and the radius of its un-oxidized boron core, r_B , it can be calculated as:

$$h_{ox} = \frac{3}{4\pi} \left[\left(\frac{4\pi}{3} r^{3}{}_{\rho\rho,0} + \Delta V_{\rho\rho} \right)^{\frac{1}{3}} - \left(\frac{4\pi}{3} \left(r^{3}{}_{\rho\rho,0} - \left(r_{\rho\rho,0} - h_{ox,0} \right)^{3} \right) - \Delta V_{B} \right)^{\frac{1}{3}} \right]$$
(6.4)

where $r_{PP,0}$ is the initial radius of a primary particle, and the volume change of the entire primary particle,

$$\Delta V_{\rho\rho} = \frac{\Delta m_{\rho\rho}}{3M_{o}} \left(\frac{M_{B_{2}O_{3}}}{\rho_{B_{2}O_{3}}} - \frac{2M_{B}}{\rho_{B}} \right)$$
(6.5)

and the volume change of the un-oxidized boron core of the primary particle,

$$\Delta V_{B} = \frac{\Delta m_{\rho\rho}}{3M_{o}} \frac{2M_{B}}{\rho_{B}}$$
(6.6)

are both calculated from the mass change of a primary particle, Δm_{PP} , which is calculated from the mass of size bin *i*, as obtained by integrating Equation (6.1) as:

$$\Delta m_{pp} = m_{pp,o} \times \frac{m_i - m_{i,0}}{m_{i,0} - m_{i,core}}$$
(6.7)

Here, m_i is the mass of size bin *i*, as defined above, $m_{i,0}$ is the initial mass, $m_{i,core}$, is the constant mass of the nonporous core, and $m_{PP,0}$ is the initial mass of a primary particle.

The calculated oxide thickness for primary particles obtained using TG traces split among different powder size bins and Equation (6.4) is shown in Figure 6.9. For all powders, as expected the oxide thickness is initially growing at the same rate. When the thickness exceeds 15 nm, discrepancies for different powder fractions are observed, which is indeed in agreement with the observed behavior of the measured TG traces at higher temperatures. Thus, the present model can be applied as long as the boron oxide thickness is less than 15 nm. It can be concluded that the powder morphology changes after this thickness is exceeded.



Figure 6.9 Evolution of the oxide thickness of primary particles with temperature for different fractions of the boron powder.

6.9 Conclusions

Using experimental TG traces for different size fractions of a commercial 95% pure boron powder with characteristically complex particle morphology, it is shown that heterogeneous oxidation of such powders can be usefully described considering boron particles as spheres with impenetrable cores and reactive porous shells. The oxidation occurs in such reactive shells volumetrically. The particle size distribution of the actual powder obtained by low-angle laser light scattering represents the size distribution of such spheres adequately. The reactive shells have an initial thickness of approximately 1.28 μ m. Furthermore, for the specific studied powder, such shells can be assumed to be composed of densely packed primary boron particles with radius of 80 nm. The obtained reactive shell thickness and primary particle size are suitable for description of the tested 95% pure boron powder. The approach developed in this work can be further applied to other boron powders with complex morphologies, which can be represented using the same impenetrable core – reactive shell model in order to quantitatively describe their oxidation. The present simplified representation of morphology of the oxidizing boron particles is expected to be useful for further analyses aimed to determine kinetics of boron oxidation. This approach is found to be valid as long the thickness of the growing boron oxide remains less than 15 nm. The approach introduced here, together with the method for experimental validation, is useful for describing a broader range of heterogeneous reactions involving porous and irregularly-shaped powders.

CHAPTER 7

HETEROGENEOUS REACTION KINETICS FOR OXIDATION AND COMBUSTION OF BORON

7.1 Abstract

The oxidation kinetics for 95% pure amorphous boron powder was studied by nonisothermal thermogravimetric (TG) analyses in an oxidizing environment. Commercial boron powders were pre-treated with acetonitrile and water to reduce the thickness of their initial hydrated oxide layer and to achieve a narrower particle size distribution. The samples were oxidized at different heating rates in an oxygen- argon gas mixture. Boron particles comprising aggregates of finer primary particles were modeled as spheres with porous shells and solid cores. Experimental TG traces were split among particles of different sizes. The split was based on the measured particle size distribution and accounted for the fraction of the measured mass gain assigned to different powder particle size bins using the core-shell particle model. Furthermore, the reactive shell was assumed to consist of densely packed spherical primary particles. The reaction kinetics was quantified to obtain both activation energy and pre-exponent factor describing oxidation of the primary particles. The early stage of oxidation is well described with the activation energy of 148 \pm 6 kJ/mol. The oxidation rate of boron particle of any size can be obtained considering the rate of oxidation of the primary particle and the introduced core-shell particle structure. The obtained oxidation model was extrapolated to the range of temperatures typical of the full-fledged boron combustion. A change in the particle morphology occurring when boron melts and the aggregates of primary particles coalesce into a single droplet was accounted

for. Burn times predicted at different temperatures were compared to those measured for boron particles burning in room air. Calculated burn times were close to those measured experimentally. Comparisons suggest that the particle surface temperature varies in the range of 3500 – 4500 K, approaching boron boiling point. It is concluded that the same heterogeneous kinetics governs both low-temperature oxidation of boron when the oxide film thickness is small and its full-fledged combustion occurring at much higher temperatures.

7.2 Introduction

Boron is an attractive fuel additive for air breathing ramjets [12, 21]; it is also explored for explosives and propellants [47] due to its high gravimetric and volumetric heat of oxidation [21]. Despite these benefits, the applications of boron combustion are limited, primarily due to its low burn rates [19, 57, 60].

In order to describe and potentially improve the processes governing boron ignition and combustion, several theoretical models, e.g., [81], [5, 30, 72, 74, 174] have been developed. It is commonly accepted that at low temperatures, the molten oxide layer inhibits diffusion for either oxygen or boron to the reaction interface. A particle heated in an oxidizing environment progressively self-heats, while forming and evaporating the B_2O_3 film [175]. Additionally, it has been argued that boron dissolves into its molten oxide to form B_2O_2 which later reacts with O_2 to produce B_2O_3 at low temperatures [60]. Either way, the net result is a heterogeneous reaction yielding B_2O_3 which is evaporating upon heating. Ignition is associated with the complete oxide removal, after which the particle temperature increases significantly leading to so-called full-fledged combustion [175]. Thus, boron oxidation rate accompanied by growth and then removal of the boron oxide determines the ignition delays, which need to be predicted in many practical calculations. Respectively, significant efforts have been made to quantify the rate of such oxidation reactions.

Some of the kinetic parameters reported for boron oxidation in air are summarized in Table 7.1. The values come from different types of measurements for boron samples oxidized as filaments, loose aggregated powders, or consolidated pellets. Ignition kinetics was described theoretically in Ref. [12] based on high-temperature combustion studies of boron-loaded propellants in air and single boron particles burning in a flat methane flame [57]. A parabolic rate law was consistently observed for boron oxidation in air from 673 to 1573 K (400 to 1300 °C) [12, 169, 176, 177], which was accompanied by the increase in thickness of the condensed oxide film [176].

Despite generally agreed upon qualitative description of boron oxidation, the reported values of activation energies (and, when available, pre-exponents) vary significantly among different reports. Table 7.1 shows low activation energies smaller than 100 kJ/mol reported in several studies dealing with boron samples coated with relatively thick oxide films. While even for these cases, the reported activation energies are inconsistent among themselves, it can be argued that all such measurements bear little relevance for situations dealing with boron ignition, when the oxide film is expected to be much thinner. Most of the activation energies reported for initial stages of boron oxidation are based on thermogravimetric (TG) measurements. Activation energies vary between 100

and 200 kJ/mol, making it difficult to choose which reaction kinetics should be used to model ignition.

A common shortcoming in interpreting TG data for oxidation of boron powders is failure to account for a broad particle size distribution or, more commonly, for surface morphology of the oxidized sample. For any heterogeneously oxidizing sample, other than a flat surface, the area of the reacting interface is changing as a function of the reaction progress. This change is easy to account for when samples are mono-sized spheres or rods; however, it is more difficult for actual poly-dispersed boron powders. An interesting early attempt to deal with this issue was reported in Ref. [177], where artificial aggregates (1-2) mm in diameter) comprised of 1.2-µm crystal boron particles were prepared and oxidized. All primary crystal particles were assumed to be equally exposed to the oxidizer. However, there was no experimental data to confirm the geometry proposed. For other work, the surface morphology of the oxidized boron was not considered at all. In a relevant recent study [178], it was found that independent of the synthesis method, boron particles consist of agglomerated primary particles with submicron dimensions. An approach to adequately represent this surface morphology is needed while interpreting results of TG measurements.

Recently, it was proposed that to describe heterogeneous oxidation, boron particles/aggregates can be modeled as spherical particles with reactive porous shells and solid cores [179]. For a common, 95% pure commercial boron powder the shell thickness was found to be 1.28 μ m. Thus, boron aggregates less than 2.56 μ m in diameter do not have the solid core. It was further shown that the shells can be treated as densely packed

160-nm diameter spherical primary particles. It is proposed here that accounting for this model and for the experimental particle size distribution for boron particles/aggregates can lead to a better quantified kinetics of boron oxidation. Obtaining such kinetics using TG measurements is one objective of this study. It is further of interest to test whether the same kinetics can describe the rate of full-fledged combustion of boron particles, occurring at much higher temperatures when the oxide film is removed from the boron surface.

Activation	Type of boron sample	Temp.	Pre-	Oxide	Ref.
Energy		range, K	exponential	thickness,	
(kJ/mol)			factor	h _{ox} (µm)	
189.12	4 μm single particle	1800-3000	$12 \cdot 10^{-7} T \cdot P_{o}$	<1	[12]
321		>2300	02		
34.72	100 µm diameter filaments	1273-1773	$77.10^{-8} \frac{p}{p_o}$	5-6	[169]
72.8			$3 \cdot 10^{-5} T$	4	[177]
82.63			$44 \cdot 10^{-3} C_{O_2}$	2	[177]
50.21	Rods	700-800	-		[176, 180]
177.06	Artificial agglomerates of crystal particles	650-950	$1.45 \cdot 10^{-6} T \cdot P_{O_2}$	0.01-0.20	[177]
122 ± 7	Electrodeposited powder	393-1073			[180]
205 ± 9	Commercial powder produced by reduction process				
120 ± 5	95% pure amorphous powder	323-1273		< 10% mass	[141]
162 ± 3	95% pure amorphous powder treated with acetonitrile			change	
106 ± 10	95% pure amorphous powder treated with toluene				
138 ± 10	99% pure crystalline/amorphous powder				

Table 7.1 Kinetic Parameters Reported to Describe Boron Oxidation in Air

7.3 Technical Approach

The particle geometry comprising a spherical porous reactive shell and solid core is used to determine the oxidation kinetics for micron-sized amorphous boron powder from nonisothermal TG measurements. The reactive shell is assumed to consist of spherical primary particles. All primary particles are able to oxidize simultaneously; oxidation of the solid core begins when the shell is fully oxidized. The interpretation of TG measurements accounts for the experimental particle size distribution of boron powders and assumes the constant thickness of the porous shell. Thus, particles smaller than the double thickness of the porous shell do not have a solid core. Data are processed using a model-free isoconversion technique. The kinetic model recovered for low-temperature oxidation is extrapolated to consider its feasibility in describing rates of full-fledged, high temperature boron combustion in air. Combustion data are obtained from experiments with single boron particles burning in room air. The fractal nature of boron aggregates and resulting surface area available for heterogeneous combustion when the aggregates melt forming a single spherical droplet is accounted for in the burn rate calculations employing the reaction kinetics obtained from TG measurements.

7.4 Materials

A commercial 95-97% pure amorphous boron powder by SB Boron Corporation was used for low- temperature oxidation studies. Because the results were expected to be compared with the reaction kinetics of full-fledged combustion involving oxide-free boron surface, the effect of natural hydrated oxide layer covering boron was to be minimized. Commonly, boron is washed with water to clean its surface [181]. Recent work showed that washing it

with acetonitrile is as effective, while also leading to a powder that is less prone to reoxidation [140, 141]. Both deionized water and acetonitrile (99.9% pure HPLC grade by Sigma-Aldrich) were used here to wash boron. Washing also enabled us to achieve a single mode particle size distribution for the powders used in experiments, simplifying the data processing as discussed below. Boron powders were washed as described earlier [141]. Briefly, 9 g of powder was loaded into a 250 mL glass beaker and agitated ultra-sonically in 175 mL of a solvent (water or acetonitrile) for three minutes. A 2" diameter titanium horn operated at 75% of maximum power controlled by a Branson Ultrasonics 910 BC unit was used. The powder stratified in two layers. The top layer consisting of ultrafine particles and including most of the dissolved boron oxide was discarded. The washing cycle was then repeated using the bottom layer with fresh solvent. The stratification occurred and the top layer was again removed. For the bottom layer, first, excess of the solvent was removed by vacuum filtration. The solids were then dried at ca. 50 °C for 2 hours at a reduced pressure of 0.5 atm using a National Appliance Company, Model 5831 oven. Two samples were prepared washed in acetonitrile and water: B_{ACN} and B_{water}, respectively.

Particle size distributions of the samples are shown in Figure 7.1. The size distributions were obtained by low- angle laser scattering using a Malvern 3000 Master sizer. A sample of each treated material was suspended in water for the analysis. For both samples, the volumetric distributions range from sub- micron to 30 μ m particles, with most particles around 10 μ m. The sample treated with acetonitrile appears to have a larger fraction of fines. As discussed elsewhere [142, 179], boron particles are agglomerates of partially fused finer primary particles. The distributions shown in Figure 7.1 represent sizes

of such agglomerates and cannot be treated as representing diameters of spheres forming upon melting such agglomerates.



Figure 7.1 Particle size distributions of boron samples treated, and size classified in acetonitrile (top) and water (bottom).

7.5 Experiment

For thermo-gravimetric (TG) analyses, 3.30 ± 0.21 mg boron samples were loaded on an alumina plate sample carrier in a Netzsch STA 409 PC/PG analyzer. The powder was heated from 298 to 1023 K (25 – 750 °C) at four rates: 2.5, 5, 10 and 20 K/min under a mixture of oxygen and argon flowing at 20 and 80 mL/min respectively. The experiments were repeated with larger mass loadings (5.11 ± 0.06 mg) and with the final temperature increased to 1223 K (950 °C) to verify the reproducibility and achieve a better signal to noise ratio.

Burn times and temperatures were measured for boron particles ignited by a CO_2 laser beam in air. As-received boron powder was used. The experimental method is described elsewhere [9]. Approximately 0.1 g of the powder was loaded on to a custom screw feeder. The particles were aerosolized and fed by air flow at 0.6 l/min into a beam of a CO_2 laser (Evolution 125 by Synrad operated at 37.5 W). The laser beam was focused by a ZnSe lens to 250 μ m diameter. Particles moved through the beam at velocities of 3 – 4 m/s. The ignited particles continued traveling vertically and burned in the surrounding room air. Optical emission produced by the luminous streaks of burning particles was recorded by two Hamamatsu R3896-03 photomultiplier tubes equipped with interference filters centered at 700 and 800 nm. The light to the PMTs was fed through a bifurcated optics bundle positioned ca. 17 cm away from the burning particles. The durations of the recorded simultaneously at different wavelengths were used to obtain their color temperatures.

7.6 Boron Oxidation Kinetics

7.6.1 Experimental results

Figure 7.2 shows the sample mass as a function of temperature for boron powders washed with water and acetonitrile measured at different heating rates. The observed mass gain shifts to higher temperatures at higher heating rates. Repeat measurements using different mass loadings are in fair agreement with each other. For samples washed with water, most traces corresponding to the same heating rates overlap in Figure 7.2. In all present TG

experiments, the theoretical mass gain corresponding to the complete oxidation of boron to B_2O_3 (220 %) was not achieved.



Figure 7.2 TG traces for boron washed in acetonitrile (top) and water (bottom) heated in an oxygen/argon flow at different rates.

Note: Dashed lines: mass load 3.3 mg; solid lines: mass load 5.11 mg.

7.6.2 Oxidation of particles of different sizes

To develop a quantitative oxidation model, the experimental data shown in Figure 7.2 need to be recast to show oxidation of particles of different sizes contained in the sample. This can be done using the measured particle size distributions (Figure 7.1) and accounting for the fraction of the surface area available for heterogeneous oxidation within each particle size bin. This approach was exploited earlier for spherical powders [182-184] and needs to be modified for the loose agglomerates making up typical boron powders. For lowtemperature oxidation of boron, it was shown recently that boron agglomerates can be described as solid, spherical cores with porous reactive shells [179]. For the powders used here, it was found that the reactive shell thickness $h_s = 1.28 \ \mu m$ [179]. Particles with diameters less than $2h_s$ are thus treated as fully porous. Furthermore, it was found that the reactive shell can be presented as consisting of densely packed, 160- μ m diameter spherical primary particles. Upon heating, the oxidation occurs at the surface of all these primary particles, whereas no reaction occurs in the core. The known shell thickness and primary particle size combined with the particle size distribution in Figure 7.1 are sufficient to distribute the mass gain shown in Figure 7.2 among different powder particle size bins and determine the thickness of the oxide layer grown at different temperatures. The initial reactive volume for a size bin, which is the volume of all porous shells, is calculated as:

$$V_i = N_i \cdot \frac{4}{3} \pi \left[R_i^3 - r_i^3 \right] \tag{7.1}$$

where V_i is the combined reactive volume of all particles in size bin *i*; N_i is the number of particles in that bin; R_i is the particle radius (from the measured data, Figure 7.1, taking particles as spheres) and $r_i = R_i \cdot h_s$, is the core radius of the particle. The corresponding mass increment for the size bin is determined as:

$$dm_i = dm \cdot \frac{V_i}{V}$$
(7.2)

where $V = \sum_{i} V_{i}$ is the combined reactive volume of all size bins and dm is the instantaneous mass gain measured by TG for the entire powder load. The TG curves for individual particle size bins, m_i(t), are then calculated by integrating Equation (7.2). To illustrate the result, relative masses m'_i = (m_i-m_{i,0})/m_{i,0} for selected particle sizes (2.5, 5.5,

10.5 and 25 μ m) are shown for measurements at 2.5 K/min in Figure 7.3. The curve reaches a constant value once the primary particles in the reacting shell are completely oxidized. Smaller particles meet this limit at lower temperatures. All particles with diameters less than 2.56 μ m have the same mass change on a percentile basis because they are treated as completely porous.



Figure 7.3 Relative masses change trends for selected particle sizes: 2.5, 5.5, 10.5 and 25 μ m, heated at 2.5 K/min.

Following earlier work [179], the mass of a particular size bin can be used to determine the mass of the primary particles, m_{PP}, that make up the agglomerates:

$$m_{PP} = m_{PP,0} \frac{m_i - m_{i,core}}{m_{i,0} - m_{i,core}}$$
(7.3)

where m_i is the mass of size bin *i*, as defined above, $m_{i,0}$ is its initial mass, $m_{i,core}$, is the constant mass of the nonporous core, and $m_{PP,0}$ is the initial mass of a primary particle. From the mass of a primary particle, the thickness of the oxide on its surface can be calculated according to the formalism developed in Ref. [179]. According to the previous work (see Figure 6.9 in Chapter 6), the redistribution of the sample mass change over boron agglomerates of different sizes as outlined above can be considered valid until the surface oxide thickness on the primary particles reaches about 15 nm. Measurement reproducibility decreases above this limit, likely due to redistribution of the accumulating liquid oxide within the porous agglomerates and resulting changes in the overall geometry. Consequently, data below this threshold can be used to determine kinetic parameters of the oxidation reaction. Figure 7.4 shows the relative primary particle mass for different heating rates. A horizontal line indicates the relative mass where the surface oxide reaches the 15 nm limit.



Figure 7.4 Relative mass of primary boron particles at different heating rates for samples washed in acetonitrile (solid lines) and water (dashed lines).

Note: The horizontal line indicates the mass where the growing surface oxide reaches a thickness of 15 nm.

7.6.3 Kinetic description

Generalized, the oxidation rate of a primary particle can be expressed as:

$$\frac{dm'_{PP}}{dt} = k \cdot f(m_{PP}) \cdot \exp\left(\frac{-E}{RT}\right)$$
(7.4)

where k is a pre-exponential factor, E is the activation energy, and $f(m'_{PP})$ describes a reaction model. The reaction rate can be stated in terms of mass of the agglomerates, mass of the primary particles, thickness of the growing oxide layer, or other parameters. Choosing the mass of the primary particles, m_{PP} (or relative mass, m'_{PP}) as the reference is consistent for agglomerates of different sizes and makes the results of the following kinetic analysis easily transferable to other parameters. Since the reaction model is unknown, a model-free iso-conversion technique [185] was used to determine the kinetic parameters for the early stages of boron oxidation. The iso-conversion method was implemented in MATLAB as in previous work [182, 183].

The result is an activation energy as a function of the reference variable, i.e., m'_{PP} , as shown in Figure 7.5. Data for both samples treated in water and acetonitrile show similar activation energies, while the latter dataset has a slightly lower variance. The data suggest that the activation energy increases at about $m'_{PP} = 0.15$, which corresponds to the oxide thickness of ca. 5 nm. The increase in the activation energy is observed for samples of boron treated in both water and acetonitrile. Flat lines in Figure 7.5 show the average activation energies, obtained for the sample treated with acetonitrile; they are 148 ± 6 kJ/mol and 162 ± 9 kJ/mol for oxidation before and after the oxide reaches 5 nm, respectively.



Figure 7.5 Apparent activation energy of oxidation of boron powder in oxygen as a function of primary particle mass, m_{PP} .

From Equation (7.4), if for a given value of m'_{PP} the activation energy *E* and the reaction rate dm'_{PP}/dt are known, the product $k \cdot f(m'_{PP})$ can be determined, although these two components cannot be separated. This is shown in Figure 7.6 for measurements performed at 2 K/min. The value declines exponentially to a relative primary particle mass change of 15 % (~5 nm) and then becomes constant at a value of ca. $6 \cdot 10^4$, supporting a change in the reaction mechanism at that point, implied by a change in the apparent activation energy (see Figure 7.5).


Figure 7.6 Product of pre-exponent, k and $f(m_{PP})$ as a function of the mass change of the primary particle mass, m_{PP} for boron washed in acetonitrile.

7.7 Boron combustion in air

From prior work, it has been proposed that at high temperatures typical of combustion, oxide layers are expected to volatilize, exposing boron surface to external gaseous oxidizer. This leads to boron combustion in air via heterogeneous surface reactions. It would therefore be useful to understand whether the kinetics predicted at low temperatures with negligible oxide thickness (i.e., at $m'_{PP} = 0$) would be applicable for high temperature surface combustion.

This section shows results of boron particle combustion experiments in air, and their relation to the kinetic description developed in Section 7.6.

7.7.1 Particle size and morphology

Analysis of the boron combustion will be based on correlation of burn time and particle size. The size distribution of the boron particles fed into the laser experiment setup was therefore determined. Without the CO₂ laser turned on, particles were aerosolized, fed through the nozzle, and collected on aluminum stubs covered with adhesive carbon tape. The stubs were positioned 2 - 3 cm above the nozzle tip exit. SEM images of collected particles were taken and processed following a similar automated procedure outlined by Refs. [186, 187]. Each aggregate identified was treated as a single particle, i.e., as a group of primary particles that would have caused a single combustion event.

Due to the complex nature of amorphous boron powder agglomerates, the primary particles (nominally 160 nm in diameter) form branch chained aggregates of varying sizes. The aggregates are refractory, and it is assumed that the bonds between primary particles do not break or fragment. Thus, it is necessary to account for the change in surface area available for oxidation when boron fractal aggregates become spherical molten droplets during combustion. The aggregates identified in the microscopic images were treated as fractal objects. Evaluating their volume, and diameter of an equivalent spherical particle, required correction for the fractal dimension. The fractal dimension, D_f of the boron aggregates was determined from SEM images at multiple magnifications (500x, 2000x and 5000x). This follows an earlier approach [187]. However, in this case, the effect of overlap is considered for the cluster morphology to obtain a true fractal dimension. It is assumed that boron particles form by the process of diffusion limited cluster aggregation (DLCA) so that their structure can be described by the following equation [188, 189]:

$$N = k_0 \cdot \left(\frac{R_g}{a}\right)^{D_f}$$
(7.5)

where *N* is the number of monomers in a cluster, R_g is the cluster radius of gyration, *a* is the monomer radius (i.e. 80 nm) and k_0 is a pre-factor of order unity dependent on the degree of overlap. To determine D_f , intermediate overlapping was assumed. Following [188], the constant k_0 was taken as 1.8, and *N* was estimated as:

$$N = 1.37 \left(\frac{A_c}{A_a}\right)^{1.11}$$
(7.6)

where A_c is the projected area of the aggregate and A_a is the projected area of the spherical primary particle. The radius of gyration, R_g was determined for each identified particle using the following approximation [188]:

$$\boldsymbol{R}_{a} = \boldsymbol{0.718} \cdot \boldsymbol{R}_{2} \tag{7.7}$$

where R_2 is half of the major axis length of the equivalent ellipse of each aggregate.

The resulting fractal dimension determined by this methodology was D_f =2.2. Note that earlier, a value of 1.8 was reported using a 2D box counting technique [187]. Using D_f =2.2, the diameters of the particles measured by SEM image analysis using ImageJ software [144] were corrected to obtain diameters of equivalent spheres [142]. The particle sizes (original aggregate size) prior to fractal dimension correction and the resulting distribution processed using the obtained value of D_f are shown in Figure 7.7. For comparison, the size distribution obtained with D_f =1.8 is also shown. Uncorrected particle diameters range from 0.1 to 30 µm. With fractal dimension correction, the particle size distribution shifts to smaller sizes. For the larger fractal dimension, the range of particle sizes extends from 0.1 to 20 μ m; while for a lower fractal dimension particle sizes varied from 0.2 to 10 μ m. The data processed with a larger D_f appears to be bimodal, similar to the uncorrected particle size distribution. Fits for all measured particle size distribution histograms were found using double lognormal functions; the fits are shown as dashed lines in Figure 7.7.



Figure 7.7 Particle size distributions for commercial boron powder fed through laser setup.

The distributions are obtained by SEM image processing: (A) is the uncorrected distribution (B) is distribution corrected by FD obtained from box counting method, (C) is obtained by FD determined by diffusion limited cluster morphology [188].

7.7.2 Combustion times and temperatures

Following the experiment outlined in Section 7.5, Figures 7.8 and 7.9 show the corresponding single particle burn times and combustion temperatures recorded for commercial boron powders burning in air. To obtain burn times, a custom MATLAB code was used to identify multiple pulses from the 700 nm filtered signal. At least 50 runs, each at a total duration of 8 seconds and a sampling rate of 100,000 samples per second were processed to obtain approximately 800 peaks. Each pulse was identified when the signal exceeded the baseline by more than 10%. The baseline was determined as the average voltage in a region with no pulses for a duration of a minimum of 10 ms. The resulting distribution of pulse durations or burn times is recorded in Figure 7.8. The distribution ranges from 0.2 to 30 ms with a number average burn time recorded of ca. 3 ms. Similar to the particle size distribution, a double log normal distribution function was used to fit the histogram. The fit is also shown in Figure 7.8.

Assuming that smaller particles have shorter burn times and larger particles have longer burn times, the cumulative frequency distributions of the log normal fits for the particle size distribution at D_f = 2.2 (Figure 7.7 (C)) and the burn time distribution (Figure 7.8) were correlated with each other. The resulting correlation can be described as burn time, t_b (ms) as a function of particle diameter, D (µm); the approximate power law is $t_b \approx$ 1.54 $D^{1.02}$.



Figure 7.8 Burn time distribution for single boron particles laser ignited and burning in air.

The temperatures for each emission peak were determined from the intensity ratio of the PMT signals at 700 and 800 nm, fitted to Planck's law. For each emission pulse, the temperatures were averaged while the emission signal was greater than 50% of the corresponding maximum peak value. Temperatures were determined for pulses where the signal to noise ratio was greater than 3 for both filtered signals. The results are shown as a scatter plot of temperature and the corresponding burn time for each peak. The plot illustrates that the temperatures range from 2000 to 4000 K, and that shorter pulses imply lower combustion temperatures than longer pulses.



Figure 7.9 Single particle combustion temperatures determined from IR PMTs filtered at 700 and 800 nm plotted against log scale value of corresponding burn time.

Note: The temperatures are determined for burning particles laser ignited in room air.

Boron particles burning in the surrounding air were also collected 4 - 6 cm above the nozzle tip on aluminum stubs by impaction. SEM images of the quenched combustion products are shown in Figure 7.10. Examples of three typical cases of particle morphology changes observed upon heating are shown. In case A, the fractal boron aggregate becomes a spherical molten droplet. In some cases, nano-metric smoke particles can be seen on the surface of the droplet. In case B, evidence of a stand- off vapor phase flame is seen where crystalline boron oxide forms upon cooling on the cold aluminum stub some distance from the spherical particle. In case C, larger aggregates appear to have initial surface oxidation occurring without drastic changes to original surface area available from aggregates. There is evidence of surface heating, initial melting and formation of oxide crystals on the surface of the aggregate.



Figure 7.10 SEM Images of combustion products of commercial boron powders laser ignited in air.

7.7.3 Rate of full-fledged combustion

In an attempt to relate the low-temperature, low-heating rate oxidation measurements to the combustion regime, particle burn times were estimated using the kinetic description established above. The activation energy determined for early oxidation is relatively constant (see Figure 7.5). For the model calculation, a constant activation energy of ca. 148 kJ/mol was therefore assumed, as determined during the initial oxide growth (less than 5 nm). However, the parameter $k f(m'_{PP})$ (see Figure 7.6) decreases noticeably with increasing degree of oxidation. To simulate a similar clean surface boron combustion regime, the initial value of this parameter was chosen when negligible oxide layer is present, i.e., $k \cdot f(m_{PP}) = 1.29 \times 10^6 s^{-1}$.

The burn rate dm/dt of a particle with mass, *m* and initial mass m_0 , is described as its initial oxidation rate, scaled by its instantaneous surface area:

$$\frac{dm}{dt} = \left(\frac{dm}{dt}\right)_{initial} \cdot \frac{A}{A_0} = \left(\frac{dm}{dt}\right)_{initial} \cdot \left(\frac{m}{m_0}\right)^{\frac{2}{3}}$$
(7.8)

where A_0 and A are respectively initial and instantaneous surface areas of the burning spherical particle.

For a particle of specific size, which could be matched with the size bin, i, so that its mass is m_i , the reaction rate is calculated from the initial oxidation rate of a primary particle:

$$\left(\frac{dm_i}{dt}\right)_{initial} = \left(\frac{dm'_{pp}}{dt}\right)_{initial} \cdot \frac{A_{i,0}}{A_{pp,0}} \cdot \frac{m_{pp,0}}{1 - 1.5 \binom{M_0}{M_B}}$$
(7.9)

where $A_{i,0}$ and $A_{PP,0}$ are respectively initial surface areas of a particle in size bin *i* and of the primary particle, M_O and M_B are molar masses of oxygen and boron, respectively. Thus, reaction rate can be calculated for any particle size. Using that rate and integrating Equation 7.9 gives an estimate for the burn time of a particle with mass *m*:

$$t_b \approx -\frac{3m_0}{\left(\frac{dm}{dt}\right)_{initial}} \tag{7.10}$$

Figure 7.11 shows burn times estimated at different temperatures for particles of different sizes. The particles are treated as non-porous, spherical molten droplets of boron, consistent with the particles observed in Figure 7.10(A) and 7.10(B). The burn times predicted from the model have been calculated for temperatures ranging from 2000 to 5000 K, similar to measured experimental combustion temperatures shown in Figure 7.9. Experimental data is depicted as a solid bold line with symbols. It suggests that combustion of boron can indeed be described using the reaction kinetics recovered from thermo-analytical measurements and that the particle temperature varied between 3500 and 4500

K. As noted earlier, the experimental trend could be described approximately using a power law with the exponent close to 1; the overall slope of that trend matches well with the slope of the calculated burn time dependencies.



Figure 7.11 Burn times versus particle size trends for boron oxidation, assuming that particles become spherical droplets and the rate of consumption is proportional to the surface area available for reaction.

Note: The dashed lines are the kinetic model predictions at varying temperatures and the bold line with symbols represents the experimental trends.

As shown in Figure 7.10 (C), some porosity may be preserved in boron particles even at combustion temperatures. Although the geometry of the particles used for initial TG measurements and determination of the kinetic parameters is unlikely to survive heating to combustion temperatures, using it to estimate burn times can still serve as a limiting case. For these estimates (shown in Figure 7.12), the porous shell, and the solid core are considered as burning in sequence:

$$t_b \approx t_{b,shell} + t_{b,core} \tag{7.12}$$

Particles with sizes less than $2h_s$, have no non-porous core, therefore $t_b = t_{b,shell}$ in these cases. Since in the oxidation model the shell oxidizes volumetrically, and consists of primary particles, $t_{b,shell} = t_{b,PP}$. The core burn times are then estimated using Equations 7. 9 and 7.10 with the mass of the core of a particle in size bin, *i*:

$$m_{i,core,0} = \frac{4\pi\rho_B}{3}r_i^3$$
(7.13)

where ρ_B is boron density and the surface area of the core $A_{i,core,0} = 4\pi r_i^2$ replacing the particle surface area in Equation (7.9).

The results from this assumption and model equation derived from the reactive shell-solid core geometry are shown in Figure 7.12. Experimental data are also shown; however, unlike Figure 7.12, the size distribution for boron in this case used as measured (uncorrected) boron agglomerate sizes. Particles less than ca. 2 μ m in diameter have the same oxidation rates, determined by the oxidation of a primary particle. As the particle size increases, increasingly longer burn times are predicted when the solid cores participate in combustion. Such larger particles present burn times with a power law trend having a slope similar to what is observed experimentally. The calculations effectively coincide with measurements for a broad range of agglomerates for the temperature of 4500 K. Note that if the experimental sizes are reduced (e.g., some coalescence of molten primary particles occurs), the trend would shift to match with the burn times corresponding to lower temperatures.



Figure 7.12 Burn times (ms) versus particle size (µm) for boron porous aggregates in air.

Note: The bold solid line represents experimental combustion data from laser ignition. The dashed lines are kinetic model predictions at varying temperatures. The model predictions are based on the assumption that the solid core and reactive shell geometry holds during combustion.

7.8 Discussion

The reaction kinetics for boron identified here and relying on TG measurements assumes that the gas phase transport of oxygen to the boron surface is not a rate-limiting process; instead, the rate is determined by the heterogeneous reaction occurring on surface of boron aggregates. Thus, kinetic parameters reported in Figures 7.5 and 7.6 cannot be applied to describe boron oxidation or combustion for fuel-rich systems, when oxygen transport can become rate limiting. They should be suitable for interpreting results of single particle combustion experiments for fine particles, for which the oxygen gas transport is expected to be fast. These are the types of experiments described in Figures 7.8 and 7.9, justifying comparisons given in Figures 7.11 and 7.12.

Reaction kinetics is derived here from measurements accounting for both particle size distribution and the complex surface morphology of boron particles, which has not been done in any of the previous studies. The pre-exponent is quantified in terms of oxidation of a primary particle; thus, conversion to the reaction rate normalized per surface area can be readily made if morphology of the oxidized or burning boron sample is known. An example of such conversion is shown in Equations 7.8-7.10. Because of the present processing for TG measurements accounting for the size distribution of boron aggregates, the kinetic description obtained here is expected to be more accurate than any of the previous assessments relying on thermal analysis, where bulk reaction rates were determined. Such bulk rates are commonly affected by varied reaction progress at the same temperature or exposure time for particles/aggregates of different sizes, which can skew both implied activation energy and pre-exponent.

The apparent activation energy of oxidation of amorphous boron particles determined by model free iso-conversion analysis changes from 148 to 165 kJ/mol when the oxide thickness reaches approximately 5 nm (Figure 7.5). Generally, these values of activation energy fall into the range of values reported earlier (see Table 7.1), however, a change in the oxidation mechanism of boron at a relatively early reaction stage has not been noted previously. The change in mechanism is also supported by the variation in the pre-exponential factor shown in Figure 7.6 and occurring at the same oxide thickness. This change could be caused by altered diffusion resistance of the growing boron oxide layer, e.g., due to a change in its structure as it thickens and becomes less affected by surface energy. However, it is likely that this change is insignificant for modeling boron ignition and combustion. In practical ignition scenarios, the heating rate is much higher than in the

present TG experiments, and particles are expected to ignite before the oxide thickness of 5 nm is reached. For combustion, boron oxide is mostly removed and thus reaction kinetics for thick oxide layers is irrelevant. Therefore, the activation energy of 148 kJ/mol should be used in the future work dealing with rapidly heated boron.

The results also suggest that particle pre-treatment with water or acetonitrile does not significantly affect the rate of boron oxidation. This implies that the present kinetics should be relevant for oxidation of various boron powders.

Extrapolating the boron oxidation kinetics to the range of temperatures expected for full-fledged particle combustion and considering the pre-exponential factor corresponding to zero oxide thickness leads to the particle burn times comparable to the experimental (Figure 7.11). The comparisons imply that the particle temperatures are between 3500 and 4500 K. The upper temperature essentially coincides with the boron boiling point, suggesting that the kinetic predictions are realistic. When it is assumed that boron retains its porous aggregate structure (see Figure 7.12 for the result and Figure 7.10 C for an example of such particle), the measured burn times for smaller particles could be matched by predicted reaction rates at temperatures at or even below 3500 K. For larger particles, the predicted burn times remain comparable to the experimental data pointing at 4500 K as the likely particle temperature. Indeed, experiments show an effect of particle size on the combustion temperature (Figure 7.9). However, the temperature estimates from the models are somewhat higher than the temperatures determined from optical emissions of burning particles. The discrepancy can be explained by the limitations in combustion temperature measurements discussed in earlier work [9]. It is suggested that the optical emissions are biased by the presence of smoke particles. Spectral emissivity of the particle

surface may also be distinct from that of a gray body and may change during combustion affecting the accuracy of the optical measurements.

In summary, the present results suggest that high-temperature reactions occurring during full-fledged combustion of boron are similar to its low temperature heterogeneous oxidation, provided that the oxide layer is sufficiently thin (less than 5 nm). This result is somewhat unexpected but can be quite useful for development of both ignition and combustion models for boron powders.

7.9 Conclusions

It is shown that presenting boron agglomerates as spherical particles with a solid core and reactive shell comprising densely packed spherical primary particles leads to an adequate description of low-temperature oxidation of boron powder that can be reduced to the oxidation of a primary particle described as:

$$\frac{dm'_{PP}}{dt} = k \cdot f(m_{PP}) \cdot \exp\left(\frac{-E}{RT}\right)$$

where relative mass of primary particle is defined through its current mass, m_{PP} , and its initial mass, $m_{PP,0}$: $m'_{pp} = \frac{m_{pp}}{m_{pp,0}} - 1$. For an early stage of oxidation of a common, 95% pure boron powder, with 1.28 µm-thick porous reacting shell and primary particles with diameter of 160 nm, the activation energy $E=148\pm 6$ kJ/mol and the pre-exponent factor $k \cdot f(m_{PP}) = 1.29 \times 10^6 s^{-1}$. This kinetics is readily transferred to describe oxidation of boron particles of different sizes, using the above reactive shell/solid core model. For powders with different purity or crystallinity, the model is expected to remain relevant; however, the thickness of the reactive shell and size of primary particles need to be determined by separate measurements, as discussed earlier [179].

The kinetics describing early, low-temperature oxidation of boron powders also predicts adequately the rates of full-fledged combustion of fine boron particles at the conditions when the gas phase oxygen transport to the particle surface is not rate-limiting. Comparisons of the particle burn times based on the derived here heterogeneous reaction kinetics and experimental data suggest that the particle surface temperature varies in the range of 3500 – 4500 K, approaching boron boiling point. It is further observed that the combustion temperatures of finer particles could be lower. Finally, at high combustion temperatures, some boron aggregates coalesce upon melting, forming single spherical droplets, while others retain, at least partially, their initial structure. Because the particle structure determines its specific surface available for heterogeneous oxidation, burn times of boron particles depend on their structure.

CHAPTER 8

EFFECT OF PURITY, SURFACE MODIFICATION AND IRON DOPING ON IGNITION AND COMBUSTION OF BORON IN AIR

8.1 Abstract

Combustion characteristics of boron powders with varying purity, surface treatment and iron dopant loadings were investigated. Particles were ignited by a CO₂ laser and burned in air. Commercial 95% and 99% pure boron powders were used as the starting materials. 95% pure boron was washed with acetonitrile to reduce the inhibiting oxide layer. All powders were doped with iron by thermal decomposition of iron pentacarbonyl. Optical emission of single burning particles was captured in order to determine combustion temperatures and burn times as a function of particle size. All materials ignited at approximately the same CO₂ laser beam energy. For all materials, two-stage combustion patterns were detected for longer emission pulses produced by particles burning in air. These two-stage patterns became difficult to resolve for the shorter burn times. It was observed that higher purity boron particles burn faster. A reduction in the natural oxide layer thickness achieved by acetonitrile wash did not appreciably change the burn time of boron particles. However, it did lead to a brighter emission during second stage combustion, oscillatory emission patterns, and formation of nitride caps on the surface of quenched boron particles. Doping boron with iron was effective for commercial 95% pure boron. It was less effective for washed boron and even less effective for boron of higher purity. Boron doped with iron burned faster than un-doped boron; the effect appeared to

scale with the amount of iron present. Additionally, boron doped with iron burned at a higher temperature than the un-doped powders. The increase in the burn rate and temperature caused by the iron doping are consistent with the proposed reaction mechanism, in which iron serves as a shuttle catalyst that is oxidized by external oxygen and then reduced by boron.

8.2 Introduction

There has been considerable interest in accelerating boron ignition and combustion due to its higher gravimetric and volumetric energy release upon oxidation, compared to more common metal fuels, such as aluminum [16, 21]. Potential applications for boron as a fuel include air-breathing ramjets, solid propellants, explosives and pyrotechnics [19, 150, 190-192].

Prior research has looked into the effect of crystallinity [22, 193], phase transitions [41], particle size [142, 194] and surface morphology of boron powders on their ignition and combustion. Effect of additives have also been explored including metals, e.g., [5, 91, 131, 195-197], metal hydrides [131], metal oxides [7, 16, 198], polymers [199] and fluorinated species [30, 200]. However, the effect of impurities present in the commercial boron powders on their oxidation, ignition, and combustion was not extensively studied. Higher purity, 99% boron samples were found that have lower hydration heat release at low temperatures (40 and 70°C) but lower onset temperature for oxidation above 400 °C compared to 95% pure powders [141]. It remains unclear whether such differences are

common. It is also of interest whether rates of these, relatively low-temperature oxidation reactions correlate with rates of full-fledged combustion for boron powders.

Most strategies aimed to improve boron as a fuel generally require large (typically >10 wt. %) quantities of additives to accelerate reactions. This results in a reduction in the energy density of the fuel. Most of the past research effort has focused on ignition, or reactions occurring at low temperatures and leading to full-fledged combustion. Studies have considered boron surface treatment using water [201] and hydrocarbons such as methanol [202-204] and acetonitrile [140, 141], that can dissolve/remove the inhibiting hydrated and un-hydrated boron oxide. Recent efforts [140] and [141] showed that acetonitrile wash and subsequent surface treatment with toluene produces boron powders with little hydrated oxide, which were stable in air and exhibited reduced ignition delays. However, washing led to no discernible effect on combustion of such powders in products of a hydrocarbon flame. Since water, CO, and CO₂ were the primary oxidizers in that case, it is of interest to investigate whether this surface treatment plays a role in boron combustion in air, when a stronger oxidizer, oxygen is present.

In other recent efforts, refractory metals like iron were explored as additives leading to accelerated boron combustion [9, 186, 205]. Iron was combined with boron using high energy ball milling [9] or surface doping [186]. It was found that as low as 1.6 wt% iron doped into boron powders was effective in reducing the burn times of boron particles in air. It is, however, unclear whether the burn rate improvements caused by boron doping with iron can be further altered by using boron washed in acetonitrile. Further, it is of interest how the observed effects of washing and doping boron compare to the effect of boron powder purity. This study seeks to bridge the gap in current data, and compare the effects of boron purity, surface modification and doping on its burn rates so that practical strategies to optimize boron powders as fuels can be developed. Possible reaction mechanisms associated with the effects observed will also be discussed.

8.3 Materials

8.3.1 Material preparation

Two commercial boron powders were used: 99% pure boron powder by Alfa Aesar (nominally -325 mesh) and 95% pure amorphous boron powder by SB Boron, referred to as B₉₉ and B₉₅, respectively. B₉₅ was washed with acetonitrile, following [141]. The wash reduced the oxide layer thickness by dissolving hydrated and un-hydrated boron oxide from the surface of boron [140]. 9 grams of B₉₅ was loaded into a 250 mL beaker with 170 mL of 99.9% HPLC grade acetonitrile by Sigma Aldrich. The mixture was agitated using a 20-kHz Branson 910BC ultrasonic system equipped with a 5.08 cm diameter titanium horn. The horn was inserted in the liquid mixture and operated at 75% of its maximum power for 3 minutes. The powder was then collected via vacuum filtration with a 55-mm diameter Whatman 1003-055, grade 3 cellulose filter (pore size 6 µm). The filter cake was reloaded into the beaker with a fresh 170 mL sample of acetonitrile to start the second cycle of treatment. The ultrasonication procedure/vacuum filtration sequence was repeated. For the last washing cycle, the filter cake was again re-loaded with acetonitrile and agitated for 2

minutes prior to recovery by filtration. The resulting filter cake product from the 3^{rd} washing cycle was stored in air for further characterization and is denoted as B_w .

Iron was doped into the boron samples (B₉₉, B₉₅ and B_w) by thermal decomposition of iron pentacarbonyl following [152-154]. The setup was placed in an argon filled glovebox. To create each doped batch, 3.17 grams of the respective starting material were loaded with 80 mL of dodecane by Fluka Chemicals (90-95% purity), 0.5 mL of CE-2000 surfactant by Lambent Technologies and a 25 mm Teflon®-coated magnetic stirrer into a 250 mL round bottom double neck glass flask. The vessel was sealed and preheated to 110 °C while maintaining a continuous flow of argon at 154 mL/min. After the sample was deoxygenated for an hour, the batch was heated to 125 °C and 1 mL of iron pentacarbonyl was injected into the batch using a 5 mL glass syringe. The sample was further heated to 190 °C to allow the decomposition to occur. The temperature was held constant for 2 hours. The exhaust from the reaction was bubbled through 400 mL of 0.1M potassium hydroxide solution in order to trap the probable decomposition products: CO and CO₂, prior to releasing the gas flow to room air. For each sample prepared by the steps outlined above, material was recovered by vacuum filtration as described above. The samples were recovered, washed and stored under hexane (by Sigma Aldrich), in an inert environment. Further details are available elsewhere [186]. The doped samples are identified by their respective starting powders as B₉₉-Fe, B₉₅-Fe and B_w-Fe.

8.3.2 Material characterization

All samples prepared were analyzed using a LEO 1530 field emission scanning electron microscope (SEM). Characteristic images of the samples are shown in Figure 8.1. Images of un-doped boron samples are shown stacked above their respective doped powders. Un-

doped boron images were taken using secondary electrons to highlight the particle morphology. Doped materials were imaged using back-scattered electrons to distinguish iron from the boron aggregates. As seen in Figure 8.1, the higher purity commercial powder includes particles with clearly distinguished crystal shapes as well as particles that appear amorphous. The lower purity samples appear as amorphous fractal aggregates. For the washed sample, larger, flake-like agglomerates appear. The corresponding doped samples show no significant morphological differences compared to their starting materials. Iron particles are not resolved in boron agglomerates at the magnifications used.



Figure 8.1 SEM Images of boron samples.

Top: commercial and un-doped boron samples (secondary electron images); Bottom: doped boron samples with different purity and surface modification (backscattered electron images).

Quantitative analysis of the samples for iron content was conducted using an Agilent 7500 series inductively coupled plasma-mass spectrometer (ICP-MS). For each sample, 0.5 grams were digested using diluted nitric acid (12% by volume). 34 μ L aliquots of the digested sample were further diluted and added to an internal standard that comprised

10 μ g/ml of Bi, Ge, In, Li₆, Sc, Tb, and Y. The results shown in Table 8.1 confirm that ca. 0.2% of iron were present in the un-doped boron powders. The data indicates that the quantity of iron successfully doped varies based on the starting material, with the highest content recorded for 95% pure un-washed boron. In that case, the sample was doped with roughly 1.3 % of additional iron. On the other hand, the lowest iron concentration was observed in the highest purity sample, with only ca. 0.3 % of additional iron. Further analysis of the filtrates recovered from the doping procedure showed that the iron produced in the cases of the B_w and B₉₉ sample remained suspended in the filtrate rather than adhered to the boron particle surface.

Table 8.1 ICP-MS Analysis of Boron Starting Materials and Doped Samples, for Iron Content

 Determination

Sample	Iron detected (ppm)	Boron detected (ppm)	Iron (wt%)
B 99	4.2	2473	0.23
B ₉₉ -Fe	9.3	1744	0.57
B 95	5.1	2304	0.28
B ₉₅ -Fe	27.9	2258	1.55
$\mathbf{B}_{\mathbf{w}}$	4.2	2387	0.23
B _w -Fe	18	2383	1.01

Combustion characteristics of the prepared samples are described in terms of burn times as a function of particle sizes. Following our previous work [143, 206], burn times are taken as durations of optical emission pulses produced by burning particles. The burn time distributions are then correlated to the measured particle sizes distributions. The main assumption is that smaller particles have shorter burn times. The distribution of particle sizes used for the correlation was obtained from processing SEM images of captured particles fed through the flow system employed in combustion experiments to inject them in the path of the laser beam. This allowed us to account for possible particle classification and/or agglomeration occurring in the flow system.

Aluminum SEM stubs coated with carbon tape were positioned 2 cm above the nozzle through which powders were fed into the laser beam. Particles traveling at velocities of 3-4 m/s were collected for 3 seconds, without the laser being powered on. Several SEM images covering the area of the stub were taken at varying magnifications to overcome the limited dynamic range of particle sizes that can be identified at a given magnification. Further details of processing are provided elsewhere [9, 142]. For each sample, the images captured were processed using a free software, ImageJ [207] to obtain the size distributions. Particles were automatically identified from their carbon tape background by applying a Gaussian blur filter with sigma value of 2 and color threshold value greater than 150. For each aggregate, the diameter of a sphere with the same surface area was determined. The diameter was further corrected by the respective sample's fractal dimension accounting for the primary particle size [142]. The fractal dimension was determined by diffusion cluster morphology theory, accounting for overlapping particles based on a 2D SEM image projection. The primary particle size was taken to be 0.16 µm, as determined recently for B_{95} [208]. It was assumed to remain the same for all powders. The fractal dimension varied between 2.2 and 2.3 for the samples investigated.

Particle size distributions are shown in Figure 8.2. All histograms appear to be bimodal. Respectively, double log-normal functions were used to fit the histograms, as shown by dashed lines. All distributions range within $0.2 - 30 \mu m$, with most particles having sizes around 1- 1.5 μm . Despite having a mixture of amorphous and crystalline particles, B₉₉ has a narrower distribution compared to B₉₅. It also has fewer fines compared

to B_{95} . The distributions show that treatment of B_{95} with acetonitrile makes the bimodal distribution more pronounced. The strong peak for coarser, 2-3 µm particles likely represents flake-like aggregates, as observed in the SEM images. In all cases, doping boron with iron appears to have negligible effect on the particle size distributions.



Figure 8.2 Particle size distributions for boron samples: doped and un-doped and with varying purity.

8.4 Experimental Details

0.1 grams of each sample was loaded into a customized screw feeder. Air flowing at 0.6 L/min served to lift particles from the threads of a stainless-steel screw turning inside a brass jacket. Powder was transported through a 10-cm long, 2.39-mm inner diameter brass tube into a nozzle placed under a laser beam. The particles were fed at a rate of 0.11 mg/min. A continuous emission Synrad Evolution 125 sealed CO₂ laser was used. During combustion experiments, it was operated at 37.5 W (30% of its maximum power). The laser beam was focused by a ZnSe lens to 250 μ m diameter. The focal spot was approximately 2 mm above the nozzle. Additional details of the setup are described

elsewhere [9, 143]. Ignited particles continued to travel vertically and burn in the surrounding room air.

To observe whether or not doping or surface modification had an effect on ignition in air, the laser power was lowered until no optical emission from particles crossing the beam could be detected.

Images of particles burning in room air were collected using a SONY DSC-H50 digital camera (exposure time of 250 ms). The camera was placed approximately 20 cm away from the nozzle.

Combustion products were collected on aluminum plates placed 4 cm above the nozzle. SEM images of the products were taken using a LEO 1530 field emission SEM coupled with Energy Dispersive X-ray Spectroscopy (EDS). EDS was used to identify elemental composition of the samples retrieved.

Two Hamamatsu R3896-03 photomultiplier tubes (PMTs) equipped with interference filters with central wavelengths of 700 and 800 nm, were used to capture optical emission pulses of the burning particles. The PMTs were connected to a bifurcated fiber optic cable. For washed and higher purity samples, the inlet of the fiber optics cable was positioned 10 cm away and at the same height as the nozzle. For doped and un-doped B₉₅ samples, exhibiting longer streaks the cable was positioned 16.5 cm away and 3 cm above the nozzle. The fields of view, within which the signal was reduced to 10% of its maximum intensity were approximately 8 and 12 cm for horizontal distances of 10 and 16.5 cm, respectively. Most particle streaks were shorter than 4 cm.

Data were collected using a 16-bit PCI-6123 National Instruments data acquisition board and LabView software for 8 seconds for each run. The sampling rate was 100,000 samples per second, resulting in a temporal resolution of 10 µs. For each material, at least 50 runs were processed to select a minimum of 1000 pulses representing combustion of single particles. Pulses were identified using a custom MATLAB code [113, 114, 206]. They were selected using the emission signal filtered at 700 nm, which had a higher signal to noise ratio. The baseline for the signals was recorded for at least 10 ms without any particle streaks. Burn times were determined as the pulse widths while the signal exceeded 10% of its maximum amplitude for each pulse. Pulses selected were further processed for combustion temperatures based on the calibrated ratio of the emission intensities from both PMTs. Particles were assumed to be gray body emitters.

Time resolved spectra of individual particle emission pulses were obtained using a 32 channel Hamamatsu H11460-01 (A10766-007-02) compact spectrometer. The instrument was coupled to a HIOKI MR8827 32 channel fully-isolated memory high speed hi-corder oscilloscope. This allowed for simultaneous collection of optical emissions by all 32 channels. Data were collected for 1 s at a rate of 500,000 samples per second for B₉₅-Fe and at 200,000 samples per second for all other materials. The spectral range covered was 373.1 - 641 nm. The spectrometer was positioned 10 cm away, at the same height as the nozzle. The ratio of intensities recorded from the PMT array at 700 nm and 800 nm and output of the compact spectrometer were calibrated using a tungsten lamp accounting for the spectral emissivity of tungsten.

8.5 Results

8.5.1 Ignition energy

Table 8.2 shows the minimum laser energy required to ignite each sample. The laser power varied slightly among the samples with B₉₅ and B₉₉ having, respectively the lowest (7.5 W) and highest (9.4 W) power required for ignition. No trend could be identified for the effect of washing or doping boron on its required ignition energy.

 Table 8.2 Minimum Laser Energy Required for Ignition of Boron Samples in Room Temperature

 Air

Sample	Laser Energy (%)	Actual Laser Power (W)
B ₉₉	7.5	9.4
B99-Fe	6.5	8.1
B ₉₅	6.0	7.5
B ₉₅ -Fe	7.0	8.8
$\mathbf{B}_{\mathbf{w}}$	6.5	8.1
B _w -Fe	7.0	8.8

8.5.2 Optical emission of individual burning particles

Characteristic images of boron particles laser ignited in air are shown in Figure 8.3. For all particles, the streaks begin with a bright spot, where the particles crossed the laser beam. The streaks become narrow as the particles moved up from the laser beam. All iron-doped particles have shorter streaks than respective starting boron powders. For doped particle streaks, insets show magnified images, which are generally similar to one another.

 B_{95} particles generally had brighter streaks compared to B_{99} and B_w particles. B_{95} streaks changed thickness and direction; less pronounced direction changes were also observed for B_{99} . Some streaks for B_w particles had oscillatory patterns as seen in Figure 8.3.



Figure 8.3 Characteristic images of single burning particle streaks of different boron powders laser ignited in air.

Typical optical emission pulses obtained from the 700-nm filtered PMT are shown in Figure 8.4. For each material, examples of short (< 5 ms) and long (> 5 ms) duration pulses are shown. Emission intensity was generally greater for longer pulses. A doublepeak structure could commonly be resolved for longer, but not for shorter pulses, as seen in Figure 8.4. For B₉₉ and B₉₅, the first peak of double-peak pulses generally had a higher intensity, consistently with earlier reports [9, 186]. For washed boron, however, the second peak was often higher than the first peak. For B₉₅-Fe, long pulses and double peaks as shown in Figure 8.4 were infrequent; more than 99% of pulses for this powder were shorter than 5 ms. Longer pulses for other doped materials (B₉₉-Fe and B_w-Fe) commonly had an extended plateau instead of the second peak, as shown in Figure 8.4. For B₉₉-Fe and B₉₅-Fe, the shorter duration pulses were symmetrical. For all other materials, short extended tails followed the pulse peaks.



Figure 8.4 Optical emission traces filtered at 700 nm for different boron powder particles laser ignited in air.

32 time-resolved emission traces filtered at wavelengths ranging from 373 to 641 nm were recorded. Examples of 641-nm traces are shown in Figure 8.5; this wavelength was selected as giving the highest signal intensity for burning particles. Similar to traces acquired in the infrared range shown in Figure 8.4, pulses in Figure 8.5 captured in the visible emission range had double peaks (in the case of B₉₅ and B_w) or sharp peaks with long tails. Also, similar to Figure 8.4, pulses for B_w sample had a stronger second peak. Time- resolved combustion temperatures were calculated assuming the emission in the visible range was that of a gray body. The obtained temperature traces for the pulses in

Figure 8.5 are also shown referring to separate vertical axes. A most reliable temperature can be inferred from the recorded emission signals when the emission intensity is high. For low intensities (e.g., by the end of the emission pulse), the temperature appears to increase clearly indicating an erroneous measurement. Thus, only a fraction of each obtained temperature trace may be usefully interpreted.



Figure 8.5 641 nm emission traces and corresponding temperatures for different boron powder particles laser ignited in air.

For un-doped boron samples (B₉₉, B₉₅ and B_w), the double peaks identified in the 700 nm filtered PMT emission traces were further analyzed to determine the characteristic times of the first and second peaks using a custom MATLAB code. This analysis was reported for B₉₅ earlier [9]. Double peaks were selected based on the number of maxima and minima identified in the derivative of the signal intensity. The respective fraction of peaks that were identified as double peaks for B₉₅, B₉₉ and B_w samples was 10%, 0.4% and 4.3%. Characteristic times are shown in Figure 8.6A, and their distributions for different

powders are shown in Figures 8.6B-D. Unexpected trends are observed, which are especially clear for B_w . It appears that smaller particles, with the total burn times less than ca. 10 ms burn differently than larger particles with longer total burn times. A minimum is detected for t_{p1} as a function of the total burn time (or particle size). For particles burning faster than 10 ms, e.g., for smaller particles, the emission intensity for the first peak increases faster for particles with increasing sizes. Conversely, for larger particles with the total burn times greater than 10 ms, the emission intensity increases slower as the particle size (and overall burn time) increase. Further, for smaller particles, the duration of the first peak and the rise time for the emission intensity during the second peak increase as the total burn times become longer. For larger particles, the duration of the first peak, t_{d1} , becomes nearly constant. The duration of the first peak is usually shorter than of the second peak.



Figure 8.6 Characteristic double peak emission trace and summary of times for un-doped boron samples laser ignited in air.

8.5.3 Statistical analysis of individual emission characteristics

Histograms showing burn time distributions obtained processing over 1000 emission pulses and their respective double lognormal distribution fits are presented in Figure 8.7. For each case, number-average burn times are noted. Burn times were taken as the widths of the 700 nm filtered emission peaks. They range between 0.1 to 30 ms. Higher purity samples (B₉₉ and B₉₉- Fe) had narrow distributions with a mean value close to 1 ms. The

effect of doping on burn times appears to be negligible for B₉₉. Samples B₉₅ and B_w had broader distributions and included longer pulses, producing the number-averaged times of ca. 3 ms. For doped powders of 95% pure boron, B_w-Fe and B₉₅-Fe, longer pulses disappeared, leading to shorter average burn times.



Figure 8.7 Burn time distributions for doped and un- doped B99, B95 and Bw samples when laser ignited in air.

Figure 8.8 shows the correlations of burn times, t, and particle sizes, D, for different powders. The correlations were made using fits shown in Figures 8.2 and 8.7 assuming that smaller particles have shorter burn times.

For commercial boron powders, particles of the higher purity B_{99} have shorter burn times compared to B_{95} particles. Surface modification by washing B_{95} with acetonitrile does not significantly affect combustion in air. In fact, finer particles of B_w have slightly longer burn times than similarly sized B_{95} particles.

Doping B₉₉ with iron led to a small change in the burn time vs. particle size trend for B₉₉-Fe compared to B₉₉. Conversely, doping B₉₅ with iron made burn times substantially shorter, particularly for larger particles, leading to a burn time vs. particle size trend that is very similar to that for B_{99} powder. A similar reduction in the burn times was observed for the washed boron sample that was also doped with iron, B_w -Fe, although smaller particles still burn somewhat longer than B_{95} .



Figure 8.8 Burn time vs. particle size trends for different boron samples burning in air.

Fitting each obtained trend using a power law, $t=a \cdot D^n$, where *a* and *n* are adjustable parameters gives values for *a* and *n* shown in Table 8.3. The values of exponents, *n*, are similar to those reported for boron combustion in air [186]. As-received 95% pure boron and 99% pure boron powders have the highest exponent values.

Sample	D- law fit		
	Pre-exponent, a	Exponent, n	
B ₉₉	0.79	0.76	
B ₉₉ -Fe	1.19	0.53	
B ₉₅	1.54	1.02	
B ₉₅ -Fe	0.86	0.53	
$\mathbf{B}_{\mathbf{w}}$	1.55	0.58	
B _w -Fe	1.11	0.52	

Table 8.3 Parameters *a* and *n* for the Burn Times, *t*, vs. Particle Size, *D*, Described as $t(ms)=aD(\mu m)^n$ for Different Materials Burning in Air

Figure 8.9 shows histograms for average particle temperatures calculated using signals from PMTs filtered at 700 and 800 nm. A gray body assumption was used. Only pulses with the signal to noise ratio greater than 3 were considered; for each pulse, portions of the emission signal exceeding 50% of its maximum intensity were processed. For reference, boiling and melting points for boron oxide, boron and iron are marked by vertical dashed lines. The measured particle combustion temperatures range from 2200 K to 4000 K. For most materials, the temperatures are close to the melting point of boron with a number average value ca. 2300 K. Although average values vary somewhat for different powders, all histograms cover very similar ranges of temperatures, except for B₉₅-Fe. For B₉₅-Fe, the temperatures are higher, approaching the boiling point of boron. The spread in the temperatures measured for this sample is higher than for other materials.



Figure 8.9 Combustion temperature distributions for single boron particles inferred from infrared emission signatures.
Further processing of recorded temperatures is presented in Table 8.4. For each particle, the time resolved temperature was averaged over the time while the emission signals exceeded 90% of its maximum intensity. For each material, the average values of these particle temperatures were calculated. Temperatures implied by the emission signals filtered in the visible and infrared ranges were calculated separately; both results are shown in Table 8.4. The error bars represent standard deviations. The temperatures suggest that combustion occurs above the boron melting point, 2350 K but below the boron boiling point, 4200 K. Consistently with Figure 8.9, higher temperatures are noted for the doped B₉₅-Fe powder. In all cases, data inferred by the visible emission suggest higher temperatures than those obtained from infrared signatures. This may be due to the effect of BO and BO₂ molecular emissions (450 nm to 650 nm), that could not be clearly resolved but could distort the black body fits for the visible spectral range. Note also that the gray body assumption used here is not separately justified and can lead to significant systematic errors in these temperature measurements.

Sample	Average combust	Average combustion temperatures (K)		
	Infrared	Visible (32 Channel)		
B 99	2200 <u>±</u> 250	3300 <u>+</u> 360		
B99-Fe	2300 <u>+</u> 150	3100 <u>+</u> 370		
B ₉₅	2500 ± 500	3000 <u>±</u> 300		
B ₉₅ -Fe	3200 <u>+</u> 870	3600 <u>+</u> 400		
$\mathbf{B}_{\mathbf{w}}$	2300 <u>+</u> 210	3800 <u>+</u> 360		
B _w -Fe	2400 ± 370	3200 ± 400		

Table 8.4 Average Combustion Temperatures for Different Boron Powders Inferred from Emission

 Signals Recorded in the Infrared and Visible Ranges

8.5.4 Boron particle combustion products from laser ignition

SEM images of combustion products of unwashed, washed and doped 95% pure boron powders are shown in Figure 8.10. Typically, spherical boron particles were observed. In the case of washed boron powders, nitride caps were observed on some of the quenched spherical boron droplets and in some instances the surface of the droplet appeared to have pores and crystalline phases.



Figure 8.10 SEM images of combustion products of different materials captured above laser beam in air.

8.6 Discussion

8.6.1 Ignition energy

Low heating rate studies [141] presented that high purity B₉₉ sample has a lower onset temperature for oxidation compared to 95% pure samples (un- treated and treated with acetonitrile). It was also reported that washing with acetonitrile resulted in shorter ignition delays for boron particles heated in the products of a hydrocarbon flame [140]. In an apparent conflict with those earlier reports, the higher purity sample, B₉₉ required a higher laser energy for ignition compared to all other materials and washing did not have an effect on ignition of B₉₅ (see Table 8.2). Considering that all materials required similar laser emission energies for ignition, an estimate was made for the temperature the igniting particles can reach upon exiting the laser beam. Because the absorptivity data for boron are lacking, as a first approximation, the characteristics of aluminum were used following [209]. The particle size of $3.37 \,\mu m$ was considered, for which the adsorption peaks for the CO_2 laser emission. Neglecting any other heat transfer terms, particles heated by the CO_2 laser emission could reach temperatures varied from 790 to 890 K using energies listed in Table 2. Doubling the value of surface absorptivity would bring the temperature up to the boron melting point, ca. 2350 K. The sensitivity of the estimated temperature to the value of surface absorptivity suggests how one could reconcile the present observations with earlier reports. The absorptivity of the laser emission for different samples tested here could be different. Indeed, surface of B_{99} is generally smoother than that of B_{95} (Figure 8.1). Thus, laser emission could be more effectively absorbed by B_{95} . Both washing and doping boron can further alter its surface properties and thus laser emission absorptivity. The present results highlight that the effectiveness of heating boron particles can depend greatly

upon presence or absence of the radiative heat transfer in addition to the convection, which primarily affected particle temperatures in earlier experiments [140].

8.6.2 Stages in boron particle combustion

Boron combustion has been extensively described as a two stage mechanism. In recent studies, the stages were associated with double peak emissions for burning particles [9, 142, 159], similar to those reported here (Figures 8.4, 8.5, and 8.6). Considering recently published phase diagrams of for B-O [160] and B-N [10] systems, it was proposed that, similar to other metals [111, 124], stages in boron combustion are caused by formation of B-O and/or B-N solutions that become metastable, resulting in a phase change accompanying the particle combustion. The phase change causes a transition from stage 1 to stage 2 combustion. Generally, the solution is formed and becomes saturated during the stage 1; it is decomposed and stoichiometric oxides (and nitrides) are formed heterogeneously during stage 2.

In addition to accounting for dissolution of oxygen and nitrogen, consider that unlike other metals, most boron particles, as shown in Figure 8.1, are aggregates of much finer primary particles. Upon melting, the aggregates collapse forming spherical droplets, as illustrated in Figure 8.10. This remarkable change in particle morphology may be occurring over a time period that is comparable to the particle burn time. Before the aggregates collapse, the rate of heterogeneous reaction is controlled by integrated surface of all primary particles accessible to oxidizer, and thus is greater than after a single droplet is formed. In other words, there may be two distinct combustion regimes occurring before and after the initial aggregates collapse into a single droplet. In addition to the formation of metastable phases inside burning particles, a switch between these two regimes can lead to the observed two-stage emission patterns.

It is reasonable to suggest that the switch between the regimes occurs when different portion of boron has reacted for particles with different initial sizes. For smaller boron aggregates, a greater portion of boron is expected to oxidize before the switch (or before the aggregates collapse into single droplets). This effect could lead to distinct overall burn time trends for finer and greater particles, which might explain a change in the slope of the burn time vs. particle size trend for B_{95} in Figure 8.8. Further, the first, rapid combustion regime will comprise a greater portion of the total burn time, which is consistent with data in Figure 8.6. An initial reduction in t_{p1} when particle size increases (Figure 8.6) could be associated with an increase in the reactive surface to volume ratio for fine aggregates when the size of the aggregate increases. However, this trend may reverse for much larger aggregates, when a portion of boron inside the aggregate becomes inaccessible for the external oxidizer. In this case, the particle can be modeled as having a porous shell and solid core similar to recent boron oxidation study [208]. Further experiments considering the evolution of morphology of burning boron particles and associated changes in their combustion regimes are desired based on the present observations.

8.6.3 Effect of boron purity on combustion

Powders of both B₉₅ and B₉₉ exhibited double peak emission pulses, suggesting that purity does not affect the overall reaction mechanism. A greater rate of combustion observed for the higher purity boron (cf. Figure 8.8) suggests that the impurities present in 95% pure boron impede boron oxidation. Analyses of B₉₅ using SEM coupled with EDS and ICP-

MS (as well as manufacturer specifications) showed the presence of magnesium (approximately 3%), silica, sodium and potassium. All the metal impurities listed may form stable oxides in presence of boron, and thus could compete with boron for oxygen. Oxides found in B₉₅ are stable and cannot be reduced by boron. They could inhibit boron surface from further oxidation, leading to longer burn times. Supporting this reasoning, it was shown that the presence of silica increases the oxidation resistance of boron [210]. Since the higher purity sample, B₉₉ does not have these impurities or less impurities present, it is less prone to surface blockage by unfavorable oxides and competitive side reactions.

8.6.4 Effect of surface modification with acetonitrile on combustion in air

The second effect explored is surface modification by washing in acetonitrile. Similar to earlier findings [140], washing had little or no overall effect on combustion in air. Results show that combustion rates are similar for washed and unwashed powders. However, emission pulses for washed boron powders were found to have stronger second peaks (Figure 8.4), and oscillatory patterns were observed in the particle streaks (Figure 8.3). Another distinct combustion feature for washed boron was presence of boron nitride caps in the quenched particles (Figure 8.10). Oscillatory patterns could, in fact, be caused by the forming nitride caps, so that the observed emission streaks support findings from the SEM analysis of the combustion behavior, a more detailed study of the washed boron surface is desired. While hydrated oxide is removed, the surface must be coated by a new layer, possibly containing nitrogen and carbon. It is this new surface coverage, which makes the washed powder stable in air [140]; it also can modify the combustion reactions occurring at high temperatures. For example, nitrogen dissolution in boron can be accelerated in the

first stage of combustion. This could make the first stage, limited by the formation of a saturated B·N solution shorter, so that greater fraction of boron would oxidize during the second stage, explaining a stronger second peak. Presence of carbon, leading to formation of B₄C, may favor formation of condensed boron nitride rather than releasing nitrogen gas and replacing it with oxygen, which is thermodynamically preferred for pure boron.

8.6.5 Effect of iron doping on combustion in air

When considering the effect of iron doping, it is important to keep in mind that different amounts of iron were added to different powders, as shown in Table 8.1. These amounts reflect the effectiveness of iron doping by thermal decomposition of iron pentacarbonyl, which depends on the boron oxide surface functionalization [211]. The doping was proposed to form when iron pentacarbonyl reacts with surface hydroxyl groups of the material at lower temperatures to form neutral iron and at higher temperatures further produces metallic nano particles or Fe^{2+} ions. The presence and nature of the boron oxide layer affects the availability of surface functional groups important for the reaction. Boron oxide grown naturally is rich in hydroxyl groups, favored by its reaction to form boric acid in moisture-containing atmospheres. Thus, removing this oxide and boric acid causes a lower iron yield, explaining the results shown in Table 8.1.

Considering the effect of iron doping on the burn times of different powders shown in Figure 8.8, it is apparent that the effect qualitatively scales with the amount of iron present. The improvement in burn rates is most significant for B_{95} -Fe, and then for washed B_w -Fe, whereas it is effectively undetectable for B_{99} -Fe. Consistently with our earlier work, even relatively small amounts of iron doping accelerate reaction rate of boron. Another interesting effect of iron doping is observed in Figure 8.9 and Table 8.5, where it is apparent that the temperature of combustion for B₉₅-Fe is higher than for other materials. A higher temperature is consistent with the observed greater burn rates and is further consistent with the proposed earlier mechanism by which iron accelerates combustion of boron [9, 186]. According to that mechanism, iron retained in burning boron particle is preferentially reacting with the ambient oxygen and then is being effectively reduced by boron. A greater rate of heterogeneous reaction naturally leads to a higher particle temperature, as observed here. Additionally, evidence of iron being retained in the burning B₉₅-Fe particles is shown in Figure 8.10, further supporting the proposed mechanism of combustion for boron doped with iron.

8.7 Conclusions

The impact of purity, washing with acetonitrile and iron doping on boron powder combustion were explored experimentally. All materials ignited at approximately the same CO₂ laser beam energy. Thus, possible differences in their low-temperature oxidation kinetics might have been offset by their differences in the absorptivity of the laser energy. For all materials, two-stage combustion patterns were detected for longer emission pulses produced by particles burning in air. These two-stage patterns became difficult to resolve for the shorter burn times. Higher purity boron particles were observed to burn faster. This effect is interpreted accounting for the impurities in commercial boron, which form stable oxides and thus compete with boron oxidizing heterogeneously. Reducing the natural oxide layer thickness by acetonitrile wash does not appreciably change the burn time of boron particles. However, boron particles modified by acetonitrile wash have brighter emission during second stage, oscillatory emission patterns, and forms nitride caps on their surface during combustion. Doping boron with iron was effective for commercial 95% pure boron. It was less effective for washed boron and even less effective for boron of higher purity. This was consistent with the mechanism of formation of iron by decomposition of iron pentacarbonyl preferentially occurring in presence of surface hydroxyl groups. Doped boron burns faster and at a higher temperature than the un-doped powder; the effect appeared to scale with the amount of iron present. The increase in the burn rate and temperature caused by the iron doping are consistent with the proposed reaction mechanism, in which iron serves as a shuttle catalyst that is oxidized by external oxygen and then reduced by boron.

CHAPTER 9

TRANSITION METAL CATALYSTS FOR BORON COMBUSTION

9.1 Abstract

Composite powders comprising 95 wt% boron and 5 wt% metal additives including Fe, Co, Ni, Hf and Zr, were prepared by high energy mechanical milling in a planetary mill using hexane as a process control agent (PCA). Additionally, composites with Fe were prepared using acetonitrile and stearic acid as PCA. Single particles of boron and all prepared materials were fed into the combustion products of a pre-mixed air-acetylene flame, in a diffusion air-hydrogen flame, and ignited in air using a CO₂ laser beam. Infrared emission pulses of burning particles were recorded. Distribution of burn times for each powder was obtained based on the durations of these pulses. Correlating the time distributions with measured particle size distributions yielded trends showing the effect of particle size on its burn time for all materials. Color temperatures were also recovered from the recorded emission signals. Additionally, constant volume explosion experiments were performed with all materials aerosolized in air. Results show that the morphology of the prepared composite powders is similar to that of boron. Single particle combustion experiments show that adding Hf leads to the most significant acceleration of combustion compared to boron. A positive effect of Hf as an additive is noted in different oxidizing environments. Adding Fe leads to an improved burn rate in air; however, there is no clear advantage in other oxidizing environments. No clear improvement is observed when other metal additives are used. Preparing B-Fe composites using different PCAs suggests that both a greater refinement of iron and a stronger acceleration in the burn rates of the prepared powders particles in air occur when acetonitrile and stearic acid are used as PCA. Unfortunately, the results of the present cloud combustion experiments were affected by too many parameters and processes making it difficult to offer their meaningful interpretation.

9.2 Introduction

Boron is an attractive fuel additive for explosives and propellants due to its high gravimetric and volumetric combustion energy densities [16, 21]. The limitations of using boron in many practical formulations are associated with its relatively slow reaction kinetics leading to long combustion times [5, 29, 42, 60] and ignition delays [22]. Additionally, in hydrogen containing environments, it forms a thermodynamically unfavorable but kinetically preferred intermediate HOBO [27, 30]. Past studies showed that boron ignition is delayed by its inhibiting oxide layer [5, 30]. It was also reported that boron burns at temperatures below its boiling point [9, 140, 142, 186] and the combustion may be rate-limited by its heterogeneous surface reaction with gaseous oxidizers [60].

Metals such as of Li [90], Al [149], Mg [5, 6, 101] and Ti [91, 197, 212, 3] have been studied as potential additives to combat the challenges associated with boron ignition and combustion. In the case of titanium, it was proposed that the intermetallic reaction with boron heats the particle surface to a temperature at which full-fledged combustion begins, thus reducing ignition delays. For magnesium, it was found that its selective oxidation leads to early ignition of B-Mg composites [196]. To date, most research focused on accelerating boron ignition [6, 213]. Recently, it was found that boron particle burn times were reduced when it was doped with iron [9, 186]. The effect was most significant when oxygen was the primary oxidizer. It was hypothesized that the iron has a catalytic effect on the heterogeneous oxidation of burning boron particles.

This work extends the efforts to consider combustion of boron doped with different metals. Included in this study are Fe, Co, Ni, Hf, and Zr. All selected metals have relatively high boiling points to ensure they are retained in burning boron particles. The mechanism by which the dopant is expected to improve combustion varies for different elements. Fe, Co and Ni are expected to serve as shuttle catalysts. They would be preferentially heterogeneously oxidized by gaseous oxidizers. Boron is then expected to readily reduce the condensed transition metal oxides. This altered reaction path might bypass formation of intermediates, including HOBO. Conversely, for Hf and Zr the mechanism by which they could potentially improve boron oxidation includes intermediate and exothermic formation of borides. This is expected to raise the particle temperature accelerating further oxidation of both boron and transition metal dopants.

All boron-based composite materials are prepared here using high-energy mechanical milling. The effect of a process control agent used during milling on the performance of boron doped with iron is also considered.

9.3 Material Preparation

Composites with 95 wt% of boron and 5 wt % of metal additive were prepared by high energy mechanical milling using a Retsch PM400 MA planetary mill. For each composite with added Fe, Co, Ni, Hf, or Zr, a batch of 50 g was prepared. The characteristics of the starting powders and sample IDs for different composites are listed in Table 9.1. For each batch, 47.5 g of boron was blended with 2.5 g of a dopant in a 500 mL steel vial. 20 mL of hexane solvent by Pharmco (reagent grade) was added as a process control agent (PCA). The vial was sealed inside an argon-filled glovebox. 10-mm hardened steel balls were used as the milling media. Each sample was milled for 4 hours at a ball to powder mass ratio of 10 and RPM of 350. The mill was set to have counter-current alternate spin every 15 minutes to improve mixing and a pause time of 15 seconds for cooling. During milling, the materials were additionally air-cooled by an external cooling unit.

Additional boron-iron composites were prepared using acetonitrile (acn) and stearic acid (st.ac.) as PCAs instead of hexane. The PCA amounts were 20 mL of acetonitrile by Sigma Aldrich (99.9% pure, HPLC grade) or 2 wt% of stearic acid (>97% purity) by Fluka. After milling, the samples were recovered at room temperature and stored dry in an argon environment. The subscripts following the sample ID are used to distinguish samples prepared with different PCAs: B-Fe_{hex}, B-Fe_{acn} and B-Fe_{St.ac}.

Material	Manufacturer	Specifications	Sample ID
Boron	SB Boron	95-97% elemental amorphous boron powder	Boron
Iron	Fisher Chemical	99% + electrolytic iron powder, < 100 mesh	B-Fe
Cobalt	Alfa Aesar	99.8% (metals basis) cobalt powder, 1.6 um	B-Co
Nickel	Alfa Aesar	99.9% (metals basis) nickel powder, 3-7 um	B-Ni
Hafnium	Atlantic Equipment Engineers	99.5% (metals basis) hafnium powder, – 325 mesh	B-Hf
Zirconium	Alfa Aesar	95%+ zirconium powder, 2-3 μm	B-Zr

Table 9.1 Starting Powders Used for Preparation of Composite Materials

9.4 Material Characterization

X-ray diffraction (XRD) analyses were performed using a PANalytical Empyrean diffractometer operated at 45 kV and 40 mA using Cu K α radiation (λ =1.5438 Å). The scan angle was in the range of 5-90°. A zero blank silica sample holder was used to minimize interference and to allow low sample quantities to be used for analyses. A JEOL JSM 7900F field emission scanning electron microscope (SEM) was used to examine structure of the prepared powders. The images were recorded using back-scattered electrons emphasize the elemental compositions of the prepared composites.

In order to correlate burn times recorded optically with particle sizes, the particle size distributions for all powders were obtained processing SEM images [9, 186]. For this analysis, particles fed through the feeder, operated at the same conditions as in the single particle combustion tests were captured and imaged using secondary electrons. This approach accounts for possible particle agglomeration or size classification occurring in the powder feeder. Details of such experiments were described elsewhere [9, 123, 159].

Particles were collected on a sticky carbon tape attached to aluminum stubs, positioned 3 -4 cm above the feeder's nozzle for up to 15 seconds. In some cases, the aluminum stubs were electrically biased at 1 kV to capture smaller particles electro-phoretically. Multiple SEM images were collected at different magnifications. For each magnification, the images were processed to measure particle size distributions using ImageJ software [144]. An automated process was used to identify each particle using color thresholding and a Gaussian blur filter [186]. The equivalent diameter was determined assuming that each particle projection had the same area as that of a sphere. Boron particles are typically aggregates of finer primary particles [178]. The diameter obtained from image processing was corrected by the fractal dimension (FD) of such aggregates determined for each composite (FD=2.2-2.5). A method based on cluster aggregation morphology theory was used [188, 189] assuming intermediate overlapping. The corrected particle diameters were used to construct the resulting size distributions. Using an approach described earlier [9, 123, 140, 142], the particle size distributions were correlated with the distributions of their measured burn times.

9.5 Experimental Setup

9.5.1 Single particle combustion tests

Combustion characteristics of were determined from both single particle and aerosol combustion studies. For single particle experiments, aerosolized particles were fed into three different combustion environments: air (where they were ignited using a CO₂ laser beam), products of pre-mixed air-acetylene flame, and products of a diffusion air-hydrogen flame.

For each oxidizing environment, approximately 0.1 g of the material was loaded onto the threads of a customized stainless-steel screw feeder. The screw located inside a brass jacket was rotated by a DC gear reduction motor. A gas jet lifted the powder from the screw and fed it through a 10-cm long, 2.39 mm inner diameter brass tube at a feed rate of ca. 0.11 mg/min. For laser ignition in air, the end of the carrier tube was positioned 2 mm below the focal point of the laser beam. The particles were fed using air flowing at 0.6 L/min. For the air-acetylene and air-hydrogen flame products, nitrogen flowing at 0.9 L/min served as a carrier gas. For the experiments with flames, the carrier tube was inserted axially into the burner. Additional details are available elsewhere [9, 113, 123, 142, 159, 186].

A Synrad Evolution 125 sealed CO_2 laser operated at 30% of its maximum power (37.5 W) was used to ignite the particles in air. The beam was focused to 250 μ m diameter using a ZnSe lens. The particles, traveling at a velocity of 3- 4 m/s continued to move vertically up and combusted in the room air. Further details are reported in Refs. [9, 143, 186].

For the premixed air-acetylene flame, the primary oxidizers for boron composites are CO₂, CO, and H₂O [142]. Air and acetylene flowing at 4.72 and 0.64 L/min, respectively, were used to create the flame with an equivalence ratio of 1.62. The gases were mixed in a 50 mm long, 19.13 mm diameter tube that was tapered to form a 5.16 mm nozzle. The particle velocity ranged from 5- 15 m/s in this experiment [9, 142].

For air-hydrogen flame, hydrogen was fed at 0.33 L/min through a central, 5.16 mm nozzle. Oxygen was fed at a rate of 0.71 L/min through an outer 47.55 mm diameter

annulus positioned around the hydrogen flow. Thus, particles injected axially could not directly react with oxygen. Note that the oxygen flow was rather weak, so that both oxygen and surrounding air were mixing with the central hydrogen jet. Hence, this flame is referred to as air-hydrogen. A diffusion flame formed around the central particle-laden nitrogen jet, generating H₂O as the main oxidizing species for the centrally injected metal. Further details are given in Refs. [9, 123].

In each of the combustion environments, a SONY DSC-H50 digital camera was used to capture images of the luminous particle streaks. Two Hamamatsu R3896-03 photomultiplier tubes (PMTs) filtered at 700 and 800 nm were used to record time resolved optical emission traces for single particles. Light from the burning particle streaks was fed through a bifurcated optics bundle. For most flame experiments, particle streaks were detected from 2 - 15 cm above the burner. In those cases, fiber optics inlet was positioned 5 cm above and 17 cm away from the burner tip. For B-Hf and B-Zr samples in the airacetylene flame, the inlet was positioned 7 cm above and 20 cm away from the burner tip to capture the emission from streaks that appeared longer than for other materials. For the B-Hf sample in the air-hydrogen flame, the inlet was positioned 3 cm above and 13 cm away from the burner tip due to the weaker signal intensity and shorter particle streaks. For laser ignition experiments, the inlet was positioned at the same height as the tip of the nozzle, 17 cm away. In this case, burning particles were detected up to 5 cm above the nozzle. The total field of view with the signal intensity decaying to 10% from its maximum was approximately 16 cm.

Data from PMTs were acquired at a rate of 100,000 samples per second for a total of 8 seconds per run using a 16-bit PCI-6123 National Instruments data acquisition system,

coupled with LabView software. A minimum of 50 runs were processed to select a minimum of 1000 of individual particle emission pulses for each sample in each environment. Using a custom MATLAB code, the particle emission signals were processed to determine the burn times and combustion temperatures [9, 113, 123, 142, 186]. For the burn time measurements, pulses were selected from the emission trace filtered at 700 nm due to the higher signal to noise ratio. The baseline was determined as the average signal recorded for a minimum of 10 ms without any particle pulses. A pulse was identified once the signal exceeded the noise in the baseline by 10%. The corresponding burn time for each particle was identified as the width of the emission pulse, where the signal amplitude was at 10% of this pulse's maximum. Weak or overlapping peaks were dismissed. Combustion temperatures were determined from the calibrated ratio of intensities of the emissions from both PMTs fitted to a Planck's curve. A tungsten lamp was used as the emission source for the calibration.

9.5.2 Aerosol combustion tests

Combustion of aerosolized powders was studied using a constant volume explosion (CVE) experiment [214]. 2 g of each boron composite powder was loaded into a reservoir under a 9.2 L, nearly spherical vessel. The vessel was evacuated to approximately 0.3 atm. The powder was aerosolized with an air blast delivered from a high-pressure reservoir and bringing the initial pressure to 1 atm. This resulted in an effective equivalence ratio close to 1.7. After a 200 ms delay, a thermite igniter placed at the center of the vessel and operated as an electric match was initiated. Each igniter contained 0.8 g of fuel-rich aluminum copper oxide thermite (4Al-3CuO) filled in a 2 cm long, 0.5 cm diameter paper tube capped with Viton. The thermite was ignited by an electrically heated, 20-cm long,

coiled tungsten wire. Pressure traces were recorded using a PX2AN1XX500PSA Honeywell pressure transducer. The experiments were repeated at least three times for reproducibility.

9.6 Results

9.6.1 Powder particle morphology: effect of metal additives

Characteristic images of the starting boron and prepared composites are shown in Figure 9.1. Boron particles appear as fractal aggregates (see Figure 9.1(A)). Each aggregate is comprised of nano-sized primary particles. For milled samples, the agglomerates are also observed. They appear to be more rounded and compact compared to boron. More angular aggregates appear for B-Hf. A broad range of aggregate sizes is seen for all materials; however, a smaller number of ultrafine particles is noted for B-Hf. Elemental contrast in images shows that bright ultrafine inclusions representing the added metals are dispersed uniformly in boron aggregates. Each aggregate examined under SEM contained some added metal inclusions. For B-Ni, larger particles of nickel were visible in some aggregates. Higher magnification images of the samples are presented in the supplemental section to illustrate the mixing between material components.



Figure 9.1 SEM Images of boron-based materials: (A) starting boron, (B) B-Fe (C) B-Co (D) B-Ni (E) B-Zr and (F) B-Hf.

9.6.2 Single particle combustion experiments: effect of metal additives

Figure 9.2 shows particle size distributions of aggregates of boron and prepared composites fed through the combustion setup. The particle sizes range from 0.1 to 30 μ m. Differences in the size distributions for the same powders fed into the burner or in the laser beam are caused by differences in the flowrate of the carrier gas. Clearly, particle size distributions are affected by the feeder setup. Double lognormal fits are shown as dashed lines for all histograms. These fits are used for correlations with the measured burn times.



Figure 9.2 Particle size distributions for different powders passed through the feeder.

Figure 9.3 shows examples of characteristic time-resolved optical emission traces obtained from the PMT filtered at 700 nm. As observed previously [9], boron shows a characteristic two-peak pulse in all three environments. The first of the two peaks observed is generally stronger than the second one. For doped boron materials, the two-peak structures were not resolved for particles burning in the combustion products of both air-acetylene and air-hydrogen flames. In air, two-peak structures were commonly observed for B-Ni and B-Zr. For B-Fe, B-Co, and B-Ni, an extended tail instead of the second peak was typically observed. For longest pulses (less than 1%) double peaks were still resolved.



Figure 9.3 Optical emission traces filtered at 700 nm for particles of different materials burning in different environments.

Images of streaks of particles of different materials burning in different environments are shown in Figures 9.4-9.6. In the air-acetylene flame (Figure 9.4), most particles burn within 2-15 cm above the burner tip. Particle streaks start as early as in the bright flame region for boron, B-Fe, B-Co and B-Ni. For the B-Zr and B-Hf, particle streaks begin higher, ca. 5 cm above the burner tip. This suggests longer ignition delays for B-Zr and B-Hf. Note also that air is slowly mixed in the flame and its concentration increases with the height. Thus, B-Zr and B-Hf burned in a more oxygen-rich environment and at a lower temperature than other materials. In most cases, a color change from yellow to green is observed, indicative of BO and BO₂ product emissions. For B-Fe, only one bright region was generally observed. Most streaks have a bright haze, indicative of a gas-phase flame around the burning particles. This observation is consistent with earlier work [9].



Figure 9.4 Emission streaks of different material particles injected in the air-acetylene flame (exposure times: 2 - 8 ms, ISO-80).'

For the air-hydrogen flame, streaks for the doped materials are largely similar to those of boron, as seen in Figure 9.5. Most particles streaks originate within the bright flame and have green emissions closer to the tip of the flame, where the temperatures are higher. Particle streaks extend outside of the flame into the surrounding air. They have less visible haze, suggesting a weaker gas phase combustion. Brighter streaks and secondary micro-explosions are noted for B-Zr, mostly for the particles outside the flame. No green emission was visible for B-Co.



Figure 9.5 Emission streaks of different material particles injected in the air-hydrogen flame (exposure time: 250 ms, ISO-400).

Powder particles ignited by the CO_2 beam in air have shorter streaks as seen in Figure 9.6. The streaks were typically white or yellow color, consistently with earlier reports [60]. The streaks typically ended within 5 cm above the nozzle (or above the laser beam). Boron particles produce streaks that appear brighter and longer than all composite powders. Among composites, B-Ni produces streaks with higher intensity, while the shortest streaks were observed for B-Fe.



Figure 9.6 Emission streaks of different material particles burning in air (exposure time: 250 ms, ISO-400).

Optical emission traces (see Figure 9.3) were processed by a custom MATLAB code to yield burn times for individual particles. The burn times are distributed into logarithmic bins to produce histograms. These histograms for all three environments for all materials are shown in Figure 9.7. Double lognormal fits are shown by dashed lines. The vertical dashed lines show average values for boron for each environment.

For the particles laser ignited in air, the burn time histograms are broader, and shift left compared to the other two environments. In air, histograms for all composite materials except for B-Co shift to shorter burn times compared to boron. A greatest fraction of particles burning with short durations, indicating the greatest reduction in burn times in air is observed for B-Fe.

For air-acetylene flame experiments, the burn time histograms appear to be narrow, with a number average or mode around 7-8 ms. A small shift to shorter burn times is seen for B-Zr and B-Hf, which were ignited higher above the burner, where oxygen could

become available as an oxidizer. The longest burn times for all materials were observed in the air-hydrogen flame. The distributions for B-Ni, B-Fe, and B-Zr appear to shift to shorter burn times compared to boron.



Figure 9.7 Burn time distributions for particles of different materials in different oxidizing environments.

Particle burn time distributions were correlated with their respective size distributions (data in Figure 9.7 vs. Figure 9.2) to produce the trends shown in Figure 9.8. The trends were determined using the respective double lognormal fits for each distribution.

In the air-acetylene flame, all composite powders burn slightly longer than boron, except for B-Hf. Comparing Figures 9.2 and 9.7, it is apparent that the effect is due to greater sized B-Hf particles exhibiting burn times similar to those of other materials.

In the air-hydrogen flame, shorter times again are seen for B-Hf particles. The burn times for all other materials are very close to those of boron. However, the effect of particle size on the burn time appears to be weaker for all composites.

In air, both B-Fe and B-Hf composites have noticeably shorter burn times compared to boron particles. Significantly longer burn times than for boron are observed for B-Zr. For B-Ni and B-Co, the effect of particle size on the burn time is weaker than for boron; as result, fine and coarse particles of these composites burn respectively slower and faster than similarly sized boron particles.



Figure 9.8 Burn time vs. particle size trends for different material particles burning in different oxidizing environments.

Obtained burn time vs. particle size trends were approximated by the common power law: $t_b = a \cdot D^n$, where t_b is the burn time in ms and D is the particle size in μ m, and a and *n* are the respective pre-exponent and exponent adjusted for the fit. The values of *a* and *n* are shown in Table 9.2. Considering that the curvature in the plots shown in Figure 9.8, the significance of these parameters as describing mechanistically boron combustion in any environment is questionable. With the above reservation, it is worth noting that all exponents shown in Table 9.2 are close to or below 1, suggesting kinetically controlled combustion. Recently, we reported similar experiments with boron and boron milled with iron powders burning in different oxidizers, where different values of a and n were presented [9, 142]. The discrepancy is caused by different method used to process particle size distributions for boron aggregates employed here. Unlike previous work, the 3-D nature of boron aggregates is now accounted for more accurately; additionally, the size of primary particles for such aggregates is better defined. Comparing the present burn time vs. particle size trends with those shown previously highlights the importance of properly assessing the size of burning particles for materials with such a complex morphology as boron.

Samples	Laser ignited in air		Combustion Products of Air- Acetylene flame		Combustion Products of Air- Hydrogen flame	
	Pre-	Exponent,	Pre-	Exponent,	Pre-	Exponent,
	exponent,	n	exponent,	n	exponent,	n
	а		а		a	
Boron	1.54	1.02	5.66	0.45	7.40	0.82
B-Fe	0.79	0.65	9.25	0.30	6.85	0.81
B-Co	1.59	0.60	6.83	0.34	7.82	0.28
B-Ni	1.67	0.75	7.21	0.35	6.72	0.55
B-Zr	3.89	0.86	8.45	0.39	10.43	0.38
B-Hf	0.79	0.90	3.97	0.45	4.08	0.58

Table 9.2 D- law Trend Fit Parameters for Doped and Un- doped Boron Composites Laser Ignited in Air and Burnt in the Products of Air- acetylene and Air- hydrogen Flames

The intensities of the filtered optical emissions from the PMTs were processed to determine the time- resolved particle combustion temperatures for each pulse. Particles were assumed to emit as gray bodies. Temperature measurements could not be made for particles burning in the air-acetylene and air-hydrogen flames generating strong background emission. Table 9.3 shows the average temperatures for particles burning in air. Two sets of emission pulses were processed separately: with the maximum signal to noise ratios exceeding 3 and 6. To reduce errors caused by weak emission, only a portion of each pulse was processed, for which the amplitude exceeded 90% of its maximum. All measured temperatures are grouped around the melting point of boron (2350 K).

Table 9.3 Average Combustion Temperatures for Particles of Different Materials Burning in Air

Material	Average temperature (K)		
	90% peak height, at S/N ratio 90% peak height, S/N		
	>6	>3	
Boron	2500±370	2400 <u>+</u> 370	
B-Fe	2400 <u>+</u> 530	2200±1080	
B-Co	2100±190	2100±260	
B-Ni	2300±250	2300 <u>+</u> 280	
B-Zr	2200±180	2100±220	
B-Hf	2300±230	2200±250	

9.6.3 Combustion of aerosolized powder clouds: effect of metal additives

Pressure traces recorded in CVE experiments are shown in Figure 9.9. In addition, corresponding dP/dt traces are shown. At time=0, the igniter is triggered. Many traces for the rate of pressure rise, dP/dt, show more than one peak. This could be associated with asymmetric shape of the propagating flame so that different parts of the flame front reach the vessel walls at different times.



Figure 9.9 Traces of pressure, P, and its time derivative, dP/dt, versus time for CVE experiments with different materials.

For CVE experiments with non-gas generating fuels, the ratio of the maximum pressure, P_{max} to the initial pressure before ignition, P_o , (P_{max}/P_o) is proportional to the combustion temperature. It is expected to be higher for samples burning more efficiently and generating more heat. The maximum rate of pressure rise, dP/dt_{max} is an indicator of the combustion rate. For a spherically symmetric flame, the time when dP/dt_{max} occurs signifies the instant when the flame front touches the vessel wall. For a flame with a finite thickness, the time when P_{max} occurs means that the rear end of the flame reached the vessel wall. Respectively, values of P_{max} , dP/dt_{max} , the times when P_{max} and dP/dt_{max} occur and the pressure at the instant when dP/dt_{max} occurs were obtained from traces shown in Figure

9.9. The results are averaged and summarized in Figure 9.10. Somewhat higher pressure ratios and pressures at the instant dP/dt_{max} occurs are observed for B-Fe, B-Co and B-Ni, suggesting greater combustion efficiencies for these materials. Higher rates of pressure rise are measured for B-Co and B-Ni. Surprisingly, lower rates of pressure rise are seen for B-Fe. Lower P_{max} and pressures at dP/dt_{max} are observed for B-Zr and B-Hf.

Similar trends are observed for pressures and times at dP/dt_{max} for different materials. Lower pressures correlate with shorter times. Interestingly, for B-Zr and B-Hf, it appears that dP/dt_{max} occurs nearly instantaneously following ignition. This suggests a very rapid initiation of most of the aerosolized powder; although its complete combustion occurs during a longer time.



Figure 9.10 Summary of time and pressure measurements for CVE experiments conducted with different materials.

To roughly assess efficiency of combustion in CVE experiments, pressures produced adiabatically by the present materials burning in a constant volume were calculated using NASA CEA code [1] accounting for the experimental powder mass, composition, and volume of the combustion vessel.Combustion efficiencies were calculated by comparing the experimental and calculated pressures.

In addition, the flame thickness, x_{th} for each aerosol was estimated as:

$$x_{th} = \frac{R_{bomb}}{t_{dP_{dt_{max}}}} \times \left(t_{P_{max}} - t_{dP_{dt_{max}}} \right)$$
(9.1)

where R_{bomb} is the radius of the vessel, $t_{dP/dt_{max}}$ and $t_{P_{max}}$ are respectively times when dP/dt_{max} and P_{max} are observed. The results are presented in Table 9.4. The calculated pressures are all close to 10 atm. The efficiencies for B-Fe and B-Co are just slightly higher than for boron. Lower efficiencies are noted for B-Zr and B-Hf. The flame thickness for B, B-Fe, B-Ni, and B-Co is close to the vessel radius. It effectively means that the particles ignited at the center of the propagating flame do not have the time to burn out before the flame reaches the vessel walls. Unreasonably large flame thicknesses are estimated for B-Zr and B-Hf, probably indicating that this simplified processing is inappropriate for the present experiments.

Samples	P _{max} , atm	P _{ad} , atm	Combustion Efficiency, %	Flame thickness x _{th} ,
				m
Boron	5.40 ± 0.20	9.97	54 ± 2.1	0.30 ± 0.24
B-Fe	5.70 ± 0.21	9.95	57 ± 2.1	0.20 ± 0.08
B-Co	5.60 ± 0.22	9.94	57 ± 2.3	0.19 ± 0.04
B-Ni	5.50 ± 0.69	9.95	55 ± 6.9	0.14 ± 0.03
B-Hf	5.00 ± 0.55	10.02	50 ± 5.5	3.10 ± 1.80
B-Zr	4.90 ± 0.70	10.02	49 ± 7.0	4.80 ± 5.30

Table 9.4 Estimated Combustion Efficiency and Flame Thickness for Different Materials

 Ignited in CVE Experiments

9.6.4 Powder particle structure and morphology: effect of PCA for B-Fe

SEM images of B-Fe composites prepared with acetonitrile, stearic acid and hexane as PCA are shown in Figure 9.11. The images show that all milled samples have similar particle morphology. They had loose, small fractal aggregates (like boron) as well as larger, more rounded composites. The higher magnification images stacked below for each corresponding composite show that iron appears to be homogenously mixed throughout boron aggregates for all samples. In samples milled with hexane and stearic acid, iron inclusions appear to be finer than in the sample milled with acetonitrile.



Figure 9.11 SEM images of iron- doped composites milled in varying PCAs.

The particle size distributions for powders fed through the feeder and analyzed from processing SEM images are shown in Figure 9.12. All distributions are bimodal. Milling with hexane results in a shift to smaller aggregate sizes. The effect is less noticeable for the sample milled with stearic acid. For the sample milled with acetonitrile, the size distribution becomes broader. Based on the double lognormal fits, there is no significant difference among the particle sizes for different materials.



Figure 9.12 Particle size distributions for boron and B-Fe powders prepared using different PCAs and passed through the feeder.

XRD patterns for B-Fe samples milled with varying PCAs are shown in Figure 9.13. In all cases, weak peaks of boron are visible at lower diffraction angles. For samples milled with stearic acid and hexane, hydrated boron oxide is clearly detected. Its peak is absent for the sample milled with acetonitrile, suggesting that the hydrated boron oxide was removed, consistently with [140, 141]. At higher angles, strong diffraction peaks of iron are visible for the composites prepared with acetonitrile and hexane; iron peaks are much reduced for the sample milled with stearic acid. This suggests an effective reduction in the iron crystallite sizes in the latter case.



Figure 9.13 X-ray diffraction patterns for B-Fe samples milled in varying PCAs.

9.6.5 Single particle combustion experiments: effect of PCA for B-Fe

Figure 9.14 shows characteristic optical emission traces filtered at 700 nm for single boron and B-Fe particles laser ignited in air. The emission profiles show that boron and B-Fe milled with stearic acid have double peaks. The second peaks are smaller than the first ones; they also appear to be weaker for B-Fe. For B-Fe milled with hexane and acetonitrile, there was one sharp peak, after which the signals decayed slowly, but did not show second peaks.



Figure 9.14 700 nm filtered particle emission traces for boron and B-Fe powders prepared using different PCAs and burning in air.

Burn times measured from the width of the emission pulses of burning particles were processed to produce the number-based frequency histograms shown in Figure 9.16. A vertical dashed line shows the average time for boron. All histograms for B-Fe shift to shorter burn times. The composites milled with acetonitrile and stearic acid have narrower distributions. Double log-normal fits are shown as dashed lines.


Figure 9.15 Burn time distributions for boron and B-Fe powders milled using different PCAs and burning in air.

The lognormal fits of the particle size distribution (Figure 9.12) and burn time distributions (Figure 9.15) were correlated to yield relationships of burn times vs. particle sizes shown in Figure 9.16. All B-Fe powders have shorter burn times than boron. The shortest burn times are measured for B-Fe milled with acetonitrile.



Figure 9.16 Burn times in air vs. particle size trends for boron and B-Fe powders milled with different PCAs.

Average combustion temperatures of B-Fe samples milled using acetonitrile and stearic acid determined as described above (see Table 9.3 and respective text) were similar to each other. Both temperatures were close to 2600 ± 400 K, i.e., slightly higher than temperatures for boron and for B-Fe milled using hexane.

9.6.6 Combustion of aerosolized powder clouds: effect of PCA for B-Fe

A summary similar to that shown in Figure 9.10 is shown in Figure 9.17 for boron and B-Fe powders milled with different PCAs. Iron- doped samples milled with acetonitrile and hexane have slightly higher pressure ratios (P_{max}/P_0) and higher pressures recorded at the maximum of the rate of the pressure rise ($P_{dPdtmax}$) compared to boron. The sample milled with stearic acid performed poorly. It had the lowest pressures recorded and the lowest combustion efficiency (see Table 9.5). It also had the lowest values for the maximum rate of the pressure rise, dP/dt_{max} , although the rate of pressure rise peaked for it rather early, showing a very short respective time to dP/dt_{max} . Similar to B-Zr and B-Hf, parameters for B-Fe milled with stearic acid imply an unrealistically large flame thickness (Table 9.5).



Figure 9.17 Summary of time and pressure measurements for CVE experiments conducted with boron and B-Fe milled using different PCAs.

 Table 9.5 Flame Thickness and Combustion Efficiencies of Boron- Iron Composites Milled in

 Varying PCAs

Samples	Combustion	Flame thickness,	
	efficiency, %	$\mathbf{x}_{\mathrm{th}}\left(\mathbf{m} ight)$	
B-Fe _{hex}	57 ± 2.10	0.17 ± 0.08	
B-Fe _{acn}	56 ± 1.70	0.12 ± 0.04	
B-Fest. acid	39 ± 1.50	6.10 ± 3.35	

9.7 Discussion

9.7.1 Particle morphology

Boron, having Mohs hardness of about 9.5, is harder than all metal additives used here, for which Mohs hardness is around 4 -5.5. This may explain the relative insensitivity of the observed morphologies of the prepared composites to the specific metal additive or to PCA

used. It appears that milling leads to break up of the boron aggregates, while primary boron particles remain intact. Conversely, powders of metal additives are refined. Continuous milling leads to re-agglomeration of boron primary particles. The newly formed boron agglomerates contain embedded refined particles of metal additives. The embedded softer metal additives may also act as a binder for boron, explaining formation of larger, rounded compacts observed in all milled materials.

9.7.2 Effect of metal additive on combustion of composite powders

Combustion of composite powders was characterized in two experiments, using single particles and CVE. In hindsight, results of CVE experiments may be affected by many more factors than single particle combustion tests, and thus interpretation of CVE experiments is quite difficult. In single particle combustion experiments, the information is retrieved from the optical emission signatures of burning particles, produced when particles reach sufficiently high temperatures to become incandescent, e.g., this information is relevant for so-called full-fledged combustion. Conversely, in CVE the information comes from pressure traces, affected by both ignition and combustion of powders. Additionally, CVE experiments involved fuel-rich environments in order to achieve reliable ignition. However, this means that gas phase transport of oxygen to burning particles could have been rate-limiting, making it difficult to identify effects associated with heterogeneous combustion kinetics. Finally, effects of possible asymmetry in the flame front propagating inside the closed vessel make it difficult to interpret the pressure traces; these effects are particularly strong for cases when the flame front is thick as is appears to be the case with the present materials. Thus, although the CVE experiments

were performed and the results are reported, the discussion here should be limited to considering results of single particle combustion experiments.

From Figure 9.8, it is apparent that B-Hf powders exhibit shortest burn times implying the most significant improvement over boron in all oxidizing environments. Considering respective particle size (Figure 9.2) and burn time (Figure 9.7) distributions, it is apparent that the effect is due to somewhat coarser composite powders exhibiting the same or slightly shorter burn times in all experiments. It was noted that in air-acetylene and air-hydrogen flames, B-Hf particles ignite later (Figure 9.4). They could have burned faster because some air mixed in with the flame combustion products at greater heights above the flame. However, a delayed ignition was also observed for B-Zr, for which no significant improvement in the particle burn rates was noted. It can thus be concluded that adding hafnium accelerates combustion of boron. Further work is needed to understand this effect. The following processes need to be considered. Both Zr and Hf readily react with boron forming respective borides. This is an exothermic reaction, which can proceed quite rapidly in the milled materials, where mixing between elements is intimate. Considering borides as intermediate products compared to boron and metal oxides, it is possible that formation of such borides actually delays full-fledged combustion, in which the oxides are formed. This could explain why the streaks of B-Zr and B-Hf particles were detected at greater heights than for other metals. When full-fledged combustion begins, different intermediate products can be formed in different environments. If HfO₂ is formed, it is unlikely to be reduced by boron; however, solutions of nitrogen and oxygen (or both) in hafnium can also form, which could be less stable in presence of boron. In air-hydrogen flame, more complex compounds involving hydrogen can form and react with boron. In air-acetylene flame, even more complex compounds involving carbon, nitrogen and hydrogen can form. Respective phase equilibria need to be considered in order to propose a combustion mechanism for B-Hf composites in different environments. A difference between the effects of Zr and Hf, which are chemically similar to each other might be associated with the difference in their respective melting points. The melting point of Zr (2128 K) is slightly lower than that of B (2350 K). Conversely, melting point of Hf is slightly higher (2506 K). This could lead to formation of difficult to reduce ZrO₂ before full-fledged boron combustion begins; however, formation of stable HfO₂ can be delayed.

The present results show that adding Co and Ni do not lead to an appreciable acceleration in boron combustion. Unlike Fe, both Ni and Co do not form multiple oxidative states. Instead, only stable CoO and NiO are known. For Fe, capable of forming FeO, Fe₃O₄, Fe₂O₃, it is deemed more likely to form a metastable oxidized intermediate that is readily reduced by boron. This may explain why B-Fe shows accelerated combustion in air; the effect of added iron in this case is comparable to that of hafnium. However, in both air-hydrogen and air-acetylene flames, the effect of iron additive diminishes. Iron is less chemically aggressive than hafnium, and thus may not be readily reacting with H₂O, CO, and CO₂ comprising primary gas phase oxidizers in these cases.

9.7.3 Effect of PCA used to prepare B-Fe composites on combustion

Powders milled with both stearic acid and acetonitrile showed a greater improvement in boron combustion rates compared to B-Fe prepared using hexane (Figure 9.16). The increase in temperature measured for both B-Fe samples prepared using stearic acid and acetonitrile is consistent with the greater burn rate for these materials. The improvement in the burn rate seen in Figure 9.16 is clearly associated with shorter measured burn times

shown in Figure 9.15, despite similar particle size distributions (Figure 9.12). As shown in Figure 9.13, PCA noticeably affects both composition and structure of the prepared composites. The sample prepared with stearic acid has significantly reduced iron crystallites, so that many fine iron inclusions that are not clearly visible in SEM images were likely formed. In other words, in this sample iron could have been distributed more homogeneously in the boron agglomerates after milling. For the material milled with acetonitrile, removal of boric acid is the most noticed feature seen in Figure 9.13. This should help with ignition of composite particles but is not expected to affect the fullfledged combustion. Iron peaks are also broadened and reduced, suggesting a greater refinement of iron compared to the sample milled with hexane. This observation is in apparent conflict with SEM images (Figure 9.11), showing what appear to be larger iron inclusions in the sample milled with acetonitrile. However, iron particles in this case could have been flattened, so they appear larger in SEM images, where thickness of particles is not detectable. Indeed, effect of acetonitrile as PCA leading to formation of ultrafine metal particles was observed for other metals [215]; its relevance for iron needs additional investigation. XRD is a more reliable tool for bulk assessment of crystallite sizes, and it suggests a greater refinement of iron for samples milled with acetonitrile compared to those prepared using hexane.

Therefore, it can be concluded that a greater refinement of iron inclusions leads to a stronger effect of iron on boron combustion. To further understand the effect of each PCA, it may be useful to consider chemical modification of the powder surfaces caused in each case. Stearic acid is likely to form carbides at the particle surfaces; a small amount of oxygen contained in PCA could also lead to formation of some oxides. Conversely, acetonitrile is more likely to lead to formation of metal-nitrogen compounds, which are readily decomposed in presence of oxygen. This might further strengthen the effect of acetonitrile as PCA when preparing B-Fe composites.

9.8 Conclusions

Comparisons of particle combustion characteristics for a range of boron-based composite powders prepared by high energy milling with 5 wt % of additives of Fe, Co, Ni, Zr, and Hf suggest that Hf leads to the most significant acceleration of combustion compared to boron. A positive effect of Hf as an additive is noted in different oxidizing environments, including air and combustion products of air-acetylene and air-hydrogen flames. Adding Fe leads to an improved burn rate in air; however, there is no clear advantage in other oxidizing environments. Other metal additives do not lead to accelerated burn rates for composite powder particles. Preparing B-Fe composites using different process control agents during milling suggests that when acetonitrile and stearic acid were used, a greater iron refinement was achieved compared to milling using hexane. A greater refinement of iron led to a stronger acceleration in the burn rates of prepared powders particles in air. The accelerated burn rates were accompanied by slight increase in the measured particle temperatures. Although experiments reported here include both single particle and aerosolized cloud configurations, only single particle experiments were considered to draw the present conclusions. It is suggested that the results of cloud combustion experiments were affected by too many parameters and processes making it difficult to offer their meaningful interpretation.

CHAPTER 10

CONCLUSIONS AND FUTURE WORK

10.1 Conclusions

Combustion and ignition characteristics of micron- sized boron powders were explored in varying oxidizing environments in an effort to establish relevant data to improve the understanding of boron reaction mechanisms that occur during combustion. The study comprised of exploring different strategies to modify boron powders to attain higher burn rates and shorter ignition delays, while maintaining boron's thermochemical properties, stability and safety. In fulfillment of the research objectives, modified materials were prepared and tested and a kinetic model was developed, which accounted for the complex geometry of boron aggregates. The model was found to be applicable for describing high-temperature combustion in air, provided that the structure of boron is accounted for during combustion.

Chapter 2 introduced the experimental methodology used to determine single boron particle combustion characteristics based on optical emission of burning particles. It was developed to allow for direct accounting for a particle size distribution of fine boron particles while interpreting particle combustion experiments. The technique began measuring and correcting for the fractal dimension of boron aggregates fed into the combustion system. Effectively described by CFD modeling, both flame environments provided temperatures over 2200 K and primarily CO₂ and H₂O as oxidizers for boron combustion. This led to burn times as a function of particle size, which could be described by a power law with an exponent of 0.75. Boron particles burned at 2600- 2800 K and fullfledged boron combustion in the products of pre- mixed hydrocarbon flames occurred in two stages.

In Chapter 3, inhibiting hydrated oxide layers were readily removed from the surface of boron powders by washing them in acetonitrile. Further treatment was done to effectively remove the solvent by rinsing with toluene and hexane. This surface modification leads to a stable powder with a protective surface, which has shorter ignition delays, compared to boron when injected in the products of an air- acetylene flame. However, full-fledged combustion was unaffected by the processing and remained slow.

To target improving boron surface reactions for combustion, 5wt% transition metal composites with boron were prepared by mechanical milling. The results are discussed in Chapters 4 and 9. Each composite particle contained nano- sized transition metal inclusions embedded in boron agglomerates. The materials were burned in the combustion products of air- acetylene and air- hydrogen flames and in air. For boron, double peak emissions were observed in all environments; each peak had sufficiently high temperatures for full-fledged combustion. In order to describe the double peaks pattern observed, a mechanism for the two-staged full-fledged combustion of boron is proposed in Chapter 5 based on previously published results and recent B-O and B-N phase diagrams. During combustion, in the first stage, a boron rich, B- O-N solution is formed. The second stages occurs when the liquid becomes saturated and undergoes through a phase change. A vapor- phase reaction zone also forms during the second stage. Combustion ends when the composition of the burning particle becomes close to that of B₂O₃. However, doped boron composites produced single peak emissions, with lower intensities, likely due to suppressed vapor

reactions. The measured flame temperatures of the composites remain similar to that of boron.

The effect of particle size on burn time was characterized for all materials and environments. Overall, the greatest acceleration of combustion (shorter burn times) compared to boron in all three environments was observed for hafnium- doped boron particles. For boron-iron composite particles, the burn times were markedly reduced only in air. The effect of other transition metals (Co, Ni and Zr) was negligible. Preparing B-Fe composites using different process control agents suggest that when acetonitrile and stearic acid are used, a greater iron refinement is achieved, which leads to shorter burn times and higher combustion temperatures in air.

A technique that is less- energy intensive than milling was explored for introducing iron into boron aggregates using thermal decomposition of iron pentacarbonyl in a dodecane/ surfactant mixture in an argon environment. In Chapters 5 and 8, the effectiveness of doping varying boron materials at different temperatures is presented. Chapter 8 also presented the impact of washing and purity of boron particles on combustion. All boron (doped or un-doped) materials ignited at approximately 9W of CO₂ laser energy. Differences in low- temperature oxidation kinetics might have been offset by variances in the laser absorptivity. During combustion, two stage patterns were detected for longer emission pulses produced by the particles burning in air. The patterns became difficult to resolve for the shorter burn times. Higher purity (99%) boron particles burn faster. The reduction in oxidative performance of commercial 95% pure boron is due to the impurities present, which compete with boron for oxygen and form stable oxides. Acetonitrile washing does not appreciably change the burn time of boron in air, but burning

particles produce brighter emission during the second stage, oscillatory emission patterns and forms nitride caps on their surface. The iron- pentacarbonyl decomposition technique produced particles containing iron, coated on the surface of the boron aggregates. Higher decomposition temperatures result in higher doped iron concentrations. The particle sizes and morphologies of boron aggregates were largely unaffected by the presence of iron. Doping by this methodology was effective for commercial 95% pure boron, but less effective for washed and 99% pure boron powders, due to preferential formation of iron in the presence of surface hydroxyl groups. At higher concentrations, iron particles aggregated affecting the homogeneity and distribution of iron on the boron surface. Overall, iron- doped boron powders burned faster and at higher temperatures than un-doped boron; the effect appeared to scale with the amount of iron present. The increase in the burn rate and temperature of B-Fe composites are consistent with the proposed reaction mechanism in which iron serves as a shuttle catalyst. In that mechanism, it is proposed that iron is oxidized by external oxygen and then reduced by boron. The reaction between boron and oxidized iron complexes occurs in condensed phase; bypass the formation of gas phase sub-oxides and generates directly condensed products, which approach the composition of stoichiometric B_2O_3 . This results in accelerating the transition to the second stage combustion.

Finally, in Chapters 6 and 7, experimental TG traces of commercial 95% pure boron powders treated with acetonitrile and water are used to describe the heterogeneous oxidation of boron aggregates with characteristically complex morphologies. In chapter 6, oxidation of two batches of boron powders with distinct but overlapping particle size distribution was characterized experimentally. It was shown that boron oxidation can be described considering boron aggregates as spheres with impenetrable cores and reactive porous shells with an initial thickness of 1.28 µm. The shells are composed of closely packed primary particles with 160 nm diameter. For 95% pure boron powder, this approach was found to remain valid up until the oxide layer thickness reaches 15 nm. A similar approach is proposed as useful for describing a broader range of heterogeneous reactions involving porous and irregularly shaped aggregates. In Chapter 7, using the porous shell/solid core geometry, a description of kinetics of low-temperature oxidation of boron powders was offered. The model derived kinetic parameters considering oxidation of primary particles comprising the reactive shell. At early stages (less than 5 nm oxide thickness), the activation energy, $E=148\pm 6$ kJ/mol and the pre-exponent factor $k \cdot$ $f(m_{PP}) = 1.29 \times 10^6 s^{-1}$ describe the reaction. The same kinetic description was shown to predict the rate of full-fledged combustion of fine boron particles at conditions when the gas- phase oxygen transport to the particle surface is not rate limiting. The burn rates were obtained using measured particle burn times in air in an experiment using a CO_2 laser beam to ignite the particles. As previously, the burn times were correlated to particle sizes, which have been corrected for fractal dimension accounting for intermediate overlapping by diffusion limited cluster aggregation. Burn rates were calculated for the cases of aggregates coalescing into a solid sphere upon melting and assuming that particles maintain their porous aggregate structure. In both cases, the model predictions indicate that the particle surface temperature varies between 3500- 4500 K. Quenched products collected indicate that some boron aggregates coalesce upon melting forming, single spherical droplets, while others retain their initial structure.

10.2 Future Work

This work has addressed single boron particle combustion primarily based on optical emissions. However, as discussed, these techniques are heavily biased to the particle spectral characteristics, which are not well known and the potential of smoke particles generated may obscure the particle emission profile. It would be therefore interesting to explore other experimental setups (including high speed imaging) and further optical processing to measure in-situ particle combustion characteristics and phase composition of molten boron droplet on a µm and microsecond resolution. This will help in improving the understanding of the double peak pattern and two-stage reaction mechanism. This work could also aid in further describing the complex morphology change that occurs during combustion. Other bulk studies are also required to account for particle – particle interaction during combustion, so as to better describe the effect of transition metal dopants in similar combustion scenarios as desired applications.

FTIR, TEM and XPS techniques would be useful to further characterize boron powders modified by acetonitrile. The results of these analyses will aid in determining the nature and composition of the surface functionalization and thickness of the resulting oxide/ hydrocarbon layer produced. A conclusion on the detailed mechanism by which boron particles are protected at low temperatures could then be presented. Other potential hydrocarbons for functionalizing boron surface could also be explored to impact not only ignition but combustion as well.

Because the primary modification to boron particles tackles surface reactions, it would be desired to explore the reaction kinetics of doped boron materials in comparison to the commercial material. This step could include non- isothermal thermo-gravimetric analyses as well as customized high-temperature experiments in an oxidizing environment that is altered to change the heat transfer mechanism (for example: O_2/N_2 , O_2/H_2 and O_2/Ar) during combustion. Furthermore, the work thus far with doped materials have only focused on combustion and could be extended to understanding the role of the dopants for ignition, whether by measuring ignition temperatures and delays.

APPENDIX A

CORRELATION BETWEEN INTENSITY AND DURATIONS OF PARTICLE EMISSION PEAKS

The correlations shown in Figure A.1 are for boron particles burned in products of airacetylene flames at varying equivalence ratios. Despite a large variance, the general trend observed indicates that the intensities of the particle emissions increase as the burn time increases.



Figure A.1 Burn times vs intensity of particle emission peaks for amorphous boron in air acetylene flame.

APPENDIX B

FLAME CONE HEIGHT AND ANGLE FOR CFD MODEL OF PRE-MIXED HYDROCARBON FLAME

It was assumed that a ring-like cone-shaped flame was produced from the annulus of the burner nozzle. The flame is assumed to form a Bunsen cone. The dimensions of the cone correlate with the flame speed.

The following example illustrates how the cone height and angle are calculated.

Assume the flame speed, $S_L = 100$ cm/s and a preheated unburned gas velocity, $u_b = 927.5$ cm/s at 450 K. The cone angle, α , is

$$\alpha = \sin\left(\frac{S_L}{u_b}\right) = \sin\left(\frac{100}{927.5}\right) = 0.108 \ rad \tag{B.1}$$

The corresponding combustion products velocities were obtained calculating their radial and axial components, labeler with subscripts *r* and *z*, respectively. For a flame with the adiabatic temperature T= 2144.2 K and the initial gas temperature of T_0 =450 K, the corresponding velocities are:

$$V_{r} = \left(S_{L}\left(\frac{T}{T_{o}}\right)\cos\alpha\right) + \left(u_{b}\cos\alpha\sin\alpha\right) = 5.73\frac{m}{s}$$
(B.2)

$$V_{z} = \left(S_{L}\left(\frac{T}{T_{o}}\right)\sin\alpha\right) + \left(u_{b}\cos\alpha\right) = 9.73\frac{m}{s}$$
(B.3)

The height of the cone was determined from the flame speed, S_L and unburnt gas velocity, u_b , the cone angle, α and the difference of the radii of the inner and outer burner tubes, r and R:

$$h_{cone} = \sqrt{\left(\left(\frac{u_b}{S_L}\right)^2 - 1\right) \times \left(\frac{\left(R - r\right)^2}{4}\right)} = 4.88 \ mm$$
(B.4)

APPENDIX C

COMPUTATIONAL FLUID DYNAMICS MODEL FOR AIR-HYDROGEN DIFFUSION FLAME

The environment in which boron particles and boron- iron composites were exposed to during the experiment is characterized using a Computational Fluid Dynamics (CFD) simulation of a jet diffusion air-hydrogen flame. The model described mixing of combustion products of the flame with stationary surrounding air accounting for an auxiliary central nitrogen jet that was used as the carrier gas in the system and additional oxygen flow from an outer annulus. The simulation was solved using COMSOL Multiphysics software version 5.3.

C.1 Model Setup and Assumptions

The model considered diffusion of equilibrium combustion products of the air-hydrogen flame at the adiabatic flame temperature and room-temperature nitrogen gas (particle carrier jet), into surrounding air. It also considered transport of hydrogen (H₂) fed from the burner tip annulus and oxygen (O₂) fed to the flame region, according to the experimental configuration. The configuration represented in the model is shown in Figure C.1.

No chemical reactions were considered. Initial temperature and composition of the air-hydrogen flame combustion products were described based on preliminary thermodynamic equilibrium calculations using NASA CEA code. The model assumed all species to behave as ideal gases. The compressible flow was modeled with a Mach value less than 0.3. The results from the CEA calculations are detailed in Table C.1.

The flame was assumed to form a cylindrical cone surrounding the central tube feeding the particle laden nitrogen flow. The assumed cylindrical symmetry enabled us to consider a 2-D model. To simplify analysis, only four most abundant gas species were accounted for: H₂O, H₂, N₂, and O₂. The focus was to establish when O₂ is mixed with H₂O to become a dominant oxidizer for boron particles.

Based on flame images and preliminary iterative CFD modeling of the mixing of hydrogen with air, it was assumed that the flame could be represented by an open cone, shown in Figure C.1. Combustion products at the adiabatic flame temperature were injected in air from that cone. To initially obtain the flame cone location, a preliminary calculation considered room temperature hydrogen, nitrogen and oxygen flowing into the computational domain and mixing with surrounding air. It was assumed that the flame front would form at the region where the mole ratio of hydrogen to oxygen was stoichiometric. At that location, a flame front at the adiabatic flame temperature was then imposed as a boundary condition in the model. Several subsequent iterations were done to further adjust the flame location.

The cone dimensions (height and radius) were adjusted to fit the calculated vertical temperature profiles to their respective experimental values, as shown in Figure 4.7. Thermal expansion and the effect of gravity were also accounted for. Radiation was neglected.



Figure C.1 Schematic diagram of the computational domain; dimensions in mm.

The model coupled calculated heat, momentum and mass transport. It accounted for changes in heat and flow properties as temperature and concentration of the species varied throughout the domain. Following related earlier work for jets and flames, the turbulence effects were modeled using Reynolds averaged Navier-Stokes k- ω shear stress transport turbulence approach [121, 122]. It was assumed that the species transport and all heat transfer were by convection throughout the fluid. The simulation was done under steady state conditions. In all simulations, the convergence was achieved when residuals stabilized at values below 10^{-4} for each segregated group of independent variables; a similar criterion was used recently describing an H₂/O₂ flame [123, 142].

The surrounding air, the central pure nitrogen and oxygen auxiliary flows were assumed to be at room temperature (298.15 K). At the boundary representing the flame cone, the hydrogen flow and diffusing oxygen from surroundings were converted into the respective combustion products (see Table 4.1) at the adiabatic flame temperature. The inner boundary of the cone was defined by linear gradients of concentration of hydrogen and temperature from feed conditions (4.5×10^{-2} molm⁻³, 298 K) to combustion product conditions (2.2×10^{-8} molm⁻³, 2409 K). A summary of the boundary conditions used is shown in Table A3.1.

The mesh was developed based on a COMSOL Multiphysics defined mesh that favored fluid dynamics. The smallest, 15 μ m, elements were located near the tip of the flame cone. The largest, 1.3 mm elements were considered away from the flame, at the open boundaries. The mesh was refined based on results of preliminary calculations with varied configurations to ensure the independence of the final results on small changes in the mesh element dimensions.

Boundary Condition	Physics		
	Turbulent k-ω Transport	Heat Transfer in Fluids	Transport of Dilute Species
Axial Symmetry	-	-	-
Carrier Gas Inlet	3.65 ms ⁻¹	298 K	$C_{N2} = 0.044 \text{ mol} \cdot \text{m}^{-3}$
Combustion Products	Vz=0.105ms-1		$C_{O2} = 4.5 \times 10^{-5} \text{ mol} \cdot \text{m}^{-3}$
Inlet (flame cone)	V _r =0.270ms ⁻¹	2409 K	$\begin{array}{l} C_{\rm H2} = 2.3 x 10^{-4} \ mol \cdot m^{-3} \\ C_{\rm H20} = 3.8 x 10^{-3} \ mol \cdot m^{-3} \\ C_{\rm N2} = 7.5 x 10^{-3} \ mol m^{-3} \end{array}$
Inner Cone boundary – Hydrogen gradient	0.410ms ⁻¹	T= 298 K-2409 K for linear height change from 0 m - 0.018m	$C_{H2}=4.5 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}-2.2 \times 10^{-8} \text{ mol} \cdot \text{m}^{-3} \text{ for}$ linear height change from 0 m-0.018 m
Open Boundary- Surrounding Air	Normal Stress =0	298.15 K	$\begin{array}{l} C_{H2} = 2.2 \times 10^{-8} mol \cdot m^{-3} \\ C_{O2} = 9.4 \times 10^{-3} mol \cdot m^{-3} \\ C_{H2O} = 1.8 \times 10^{-4} mol \cdot m^{-3} \\ C_{N2} = 3.5 \times 10^{-2} mol \cdot m^{-3} \end{array}$
Walls	Wall functions	Thermal insulation	No flux

Table C.1 Boundary Conditions used for COMSOL Flame Modeling air- hydrogen flame

C.2 CFD Results

Following an earlier approach [123, 142], the temperature profile predicted by the CFD calculations were compared to those obtained experimentally. Results are shown in Figure 4.7. Based on the minimum discrepancy between the predicted and measured vertical temperature profile, the flame height and radius selected were 18 mm and 7 mm respectively.

Vertical concentration profiles of the species, N_2 , H_2 , O_2 and H_2O , are shown in Figure 4.7 along the flame's axis. The model predicts that at low heights close to the tip up to 10 mm, particles fed are primarily exposed to H_2 and N_2 . As they ascend beyond 20 mm, N_2 , O_2 and H_2O become the primary environment. The dominance of H_2O as a preferential oxidizer is short lived and ends within 35 mm above the burner tip, where most particles appeared to be burning. Model- calculated temperatures implied that the combustion products cool sharply from the adiabatic flame temperature up to 30 mm and then steadily declines as the height increases. Conversely, experimental data show an increase in the temperature at the heights of up to 5 mm, then a decline. This discrepancy may be indicative of the flame reaction.

Calculated radial profiles for the temperature and concentration at different heights are shown in Figure C.2. Temperatures remain higher (above 1500 K) at lower radial distances and steadily decline moving further away from the flame. At low heights (below 20 mm), temperatures appear to be initially low then steadily climb to a maximum before declining to room temperature. The gas compositions near the flame's axis remain mostly defined by excess nitrogen and water. The water concentration profile follows the temperature trends at each height. Concentration profiles for nitrogen show that an increase in the nitrogen concentration effectively coincides with the increase in concentrations of O₂, while H₂O decreases. The degree of mixing with external air extends to 30 mm away from the flame axis. Based on the observed locations of streaks produced by burning boron particles, combustion mostly occurred in that central zone of the flame, containing mostly water, remaining oxygen and nitrogen rather than oxygen from surrounding air.



Figure C.2 Calculated radial temperature and selected concentration profiles plotted for different heights above the burner for flame.

Similar temperature and concentrations trends are shown at varying radial distances from

the flame axis. At radial distance of 25 mm away, flame effects are negligible.



Figure C.3 Calculated vertical temperature and concentration profiles for different horizontal distances away from flame axis. Experimental values are shown as circles.

APPENDIX D

PARTICLE SIZE DISTRIBUTIONS OF DOPED AND UN-DOPED BORON POWDERS OBTAINED USING LOW ANGLE LASER LIGHT SCATTERING

The commercial reference sample, 95% pure boron and samples of the prepared materials by thermal decomposition of iron pentacarbonyl, (B-Fe190 and B-Fe125) were analyzed using a Mastersizer 3000 by Malvern Instruments. The system was equipped with a 120 mL Hydro MV wet dispersion unit. Samples of the materials were dispersed in hexane solvent and analyzed using He-Ne laser diffraction pattern for particle sizes from 10 nm to 3500 µm. The results from the analyses are shown in Figure D.1.



Figure D.1 Particle size distributions of boron and doped- boron materials by commercial laser scattering technique.

The results show that most aggregates measured have sizes ranging from 0.2 to 100 μ m. In the case of the doped boron samples, B-Fe 125 and B-Fe190, the size distributions seem to be unaffected by the temperature the iron pentacarbonyl was injected to the sample.

APPENDIX E

PARTICLE IDENTIFICATION FOR AUTOMATED SEM IMAGE PROCESSING FOR PARTICLE SIZE DISTRIBUTIONS

Preparing samples for these analyses is described in the article. The identification of particles from the collected images used the following image processing sequence. First, a Gaussian blur filter with sigma radius ranging between 1 to 2 pixels was applied, which was necessary to avoid identifying each particle in a boron agglomerate as an individual object. Filtering also eliminated pixel noise from the background by applying a convolution with a Gaussian function for smoothing the image. The image was then thresholded to distinguish the particle agglomerates from their carbon tape background. For each aggregate identified, the diameter equivalent to the area measured (assuming spherical shapes) was determined. The diameters were corrected by the fractal dimension (FD=1.8), determined using the box counting method [142]. An example of particle identification using image processing is shown in Figure E.1. Further details of processing are provided elsewhere [142]. A sample image of a group of particles is shown on the left. The zoomed in images of a selected particle thresholded before (image A) and after (image B) applying the Gaussian blur filter are shown for comparison. Without filtering, small fragments of the boron agglomerate were identified as individual particles; it is considered highly unlikely that such fragments will burn separately. When filtering was applied, the entire agglomerate was counted as one particle, which is how it is expected to burn.

Images with magnifications 500 x to 5000 x were used for collecting the particle size data to include a broad range of particle sizes. While the settings for automation were held constant, the threshold range had to be changed due to variances in the carbon tape background brightness and SEM settings used for imaging.



Figure E.1 SEM image of doped boron powder B-Fe125 obtained using secondary electrons for image processing with one of the particle agglomerates selected in a dashed rectangle to illustrate image processing.

Thresholded images of the selection are shown in images (A) and (B): (A.) Thresholded image without filtering, in which 7 separate particles are identified. (B.) Thresholded image after application of the Gaussian Blur filter, in which only one particle is identified.

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