Nanoenergetics by Plasma Processing

PennState
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**CHEMICAL
ENGINEERING**

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March, 25, 2020

Motivation

Jet Propellants

Volumetric Enthalpy of Combustion: 34 KJ/cc

How to extract more energy in volume limited propulsion systems?

Adding solid additives

Ojha et al. Progress in Aerospace Sciences 2018,100, 18-45.

Favorable size of solid additives?

Nanometer sized additives have distinct advantages

Key issue in using nanoparticles?

Poor Stability due to aggregation

Rapid
Settlement of
particles

Clogging of fuel
injection
systems

**Which solid additives have high potential in nanoenergetics?
&
How to control aggregation and other problems due to nanometer size?**

Boron nanoparticles (BNP) have drawn maximum attention of researchers to be used as additives

Dreizin E.L., Progress in engineering and Combustion Science, Vol 35 Issue 2, Pages 141-167, 2009

Highest volumetric & gravimetric enthalpy of combustion
(140 KJ/cc, 58 KJ/g)

Good choice for volume limited combustion systems

Volumetric combustion enthalpy of ethanol (KJ/cc)

Effect of Boron loading on Ethanol

10% loading

+19% in Energy density

Energetic potential of B can be harnessed in nanoparticulate form. But some **roadblocks** are there!

Various reduction methods are available in literature

Novelty - Non-thermal hydrogen plasma (HP) can be used to reduce native oxide layer from BNP

Previous work/Literature
Reduction of native oxide
from Cu, Ru, Ge, Si surfaces

Thermodynamic Feasibility
At low temperatures

Driving Force of Reduction
Highly reactive hydrogen atoms, ions &
vibrationally excited H_2 molecules

Advantages

- **Dry process.** Does Not involve many chemicals and post processing separations
- **By-product - Water vapor,** not an environmental threat

How to prevent re-oxidation after reduction of native oxide?

Surface modification for passivation & forming stable dispersions in fuels

Capping with Octyloxy groups

Pickering et al., RSC ChemComm, 2007

Surface Functionalization using Halogens

Bellott et al., RSC ChemComm, 2009

Capping with Silane

Meijie et al., Fuels, 2017

High energy Milling using oleic acid

Anderson et al., Energy & Fuels, 2009

Problems

Longer processing/separation
times/achieving both passivation &
stable dispersion

Both passivation and stable dispersions can be achieved by method developed by our lab

Plasma Enhanced Chemical Vapor Deposition (PECVD)

- Tailoring of coating chemistry
- Nanometer level control on coating thickness

- Water Contact Angle: 125°
- Passivation against air & humidity
- Can provide Improved dispersibility in liquid fuel

Goal – To combine HP reduction and PECVD passivation to produce energetically enhanced BNP

- To reduce native oxide
- To form a passivation barrier against air & moisture
- To form stable dispersions in jet propellants

Non-thermal plasma experimental setup

Components

- Vacuum Pump with LN trap
- RF generator with matching box
- Tubular Reactor
- Magnetic Stirrer
- Hydrogen Transport System
- Argon assisted precursor delivery system

Experimental Methods

Treatments

Non-thermal
Hydrogen Plasma

Different time periods
85 & 120 min

Plasma Enhanced
Chemical Vapor
Deposition

Constant time period
15 min

Average Particle Size
BNP: 70 nm

Operating Conditions

Non-thermal
Hydrogen Plasma

- RF Power = 40 W
- Pressure = ~100mTorr

Plasma Enhanced
Chemical Vapor
Deposition

- RF Power = 30 W
- Pressure = ~100 mTorr

Pressure

Characterization methods to get reduction, passivation & energy evidences

High Resolution TEM images give evidences about thickness of oxide layer & coating

Untreated BNP

PECVD (15) treated BNP

High Resolution TEM images suggested reduction of native oxide layer

HP(85) PECVD(15)

HP(120) PECVD(15)

STEM-EDS in HAADF shows evidence of reduction of atomic concentration of oxygen through elemental analysis

Quantitative Analysis is done by calculating relative atomic composition of Oxygen to Boron (O/B)

Without HP treatment

Summary of HAADF EDS Results

Treatments on Boron Nanoparticles (Time is shown in brackets in minutes)	O/B * 10 ⁻²
Untreated Sample	9.6
HP (85) PECVD (15)	2.5
HP (120) PECVD (15)	0.68

High Resolution XPS is done to extract quantitative information on the surface

Sampling Depth: ~10-15 nm

Untreated BNP; B^{+3} =12.4%

HP(120) PECVD(15) ; B^{+3} = 4.9%

Summary of XPS Results

Treatments on Boron Nanoparticles (Time is shown in brackets in minutes)	B ⁺³ Concentration (%)
Untreated Sample	12.74
HP (0) PECVD (15)	12.43
HP (85) PECVD (15)	8.79
HP (120) PECVD (15)	4.99

Weight change of untreated & plasma treated BNPs were measured & compared using TGA

Simultaneous DSC|TGA

Method

- Heating Rate: 30°C/min from ~25°C to 1400°C
- Oxidizer used: Air (100ml/min)

Gravimetric Energy density of untreated & plasma treated BNPs were measured & compared using DSC

Simultaneous DSC|TGA

Method

- Heating Rate: 30°C/min from ~25°C to 1400°C
- Oxidizer used: Air (100ml/min)

Summary of DSC Results

Treatments on Boron Nanoparticles (Time is shown in brackets in minutes)	Enthalpy of Combustion (KJ/g) with error of +/- 2%	% Increase with respect to the reference (untreated BNP)
Untreated Sample	24.69	0 (Reference)
HP (0) PECVD (15)	25.62	+3.7
HP (85) PECVD (15)	27.90	+13
HP (120) PECVD (15)	29.42	+19

Summary

- Developed unique in-situ method of non-thermal plasma reduction + passivation of BNP

- Significant reduction in native oxide layer (diffusion barrier for oxidizer)
- Formation of passivation barrier which is preventing re-oxidation for at least 2 months

- Enhanced gravimetric energy density of BNP as a result of oxide layer reduction

Acknowledgements

Dr. Themis Matsoukas

Dr. Rob Rioux

Toni & Troy (TT)