Metal Particle Combustion

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Purdue Energetics Research Center

Metal Particle Combustion

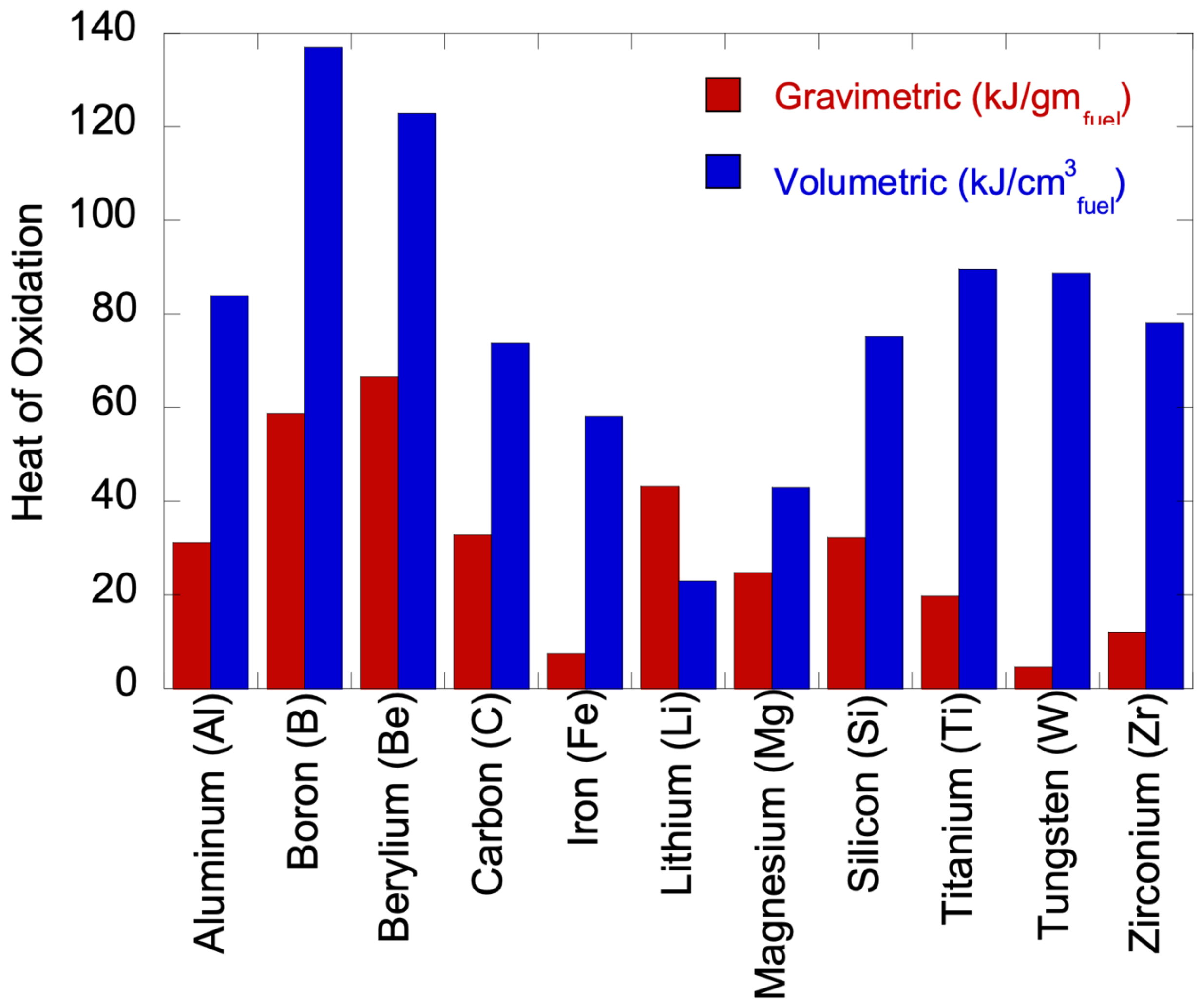
- Metals (mostly Al) are ubiquitous in propellants, explosives, solid fuels (for example for hypersonics), and pyrotechnics (igniters, countermeasures, etc.)
- Could metals also be used in energy storage and transportation?
  - That is, metals as energy mediums?
  - McGill University has explored this some
  - Netherlands and other are researching this also
- Alloys and composite particles could significantly improve each of these areas (see Son (2024))

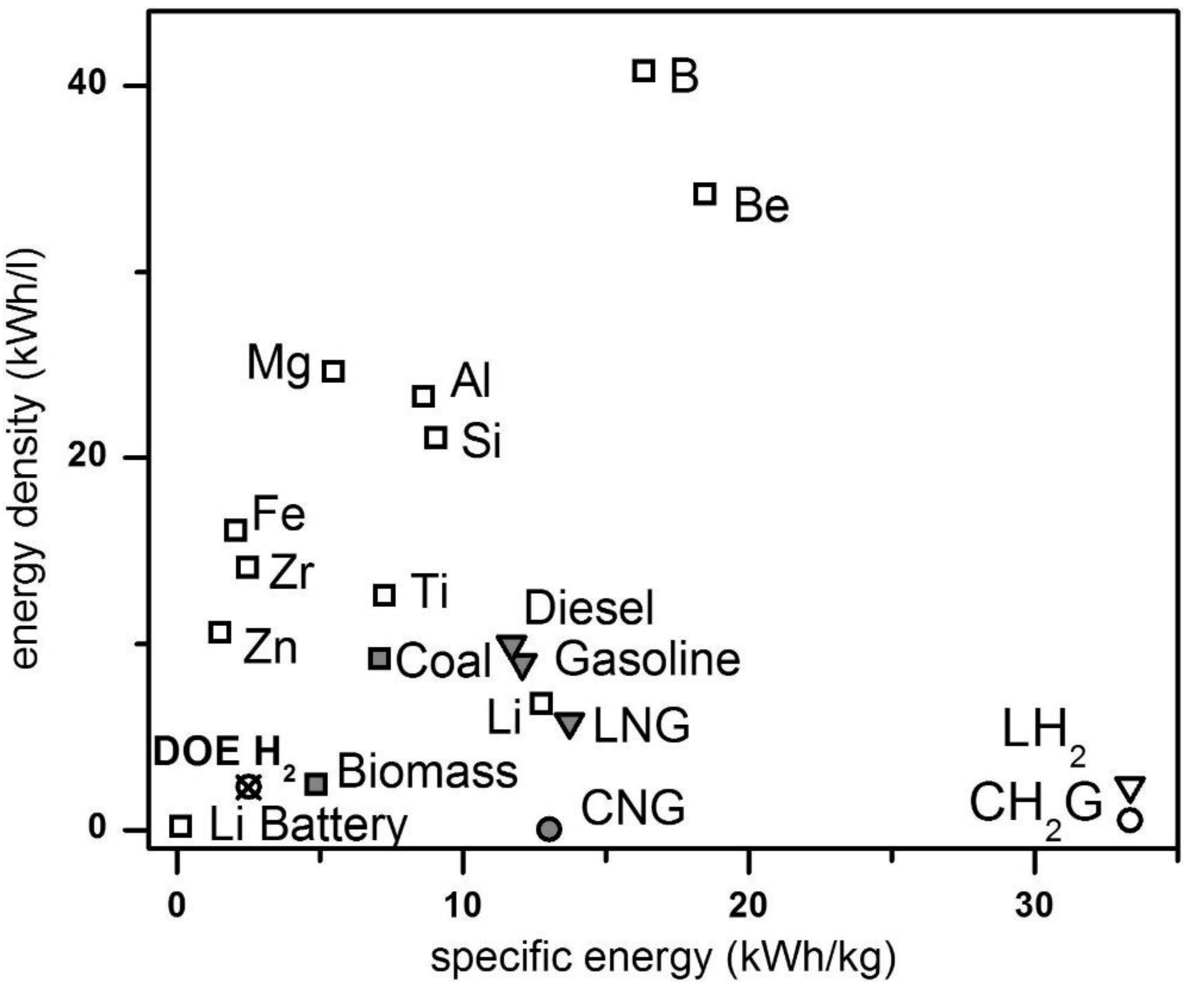
Son (2024) “Opportunities in Engineering Energetic Materials”

Metal Particle Hazards

- Pyrophoricity
  - Some metals react on contact with air
  - Passivation, coatings and protective polymers can mitigate this
- Dust explosions
  - Hazards are similar to other solid fuel particle
  - Mitigations are similar also (must minimize accumulation, dispersion and ignition)
- Electrostatic discharge (ESD)
  - Some (mainly nanoscale metal particles are ESD sensitive
- Most of our work is not on safety

Heats of Oxidation of Several Materials



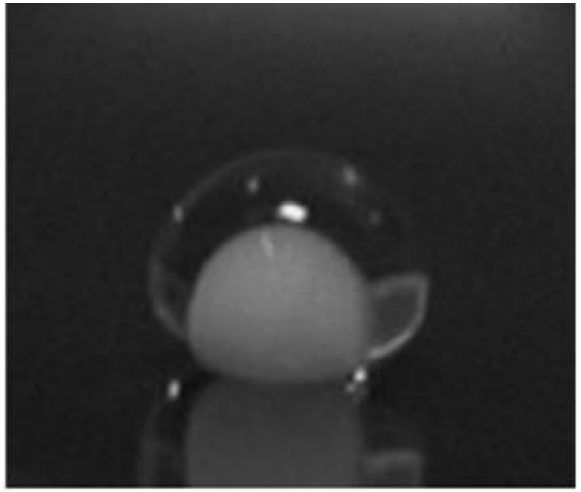


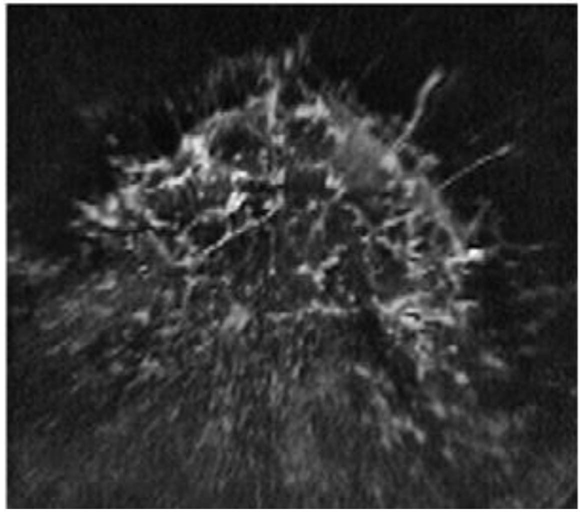
Neat Aluminum Propellant

(1000 fps, 10 μs exposure)

Metal agglomeration in propellants is an ongoing problem!

Emulsion Microexplosive Liquids





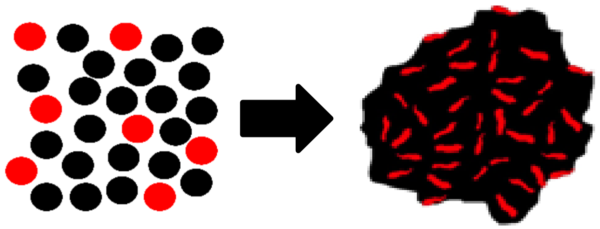
- Microexplosive liquid fuels have been investigated since the early 1960's
- Mixtures of high/low volatility constituents
- The multicomponent fuels can be emulsions (e.g., oil/water, left)
  - Rapid boiling of volatile component produces microexplosions
- Has been shown to:
  - Promote fuel atomization
  - Reduce residence times
  - Increase completeness of combustion
  - However, there are other options to achieve atomization with liquid fuels (e.g., increasing ΔP in injector)

Images: Wang, C.H., X.Q. Liu, and C.K. Law, ***Combustion and microexplosion of freely falling multicomponent droplets.*** Combustion and Flame, 1984. **56**(2): p. 175-197.

Modified Particles: Analogies to Metallic Fuels

Emulsion Fuels

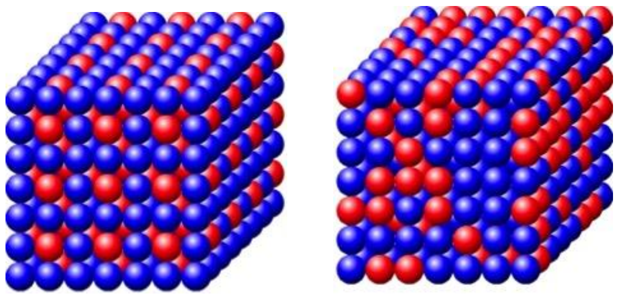
- Mechanical activation (MA, ball milled) can create composite particles with nanometric inclusion material (e.g., polymer) (See several papers by Sippel et al.)



Constituents Nanocomposite Particle

Missive Fuels

- Metal alloys can yield particles that have constituents mixed at the molecular scale (Our focus here, specifically Al-Li)



New Phase Solid Solution

Other "emulsion" examples: Coatings, encapsulated or core-shell

- Why?
  - Could promote ignition and fuel "self-atomization", leading to reduced burning times. We could tailor atomization (few alternatives -- no injectors in energetic materials!) to achieve nAl combustion properties, w/o drawbacks
  - Could disrupt ignition process
  - Could decrease two-phase flow losses (5-10-% loss in motors) and improve combustion efficiency (small motors)

Right Images: http://www.spaceflight.esa.int/impress/text/education/Images/Solidification/Intermetallics/Intermetallic%20versus%20alloy.jpg

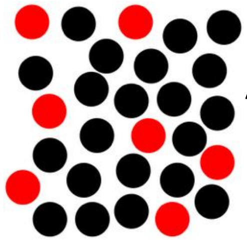
Emulsion Analogy: Fuels with Nanoscale Inclusions

Mechanical Activation (MA)

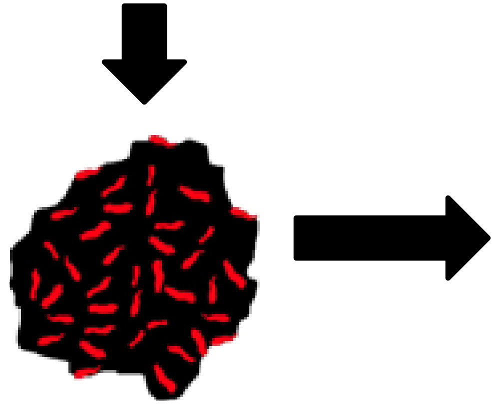
High Energy

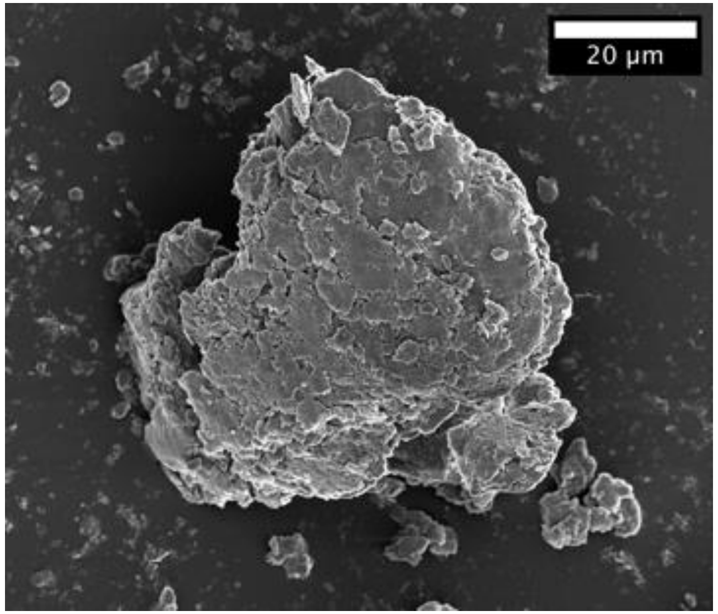
Low Energy

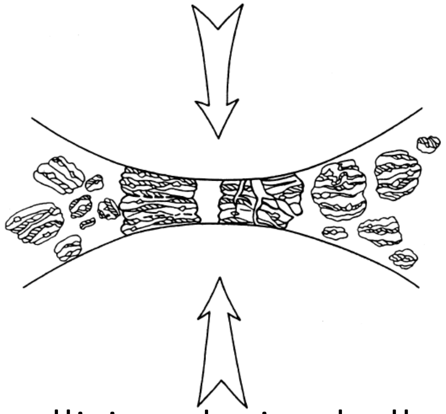
Fuel-rich Al+ PTFE Powder Mixture



Al (black)
PTFE (red)





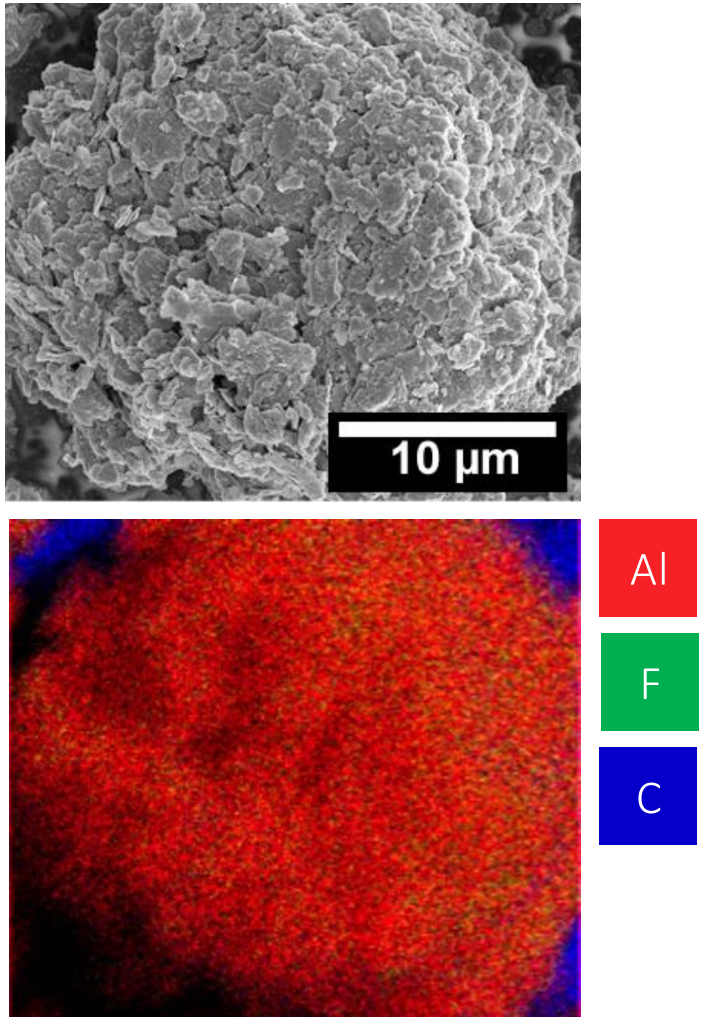


Media collision during ball milling mechanical activation

Precursor Materials

	Aluminum	**PTFE $(C_2F_4)_n$**
wt.%	70%	30%
ρ (g/cm^3)	2.7	2.31
ΔH_c (kJ/g)	31.0	10.7
D_{avg} (µm)	35	35
SSA (m^2/g)	0.06	0.07

Emulsion Analog: Inclusion Fuels



- Have been shown to:
  - Modifies ignition and combustion with little oxide
  - Micron-scale morphologies (moderate SSA) produce particles that can be a drop in replacement
- Can be tailored to achieve desired material properties and combustion characteristics

Inclusion materials can be interacting or non-interacting (no analogy with emulsions)

Images modified from: Sippel, T.R., S.F. Son, and L.J. Groven, ***Modifying Aluminum Reactivity with Poly(Carbon Monofluoride) via Mechanical Activation.*** Propellants Explosives Pyrotechnics, 2013. **38**(3): p. 321-326.

Flame Tests Show Altered Ignitability

Al/PTFE (70/30 wt.%)
Precursor Physical Mixture

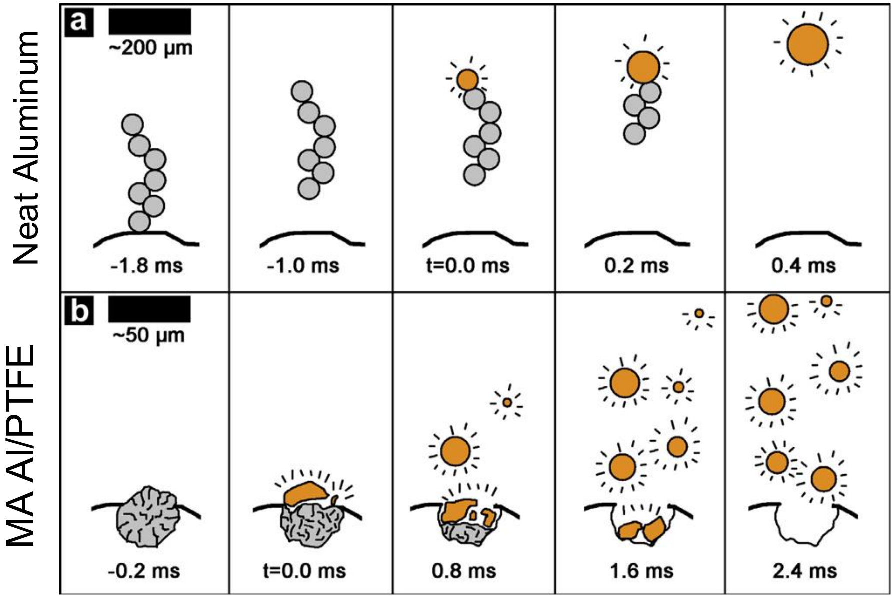
nAl (50 nm)

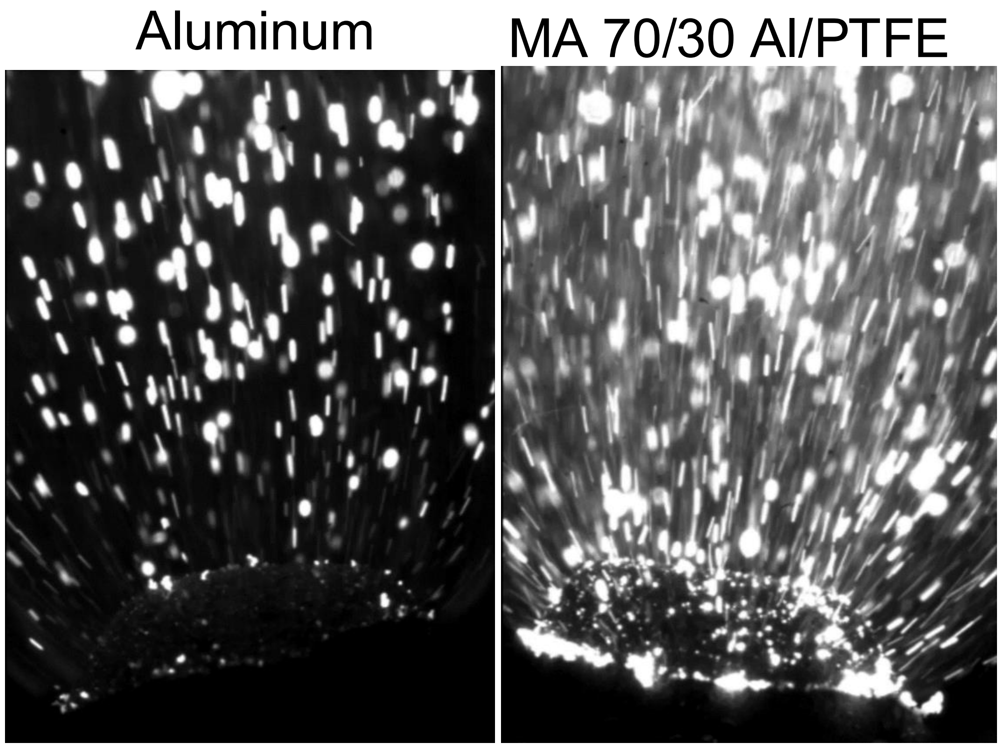
Al/PTFE (70/30 wt.%)
60 min

Modified Al ignites much more easily than µAl and burns quickly

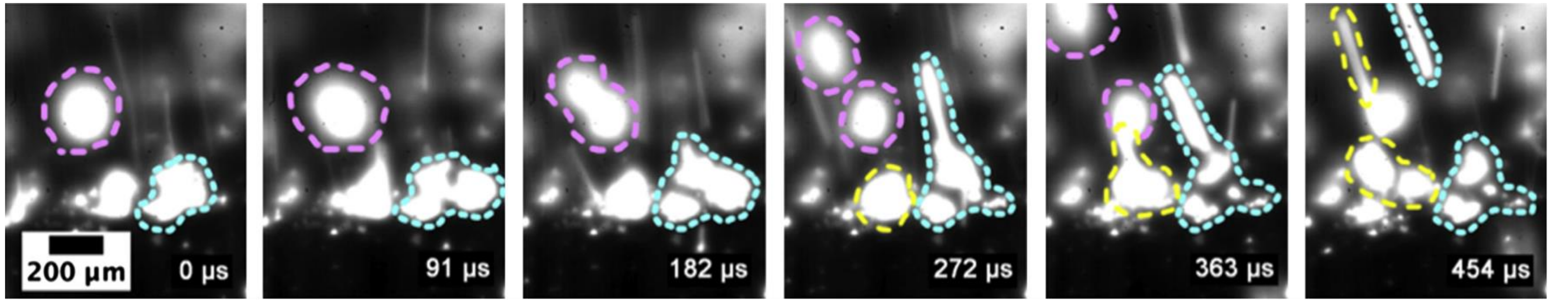
Sippel, T.R., S.F. Son, and L.J. Groven, *Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles.* Combustion and Flame, 2013(0).

MA Powders in Solid Propellants



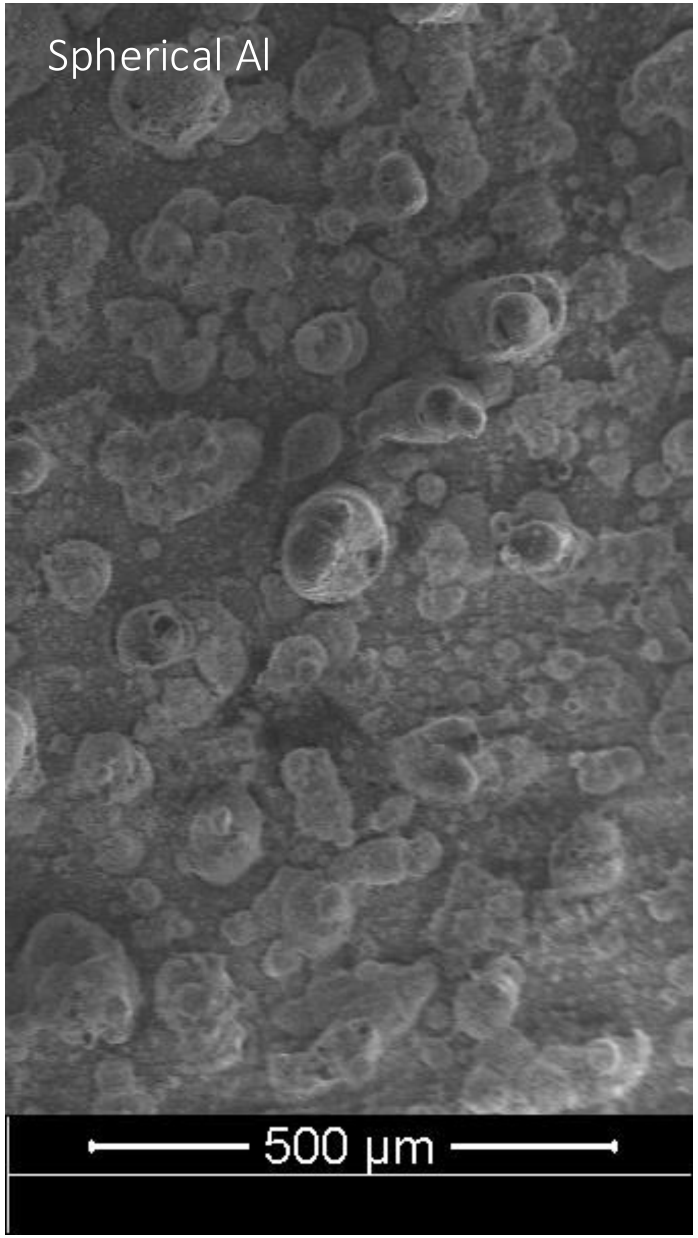


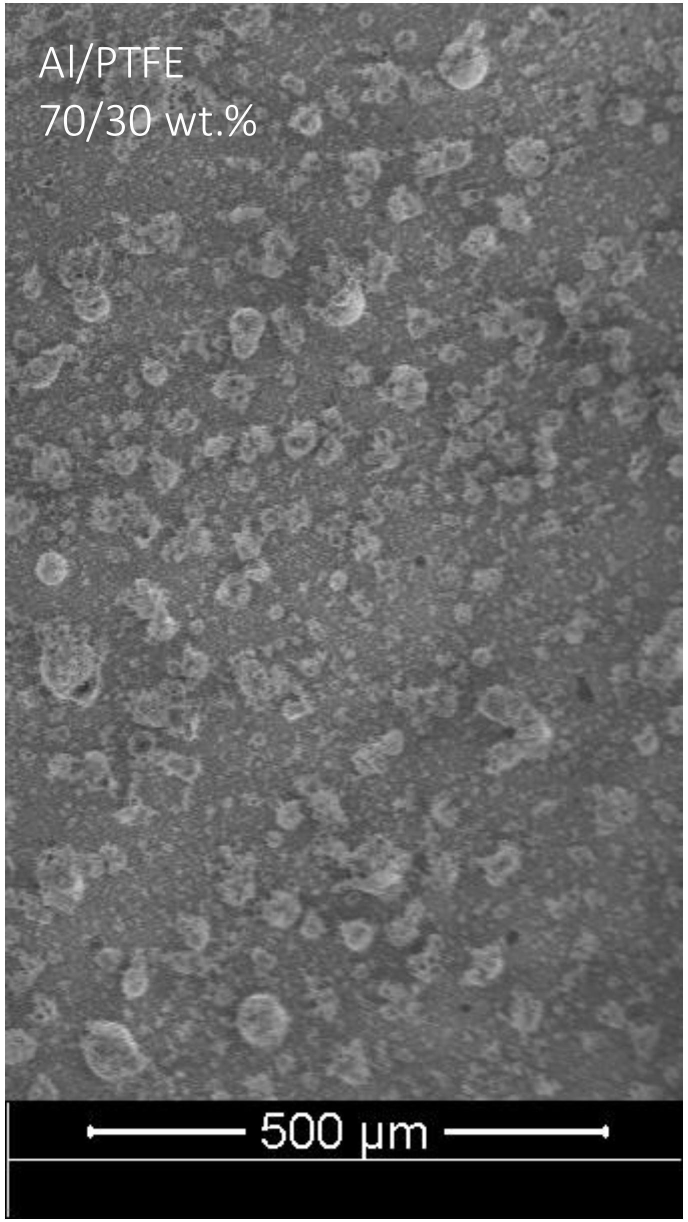
Prompt ignition and particle breakup both important



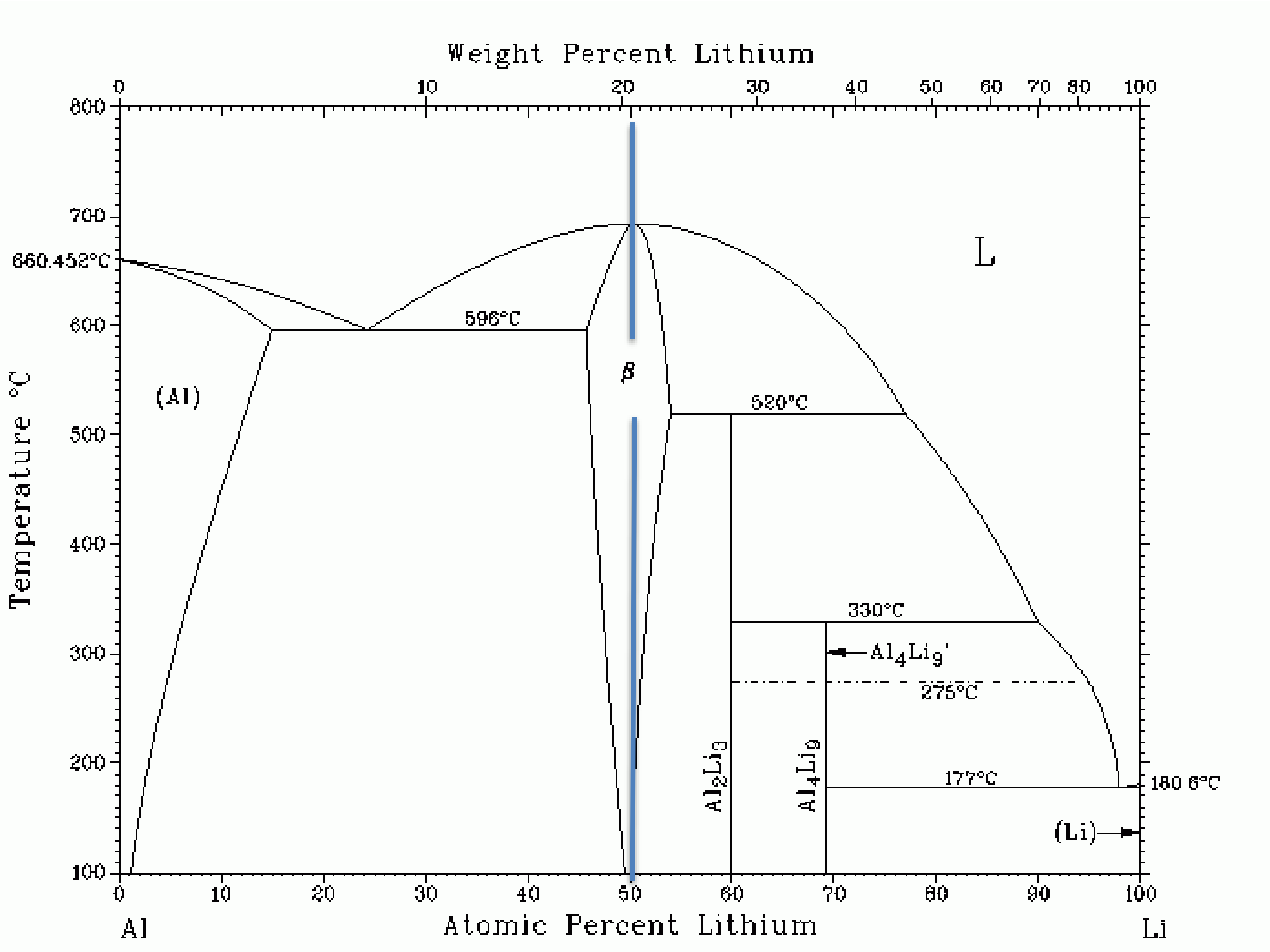
Images: Sippel, T.R., S.F. Son, and L.J. Groven, ***Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles.*** Combustion and Flame, 2013(0).

Quenched Products (68 atm) Show Reduced Agglomeration





Miscible Fuel Analogy: Alloy Fuels Example

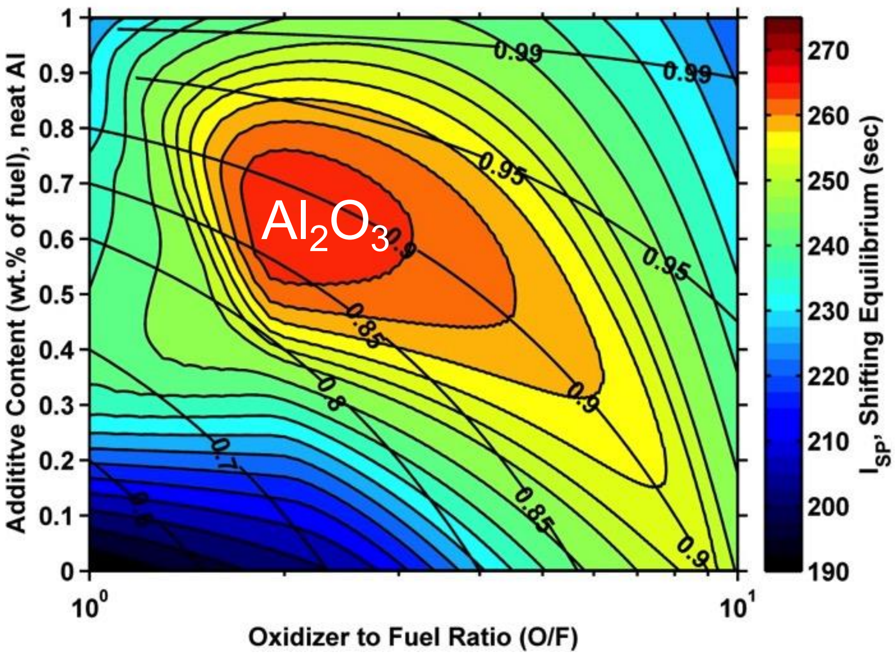


Notes: $T_{bp,Li}$ = 1342 °C; $T_{bp,Al}$ = 2519 °C; m.p. of alloy slightly higher

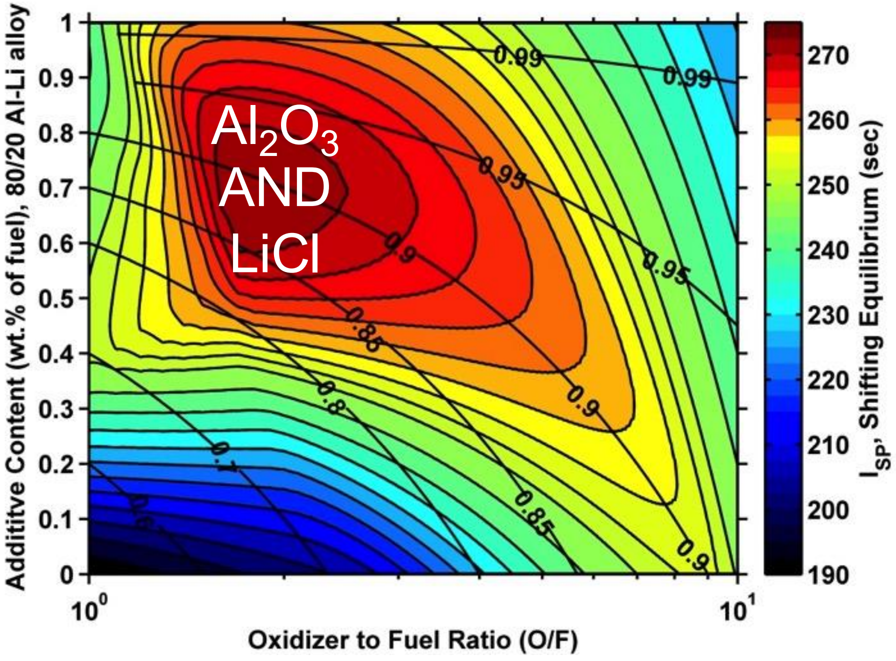
http://www.himikatus.ru/art/phase-diagr1/Al-Li.gif

Thermochemical Predictions (CHEETAH)

Neat Al



80/20 Al-Li Alloy



Additive	Max I_{SP} [sec]	$\Delta h_{Chamber\text{-}Exit}$ [kJ g^{-1}]	Temperature [K]	Molecular Weight [kg $kmol^{-1}$]	Cl → HCl [%]
Neat Al	264.8	3.4	3614	27.9	98.3
Neat Li	263.4	3.3	3204	27.3	1.8
80/20 Al-Li	271.9	3.6	3553	26.2	1.9

B.C. Terry, T.R. Sippel, M.A. Pfeil, I.E. Gunduz, S.F. Son, J. Hazard. Mater. 317 (2016) 259–266,

Alloy Powders – Solid Propellant (1000 fps)

26.80/61.48/11.72   Metal/AP/HTPB

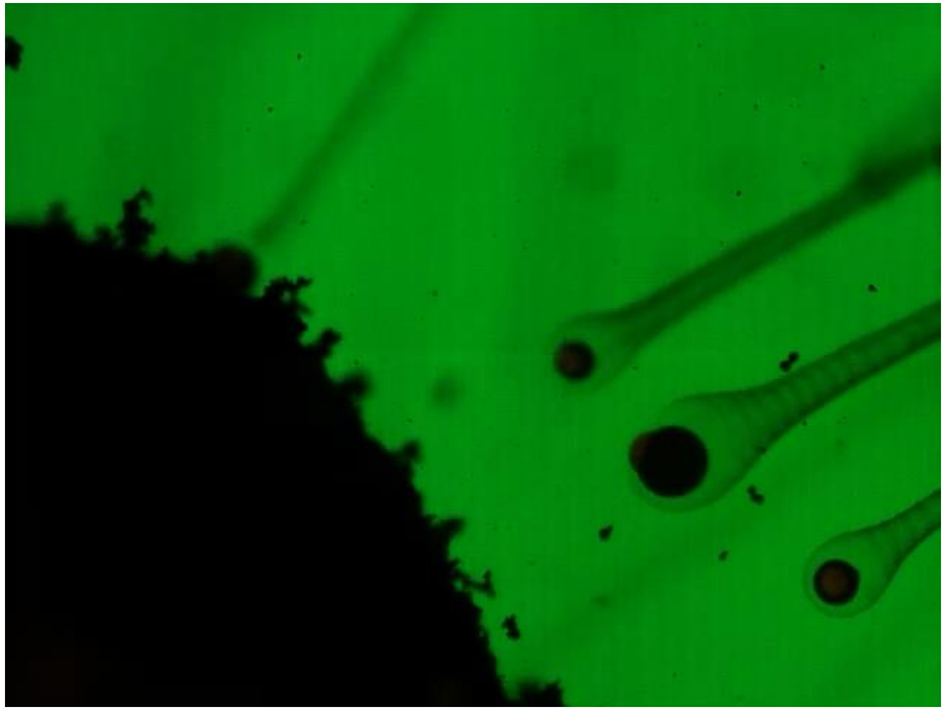
Neat Al

80/20 Al-Li Alloy

Appears to be less coarse product agglomeration from the Al-Li propellant

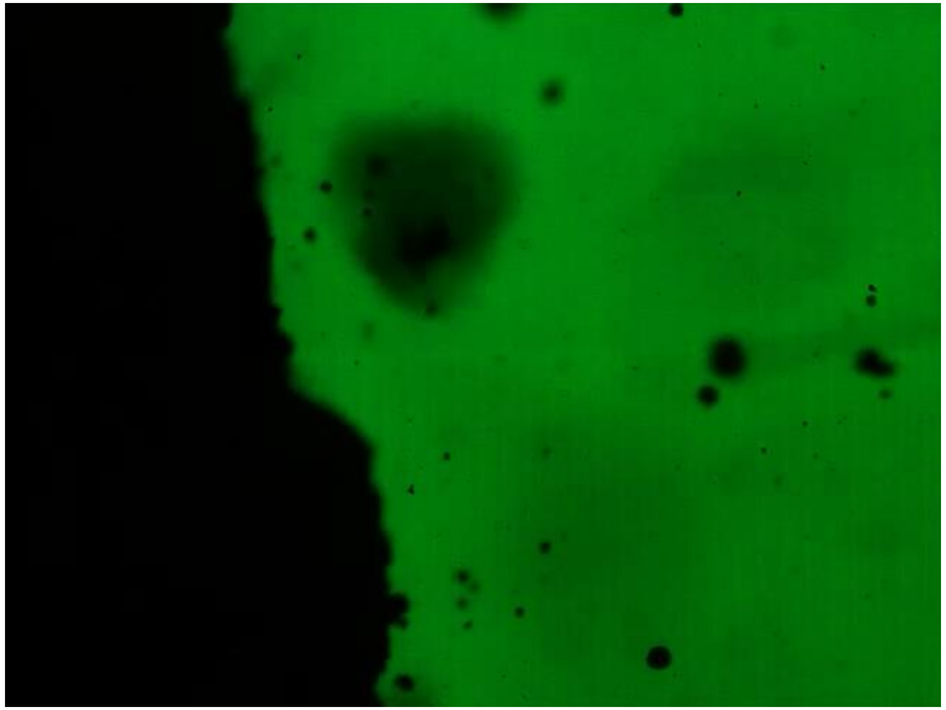
Alloy Powders – Propellant Surface (9900 fps)

Neat Al based propellant



Aluminum sinters and agglomerates on the propellant surface

Al-Li alloy based propellant



Al-Li forms a surface melt layer, and the Al-Li droplets appear to microexplode

Terry, et al., 2016, Proceedings of the Combustion Institute

Other alloys, lower Li content alloys?

- 1:1 atomic alloy being developed by Anduril (previously Adranos)
- We are exploring other alloys as well as lower Li, Al-Li alloy
  - This shows promise to be a better balance between safety (passivation) and performance
  - We have a patent disclosure in this area

Possible Aluminum Based Alloys

METAL	BOILING POINT (°C)	PBR
Aluminum	2441	**1.28**
Beryllium	2475	**1.76**
Boron	3927	**~3.1***
Gallium	2400	**1.8**
Indium	2072	~1.2
Lithium	1330	**0.57**
Magnesium	1090	**0.81**
Silicon	3280	**2.15***
Sodium	884	**0.55**
Zinc	910	**1.58**

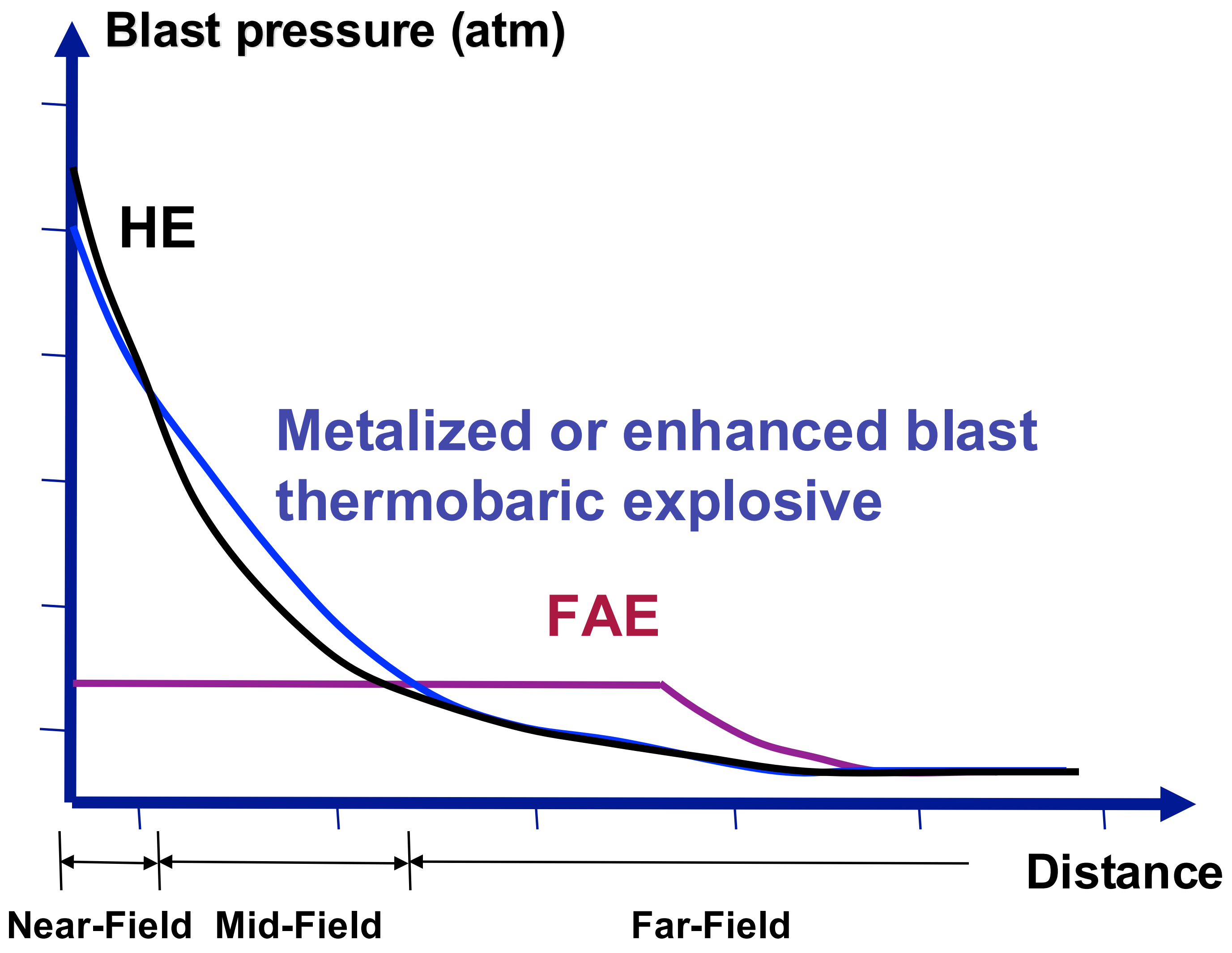
- Al-Li, Al-Mg, Al-Na, Al-Zn (or Be based alloys…toxic)have potential for micro-explosion
  - Theoretical Isp of Al-Li can be higher, while others decrease with alloy content (optimal near where Li is fully oxidized by Cl and Al by O_2) (Blackman and Kuehl, 1961)
  - Li is halophilic (reacts with Cl in APCP), so reduces HCl dramatically (Terry et al., 2016)
  - Al-Mg, Al-Zn alloys reduce agglomeration and increase flame temperature. Have better density Isp than Al-Li
- Passivation can be an issue with some alloys (Pilling-Bedworth is the volume of the oxide to the metal or *how well the oxide fits on the metal*)
- Other alloys such as Al-Ga and Al-In can disrupt the oxide and improve ignition and combustion also (Harper, 2025; Harper et al., 2025)
- Al-Si lowers the melting point, but has minimal effects on agglomeration and burning rate (Terry et al., 2019)

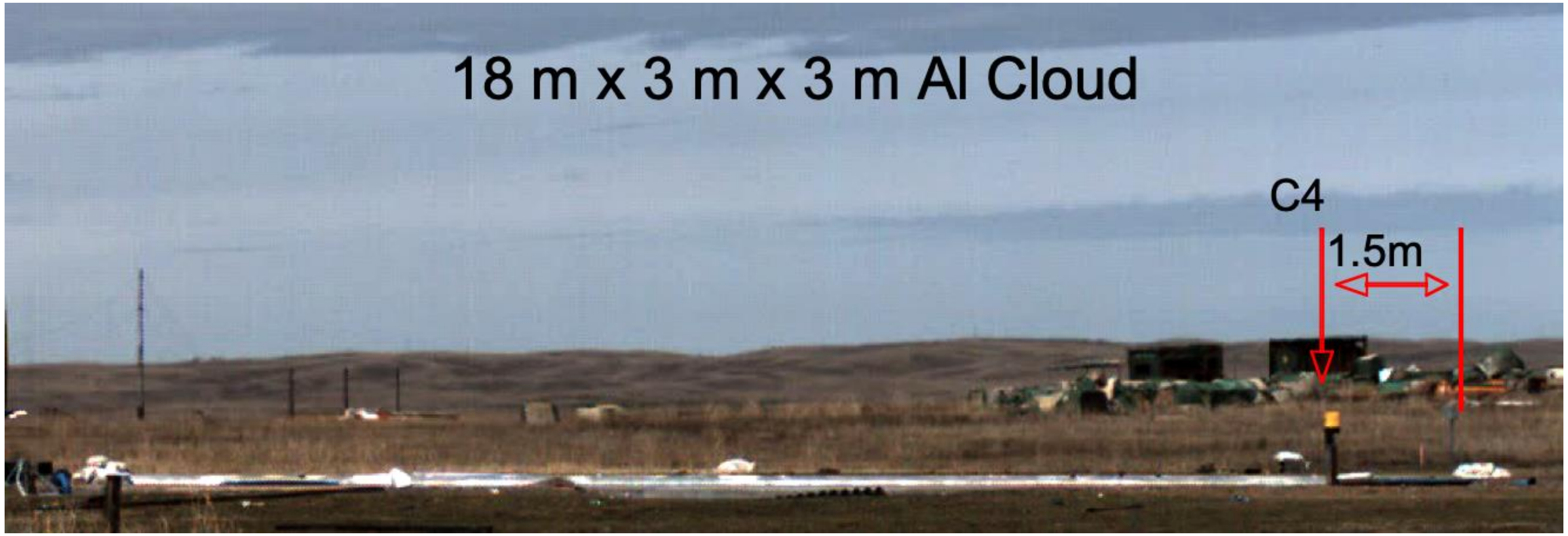
Metal Combustion in Explosives

- Metal sometimes added to explosives
  - underwater explosives
  - enhanced blast
  - fuel-air explosives (FAE)

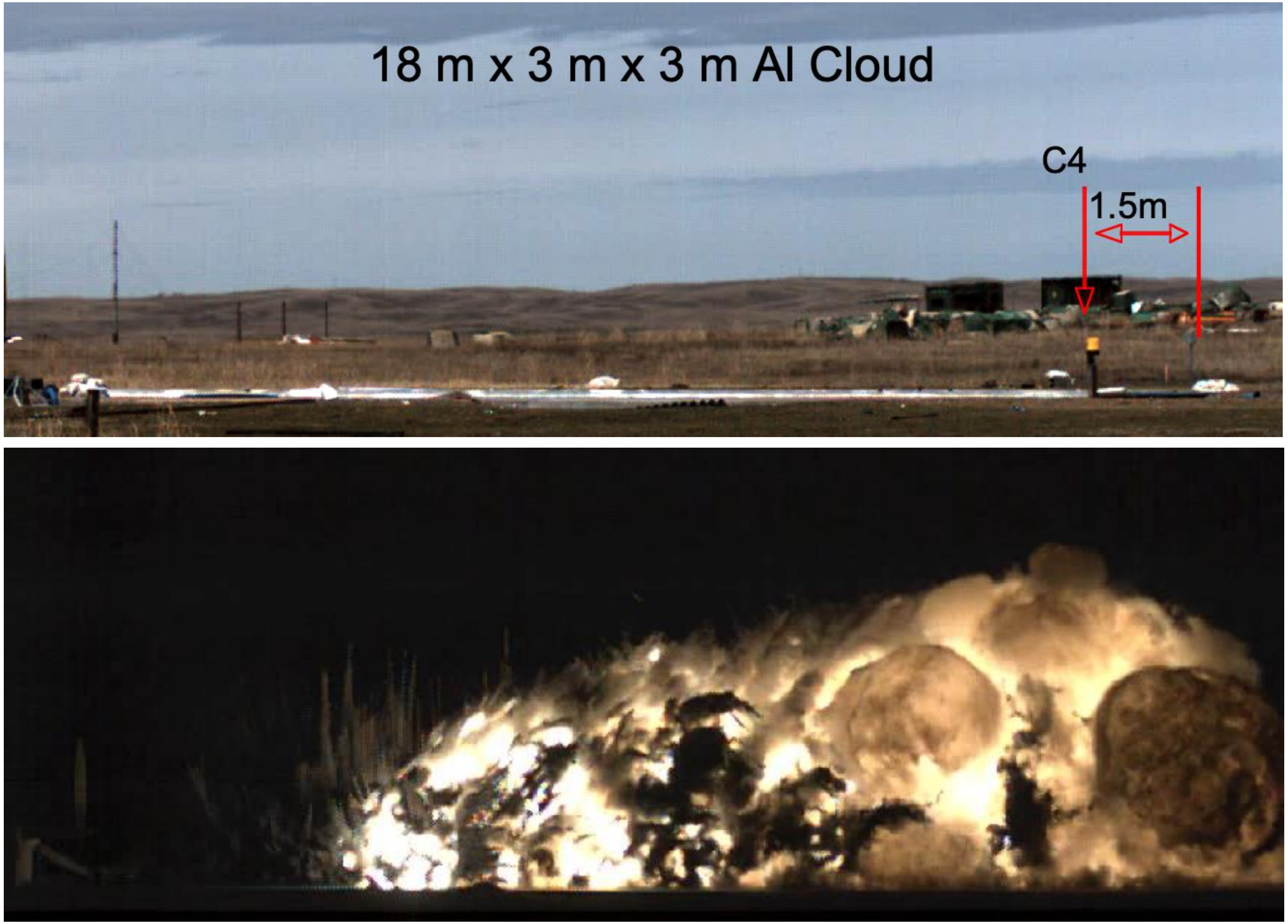
Aluminized Explosive
(failure to ignite Al)
Zhang et al. 2007

Aluminized Explosive
(Al ignited, larger, smaller Al)
Zhang et al. 2007


Blast pressure (atm)
HE
Metalized or enhanced blast
thermobaric explosive
FAE
Distance
Near-Field
Mid-Field
Far-Field



Zhang et al. (2007)

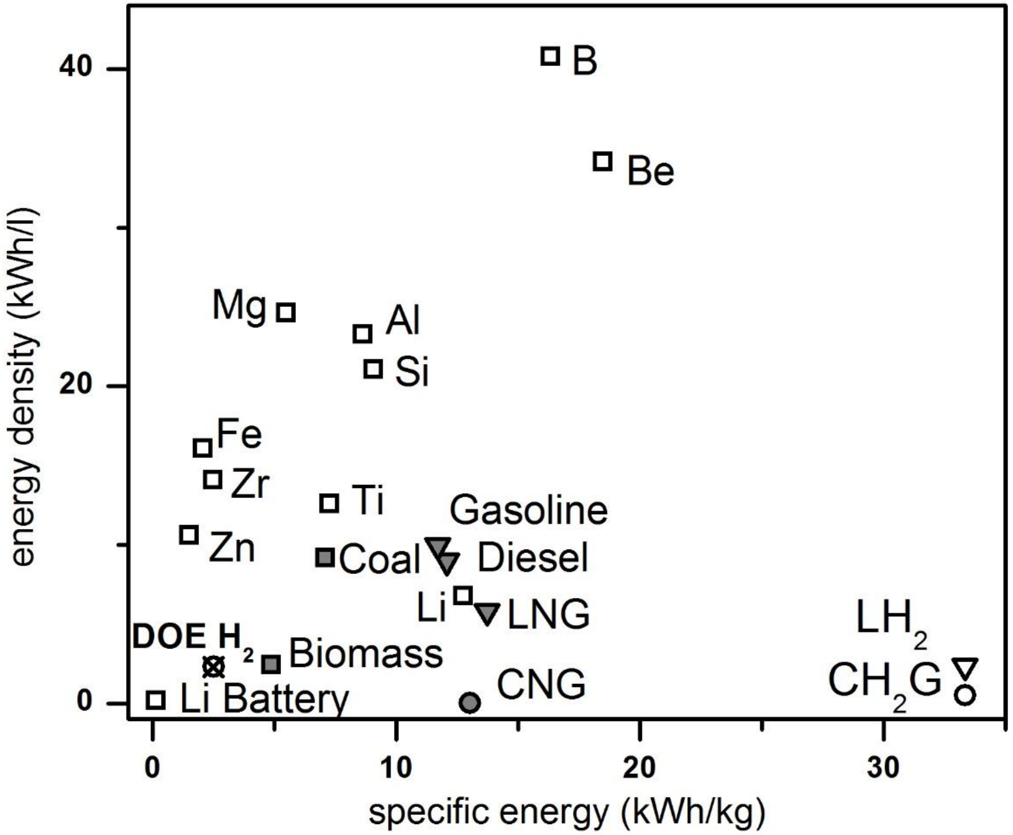


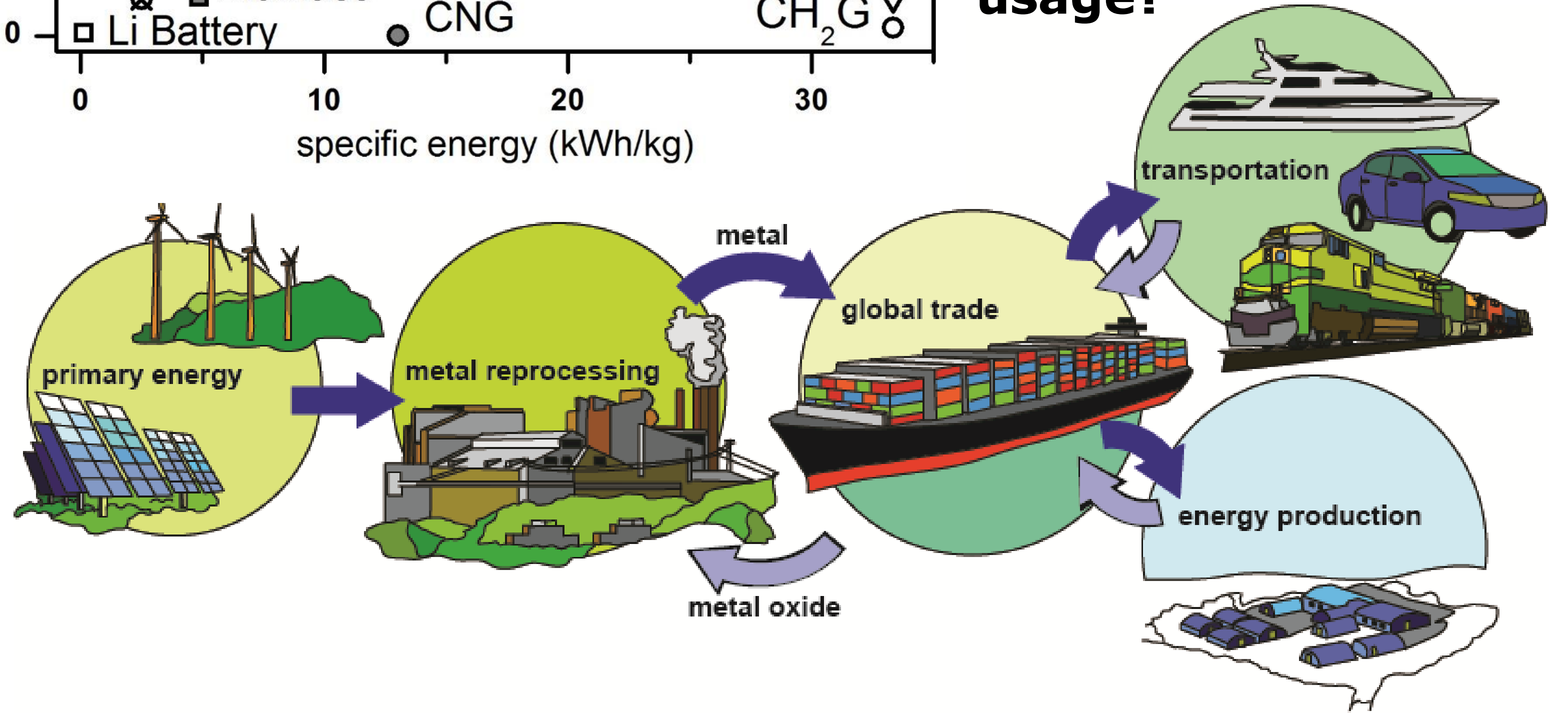
Zhang et al. (2007)

Metals as recyclable, high energy-density fuels

- Zero-carbon emissions
- No storage issue (e.g. H_2)
- Recyclable using existing techniques
- Tradable commodity

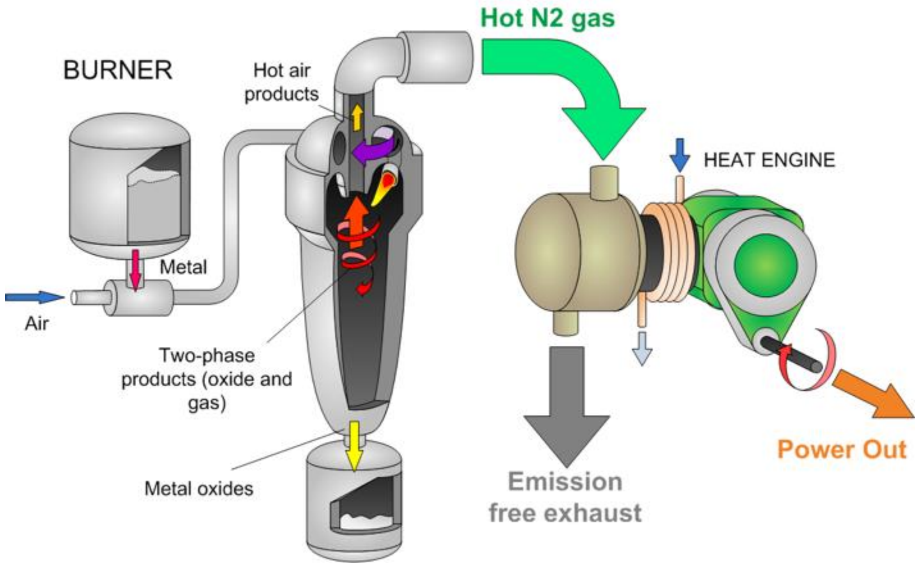
Can metal fuel usage replace hydrocarbon fuel usage?





Other Applications

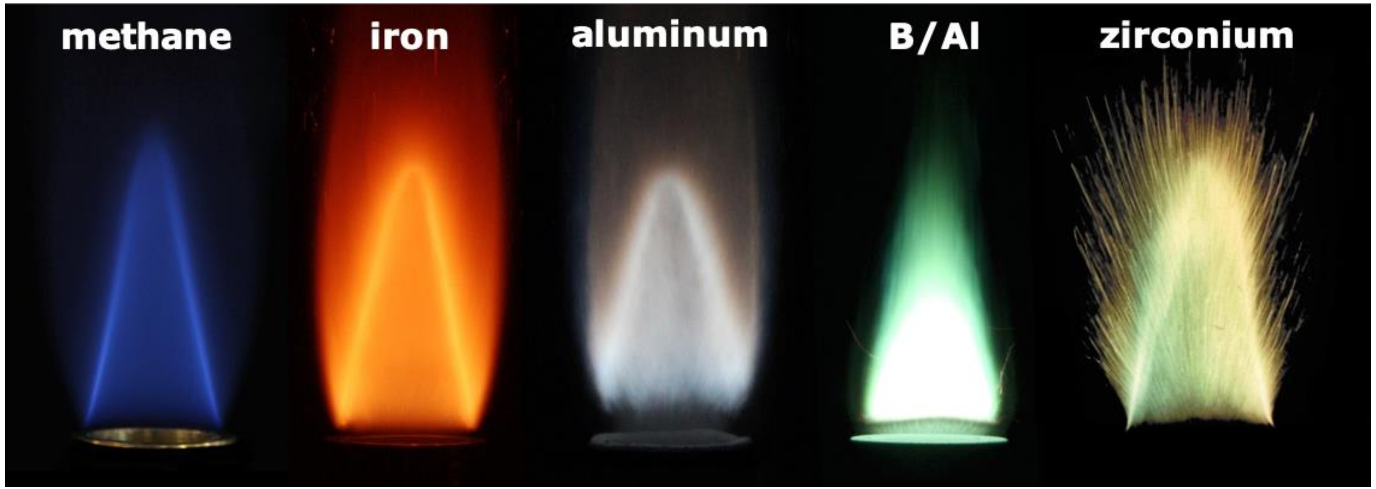
- Metal fuels for external-combustion engines
  - Metal fuels can be directly burned with air
  - High-grade and clean thermal energy can power heat engines



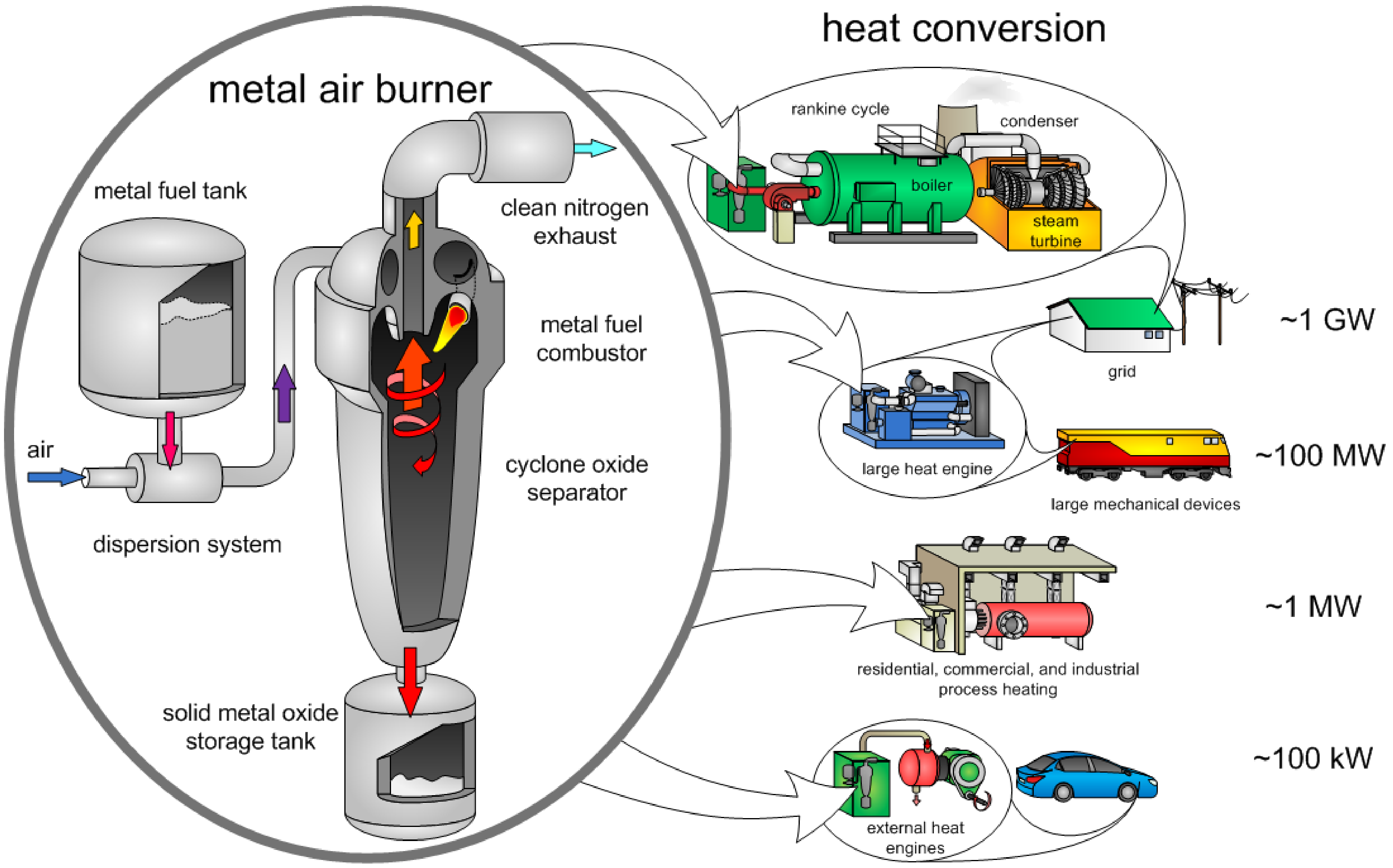
Metal-air combustion system with external-combustion engine

Bergthorson, J. M., et al. "Direct combustion of recyclable metal fuels for zero-carbon heat and power." *Applied Energy* 160 (2015): 368-382.

Metal flames



Metal-air flames for high-power applications

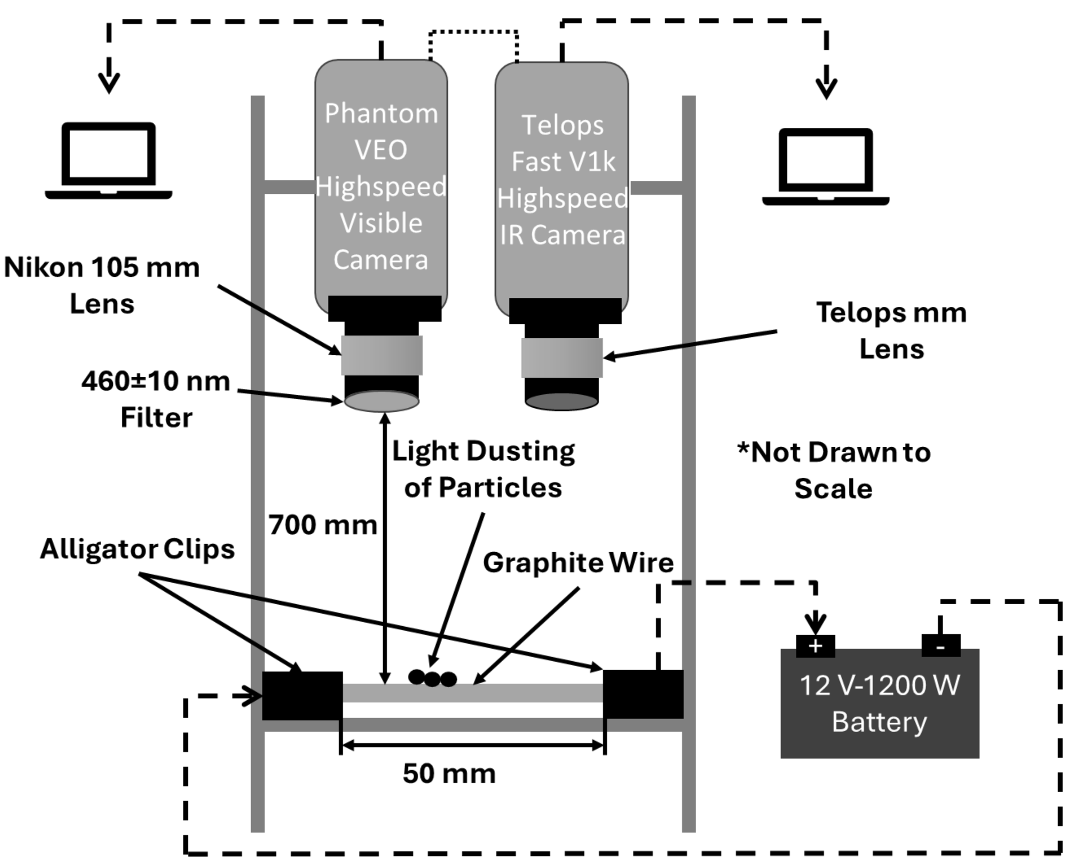


Bergthorson, Goroshin, Soo, Julien, Palecka, Frost & Jarvis (2016)

Other Alloys and Composites Could improve propellants, explosives and pyrotechnics – and Other Applications

- Could alloys and engineered composites yield improved explosives and pyrotechnics?
  - We have patent disclosures in this area
- We also have patented technologies to print metals with fluoropolymers (FDM)
  - This could be used for reactive structures
- Exploring composite particles including crystal inclusions of metals

Ignition Temperature Characterization



Schematic of Particle Ignition Experiments.

- By varying number of batteries and dimensions of graphite test strips, the heating rate can be varied

Purdue Metal Combustion Capabilities

- Bomb calorimetry & detonation chambers (up to 250 g TNT eq.)
- Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) with mass spec
- Particle ignition with imaging and other diagnostics
- Particle combustion (burning time)
- Entrained particle jet combustor
- Opposed flow particle burner
- Fabrication and testing of metalized solid propellants
- Fabrication and testing of metalized explosives
- Impact, friction, ESD safety testing
- Other: Battery fire mitigation/characterization, solid state fire extinguishment, and flammability of refrigerants