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Innovative Nitrogen-Doped Boron Propellants

Presented by:

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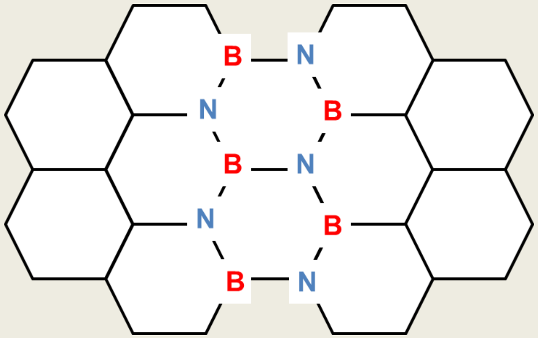
OUTLINE

- **The Problem**
- **Status/Testing**
  - Experimental Section
    - Propellant Processing
    - Closed Bomb Test
    - Propellant Wear and Erosion Test
- **Prior Art and Advantages Over Prior Art Status/Testing**
  - Results and Discussion

    Nano-Boron Nitride
  - Burn Rates
  - XPS/SEM/TEM
- **Conclusions / Future Work**

THE PROBLEM

- Army needs more powerful and balanced propellants
- Barrel wear and erosion is a problem
- BN is interesting because:
  - Hexagonal BN is lubricating
  - Boron doping of steel improves its hardness
  - Boron has low molecular weight
  - Resistant to chemical attack



The Problem

- Currently fielded 155mm artillery propelling charge, M232/M232A1, has exhibited spiral wear and erosion problems.
  - Wear reducing liner

Prior Art and Advantages Over Prior Art

- Many Low Vulnerability (LOVA) Propellant Formulations contain RDX.
  - RDX is highly chemically erosive
- New, experimental low-erosivity LOVA propellants have been produced by
  - Reducing RDX content
  - Introducing nitrogen-rich energetic binder or filler compounds.
  - Compromises between performance, sensitive and erosivity must be reached in these cases

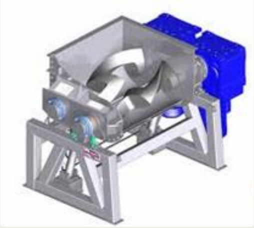
Prior Art and Advantages Over Prior Art

- Ceramic additives to the propellant can theoretically reduce barrel deterioration by coating the inside of the barrels[3]
  - Challenges with dispersing the particles in the propellant, and due to abrasion from incomplete sublimation, propellant and ceramic composites that produce regenerative wear-resistant coatings have not been demonstrated
- Ceramic Barrel Liners have been identified as a promising technology for some time.
  - Very good wear characteristics and thermal resistance
  - Susceptibility of ceramics to fracture, driven by stress, induced by the different thermal expansion properties of steel and ceramics

Detailed Description

Approach:

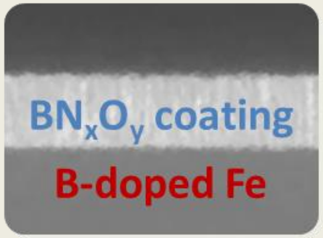
Additive + Propellant



Mix and extrude

Propellant Composite

Propellant Fired



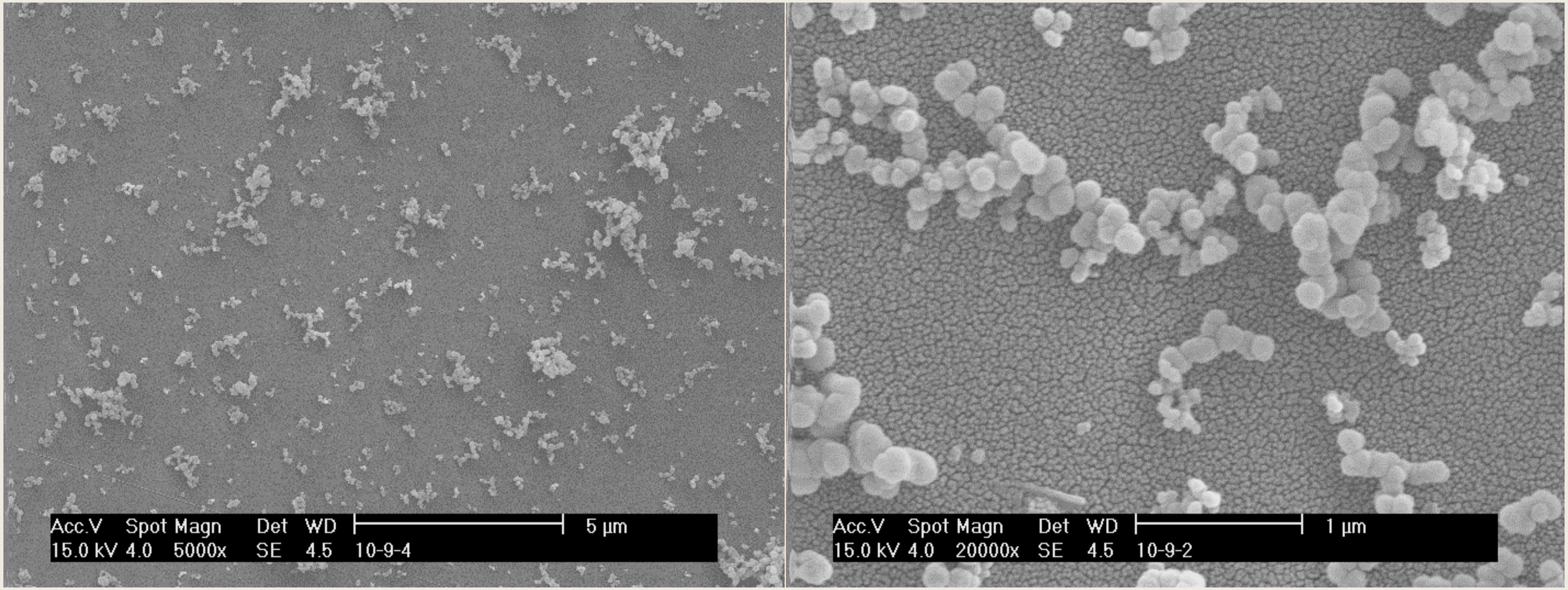
(dramatized image)

Coated and Hardened Barrel

Particles Size / Surface Area Control

Synthesis Condition	Surface Area (m^2/g)	Calculated Particle Diameter (nm)
High Conc. A	20.0	143
High Conc. B	23.0	124
Intermediate Conc. A	37.8	76
Intermediate Conc. B	51.2	56
Low Conc.	77.4	37

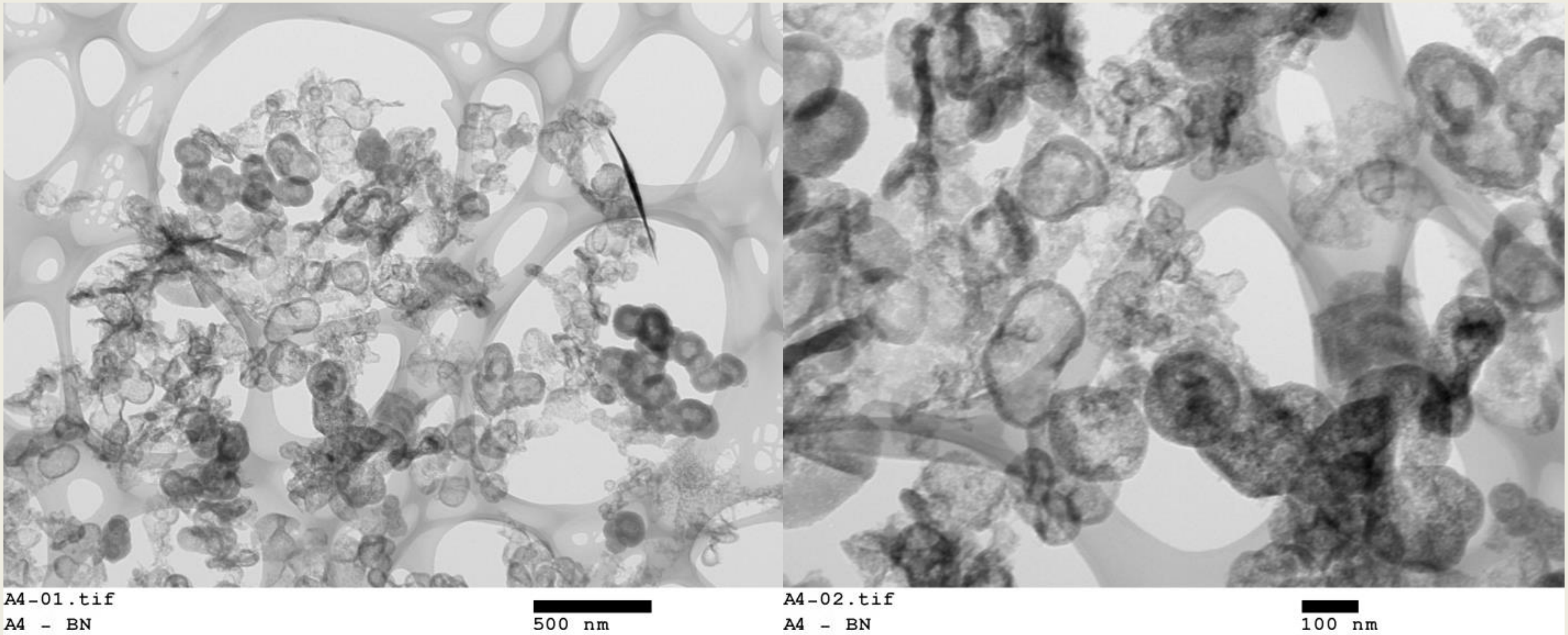
SEM Imaging



BN NANO-PARTICLE SPHERES

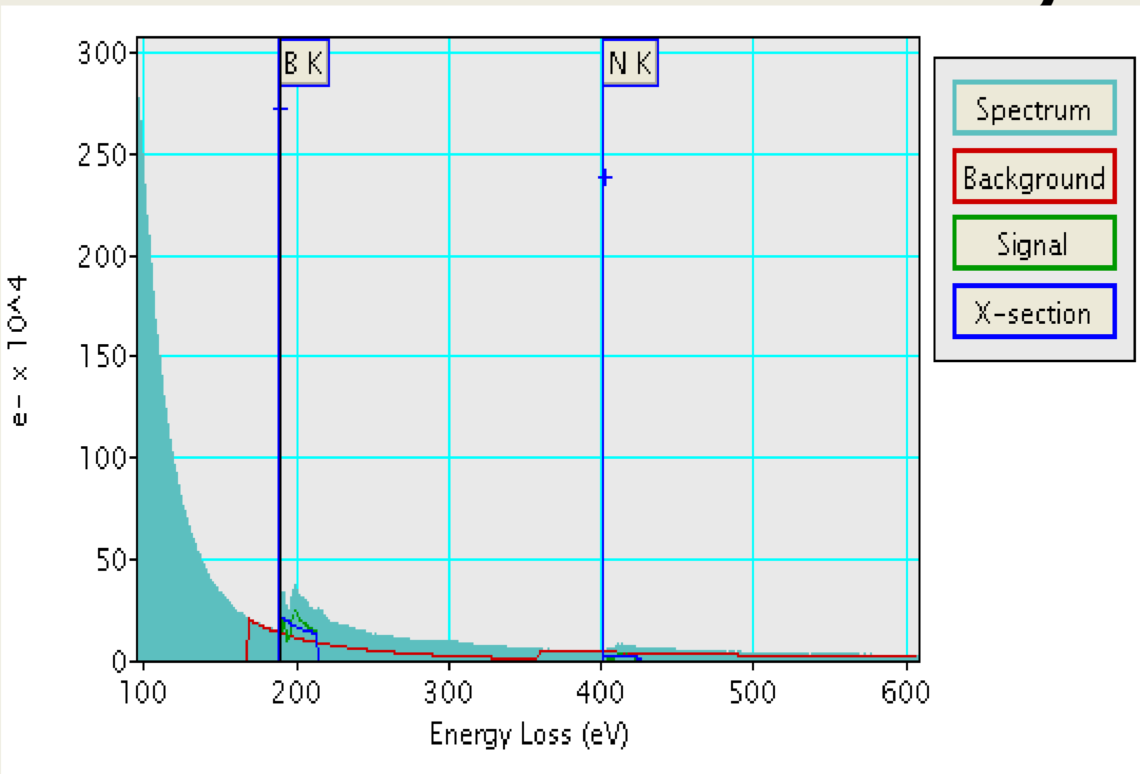
- ❑ Particle agglomerate upon drying
- ❑ Individual particles are spheres
- ❑ Spheres with diameters in the nanometer range.

TEM Imaging



TEM images showing nano-spheres of boron nitride used for propellant additive testing (US Patent Pending).

EELS Analysis



Experimental Conditions

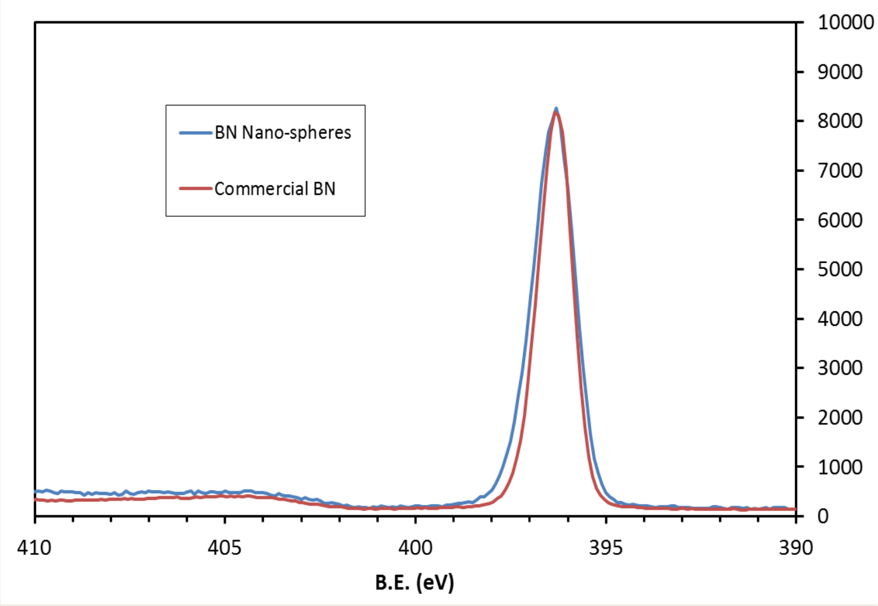
Beam Energy: 200 keV
Convergence Semi-Angle: 5 mrad
Collection Semi-Angle: 1.5 mrad

Composition Information

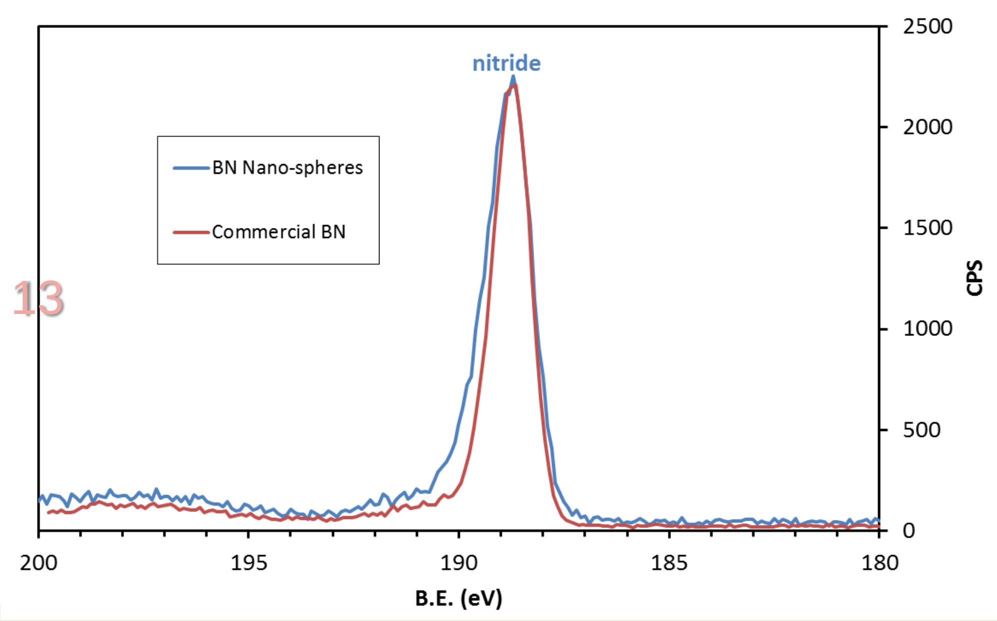
Elem.	Atomic ratio (/B)	Percent content
B	1.00 ± 0.000	52.37
N	0.91 ± 0.129	47.63

EELS Analysis, showing the material has a 1:1 B:N ratio (US Patent Pending).

XPS Analysis – N 1s Region



XPS Analysis – B 1s



XPS Analysis showing (a) the N 1s region, and (b) the B 1s region for the BN nano-particle propellant additive compared to a commercial hexagonal boron nitride sample.

IMR-4198 Composition

Propellant Name	Nitrocellulose Composition (wt%)	Dinitrotolulene Composition (wt%)	Other Components (wt%)
M1	86%	9.9%	3% Dibutylphtalate 1% Diphenylamine
M14	90%	8%	2% Dibutylphtalate 1% Diphenylamine 0.7% Residual solvent 0.6% Moisture 0.2% Graphite
IMR 4198 (Hodgdon)	>85%	<10%	<10% Non-hazardous additives

DSC Testing

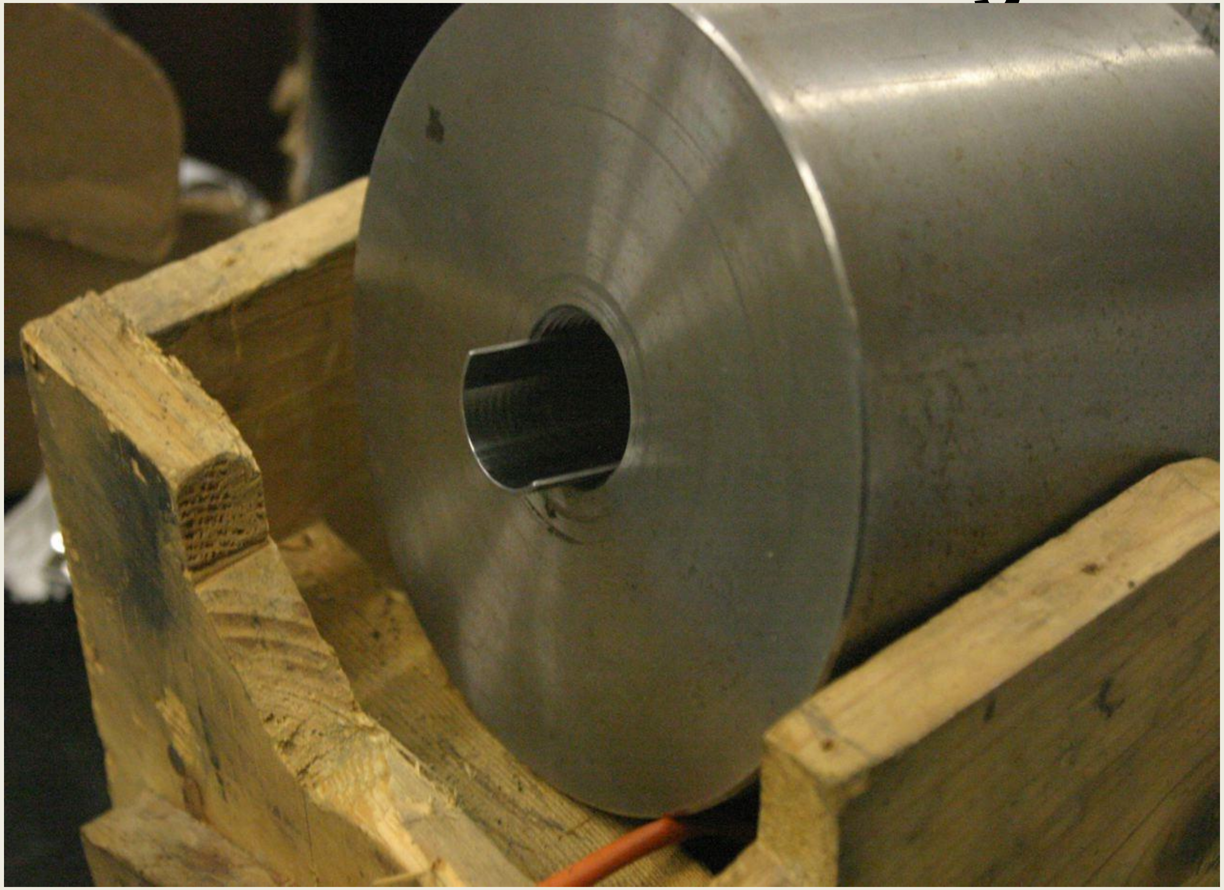
Propellant Material Tested	Heating Rate (°C/min)	Sample Amount (mg)	Exotherm Onset (°C)	Exotherm Peak (°C)	Exotherm End (°C)
IMR4198 w/o BN	10	0.36	162	206	265
	10	0.15	162	207	265
	10	0.58	159	207	265
Average			161	207	265
IMR4198 w/ BN	10	0.22	163	207	265
	10	0.40	158	207	265
	10	0.45	161	207	265
Average			161	207	265

Propellant Testing

Heat of Combustion

Material Tested	Heat of Combustion; ASTM D240 (J/g)
IMR-4198 w/o BN	10038
IMR-4198 w/ BN	10036

Closed Bomb Testing



200 CC CLOSED BOMB

Closed Bomb Testing

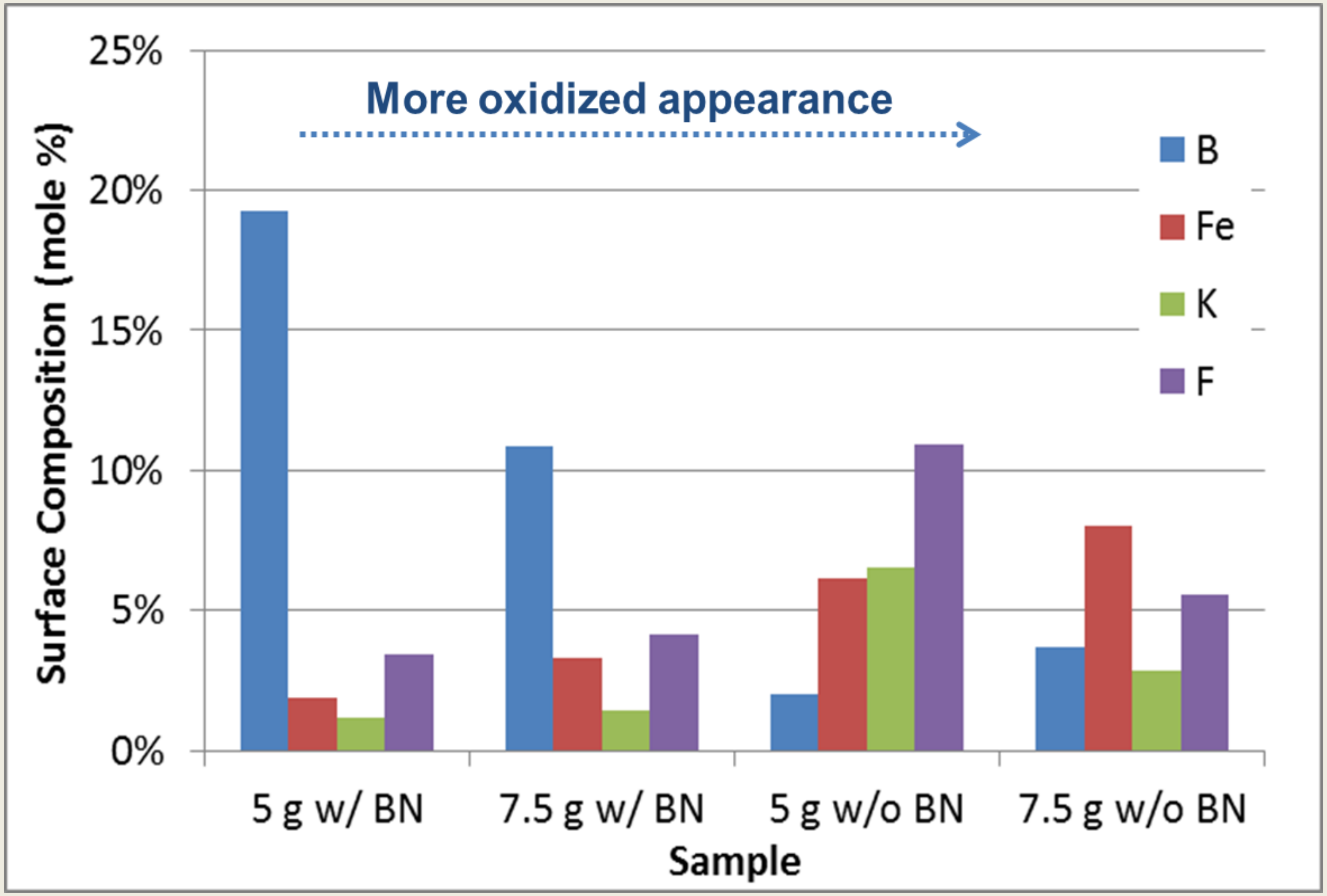
Material Tested	Amount (gram)	Closed Bomb Chamber pressure (psig)	Observations
IMR-4198 w/o BN	5.0	10k	Oxidation (rust color)
	7.5	15k	Deep oxidation (rust)
Mix 50/50 of pure and composite (WITH A% BN)	5.0	10,250	Black residue on the surface, no visible oxidation
IMR-4198 w/ BN	5.0	10k	Black residue on the surface, no visible oxidation
	7.5	15k	Possible slight oxidation (green color)
IMR 4198 as received	5.0	9,170	Reference sample, used high speed DAQ system.
	7.5	15,470	Reference sample, used high speed DAQ system.

Closed Bomb Inserts

Characterization

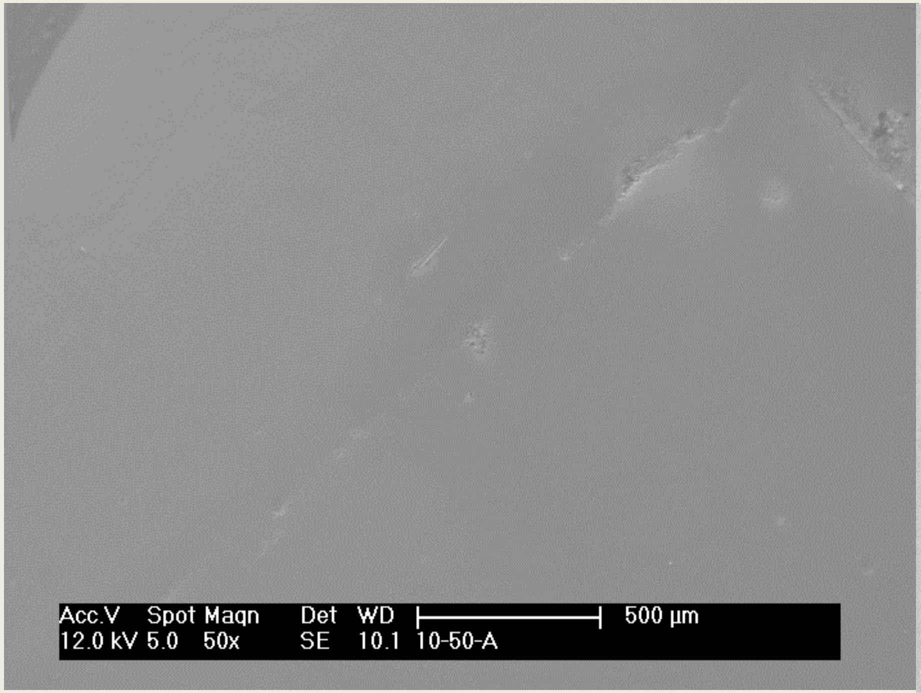
Closed Bomb Inserts

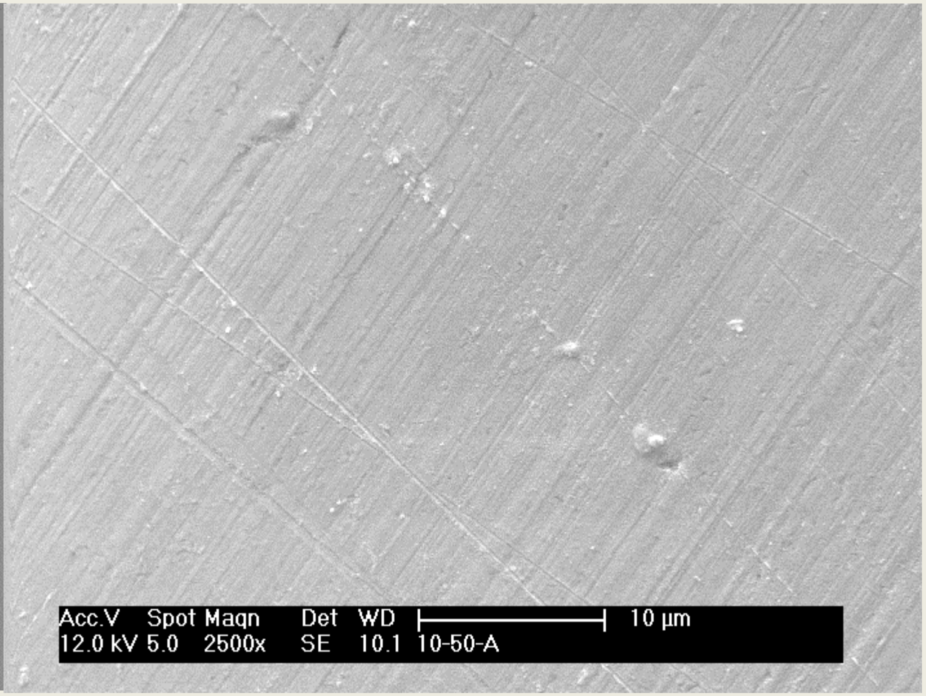
XPS Analysis



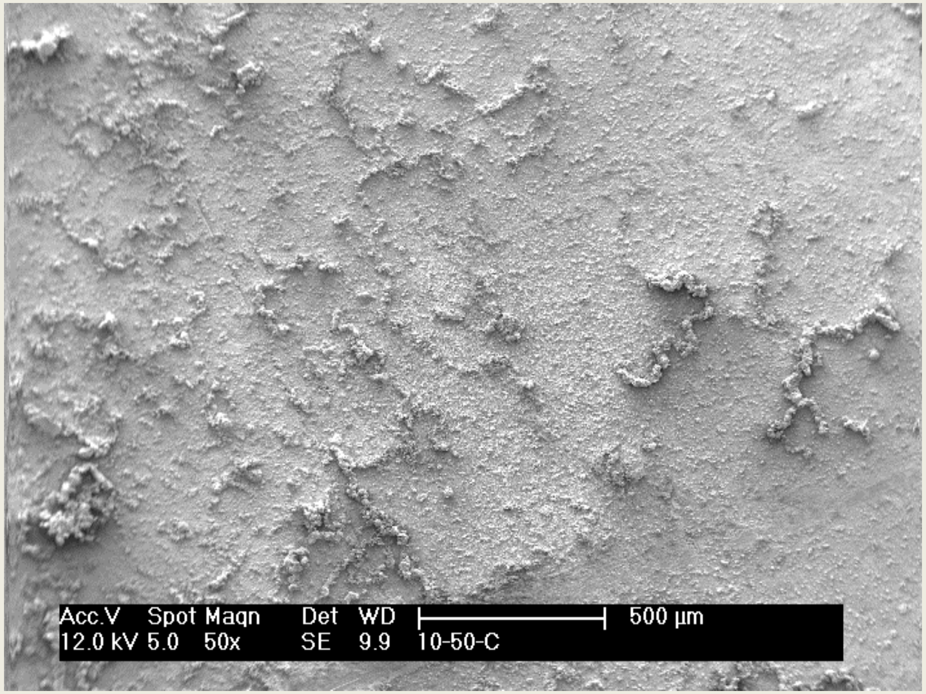
Characterization

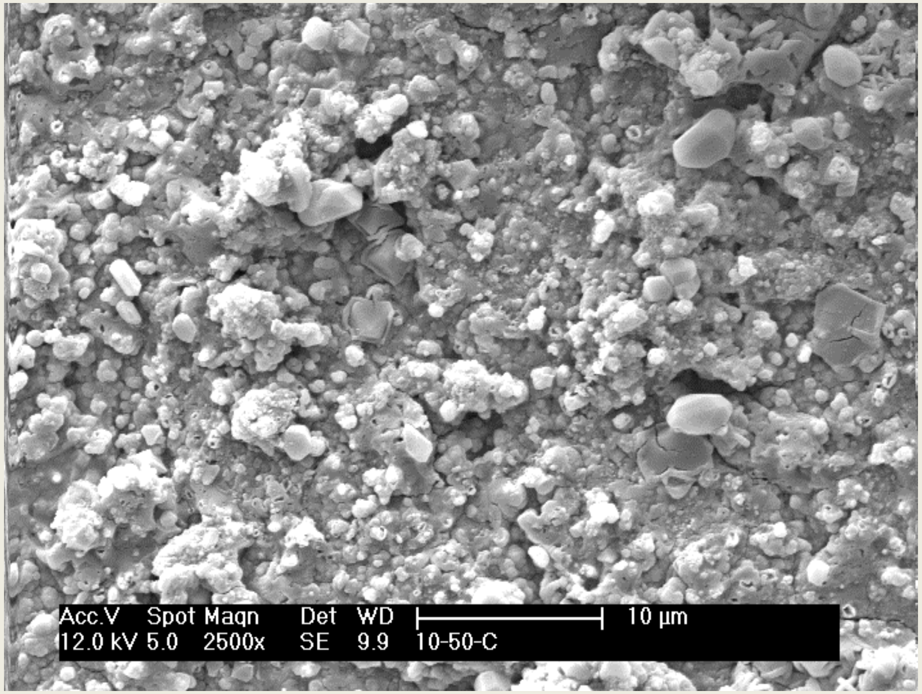
SEM – Fresh Insert





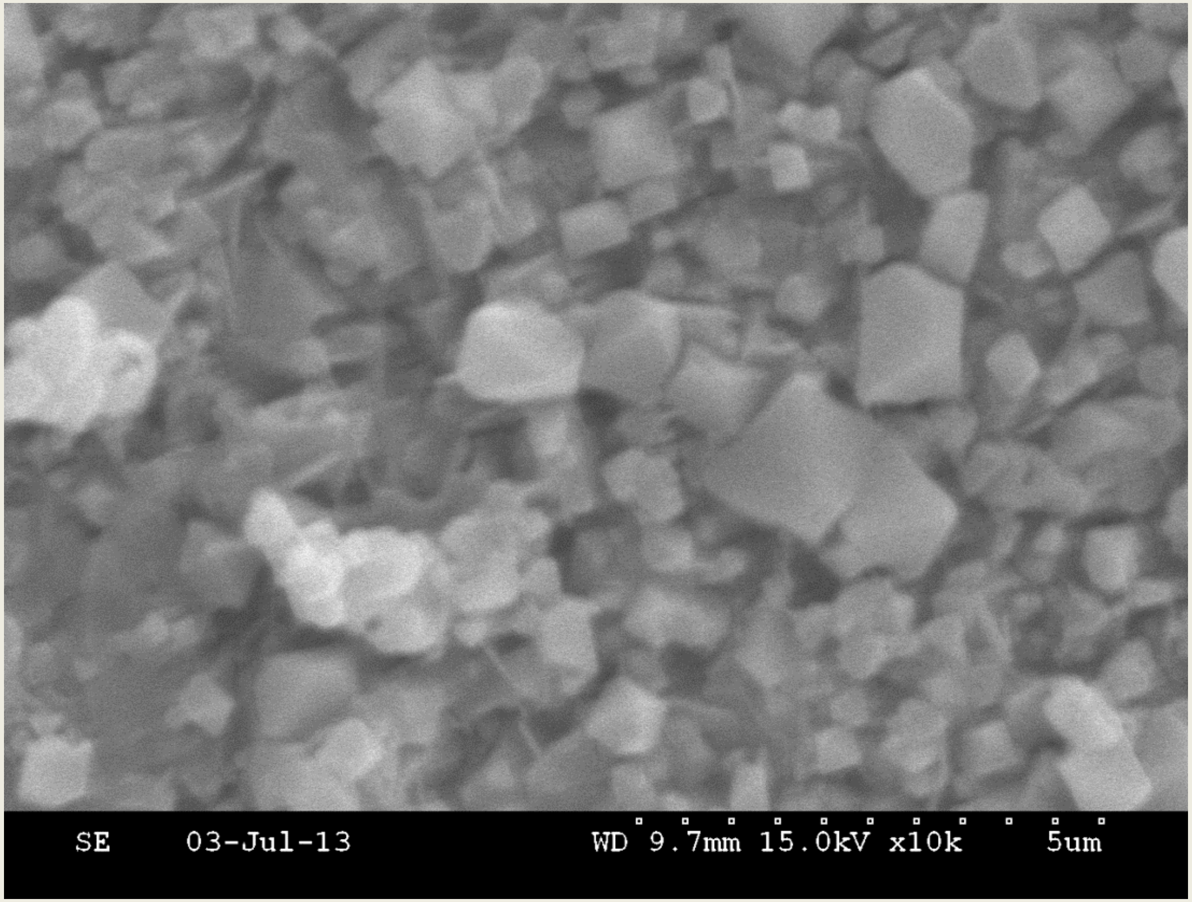
SEM – Insert Fired w/o BN





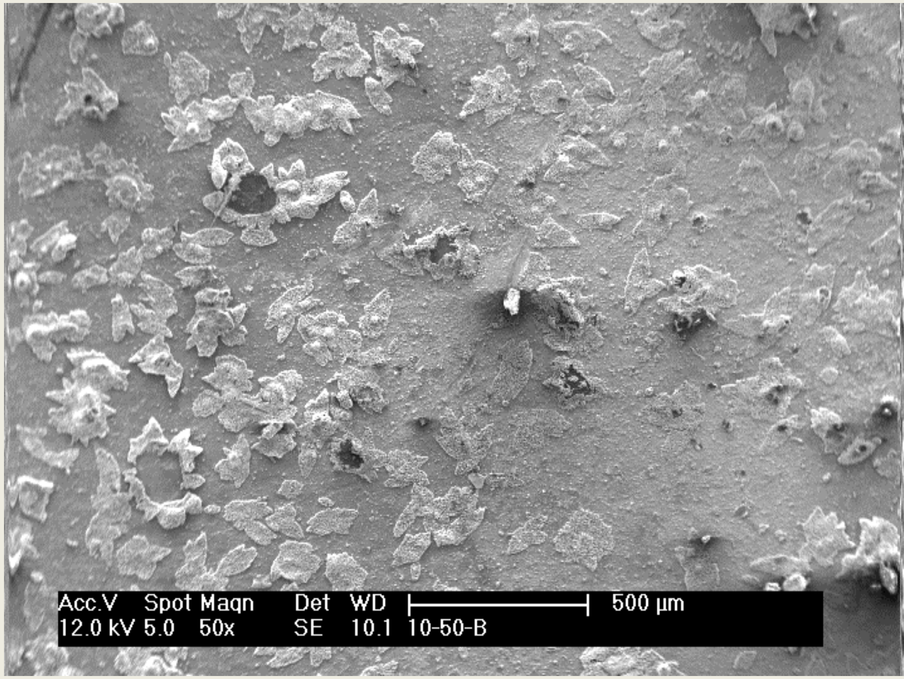
Characterization

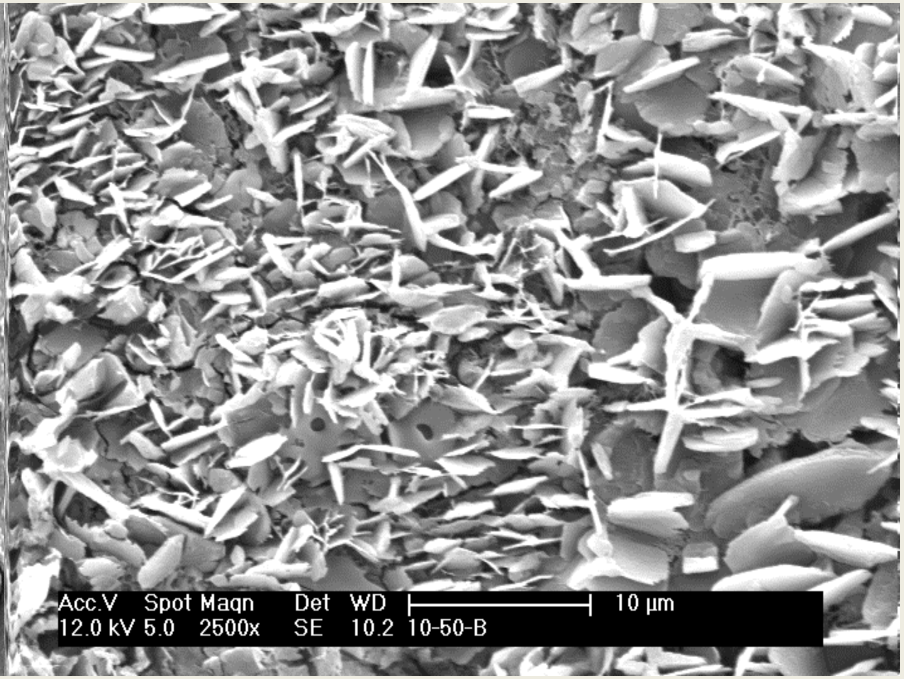
SEM – Insert Fired w/o BN



Characterization

SEM – Insert Fired with BN





Wear and Erosion Test

Figure 1: RPD380 w/o BN - Single Perf grain used in erosion testing

Figure 2: RPD-380 w/BN Single Perf grains used in erosion testing

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Wear and Erosion Test Results

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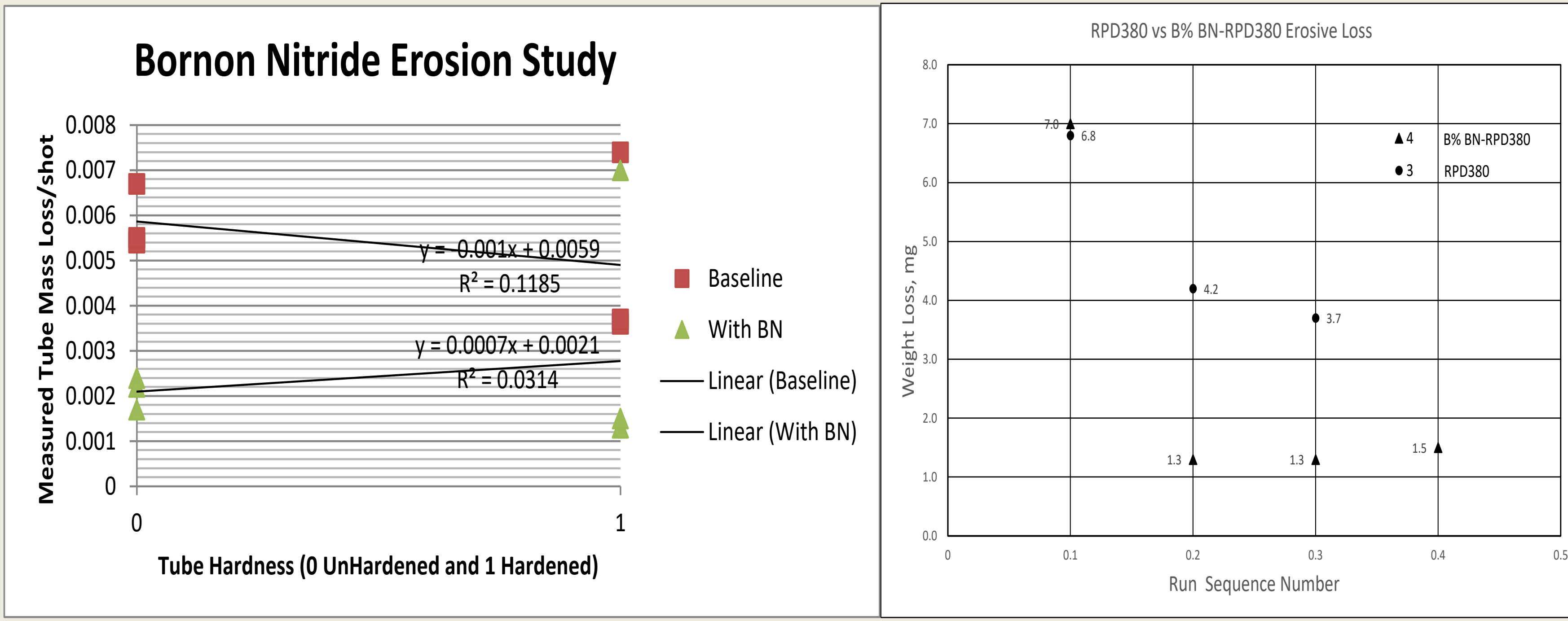

Figure 10: Wear and Erosion Test Results for hard and unhardened sleeves (US Patent Pending). Note: Sleeves 1 and 2 were hardened to approximately Rockwell Hc 41. Sleeves 3 and 4 were approximately Rockwell Hc 12. See ICP

The effect of the BN propellant additive (US Patent Pending) suggests an apparently significant reduction in the mass loss for both hardened and unhardened insert sleeves relative to baseline RPD-380 propellant. The results look compelling at 2.8 and 1.8 times life increase for hard and unhardened insert sleeves, respectively

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Wear and Erosion Characterization

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- **SEM:**
  - Hardened and cleaned – both with and
    without BN
  - Unhardened and un-cleaned – imaged cleaned areas of both with and without BN (un-cleaned areas were too resistive).
- **ICP:**
  - Hardened and cleaned – both with and without BN
- **XPS:**
  - Hardened and cleaned – both with and without BN
  - Unhardened and cleaned –
  - Unhardened and un-cleaned coating
  - Saw material –

❖ **Moh's Hardness Testing:**
  - Hardened and cleaned – both with and without BN
  - Unhardened and cleaned – both with and without BN

WEAR AND EROSION SLEEVE INSERTS

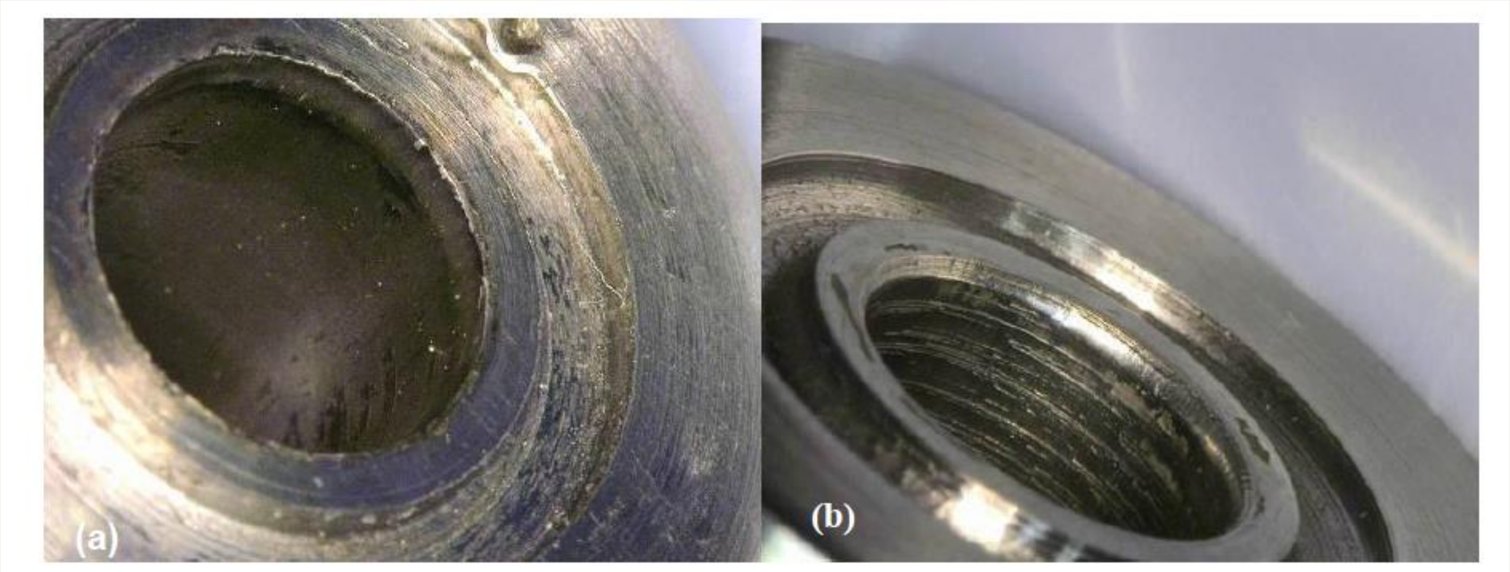


Figure 3: Hardened Steel Sleeves (a) RPD380 P2 flow entrance end, sleeve 1. (b) BN-RPD380 P5 Flow Exit end, sleeve 2 – cleaned after 3 shots

Wear and Erosion Sleeve Inserts

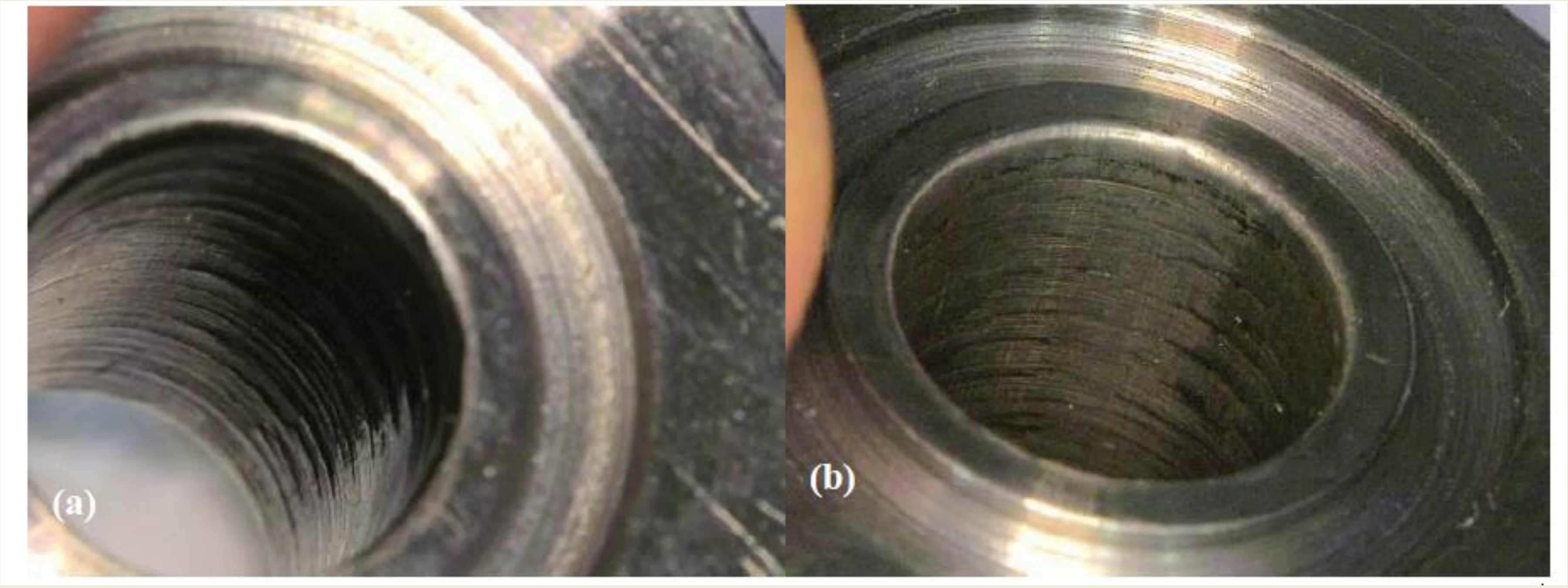
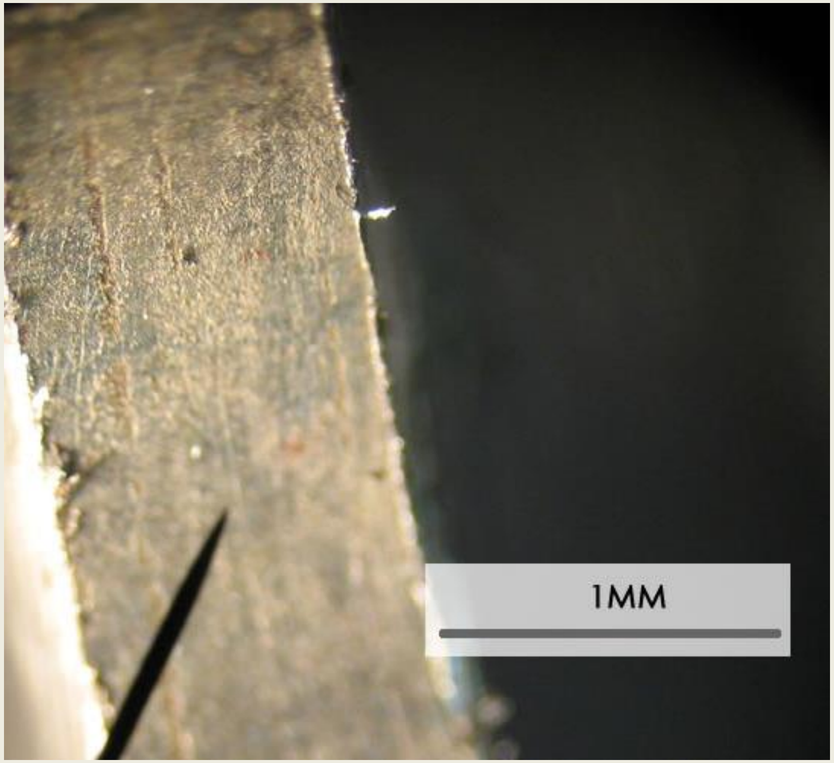
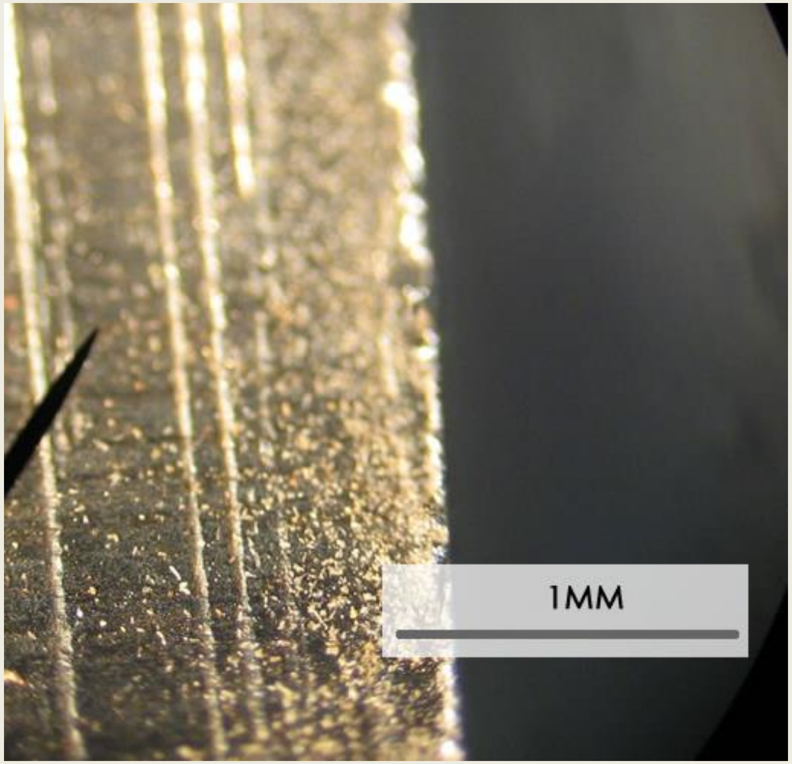


Figure 4: Insert Sleeve 2 – (a) hardened Steel, after firing 3 shots RPD380 Propellant (Cleaned) , RPD380 P - Flow Entrance End – cleaned after 3 shots (b) RPD380 P - Flow Exit End – cleaned after 3 shots

Light Micrographs

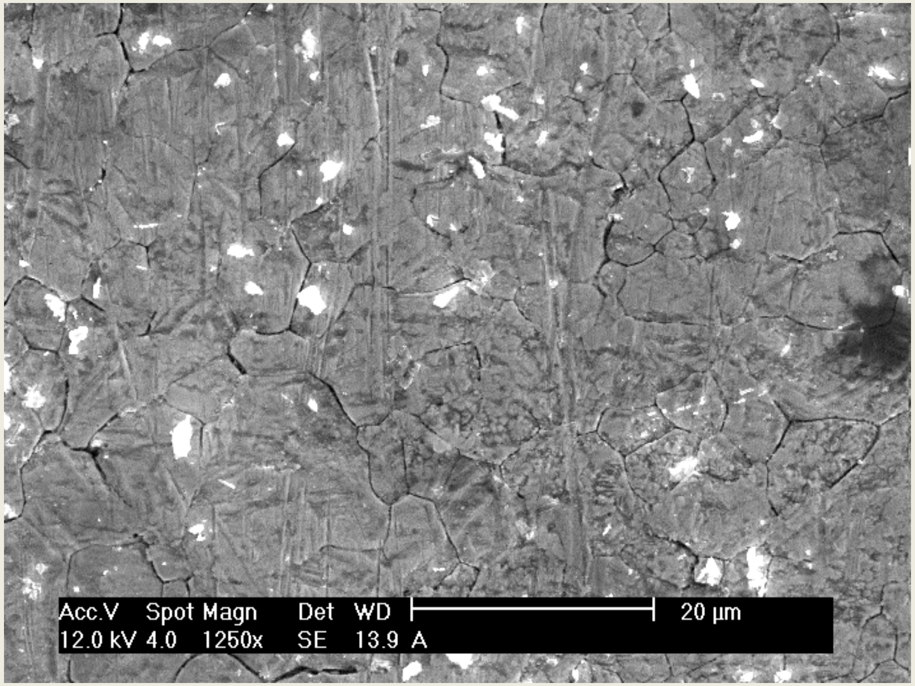


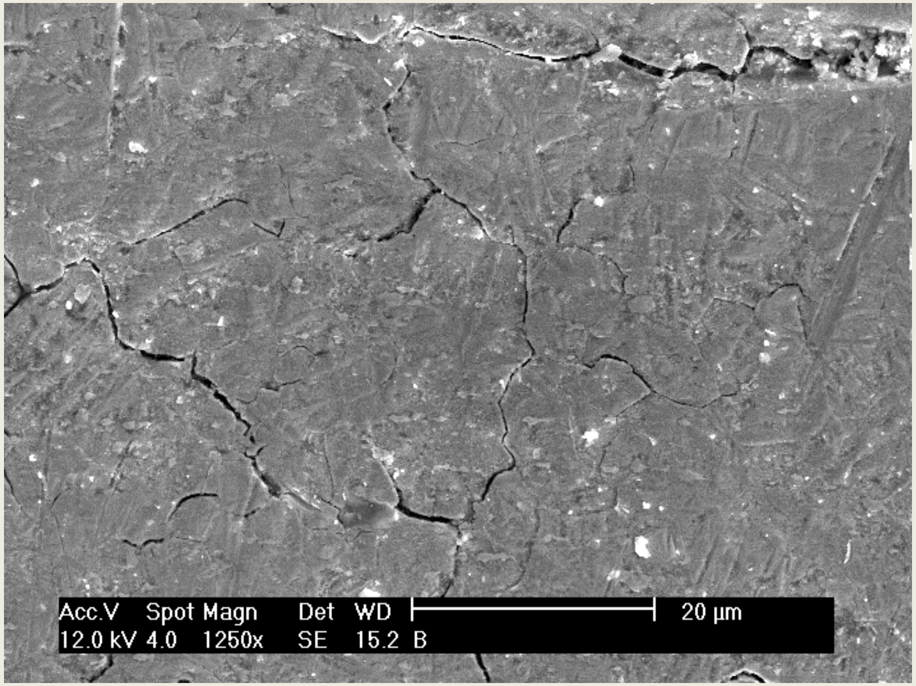


Hardened, Cleaned

Without BN **With BN**

SEM (1,250x)

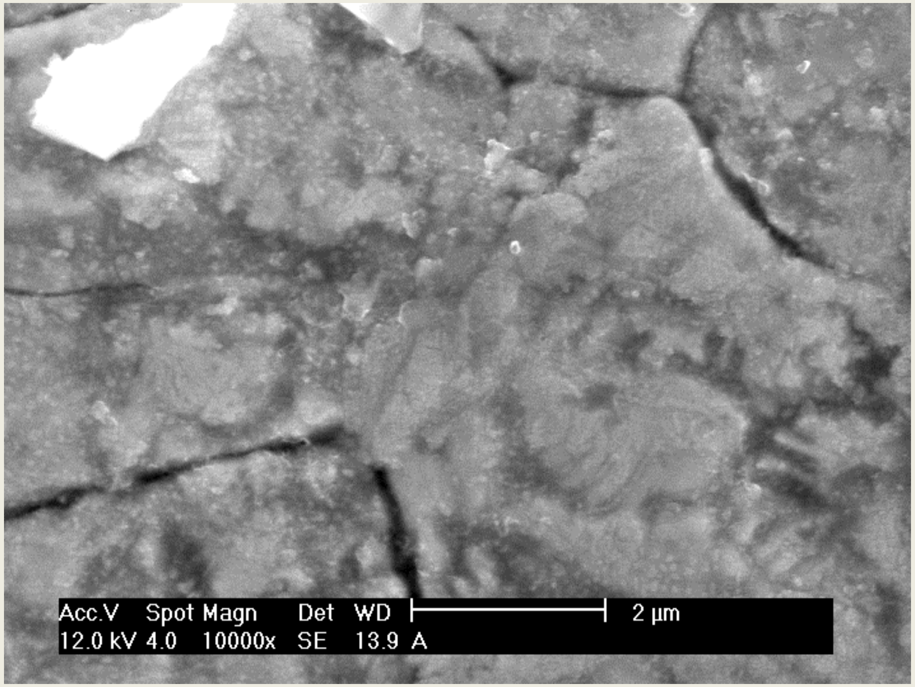


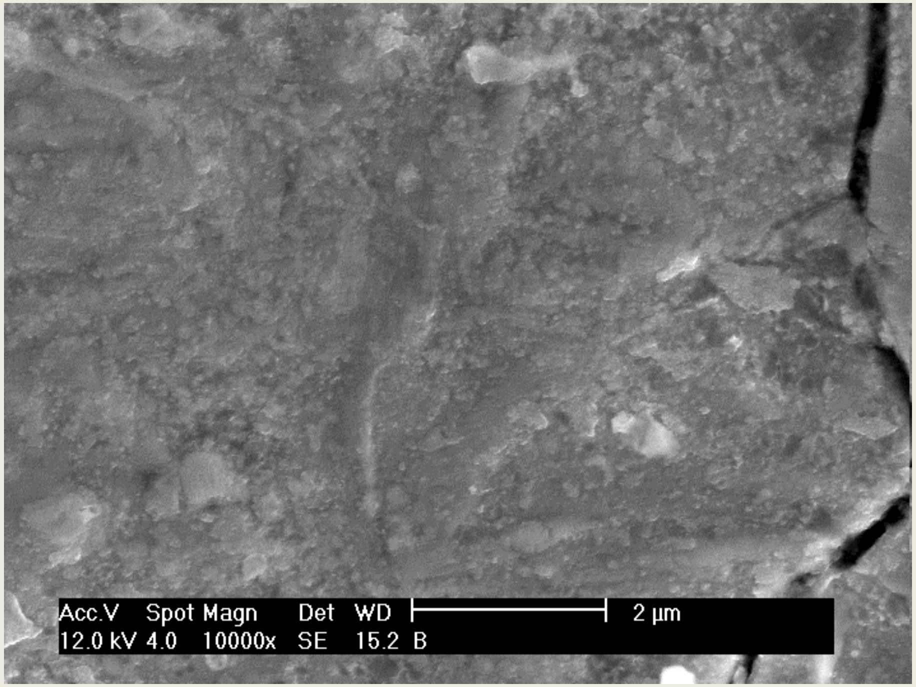


Hardened, cleaned

Without BN **With BN**

SEM (10,000x)



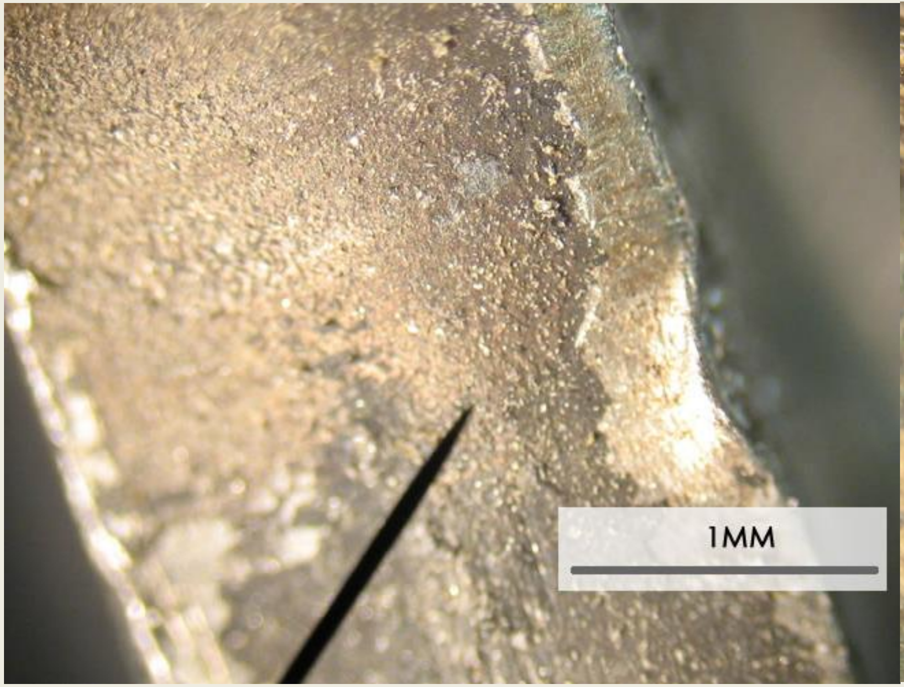


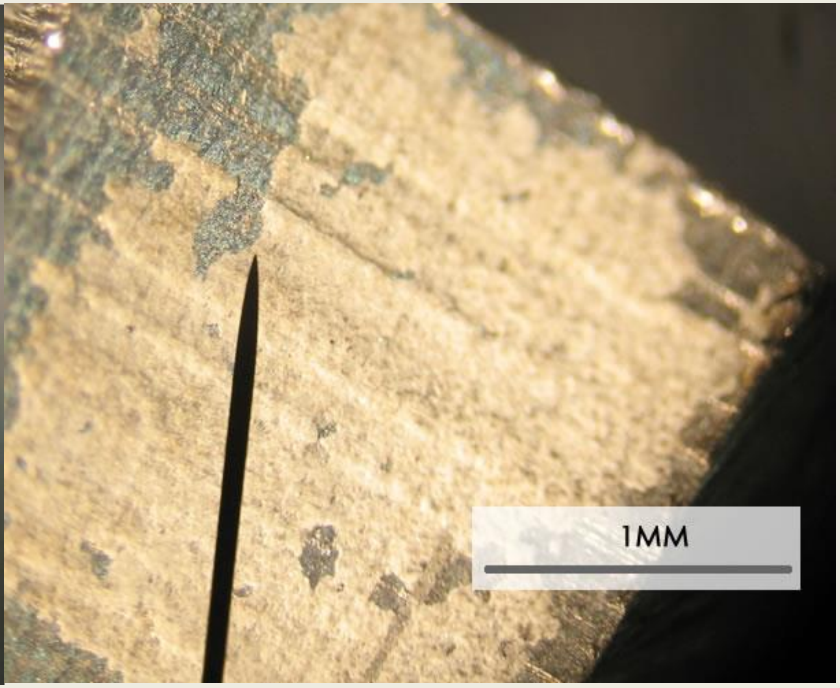
Hardened, Cleaned

Without BN

With BN

Light Micrographs



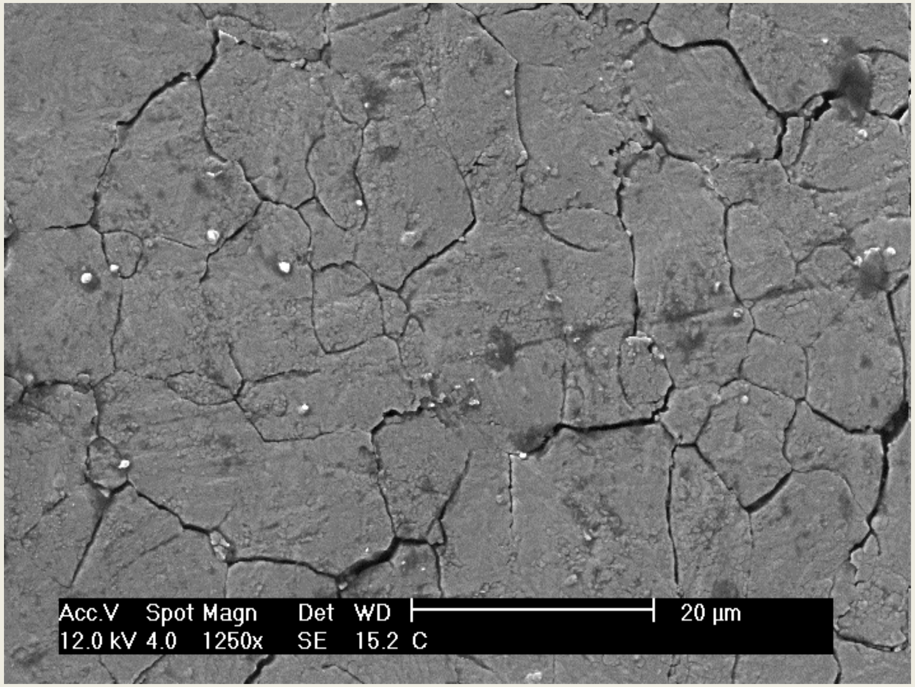


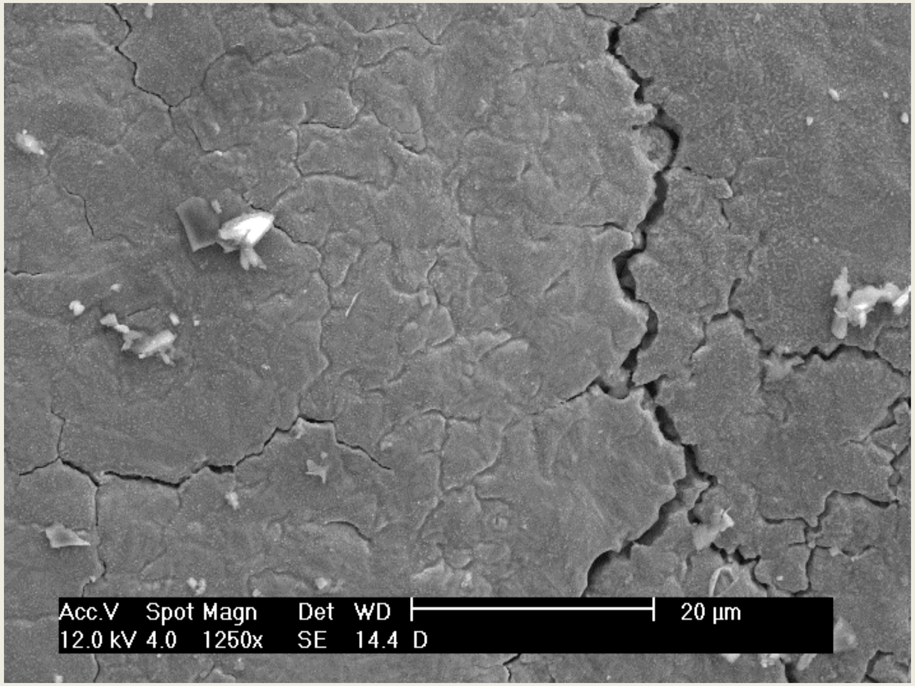
Unhardened, un-cleaned surface

Without BN

With BN

SEM (1,250x)

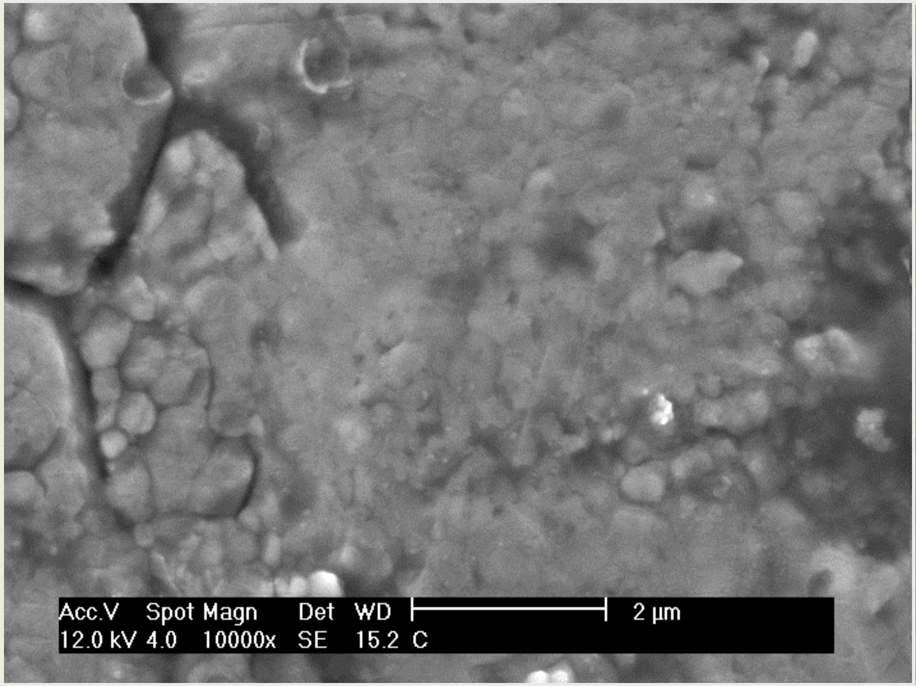


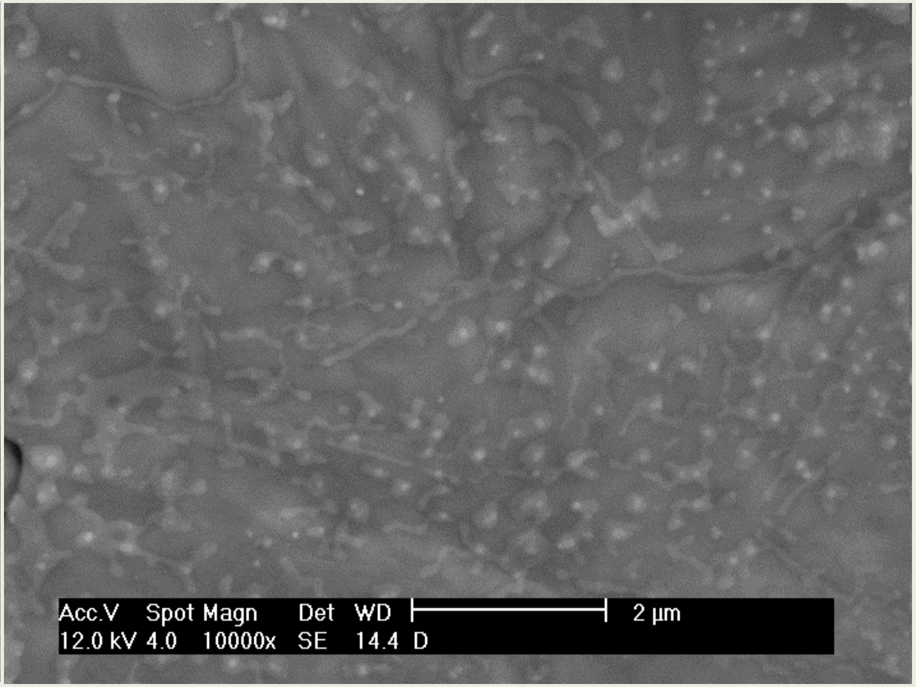


Unhardened (clear area)

Without BN **With BN**

SEM (10,000x)





Unhardened (clear area)

Non BN **With BN**

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XPS and ICP Analysis

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Relative Composition					
Element	Hardened (0% BN)	Hardened (B% BN)	Unhardened (B% BN)	Unhardened (B% BN)	Coating from Unhardened B% BN
C	65.2%	19.9%	29.9%	13.1%	64.6%
B	0.0%	0.0%	0.0%	0.4%	2.3%
N	2.8%	1.4%	0.0%	0.9%	5.2%
Fe	32.0%	78.7%	70.1%	85.6%	27.9%

Hardened and cleaned surface composition

- After firing, the samples were analyzed by XPS to determine surface composition, and ICP analysis to determine the bulk composition.
  - Relative surface composition for samples fired in wear and erosion testing.
  - ICP analysis showed less than 0.01% B in all samples, and the remaining composition is consistent with the respective steel specification.

HARDNESS AND TESTING

Sample	Hardness
Unhardened steel reference	5.5
Hardened, without BN	7.0
Hardened, with BN	7.5
Unhardened, without BN	5.5
Unhardened, with BN	7.5

HARDNESS AND TESTING

Sample	Hardness
Unhardened steel reference	5.5
Hardened, without BN	7.0
Hardened, with BN	7.5
Unhardened, without BN	5.5
Unhardened, with BN	7.5

CONCLUSIONS

- Evidence for reduced erosion observed.
  - The results look compelling at 2.8 and 1.8 times life increase for hard and unhardened insert sleeves, respectively.
- Propellant with BN generates a lower flame temperature.
- Increased hardness was observed in unhardened steel fired with BN additive.
- SEM imaging showed less surface crack density in the samples fired with boron nitride.
- No destabilizing effects on propellant.
- Boron-based coating was observed.

Future Work

- More quantitative hardness testing after extended firing would be useful to verify a hardening mechanism
- Characterization of the boron, possibly in or on the steel surface, would also be beneficial.
- Further wear and erosion testing of the propellant additive is in progress in a 25mm gun test fixture/projectile test stand that will simulate the conditions of 155 mm artillery.
  - Larger amount of propellant necessary to support a sufficient number of firings to generate supportable statistical conclusions
  - Alternate grain form to allow larger bomb loading density

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