Innovative Boron Nitride-doped Propellants

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Abstract

The U.S. military has a need for more powerful propellants with balanced/stoichiometric amounts of fuel and oxidants. However, balanced and more powerful propellants lead to accelerated gun barrel erosion and markedly shortened useful barrel life. Boron nitride (BN) is an interesting potential additive for propellants that could reduce gun wear effects in advanced propellants (US Patent Pending 2015-026P). Hexagonal boron nitride is a good lubricant that can provide wear resistance and lower flame temperatures for gun barrels. Further, boron can dope steel, which drastically improves its strength and wear resistance, and can block the formation of softer carbides. A scalable synthesis method for producing boron nitride nano-particles that can be readily dispersed into propellants has been developed. Even dispersion of the nano-particles in a double-base propellant has been demonstrated using a solvent-based processing approach. Stability of a composite propellant with the BN additive was verified. In this paper, results from propellant testing of boron nitride nano-composite propellants is presented, including closed bomb and wear and erosion testing. Detailed characterization of the erosion tester substrates before and after firing was obtained by electron microscopy, inductively coupled plasma and x-ray photoelectron spectroscopy. This promising boron nitride additive shows the ability to improve gun wear and erosion resistance, without any destabilizing affects to the propellant. Potential applications could include less erosive propellants in propellant ammunition for large, medium and small diameter fire arms.

Keywords: nano-Boron Nitride; additive; lubricant; gun barrel; wear and erosion; gun propellant

1. Introduction

The U.S. military has a need for more powerful propellants with balanced/stoichiometric amounts of fuel and oxidants to provide an advantage to its warfighters. The useful life of each gun is limited either by the effects of barrel erosion on its performance or metal fatigue. The enlargement of the origin of rifling or the down bore area can affect ammunition performance resulting in range and accuracy loss, fuze malfunctions, excessive torsional impulse and excessive muzzle flash and blast overpressure. With increased demands for guns that fire faster, farther, and more accurately, barrel erosion has worsened and become a major limitation in developing better guns [1,2,3]. For example, with advanced propellants 155 mm artillery barrels may only survive a couple hundred rounds before they must be replaced at a cost of over $70,000 [4].

Many Low Vulnerability (LOVA) propellant formulations contain RDX, and it has been convincingly shown by several investigators that RDX is highly chemically erosive. New, experimental low-erosivity LOVA propellants have been produced by reducing RDX content and introducing nitrogen-rich energetic binder or filler compounds. The resulting propellant combustion gases, rich in nitrogen, act to re-nitride bore surfaces during firing and inhibit erosive surface reactions. The result is increased bore hardness, increased resistance to melting, and reduced chemical erosion. The lowered hydrogen

concentration in the combustion gas of some of these propellants may also reduce hydrogen-assisted cracking of the bore surface. Of the high-nitrogen propellants under development, the majority possess impetus and flame temperatures lower than RDX: a compromise between performance, sensitiveness and erosivity must be reached in these cases.

Significant effort has recently been directed at understanding the erosion mechanisms for barrels coated with protective refractory metals. The most plausible mechanism is that micro-cracks in the coatings, present from the time of manufacture, propagate due to pressure and thermal stress cycling and eventually reach the gun steel substrate. Through numerical modelling and analysis of eroded barrels, a number of investigators have shown that once cracks reach the substrate, chemical erosion, gas wash, and high interfacial temperatures cause pitting of the substrate and eventually undermine the coating. Segments of coating are subsequently removed by the flow or engagement with the projectile, and at this point the erosion rate of coated barrels may exceed that of steel barrels. A number of ways to mitigate this erosion pathway have been suggested, including: development of better coating techniques to avoid the initial micro-cracks, pre-nitriding the gun steel before coating to slow substrate erosion, introducing a protective interlayer, and controlled barrel storage and post-firing treatment to prevent oxidation of exposed substrate. Modelling and experiments have additionally shown that, with the notable exception of chromium, the erosion resistance of refractory metal coatings varies amongst different propellant gas chemistry environments. Ceramic additives to the propellant can theoretically reduce barrel deterioration by coating the inside of barrels, but implementation of composite propellants with conventional ceramics (i.e. alumina) has not resulted in improved wear resistance to date. Due to 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. Due to very good wear characteristics and thermal resistance, ceramic barrel liners have been identified as a promising technology for some time. However, the susceptibility of ceramics to fracture, driven by stress induced by the different thermal expansion properties of steel and ceramics, have prevented their widespread use.

The currently fielded 155mm artillery propelling charge, M232/M232A1, has exhibited spiral wear and erosion problems. This was due to either the wear reducing liner, containing titanium dioxide, talc and wax, and other contributing factors. This resulted from the propellant chemistry and interaction of the combustion products within the gun tube wall. Modeling & Simulation studies performed by Dr Samuel Sopok from Benet Labs has determined that the reaction of titanium dioxide with the talc and wax produced a residue that was hard to remove[5]. This product was an abrasive residue (number 80 ceramic grit) that built up in the gun barrel. This caused a spiral rifling imbalance and accelerated gun barrel erosion which markedly shortened gun barrel life. Boron nitride is an interesting potential additive to propellants that could reduce gun wear effects in advanced propellants. It has the properties of providing metal coating/lubricating, and steel hardening properties and nitrogen cooling effects.

On the other hand, Boron Nitride (in the form of crystalline hexagonal BN or amorphous BN) has interesting properties for a propellant additive (US Patent Pending). BN can form a lubricating coating on barrel walls. BN coated ammunition is currently used commercially for small arms to lubricate barrels and ammunition [2]. Further, boron can be used to dope steel, which drastically improves its strength and wear resistance. Boron-doped steel is used to reduce wear in numerous industrial applications, and is typically produced by annealing steel that has been packed in boron oxide [6-12]. In this paper, we explore a new concept where BN is used as a propellant additive that can regeneratively coat and harden steel barrels. The BN is in the form of a nano-particle that can be evenly dispersed in the propellant without negative impact on its performance. Dispersion studies were performed to determine how easily the amorphous BN nano-particles could be dispersed in propellants. Scanning Electron Microscope (SEM) image of the BN in a commercial off-the-shelf double base propellant (1:1 by weight) dispersed with acetone/alcohol is shown in figure 1 below. The BN nano-particles were evenly dispersed, and measured 38 nm on average.
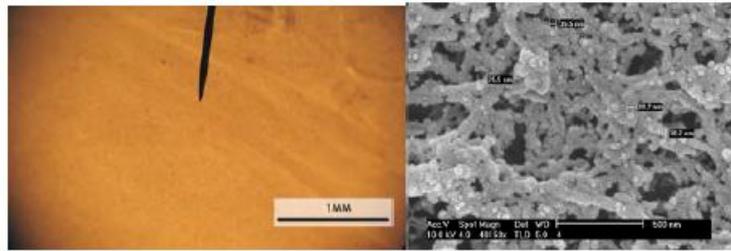
Figure 1. SEM image of double base powder and amorphous BN (1:1 by weight) dispersed with acetone/ethanol using a sonic horn, and deposited onto a glass slide (48,000X magnification); the BN nano-particles were evenly dispersed, and measured 38 nm on average.

Further, the production of the nano-scale boron nitride is economical. An economic model was constructed to project the cost of producing BN nano-particles from raw materials at the anticipated commercial scale (50,000 kg/yr**).** Based on this analysis, the projected cost of BN at the 50,000 kg/yr scale was found to be $91.15 per kg. This cost is reasonable because we use such a small percentage in the propellant formulation.

2. Experimental Section

2.1 X-ray Photoelectron Spectroscopy (XPS)

For XPS analysis, powder samples were pelletized by hand and loaded into a steel pellet sample holder. The samples were loaded into a Kratos Axis Ultra XPS, and pumped down overnight to achieve ultra-high vacuum levels. All samples were first analyzed in a survey scan from 1200 to 0 eV to determine the elements present on the surface. All samples analyzed contained B, N, and lower levels of C, and O. The carbon and oxygen is typical from atmospheric contamination (dust and oils). Detailed scans were run for B 1s and N 1s regions to determine the oxidation state and ratio of species, with a charge neutralizer applied to the samples to prevent spectra shifting.

2.2. Differential Scanning Calorimetry (DSC) and Vacuum Thermal Stability (VTS) Tests

Testing was conducted per NATO PIP US/202.01.020 *"Differential Scanning Calorimetry (DSC)" which is also described in* ASTM E537 - 07 *"Standard Test Method for the Thermal Stability of Chemicals by Differential Scanning Calorimetry"* and MIL-STD 1751A Method 1072 *"Differential Scanning Calorimetry (DSC)."* A Differential Scanning Calorimeter (TA Instruments Model 2910) was utilized to determine the ignition temperature (exothermic peak) and melting temperature (endothermic peak) of the material. The test was carried out in nitrogen gas. The temperature ranged from room temperature to 400°C. The sample container (aluminum pan and cover) containing the material was placed into the measuring cell and heated at a rate of 10°C and 20°C per minute. The peak temperatures (corresponding to exothermic decomposition and endothermic melting) along with onset temperature were determined and recorded.

Vacuum stability testing is performed in accordance to STANAG 4556 ED.1 (*Explosives: Vacuum Stability Test).*This standard testing procedure measures the stability of an explosive at an elevated temperature under vacuum. The stability of a candidate explosive is determined by the amount of gas evolved. To qualify as a chemically stable material, no explosive may produce more than 2ml of gas per gram. The material is tested for 48 hours at 90 degrees Celsius.

2.3. Closed Bomb Testing

One of the ways to assess propellant performance is through combustion testing. The closed bomb test is a standard device used to measure gasification rates for energetic materials. Knowledge of propellant chemical formulation and geometry allows for calculation of a linear burn rate from the measured pressure versus time data. Performance is given in terms of relative quickness (RQ) and relative force (RF). Relative quickness applies to the speed with which the material burns and is a comparison of the pressurization rates (dP/dt). Relative force is a comparison of the peak pressure levels observed in the bomb (Pmax). There were two closed bomb tests conducted using the procedure P1-BPP MIL-STD-286C, Section 801.1.2 and guided by STANAG 4115. For the first test, two shell-shaped inserts of heat-treated and polished 4340 steel were placed inside the chamber to determine if any reactivity occurs between the BN and the steel, and to determine if a boron-based coating forms. The second test was performed to determine the burn rates of the RPD-380 composite propellant with and without BN in preparation for the wear and erosion test.

2.4 Composite Propellant Preparation for Wear and Erosion Test

It is hypothesized that boron nitride (BN) in nano-particle size range incorporated into a propellant during mixing may reduce the erosion that propellant combustion gases cause to a gun bore. In order to provide an initial test of this proposal, two batches of nominal double base propellant composition RPD-380 were fabricated using a solvent mixing process. The two batches consisted of the baseline RPD-380 formulation and the same formulation with nano-scale boron nitride sample provided. The propellants were extruded in single perforation strand form and cut to grain length, as shown in figures 2 and 3, respectively. Closed bomb testing was conducted on each of the materials and then analyzed for acceptable burning properties and burning rate. Both propellants are high energy propellants with high flame temperatures. Using the MCVEC[13] thermochemical equilibrium program, baseline RPD-380 calculated heat of explosion is 1156 cal/ gram, with a flame temperature 3573 K at loading density 0.13 gram/cc; the baseline RPD-380 with BN composition has a calculated heat of explosion of 1100 cal/gram and flame temperature of 3451 K at the same loading density.

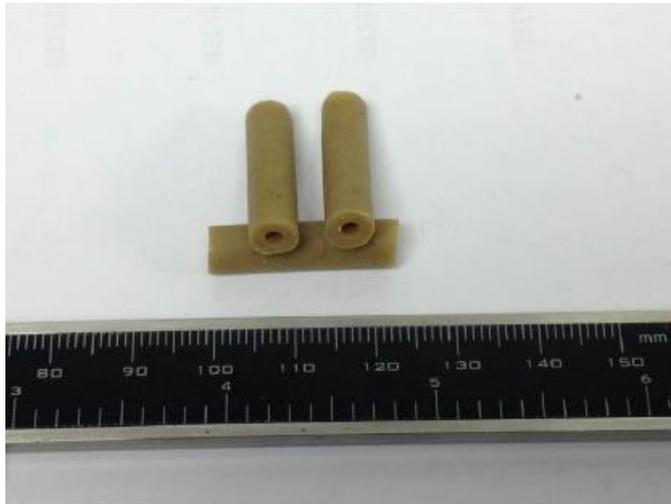**Figure 2:** RPD380 without BN - Single Perf grain used in erosion testing

Figure 3: BN-RPD380 (US Patent Pending) Single Perf grains used in erosion testing

2.5. Propellant Wear and Erosion Testing

The goal of this testing is to determine whether the addition of the nano-scale BN to a propellant does reduce the erosion on typical gun steel, and to provide gun steel samples exposed to erosive gas flows for further analysis. The ARDEC erosion tester used, produces the erosive environment by burning a known amount of propellant in a high pressure vented 200 cc bomb, and recording the weight of a metal insert sleeve before and after firing. The loss in weight of the insert sleeve is the erosive loss. The erosion tester is a modified closed bomb that has a burst disk which breaks at a certain pressure (determined by the thickness and material of the disk) and then vents the bomb gases outward through the bore of the cylindrical steel test insert sleeve.

The two propellants were each fired using two steel sleeves of different hardness. Prior to firing the baseline or propellant with BN, all sleeves had a shot of JA2 fired through them with the intent to smooth out machining defects in the sleeves and have them be at a more uniform initial state prior to testing. The hardened steel sleeves had three shots each fired in them; these were sleeves labeled 1 and 2, with the baseline propellant fired in sleeve 1 and the propellant with BN in sleeve 2, shown in figures 4 and 5 respectively. The unhardened sleeves had four (baseline) or five (with BN) shots each fired in them, with the baseline propellant in sleeve 3 and the propellant with BN in sleeve 4. The final shots in sleeves 3 and 4 were not cleaned and the sleeves were not weighed after those shots so that the residue could be retained for analysis.

The propellant with added BN burned at a lower rate than the baseline, so based on a closed bomb calculation an extra gram of that propellant was fired in each of its shots to account for the pressure difference and thus provide a better pressure match with the shots generated by the baseline propellant. In order to get the best and most accurate results it is important to keep conditions in the erosion tester as similar as possible. In the present tests the maximum pressure range of 20,000-22,000 psi typically used for routine erosion tests was targeted. The thermo-chemistry, burning rate and form function of the propellant grains to be tested resulted in required propellant sample loading densities (grams of propellant per unit bomb volume) nearly 50% lower than is typically employed. Consideration of the propellant weight burned obviously affects the flow time of the combustion gases through the insert sleeve. In addition, in comparing individual tests, there are always some minor variations in the burning process and the peak pressure developed at burst disk rupture.

The 26.4 grams of baseline propellant and 27.3 grams of propellant with BN were fired. The propellants did not have the exact same weight due to variation in weights of individual grains. An extra shot was fired in sleeve 4 due to having enough remaining material. All shots were ignited by using an electric match initiated 1-gram sample of M38 ball powder. Using ball powder rather than black powder as an igniter reduces the sulfur and potassium compound content of the combustion products to a very low level.

The sleeves are marked with a number of small indentations equal to their sleeve number to identify them and to ensure that the sleeve was facing the same way on every shot. Each sleeve was cleaned and weighed before and after every shot (excluding the last shots on sleeves 3 and 4, as mentioned above) in order to measure the weight loss that each shot caused. Sleeves were cleaned with soap and water until no visible residue remained and then thoroughly dried prior to weighing.

Figure 4: Hardened Steel Sleeves (a) RPD380 P2 flow entrance end, sleeve 1. (b) BN-RPD380 P5 Flow Exit end, sleeve 2 – cleaned after 3 shots.
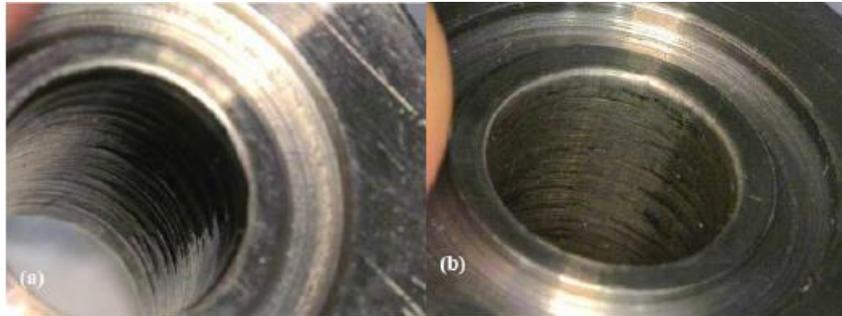

Figure 5: Insert Sleeve 2 – (a) hardened Steel, after firing 3 shots RPD380 Propellant (Cleaned) RPD380 P - Flow Entrance End –cleaned after 3 shots   (b) RPD380 P - Flow Exit End –cleaned after 3 shots

3. Results and Discussion

3.1 Boron Nitride Characteristics

Under this project, a proprietary process for production of dispersible boron nitride nano-particles to use as a propellant additive was developed. The process does not use a catalyst, and the boron nitride precursor is free (<1 ppm detection limit) of metal contamination. The process involves nucleation of a boron and nitrogen based precursor, so the product particle size can be controlled based on the reactant concentration. Typical bulk BET surface areas range from 20 m^2/g to 80 m^2/g, depending on process conditions, consistent with spherical particle diameters from 143 nm down to 37 nm.

Electron microscopy of the BN product shows that the morphology of the BN is indeed nano-particle spheres. Figure 6 shows SEM images of typical particles. Although the particles agglomerate upon drying, it is clear from the images that the individual particles are spheres with diameters in the nanometer range.
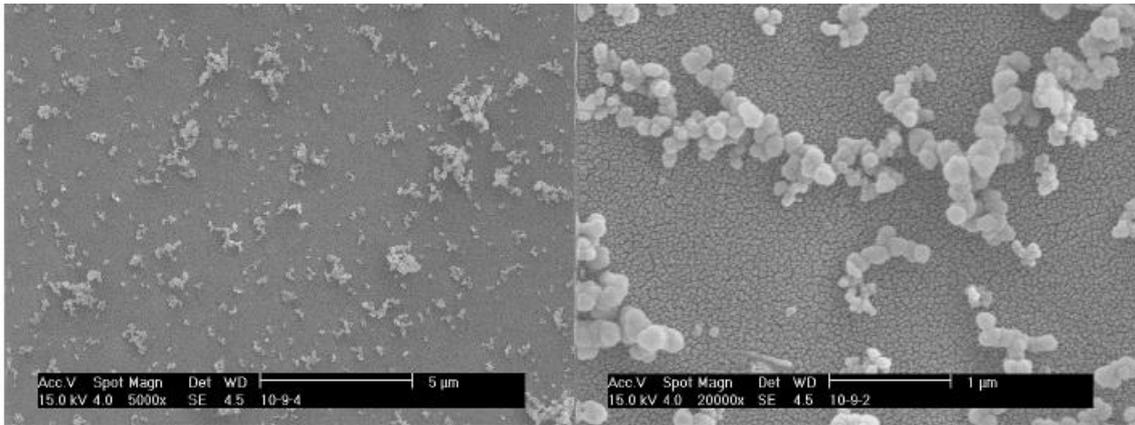
Figure 6: Scanning electron micrographs of BN nano-particles (US Patent Pending) used for propellant additive testing.

The surface of the BN nano-particles was characterized to verify the material composition and how it may interact with propellant. X-ray photo-electron spectroscopy (XPS) was used for this characterization. XPS analysis is sensitive to the first few atomic layers of a material, so it can be considered a surface analysis tool.

Figures 7a and 7b show the N 1s and B 1s regions for the samples respectively. The BN nano-particles prepared are compared to conventional commercial hexagonal boron nitride obtained from Alfa Aesar. As can be seen from these figures, the ratio of B:N is the same for both materials. Further the oxidation states of the boron and the nitrogen are the same in each sample. The binding energy (oxidation state) for boron is consistent with literature values for boron nitride. It should be noted that XPS analysis has been repeated on materials that were aged in air for 6 months, and no change in oxidation states were observed.
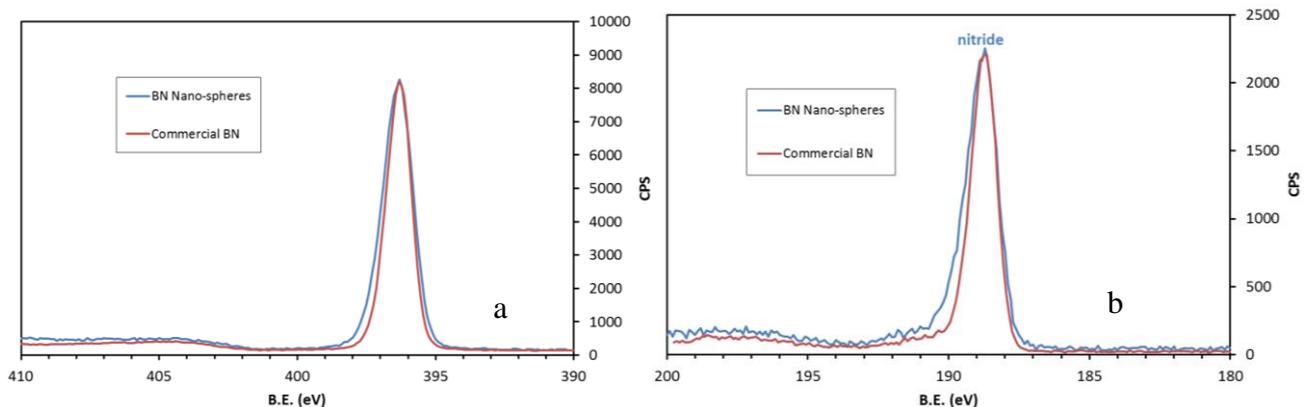

Figure 7: XPS analysis showing (a) the N 1s region, and (b) the B 1s region for the BN nano-particle propellant additive compared to a commercial hexagonal boron nitride sample.

Transmission electron microscopy (TEM) imaging in conjunction with electron energy loss spectroscopy (EELS) was also run on the material to characterize the BN particles. Figure 8a shows the TEM images of the particles, which appear to be amorphous spheres. Figure 8b shows the EELS analysis, within the accuracy of the measurement, verified that the material has a 1:1 B:N ratio, consistent with boron nitride.
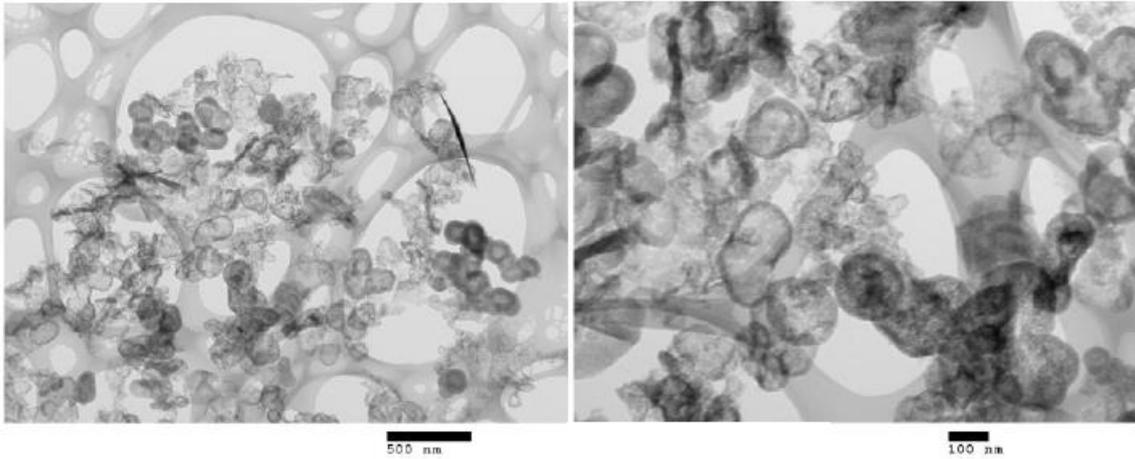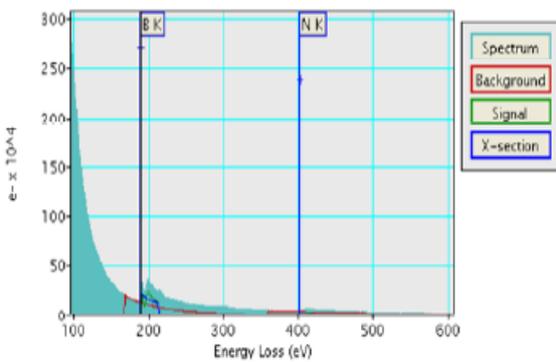
Figure 8a: TEM images showing nano-spheres of boron nitride used for propellant additive testing(US Patent Pending).

Figure 8b: EELS analysis, showing the material has a 1:1 B:N ratio (US Patent Pending).

3.2 Composite Propellant Testing

In the first round of testing, a composite propellant was prepared using a commercially-available nitrocellulose double-base propellant, IMR-4198 (Hodgdon). Preparation of composite propellant was conducted under solvent (acetone:ethanol 1:1) in a small rotating mixing chamber, with sufficient solvent added to soften the propellant to a dough-like consistency. Two batches were prepared, one with additional B-wt% BN nano-particles, the other without addition of BN. Both propellants were subjected to the same mixing conditions (~2 days in the mixing chamber) to provide a control comparison in testing.

RPD-380 nitrocellulose based propellant with and without BN were prepared using the conventional solvent process in a horizontal sigma blade mixer. The propellants were extruded into single perforated geometry.

3.2.1. Differential Scanning Calorimetry and Vacuum Thermal Stability Tests

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DSC measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. This test method is recommended as an early screening test for detecting the thermal hazards of an uncharacterized substance. For explosives and energetic materials study or development, a DSC may be used to measure safely, the energy released by a small amount of a sample without any catastrophic consequences.

DSC tests were performed in triplicate on the materials (both IMR 4198 and IMR 4198 with B-wt% BN) to determine the combustion initiation temperatures. The onset temperature is indicated by examining any deviation in the reaction mass temperature from the heating rate. The peak height or area under the curve indicates the magnitude of the energetic activity. The DSC test results showed the average onset exothermic reaction at heating rate of 10°C/min was 161°C and the average peak exothermic was 207°C for both samples tested. It appears the addition of BN (B wt %) did not have any significant effect on DSC thermal test results, indicating the BN does not destabilize the propellant under the DSC conditions. The heat of reactions also remained unchanged within the measurement capabilities of the technique.

VTS is performed in accordance to STANAG 4556 ED.1 (Explosives: Vacuum Stability Test).This standard testing procedure measures the stability of an explosive at an elevated temperature under vacuum. The stability of a candidate explosive is determined by the amount of gas evolved. To qualify as a chemically stable material, no explosive may produce more than 2ml of gas per gram. The material was tested for 48 hours at 90 degrees Celsius. Based on test results, which were conducted in accordance with the defining criteria of STANAG 4556 ED., the RDD24F-001T5 propellant lot with B% BN produced less than 2ml of gas per gram for a five gram sample and therefore passes vacuum stability criteria according to military specifications.

3.2.2. Bomb Testing with Steel Inserts

The first closed bomb test was used to determine the Relative Quickness(RQ)/ Relative Force (RF) to characterize propellant samples and the resulting coating formed on steel inserts. An overview of the results of the tests is given below in Table 1A. Pure IMR-4198 and the B% composite propellant were tested at different loadings. Additionally, a physical mixture of 1:1 IMR-4198 and the composite were tested to obtain B% BN composite. The maximum pressure was measured with a high speed DAQ system for the pure IMR-4198 and the B% BN composite.

Propellant	Amount (g)	Pressure (psig)	Insert in Figure 9	Observation
IMR-4198	5.0	9,170	(a)	Rust color
IMR-4198	7.5	15,470	(b)	Rust color
A% BN	5.0	10,250	(c)	Black
B% BN	5.0	~10,000	(d)	Black
B% BN	7.5	~15,000	(e)	Black/green

Table 1A: Overview of Bomb Tests with Steel Inserts (A<B).

A photograph of the steel inserts that resulted from this testing is shown in Figure 9. Stark differences in surface oxidation of the steel inserts were observed. Visually, there were some dramatic differences between steel inserts that were fired without an additive, versus inserts with BN additive.

Samples (a) and (b) did not have any additive, and both samples looked oxidized with a distinctive orange rust color. The oxidation was worse for the higher propellant loading (higher chamber pressure). Samples (c) and (d) with B% BN respectively at 5 grams loading each were darker after firing, but did not have an orange color indicative of steel oxidation. Sample (e) was fired with 7.5 grams of IMR-4198 with B% BN and had a green color. These initial results are promising, as it seems BN may be preventing steel oxidation; however, more work remains to understand the nature of this coating and verify any effect on wear and erosion resistance.
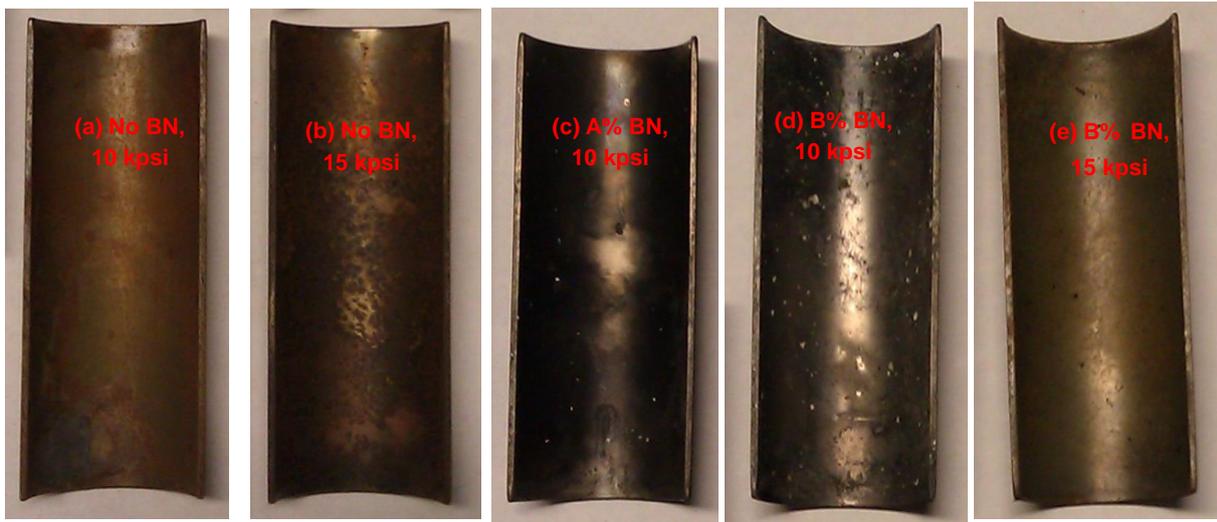

Figure 9: Photographs of steel inserts after closed bomb testing at ~10,000 psi and ~15,000 psi; listed in Table 1; Steel inserts after bomb testing samples fired with a composite propellant containing BN (A<B) had less oxidation than sample fired with pure propellant.

A 200cc high pressure closed bomb testing of the RPD-380 baseline propellant was also performed to determine the burn rates with and without BN added in the propellant, shown in Table 1B. The RQ, RF and Relative Vivacity (RV) values less than 100% value can be explained as due to the high percentage of BN added in the propellant formulation to simulate the worst case scenario of adding an inert additive. The propellants burned much better than their appearance might have indicated and followed the form function geometry of a single perforated grain geometry, shown previously from figures 2 and 3. The graphite was not incorporated. Using the data obtained from this test, the burn rate can be predicted using the Vielle's burn rate law shown in equation 1, wherein P is the pressure in the chamber, α is the burn rate coefficient, and β is the burn rate pressure exponent [2,4].

$$\text{Burn Rate} = \alpha P^{\beta} \tag{1}$$

Propellant Lot Number	α , Pressure Coefficient	β , Pressure Exponent
-0192 (no BN)	0.6515E-03	0.9309
-0193 (with BN)	0.7736E-03	0.9089
RQ = 90.79%		
RF = 96.68%		
RV = 94.28%		

Table 1B: Closed Bomb Test Results for RPD-380 baseline propellant with and without BN.

3.2.3. Steel Insert Characterization

In order to better understand the first closed bomb test results, the steel inserts were characterized by XPS and SEM. Insert samples were first characterized by XPS to determine surface composition and element oxidation states after firing. All fired samples contained B, C, N, O, F, K, and Fe on the surface. The fresh sample had only C, N, O, and Fe on the surface, indicating some of the C, N, and O was in the steel or originated from atmospheric contamination. The first sample fired contained boron, so apparently boron in the chamber re-deposited on samples that were fired in a non-boron propellant; however, the amount of boron in non-BN inserts was significantly less, as will be discussed. The K and F likely originated from the propellant, and remained on the inserts after firing and rinsing. Figure 10 shows the relative abundance of B, Fe, K, and F in the samples. It should be noted that all samples had a similar amount of C (33-44%), and O (33-41%). Clearly the samples fired with the BN composite propellant had more boron, with the 5 gram sample, which was the least oxidized, having the most boron coverage. The amount of iron on the surface increased steadily with the extent of apparent surface oxidation. Based on binding energies of these species, it was apparent that the BN additive is at least partially oxidized on the surface during propellant firing, and that the presence of boron does not seem to affect the iron oxidation state. However, ppm levels of boron doping in the steel would improve hardness, and would not be detectable from XPS analysis of the iron. Samples fired with a composite propellant containing BN exhibited less oxidation than samples fired with pure propellant. Clearly, the less oxidized samples had less iron on the surface, which was generally displaced by boron.
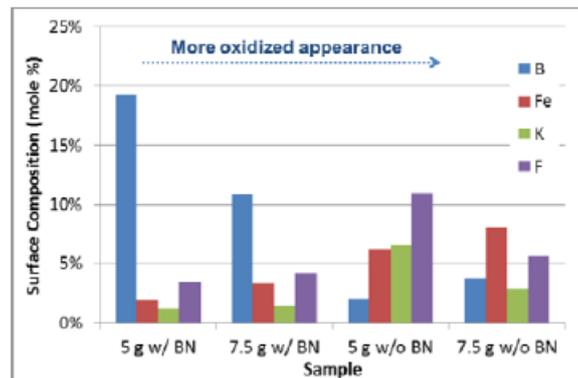

Figure 10: Surface elemental compositions for steel inserts after firing in bomb tests.

SEM with energy dispersive x-ray (EDX) spectroscopy analysis of sample surfaces was performed to characterize the morphology of any coatings formed during propellant firing tests. For reference, an unfired steel insert was imaged, as seen in Figure 11a. The steel insert showed few features at 2500x magnification, as only straight grooves were visible. Figures 11b and 11c compare steel inserts fired without and with BN additive respectively. Both samples seemed to have rougher surfaces compared to unfired steel. At 2500x major differences were visible in the surface morphology. The surface of the sample fired with BN had what appeared to be micron sized platelets covering the surface. These platelets are consistent with the shape of hexagonal BN. The sample fired without BN had spheres and pits, and what appears to be octahedral crystals consistent with Fe_3O_4. EDX elemental analysis confirmed that the samples fired with BN additive were mostly boron, oxygen, and carbon on the
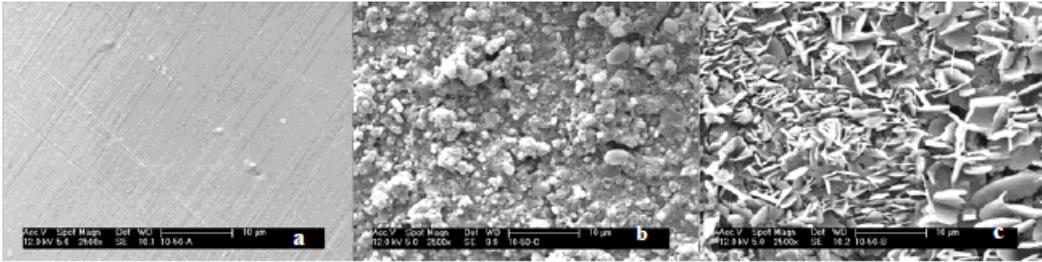
Figure 11: SEM images of (a) unfired steel insert (b) steel insert fired with 5 grams of IMR-4198, and (c) steel insert fired with 5 grams of B% BN composite propellant.

surface. The samples fired without BN did not have any B detectable by EDX, and were mostly Fe, K, and F. This analysis supports that hypothesis that the inserts fired with BN-containing propellant formed a boron-based coating, that apparently covers the iron and reduces the extent of oxidation. It is not clear if the crystals are partially oxidized hexagonal BN or mostly oxidized boron.

3.1.4 Wear and Erosion Test Results

The two types of insert sleeves used for these tests were prepared much earlier for another test. The initial bore surface roughness in both sets of inserts used were of a lower quality than ideal. Based on prior experience with high flame temperature propellants, imperfections in the bore surfaces are usually rapidly removed due to much higher mass loss rates than were observed in tests with highly energetic propellants. From the photos shown in figures 4 and 5, it can be seen that the hardened inserts had rough surfaces with extensive machining features, even after firing. With these features, and the corresponding higher surface area, the mass loss for the hardened inserts is higher than the annealed inserts despite the higher hardness. In both cases with the hardened inserts the shot to shot variation in mass loss is reasonable. The unhardened inserts apparently had less severe initial machining roughness, which apparently accounts for the lower mass loss values despite the lower hardness. From the data shown in figure 12, it appears that the first shot in each group of unhardened inserts experienced a much larger weight loss than the following shots. The small number of shots limits the ability to demonstrate statistically supportive conclusions.

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. The results look compelling at 2.8 and 1.8 times life increase for hard and unhardened insert sleeves shown in figures 13 and 14, respectively. These results must be considered in light of the less than ideal test insert bore surface conditions mentioned above. However, since the propellant formulation with B% BN has a theoretical flame temperature only approximately 100 K less than the baseline composition, mechanisms other than thermal (bore heat transfer) leading to the reduced mass loss must be considered. The presence of particles in the wall boundary layer during flow typically relates to heat transfer alteration to the substrate. The un-cleaned insert sleeves shown in figure 15 following BN-propellant firing show deposits collected as a result of the entire blow-down process of the bomb gas emptying process. Due to the limited number of exposures of the inserts to the combustion products containing BN derived materials, alteration of the steel would seem to be minimal. The very limited number of shots with the BN propellant does not show a progressive reduction in mass loss on subsequent shots after the initial shot. Probing of the steel surface layers and the coating residue may provide added information.
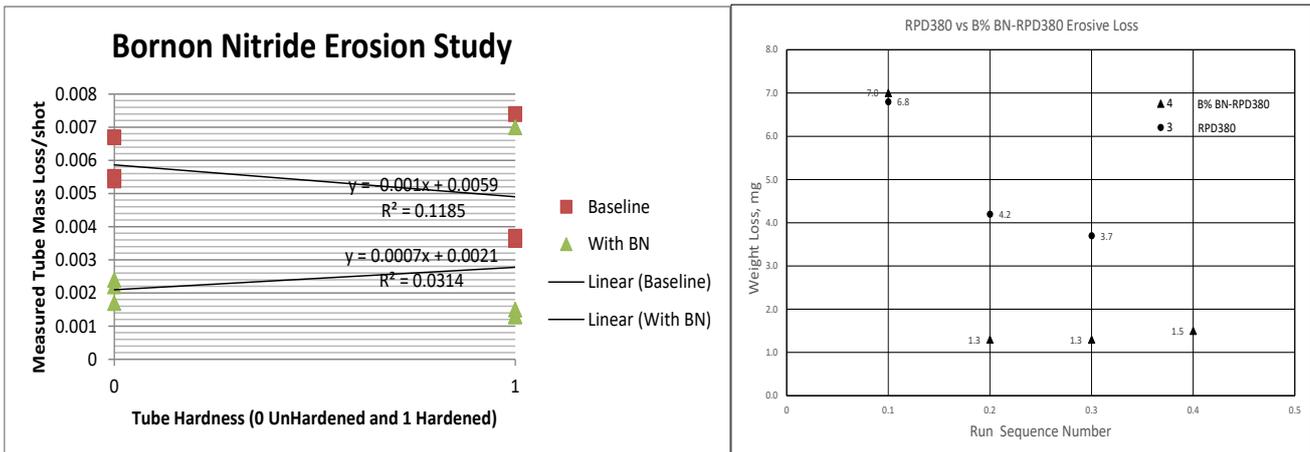
Figure 12: Wear and Erosion Test Results for hard and unhardened sleeves (US Patent Pending). Note: Sleeves 1 and 2 were hardened to approximately Rockwell Hc 41. Sleeves 3 and 4 were approximately Rockwell Hc 12.

4. Characterization of Steel Inserts after Wear and Erosion Testing

4.1. Composition Analysis.

After firing, the samples were analyzed by XPS to determine surface composition, and Inductively Coupled Plasma (ICP) analysis to determine the bulk composition. A number of elements were detected on the surface, including Pb, Fe, Cu, Zn, Sn, Si, Al, S, F, O, N, and B. Since many of the elements may only be surface contamination from the test, and not significant to erosion effects, we focused the analysis on Fe, N, C, and B. A breakdown of the surface composition is given in Table 2 below. After cleaning, very little boron remained on the surface. Only the unhardened sample fired with B% boron contained a detectable amount of boron (0.4%); the detectable limit is about 0.1%. Boron was detected in the coating that was scraped from the surface, but it was lower than the amount present during closed bomb testing, and less than the amount of iron removed with the coating. The bulk ICP analysis showed less than 0.01% B in all samples, and the remaining composition is consistent with the respective steel specification. This low boron content in the 1 mm thick sample indicates that the weight loss differences are real and not due to build-up of boron on the steel.

A large amount of carbon was found on the surface of all samples, but less was present in samples fired with boron. It is not clear if this surface carbon is related to erosion, but iron carbides are softer and melt at a lower temperature than iron. It is possible the boron, apparently in small amounts, could dope (or coat) the steel and block carbide formation. It is also possible, as will be discussed below, that boron dopes the steel in small amounts, resulting in hardened steel. Again, similar to closed bomb tests, based on the oxidation state of boron in the XPS analysis (data not shown) the boron nitride is at least partially oxidized. The iron oxidation state (data not shown) indicates that the iron is mostly 3+ on the surface with a small amount of reduced iron as well.

Relative Composition					
Element	Hardened (0% BN)	Hardened (B% BN)	Unhardened B% BN)	(Unhardened (B% BN)	Coating from Unhardened B% BN
C	0.652	0.199	0.299	0.131	0.646
B	0	0	0	0.004	0.023
N	0.028	0.014	0	0.009	0.052
Fe	0.32	0.787	0.701	0.856	0.279

Table 2: Relative surface composition for samples fired in wear and erosion testing.

4.2. SEM Imaging.

SEM images of the cleaned and uncleaned samples fired in the erosion test stand are shown below. The steel had a number of surface cracks, but the crack density appeared to be less, or cracks were filled in, for the samples fired in boron nitride shown in figures 13, 14 and 15. The surface also appeared to be smoother and less pitted for the samples fired with boron.
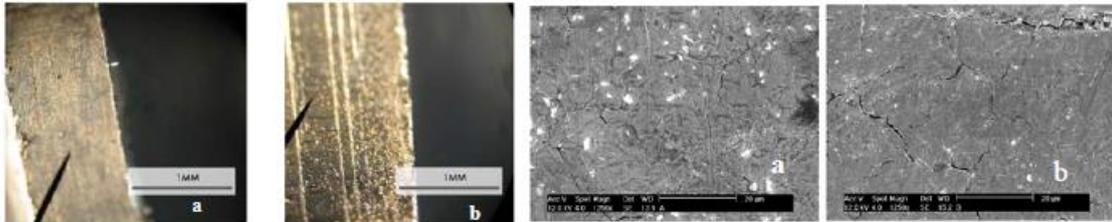

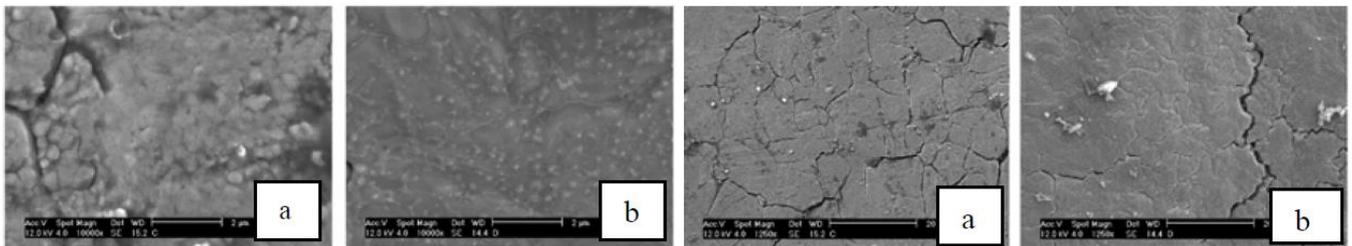**Figure 13:** Hardened Steel Fired (a) no BN (b) with BN

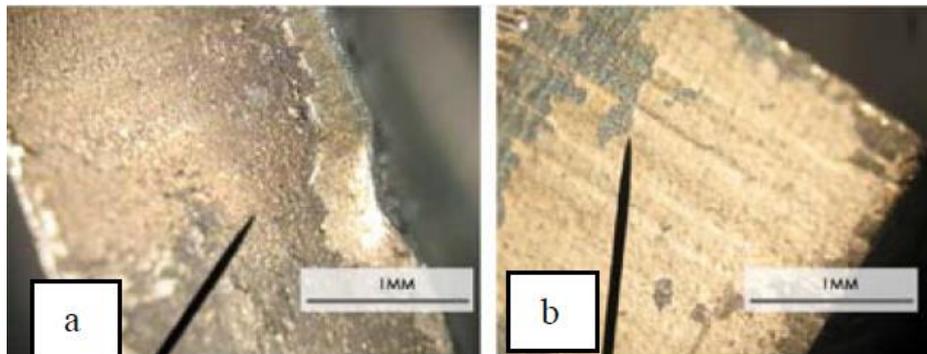**Figure 14:** Un-Hardened Steel Fired (a) no BN (b) with BN

Figure 15: Un-Hardened Un-cleaned Steel (a) no BN (b) with BN

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4.1. Hardness Testing

A simple Moh's hardness test was performed on the samples after erosion testing to determine if the boron is playing a role in hardening the steel. Table 3 shows the results of this analysis. A reference unhardened steel sample was measured to have a hardness of 5.5, typical for steel. Surprisingly, the unhardened steel samples showed an increase in hardness up to 7.5 after being fired with boron in the propellant. The sample fired without any boron remained at 5.5. The hardened sample fired with boron was also 7.5, and the hardened sample fired without boron was approximately 7.0. Based on these results, it is possible that boron doping could regeneratively harden the steel, thus reducing erosion. However, more quantitative testing, such as Rockwell Hardness testing, after extended firing tests would be beneficial to verify this possible mechanism. Further, improved characterization of how the boron may or may not be infiltrating the steel in small amounts would be beneficial to determine if the reduced erosion results from a chemical mechanism (i.e. increased hardness from B doping) and/or a more physical mechanism (i.e. protection of the steel surface or cracks through a coating).

Sample	Hardness
Unhardened steel reference	5.5
Hardened, 0% BN	7.0
Hardened, B% BN	7.5
Unhardened, 0% BN	5.5
Unhardened, B% BN	7.5

Table 3: Hardness Testing Results for insert sleeves fired in wear and erosion test apparatus.

5. Conclusion

A scalable and economical proprietary process for production of BN nano-particles has been developed. An economic model was constructed to project the cost of producing BN nano-particles from raw materials at the anticipated commercial scale (50,000 kg/yr**).** Based on this analysis, the projected cost of BN at the 50,000 kg/yr scale was found to be $91.15 per kg. This cost is reasonable because we use such a small percentage in the propellant formulation.

These particles were confirmed to be spherical, with an average size less than 100 nm, and can be dispersed in propellants using the conventional solvent approaches. The particles were confirmed to not destabilize the nitro-cellulose based propellants such as the RPD-380 and IMR 4198. To simulate the interaction of BN nano-particles with gun barrels under combustion environments, steel inserts were fired in a closed bomb test chamber in the presence of propellant compositions with and without the BN additive. Samples fired with BN additive in the propellant showed signs of less oxidation in this testing. XPS showed that boron oxide coated the surface of samples fired with BN additive, and less iron was present on the surface in samples that were less oxidized. SEM and EDX analysis showed stark differences in surface morphology and composition for samples fired with or without BN additive. Samples fired with BN had a boron oxide surface coating of flat platelets, and seemed to lack significant iron oxide (less than 10%). Samples fired without BN were covered with pits, bumps, and octahedral crystals indicative of Fe_3O_4. Hardness testing of the insert surfaces was performed to quantify any differences between samples, but the results for these samples were inconclusive.

While at first glance, the results do show that the propellant with the added BN propellant shows less erosion than the baseline propellant, the sample size is clearly too small for the results to be considered proof that the BN does reduce erosion. Further testing of the propellants is recommended. Other differences in the two propellants or side effects from the addition of the BN could also be the cause of the lower erosion seen, for example, the lower flame temperature that the propellant with BN generates. Better control of the insert bore surface roughness is needed in future tests. Only a small amount of boron remained on the surface after firing and cleaning, but ppm levels of boron doping can harden steel, and an increased hardness was observed in unhardened steel fired with boron nitride additive. SEM imaging showed less surface crack density in the samples fired with boron nitride. Important considerations for any further tests are an alternate grain form to allow larger bomb loading density, and the corresponding larger amount of propellant necessary for that condition, as well as to support a sufficient number of firings to generate supportable statistical conclusions. More quantitative hardness testing after extended firing would be useful to verify a hardening mechanism, and better 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 planned in a projectile test stand that will simulate the conditions of 155 mm artillery.

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Acknowledgements

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