

Combustion Behavior of Boron-Based BAMO/NMMO Fuel-Rich Solid Propellants

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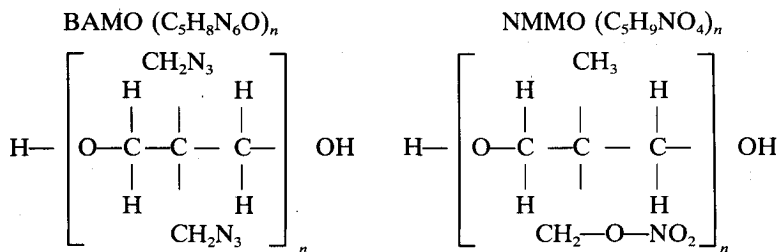
Combustion characteristics of boron/poly(BAMO/NMMO) fuel-rich solid propellants have been studied due to their potential application to solid-fuel ramjets (SFRJ). For the same boron content, BAMO/NMMO copolymer-based fuels are superior to conventional hydroxyl terminated polybutadiene (HTPB) fuels due to their vigorous pyrolysis characteristic for dispersing boron particles into the main reaction zone. However, their specific impulses are generally lower than that of HTPB, in spite of high positive heats of formation. Formation of hexagonal crystalline boron nitride (BN) has been found in the combustion of this family of propellants studied. Favorable conditions for the formation of BN have been identified. BN also has a significant effect on the theoretical performance for high equivalence ratio conditions. The burning rate was found to depend strongly upon pressure and nonmonotonically on boron content. An "energy sink" hypothesis is proposed to explain this observation. Fine-wire thermocouple measurements support this hypothesis.

I. Introduction

THE continuous search for more energetic and denser binder materials for solid propellants and fuels has, in recent years, prompted the synthesis and development of novel polymers with azide, nitro, or nitrate groups.¹ Performance increases can be expected by replacing the conventional non-energetic polymeric binders with polymers that could contribute energy to the formulation. These polymers are generally characterized by high positive heat of formation, high density, relatively low decomposition temperature, high nitrogen content, ease of ignition, fast pyrolysis, and low oxygen consumption for combustion. In particular, copolymers of nitrate esters, such as 3-nitratomethyl-3'-methyloxetane (NMMO) with (azidomethyl)-oxetane polymers, such as 3-azidomethyl-3'-methyloxetane (AMMO) and 3,3'-bis(azidomethyl)-oxetane (BAMO) have recently received much interest as potential candidates for energetic propellant fuels.^{2,3} Evaluation of solid propellants, using poly(BAMO/NMMO) polyether glycol as a binder, has shown high-performance capability in terms of volumetric specific impulse and excellent mechanical properties, especially in terms of elongation.³ The molecular structures of BAMO and NMMO polymers are

Boron, on the other hand, is well-known for its high heat release during oxidation or fluorination.⁴ It can provide more than three times the volumetric energy density of conventional hydrocarbon solid fuels used in air-breathing ramjet propulsion systems. However, problems associated with the ignition and combustion efficiency of boron particles have been an obstacle in utilizing boron-containing solid fuels or propellants in ramjet engines. It has been shown in a recent study by Chen et al.⁵ that the combined effect of very high heat release by exothermic decomposition reactions and the highly turbulent nature of the pyrolyzed gases of BAMO/NMMO copolymer binders enhances the ignition of the boron particles in BAMO/NMMO-based fuel-rich propellants. In addition, it may be expected that high performance can be obtained, due to the combination of two energetic fuel components, and also higher regression rates, caused by exothermic solid-phase or surface reactions, which is usually very desirable in solid-fuel ramjets (SFRJ).

It is known that oxidation of boron is highly exothermic. Under oxygen-rich conditions within adequate temperature and pressure ranges, the combustion products of boron will be boron oxides (e.g., B₂O₃, BO, BO₂, HOBO, H₃BO₃).



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However, when the oxygen concentration is limited, not all of the boron fuel can be oxidized. Instead of losing the heat of reaction of unoxidized boron, it is useful to consider the reaction of boron with other elements such as fluorine and nitrogen. This is why certain fluorine compounds are sometimes introduced into the formulations of solid fuels and propellants. To the best of the authors' knowledge, boron nitridation has not been considered in the performance evaluation of boron-based solid fuels. One exception is attributed to Weber and Mueller in their consideration of metal combustion in the Martian atmosphere.⁶

Preliminary thermochemical calculations and strand-burner tests conducted in this study have shown that under certain conditions (e.g., high equivalence ratios) nitridation of boron can indeed take place to form hexagonal crystalline boron nitride (BN). The heat released in this reaction (23.2 kJ/g boron) is less than one-half of that released in boron oxidation. This phenomenon has surprisingly received no particular attention in the propulsion literature, as mentioned above.

The overall goal of the work described herein is to study the propulsion-related combustion behavior of the newly developed boron/poly(BAMO/NMMO) fuel-rich solid propellants with the following specific objectives: 1) assessment of the applicability of these fuel-rich propellants to SFRJ engines; 2) conduction of thermochemical and thermoanalytical studies to achieve a better understanding of the pyrolysis process; 3) determination of the burning rate as a function of the boron content and pressure by using a windowed strand burner; 4) measurement of the thermal wave structure by fine-wire thermocouples; 5) determination of the favorable combustion environment for the formation of boron nitride by examining the combustion residues with scanning electron microscope (SEM) and x-ray diffraction analyzer; and 6) identification of the source of nitrogen for boron nitridation by conducting strand-burner tests in both air and oxygen/argon atmospheres.

II. Thermochemical and Thermoanalytical Studies

Thermochemical Equilibrium and Performance Calculations

The fuel-rich propellants used in this study were synthesized and provided by G. E. Manser of Aerojet Solid Propulsion Company. They are based on the BAMO/NMMO copolymer as a binder with 70/30 mole ratio, respectively, which yields the molecular formula ($C_5H_{8.34}N_{4.30}O_{2.02}$) for the repeating unit. This energetic formulation has a heat of formation of +1,378 J/g (53 kcal/mole). The mass fractions of nitrogen and oxygen in the copolymer are 37.4% and 20.1%, respectively, with the nitrogen coming mostly from BAMO. This copolymer was mixed with a boron powder of submicron particle size (median particle diameter of 0.5 μ m) at several mass fraction ratios: 0, 5, 10, 17.6, and 29% boron. In addition, a formulation containing 40% bimodal boron powder with particle sizes of 0.5 μ m (30%) and 20 μ m (10%) was prepared and supplied. The pure copolymer tested in this study had a density of 1.26 g/cm³.

Computer runs of the CET 86 chemical equilibrium transport code⁷ for the combustion of the above-mentioned compositions with air at various equivalence ratios ϕ , combustion pressures, and air temperatures, ranging from 0.6–4.0, 0.207–1.034 MPa (30–150 psia), and 298–537°K, respectively, were conducted to evaluate the performance of these propellants in solid-fuel ramjets and obtain information on the global equilibrium combustion products.

Complete combustion of pure poly(BAMO/NMMO) with air yields N_2 , CO_2 , O_2 , and H_2O as the major combustion product species for fuel-lean conditions ($\phi < 1$), as expected. For fuel-rich combustion ($\phi > 1$), as ϕ increases, CO_2 converts gradually into CO and unburned carbon, whereas H_2O is replaced by gaseous hydrogen. A theoretical adiabatic flame temperature of 2607°K is obtained for $\phi = 1$, a combustion pressure of 0.685 MPa, and a flight speed of Mach 2 at sea level. It was found that the effects of both pressure and air temperature are small in the range studied.

When boron is added to the poly(BAMO/NMMO) binder, the major equilibrium combustion products also contain boron oxides, mainly HBO, B_2O_3 , and B_2O_2 . The CET 86 chemical equilibrium transport code reveals that as less oxygen is available for $\phi > 1$, some boron nitridation takes place. The mole fraction of boron nitride (BN) in the combustion products increases with the equivalence ratio and the boron content. Table 1 lists the major theoretical equilibrium com-

Table 1 Major products of combustion of boron/poly BAMO/NMMO (containing 29% boron by weight) with air at 0.690 MPa (100 psia)

Combustion products, mole fraction, %	Equivalence ratio, ϕ		
	1	2	4
N_2	74.56	60.36	30.86
CO_2	5.93	0.01	—
HBO	5.72	0.80	0.01
H_2O	3.95	0.04	—
CO	3.06	15.29	22.46
B_2O_3	2.08	2.93	0.01
H_2	—	10.18	16.91
BN(s)	—	2.04	22.38
HBO	0.02	4.00	2.12
B_2O_2	—	2.46	0.29

bustion products for a composition containing 29% boron burned at 0.690 MPa and equivalence ratios of 1, 2, and 4 with air, which has enthalpy corresponding to a flight speed of Mach 2 at sea level. Crystals of hexagonal BN were found in residues from strand-burner tests in this study, as described in the following section. Boron nitridation releases 23.21 kJ/g boron, as compared to 58.74 kJ/g boron for oxidation to B_2O_3 . When an SFRJ is operating under certain conditions (such as high-altitude, high-angle-of-attack flight, or an accelerating climb), combustion of solid fuels will occur at high equivalence ratios. Under such conditions, the amount of heat release due to chemical reaction comes not only from boron oxidation but also from boron nitridation. Chemical-equilibrium calculations show that the portion of unoxidized boron nitridation increases with pressure, as confirmed by the experimental testing conducted in this study.

Detailed studies of the finite-rate chemical kinetics of BN formation under actual fuel-rich SFRJ operating conditions should be conducted. Investigation of various researchers indicated that there are some kinetic limitations of boron nitridation.⁸

In addition to the chemical-equilibrium calculations, the CET 86 code was used to calculate the theoretical performance of an SFRJ by assuming complete equilibrium combustion. A performance comparison was made between boron-based poly(BAMO/NMMO) and HTPB fuels for the same boron mass fractions at the Mach 2 sea-level flight condition. The calculated results show that for the same equivalence ratio in the range of $\phi = 0.6$ –4.0, boron-based poly(BAMO/NMMO) fuels have considerably lower gravimetric specific impulses than those of boron-based HTPB fuels. This is caused by the higher heat of combustion of the HTPB binder, which overcomes the high positive heat of formation of the poly(BAMO/NMMO) binder. The difference in performance between these two types of fuels becomes much smaller in terms of volumetric specific impulse, which is very important for volume-limited propulsion systems. Figure 1 shows plots of the theoretical volumetric specific impulse as a function of equivalence ratio for pure poly(BAMO/NMMO) and HTPB fuels and the same fuels mixed with 40% boron, all burning at 0.690 MPa in an SFRJ engine at Mach 2 sea-level flight. The density and heat of formation of HTPB were taken as 0.92 g/cm³ and 0 J/g, respectively. The relatively high performance of the boron-loaded fuels at high equivalence ratios is obtained due to boron nitridation. The same performance is plotted vs air/fuel ratio in Fig. 2. The stoichiometric air/fuel ratios for various fuels are also given in Fig. 2. For low air/fuel ratios, the poly(BAMO/NMMO) fuel is superior to the pure HTPB fuel, due to the larger oxygen deficiency of the latter. As the air/fuel ratio increases, the performance of the HTPB-based fuels becomes gradually greater. It should be recalled that the hydrocarbon mass fraction of poly(BAMO/NMMO) is only 42.5%, as compared to almost 100% hydrocarbon for HTPB.

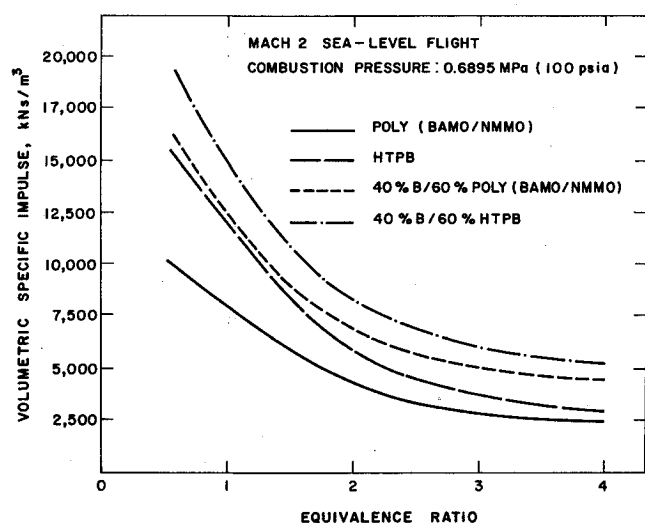


Fig. 1 Comparison of volumetric specific impulse of BAMO/NMMO copolymer and HTPB fuels with 0 and 40% boron at various equivalence ratios.

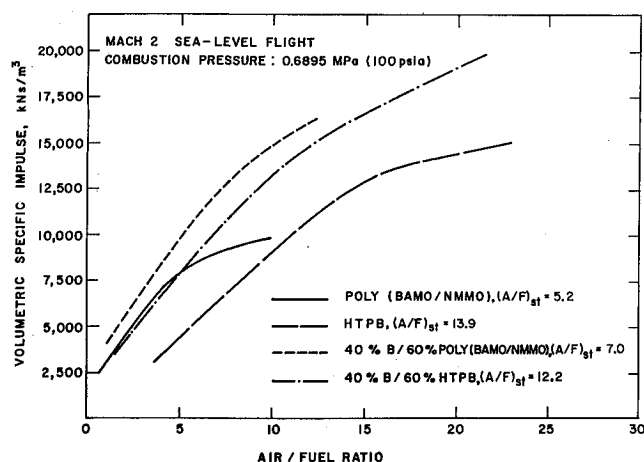


Fig. 2 Performance comparison of BAMO/NMMO copolymer with HTPB fuels containing 0 and 40% boron at various air/fuel ratios.

Thermoanalytical Studies

Extensive studies of the thermal decomposition of energetic monomers and polymers have been conducted by Farber et al.⁹ and Oyumi and Brill.^{2,10,11} An interesting finding by the latter with regard to poly(BAMO/NMMO) was that the two polymers decompose more or less independently despite being copolymerized. It was also revealed that pressure and heating rate exert relatively little influence on the concentration of the gaseous decomposition products. Mass spectrometric and rapid-scan Fourier-transform infrared spectroscopy (RSFTIR) tests have shown that both BAMO and NMMO polymers decompose thermally in two stages. In the first stage (primary decomposition), rupture/destruction of the side groups takes place, and in the second stage, decomposition of the polymer oxetane backbone occurs. Farber et al.⁹ conducted mass spectrometric studies of the thermal decomposition of BAMO polymer at 10^{-7} Torr, and reported a start of decomposition at 130°C by release of molecular nitrogen due to the rupture or scission of the azide bond structure. Much higher rate of N_2 evolution is observed at temperatures above 160°C. The three-carbon backbone starts to decompose into small fragments, such as HCN, CH_2 , OH, and CH_2O , at 160°C and the thermal decomposition rate increases rapidly with temperature. Similar results were obtained by Oyumi and Brill,¹⁰ by slow and rapid thermolysis of BAMO at a wide range of pressures using RSFTIR. The decomposition temperature of

the BAMO polymer was determined to be 463°K by slow heating at atmospheric pressure of argon.

The mass spectrometric studies of the thermal decomposition of NMMO polymer conducted by Farber et al.¹² revealed that decomposition starts at about 100°C, with the release of NO_2 and CH_2O by the rupture of the nitrate bond ($O-NO_2$) and the bond destruction in the nitrate ester side group. The onset of the oxetane backbone decomposition occurs at approximately 150°C. Oyumi and Brill¹⁰ suggest that considerable condensed phase reactions take place in the decomposition of poly(NMMO), which is assumed by them to start with the release of CH_2O or CO. They claim that the decomposition temperature of poly(NMMO) is 187°C. Manser is quoted as suggesting that the backbone of NMMO polymer might be less thermally stable than the nitrate ester.^{11,12}

Thermogravimetric analysis (TGA) tests in a 0.1-MPa argon atmosphere were conducted in this study on fuel-rich compositions with various boron content, using a Perkin Elmer TGS-2 thermogravimetric analyzer at a heating rate of 20°C/min. Weight loss of pure poly(BAMO/NMMO) samples started at 150–155°C at a very slow rate and rapid pyrolysis took place at a temperature between 205 and 210°C, leaving residues between 1 and 2%. The addition of 5, 10, and 18.3% boron did not substantially affect the temperatures of the start of weight loss and rapid pyrolysis, but the dispersion in the measured values of these temperatures was higher than that of the pure copolymer. The residue increased to between 2 and 3%. A single test with a composition containing 40% boron showed an onset of weight loss at about 120°C and rapid pyrolysis at 210°C, leaving a residue of only 1.2%. No definite conclusion for this difference can be drawn, due to the small number of experiments. However, it must be noted that in all tests, eyeball observations revealed a very rapid and violent pyrolysis process, in which the pyrolyzed gases of the copolymer dispersed the boron powder in the gas phase in the form of a brownish cream-colored cloud. A single TGA test with a sample of HTPB-based fuel with 30% boron was also conducted for comparison. In this case, the weight loss started at about 160°C and proceeded slowly until the rate was substantially increased between 420 and 480°C, leaving a black residue of 34%. The shape of the curve agrees well with published TGA thermograms for pure HTPB fuel.¹³ Figure 3 shows the above-described TGA thermograms of 40% boron-containing poly(BAMO/NMMO) and 30% boron-containing HTPB fuels. In view of the close similarity of the TGA thermograms of pure HTPB¹² and the boron/HTPB fuel of this study, one may conclude that the boron content has an insignificant effect on the decomposition process of HTPB for temperatures up to the completion of decomposition (~450°C). The only noticeable effect is that the boron-containing fuel has a higher percentage of residue.

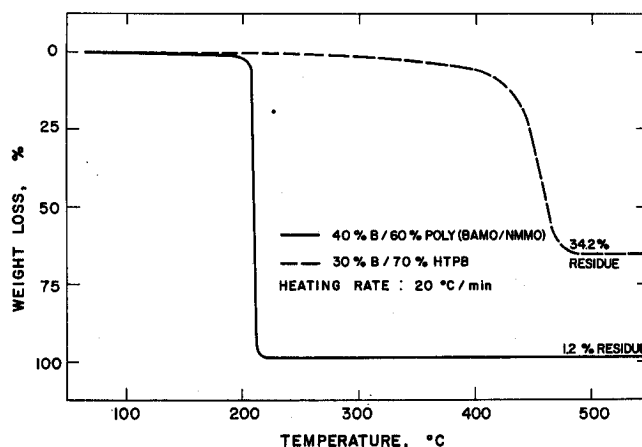


Fig. 3 TGA thermograms of poly(BAMO/NMMO) and HTPB fuels containing boron.

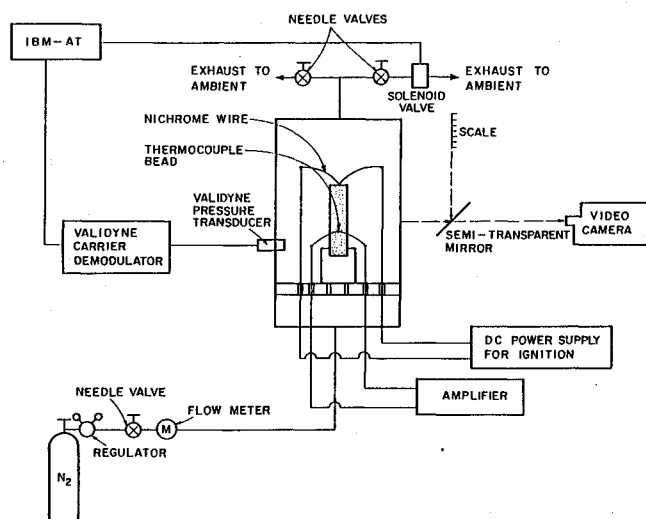


Fig. 4 Schematic diagram of experimental apparatus used in strand-burner tests.

III. Strand-Burner Tests

Experimental Approach

In this investigation, a windowed strand burner was used to study the combustion behavior of boron/poly(BAMO/NMMO) fuel-rich solid propellants. Figure 4 shows a schematic diagram of the windowed strand burner. A sample (5 mm in diameter and 60 mm in length) was mounted vertically in the chamber. Ignition of the sample was achieved by sending an electric current to a nichrome wire, pierced through the test sample about 3 mm from the top surface. To determine the burning rate of the test sample, the image of a scale was optically overlapped on that of the test sample by a semi-transparent mirror. During a test, both images of the scale and the test sample were recorded by a video-recording system. With this technique, the burning rate could be determined accurately from the length of the sample burned in a certain time duration.

Different gaseous mixtures were used to pressurize the strand burner for studying the effect of ambient gas environment on the combustion behavior of boron/poly(BAMO/NMMO) fuel-rich solid propellants. The chamber pressure was maintained at a preselected level by a computer-controlled gas supply system. Fine-wire thermocouples (platinum/platinum-13% rhodium) were embedded in the test sample to measure the thermal-wave structure. Detailed descriptions of the computer-controlled gas supply system, preparation of the fine-wire thermocouples, their embedding in the propellant samples, and the data acquisition system can be found in Refs. 14 and 15. The combustion residues from the strand-burner tests were collected and examined by an SEM. The boron compounds in the combustion residues were determined with an x-ray diffraction analysis technique.

The effect of the boron content and chamber pressure on the burning behavior of boron/poly(BAMO/NMMO) fuel-rich solid propellants was examined by testing five compositions with different boron weight percentages (0, 5, 10, 29, 40) at various pressures ranging from 0.241–1.034 MPa (35–150 psia).

Results and Discussion of Strand-Burner Tests

The measured strand burning rates in air as a function of pressure for the five compositions of test samples are shown in Fig. 5. Error bars given in this figure are defined as $\pm 2\sigma$ (standard deviation). The burning rates for all compositions increase as the pressure increases. It is interesting to note that the burning rate increases with increasing boron weight percentages up to a certain boron content and then decreases.

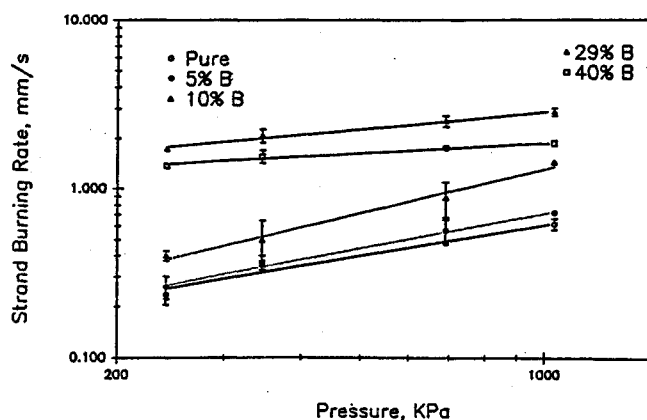


Fig. 5 Measured strand-burning rate as a function of pressure for boron/poly(BAMO/NMMO) solid fuel with different weight percentage of boron.

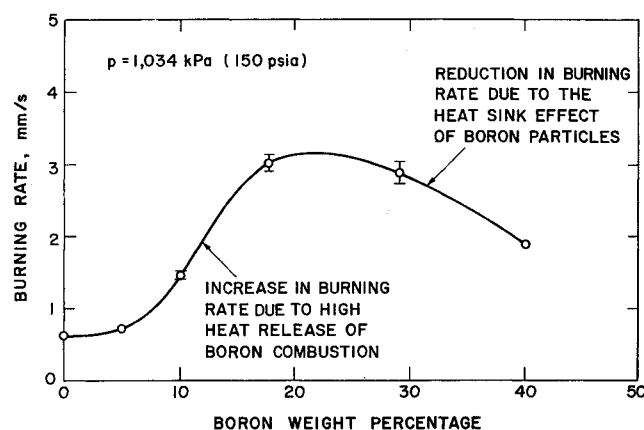


Fig. 6 Effect of boron weight percentage on burning rate of boron/poly(BAMO/NMMO) solid fuels at a fixed pressure.

In order to examine this effect, the burning rates for the five types of test samples at 1.034 MPa (150 psia) along with the burning rate data for 17.6% boron/poly(BAMO/NMMO) from Ref. 5 are plotted in Fig. 6. It was found that the highest burning rate occurs between 17.6 and 29% boron content.

Figure 7 shows the measured temperature profile obtained using a 50- μ m R-type thermocouple embedded in a 29% boron/poly(BAMO/NMMO) sample, at a combustion pressure of 0.345 MPa (50 psia) in air atmosphere. The burning surface temperature, indicated by a sudden jump in the slope of temperature near the surface, was found to be 205°C. This measured burning surface temperature agrees well with the decomposition temperature of the fuel-rich propellant sample from TGA tests at a pressure of 1 atm. The burning surface temperature T_b for 29% boron/poly(BAMO/NMMO) increases monotonically with chamber pressure, ranging from 200°C at 0.24 MPa (35 psia) to 300°C at 1.03 MPa (150 psia). The burning surface temperature is also found to be a function of boron weight percentage. At 1.03 MPa, T_b is nearly constant (≈ 300 – 310°C) for samples containing 5, 10, 17.6, and 29% boron particles; it drops to 260°C for the sample with 40% boron particles. It is noted that the subsurface temperature profile shown in Fig. 7 does not follow the exponential form, which is commonly observed or theoretically derived for inert heating zones with constant thermal properties. This departure from the exponential form is believed to be caused mainly by the subsurface reactions of poly(BAMO/NMMO) binders, as discussed in the earlier section. Beyond the burning surface, the thermocouples continue to measure the temperature of the media in the two-phase reacting region. Some irregularities of the temperature-time trace are noticeable;

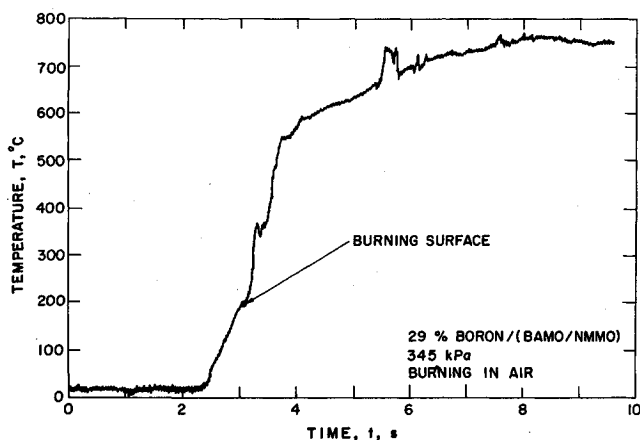


Fig. 7 A typical measured temperature-time trace from a strand-burner test using a 50- μ m fine-wire thermocouple.

the irregularities could be caused by the complex structure of the reacting zone described below.

A schematic description of the physicochemical processes occurring in the combustion of boron/poly(BAMO/NMMO) fuel-rich solid propellant, together with the temperature profile in the condensed and two-phase reacting regions, is shown in Fig. 8. Several zones can be defined based upon the major physicochemical processes taking place in the specified domains. In zone 1, the condensed phase material is being heated and there are no chemical reactions whatsoever. At the boundary between zone 1 and zone 2, decomposition of BAMO polymer starts around 130°C (measured under vacuum).⁹ As one approaches a higher temperature region near the "burning surface," decomposition¹¹ of NMMO polymer occurs near 190°C. The measured temperature of the so-called "burning surface" is around 205°C. Near the interface between the subsurface reaction zone (zone 2) and the first-stage combustion zone (zone 3), there are certain residues (containing

B_2O_3 , H_3BO_3 , B, BN, etc.) accumulated on the "burning surface."

In the lower portion of the first-stage combustion zone, the boron particles, coated with a thin layer (on the order of tens of Angstroms)¹⁶ of solid boron oxide, enter the hot combustion environment as low temperature solids. As described by King¹⁷ and Faeth,¹⁸ heat transfer from the reaction zone causes the particle temperature to rise with the B_2O_3 layer melting at roughly 455°C. Boron and/or oxygen diffuse across the oxide layer and tend to react more rapidly with the increase of particle temperature as particles move in the upward direction. This gives rise to a first-stage ignition of B/ B_2O_3 particles, where reaction rates suddenly increase with appearance of luminosity. According to a number of researchers' observations summarized by Faeth,¹⁸ this first-stage reaction appears to slow down almost immediately after the appearance of luminosity. This reduction of luminosity is believed to be caused by the thickening of the boron-oxide layer. Further increase of B/ B_2O_3 particle temperature causes rates of evaporation of boron oxide to increase, thus reducing the thickness of the oxide layer. Eventually, when the evaporation rate of the oxide layer is sufficiently large to remove the oxide layer, a second-stage ignition is attained at about 1627°C. From there on, the boron particles are exposed directly to the ambient oxidizers and relatively fast boron combustion takes place. The above-mentioned processes are depicted in Fig. 8.

To explain the dependence of burning rate as a function of boron weight percentage (as shown in Fig. 6), it is useful to consider the measured temperature-time traces under various conditions. As mentioned above, the surface temperatures of the burning fuel-rich propellant sample tested in this study are quite low ($\sim 205^\circ\text{C}$). The boron particles with oxide coating, ejected into the gas phase, serve as an "energy sink" to absorb a part of the energy generated by the reaction of pyrolysis products of the energetic BAMO/NMMO binder. When the boron weight percentage is low ($\leq 20\%$), the B/ B_2O_3 particles can reach the second-stage ignition temperature of 1900°K (1627°C). A high amount of heat release is

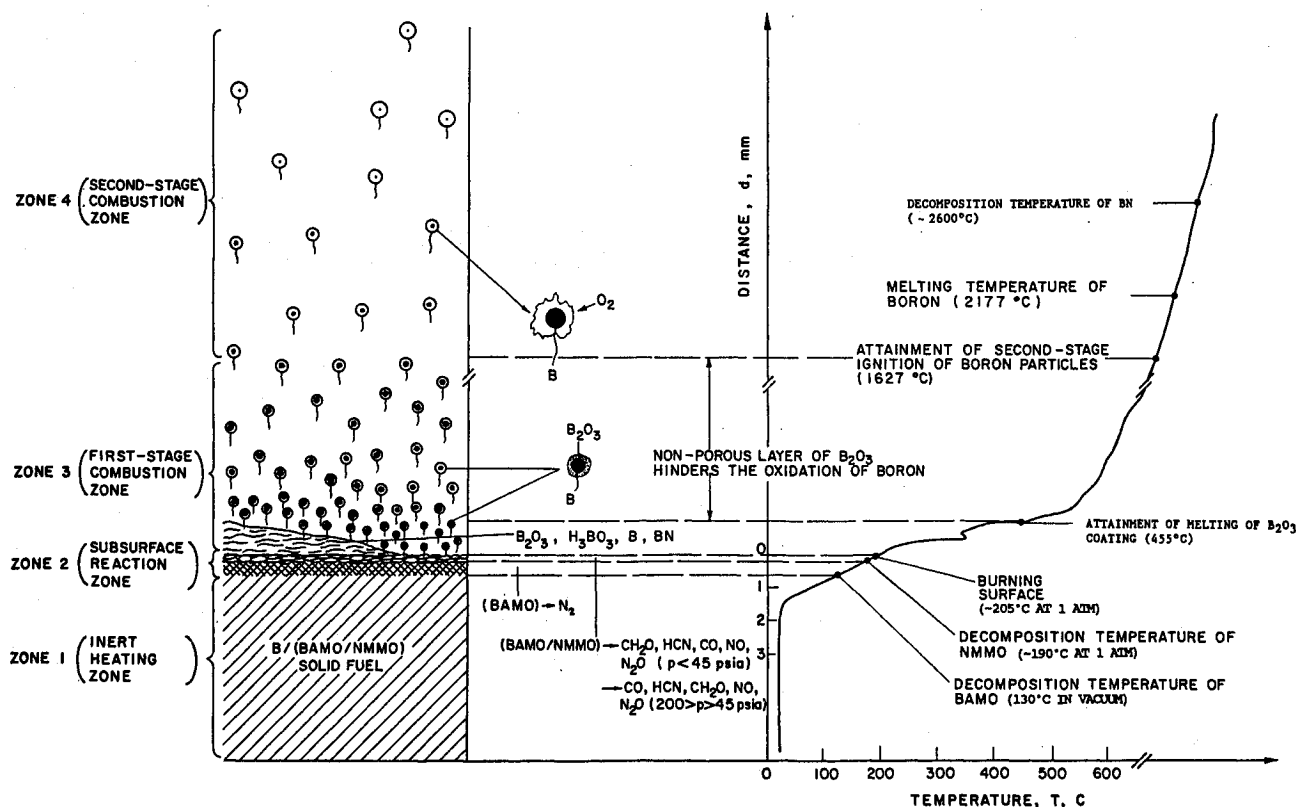


Fig. 8 Physicochemical processes in the combustion of boron/poly(BAMO/NMMO) solid fuel in air.

Table 2 Measured maximum combustion product temperatures for poly(BAMO/NMMO)-based solid fuels with various boron content ($p = 1.034$ MPa)

Boron weight percentage	5.0	10.0	17.6 ^a	29.0	40.0
Maximum temperature, °C	>1800 ^b	>1800 ^b	>1800 ^b	970	760

^aFrom Ref. 5.

^bDuring the tests, the output voltage of R-type thermocouples exceeded the calibration range.

Table 3 Presence of boron nitride in combustion residues of boron/poly(BAMO/NMMO) fuel-rich solid propellants burned in air

Boron weight percentage	Pressure, MPa			
	0.241	0.345	0.690	1.034
5.0	None	None	None	None
10.0	None	None	None	None
17.6 ^a	None	None	None	Small amount
29.0	None	None	Small amount	Significant amount
40.0	None	None	None	Small amount

^aFrom Ref. 5.

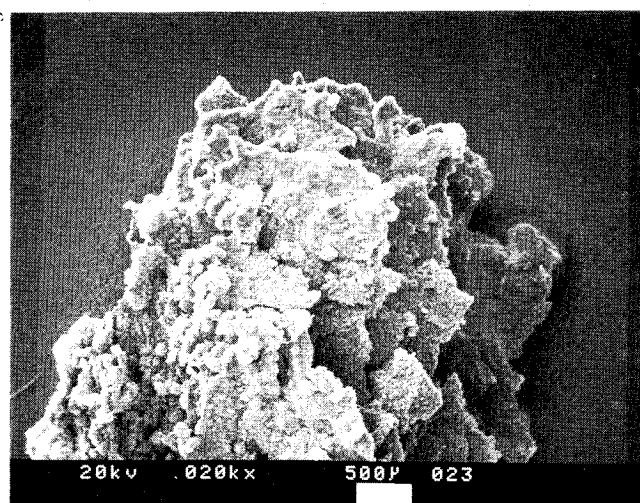
obtained due to efficient boron combustion. The heat feedback to the burning surface is high, and the burning rate is enhanced by the increase of boron content in the fuel-rich propellant. However, as the boron content exceeds a certain critical value ($\sim 20\%$), the "energy sink" effect becomes a dominant factor in reducing the heat feedback to the burning surface. This reduction is due either to the unattainment of the so-called second-stage ignition temperature or the extension of the active reaction zone to a much further distance from the burning surface.

To verify the above-mentioned hypothesis, temperature measurements of the combustion products of the two-phase reacting media were made with fine-wire thermocouples. The maximum temperatures measured from the combustion of solid fuels with different amounts of boron content are listed in Table 2. It is useful to note that when the boron percentage is 17.6% or below, the measured maximum temperature exceeds the second-stage ignition temperature of boron of 1627°C. For 29 and 40% boron, the measured maximum temperatures were much lower. This finding supports the "energy sink" postulation for explaining the burning-rate behaviors of fuel-rich solid propellants with various boron contents. Besides the "heat sink" postulation, the effect of agglomerate sizes generated from fuel-rich solid propellants with different boron contents can also be used to explain part of the burning-rate behavior observed in this study. The size of the boron agglomerates, which are ejected from the surface in the burning process, may increase significantly for higher boron concentration. The large agglomerate size may result in poor ignition/combustion characteristics, and consequently in lower flame temperature, lower heat feedback, and lower burning rates. However, this agglomerate size effect can only be adopted to explain why the burning rate decreases with increased boron content, when the boron content is greater than 20%. This reasoning cannot be used to explain the fact that when the boron content is less than a critical percentage, the burning rate increases with the boron content as observed in this study.

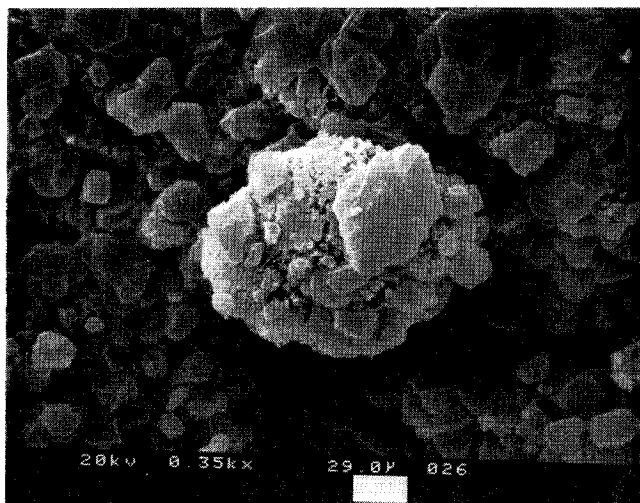
After each strand-burner test, the combustion residues were collected for SEM examination and x-ray diffraction analysis. From the results of x-ray diffraction analysis, significant amounts of boron nitride (BN) in hexagonal crystalline form were found for the tests conducted at 1.034 MPa (150 psia) with 29% boron/poly(BAMO/NMMO). For other tests, the amounts of BN found in the combustion residues were much lower, as

indicated in Table 3. Besides BN found in certain test conditions, other major boron compounds detected by x-ray diffraction analysis were B_2O_3 and H_3BO_3 . These two compounds were found in residues from all test conditions listed in Table 3. The importance of this finding of BN was discussed in the earlier part of this paper. It is useful to note that the amount of residue recovered from strand-burner tests increases with the percentage of boron. No residue was found after tests with pure BAMO/NMMO copolymer. The flame is generally faint at low pressures, but at high pressures ($p > 0.69$ MPa), the flame becomes much brighter. Some streak lines of the burning B/B₂O₃ particles can be seen from high-speed video images.

Figures 9 and 10 are SEM pictures showing the H_3BO_3 and BN crystal structures in the combustion residues from tests with 29% Boron/poly(BAMO/NMMO) in air at 0.345 MPa (50 psia) and 1.034 MPa (150 psia), respectively. In order to identify the source of nitrogen in the formation of boron nitride, a set of strand-burner tests using Boron/poly(BAMO/NMMO) solid fuel with 40% boron were conducted with a mixture of 21% O₂ and 79% Ar (volumetric ratio) at 1.034 MPa (150 psia). In contrast to the test condition with air,

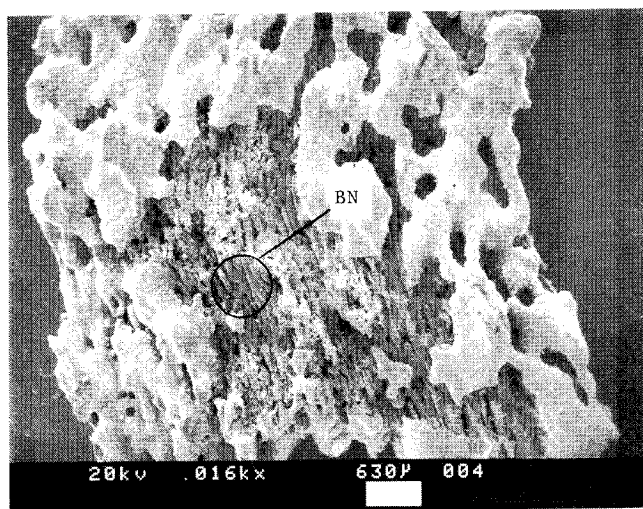


a) Magnification 20X

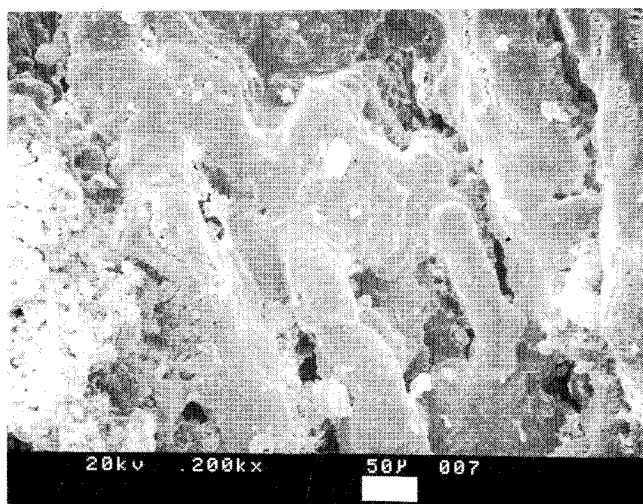


b) Magnification 350X

Fig. 9 SEM pictures showing the crystal structure of H_3BO_3 in the combustion residue of boron/poly(BAMO/NMMO) solid fuels (with 29% boron) burned in air at 0.345 MPa.



a) Magnification 16X



b) Magnification 200X

Fig. 10 SEM pictures showing the presence of boron nitride (BN) in the combustion residue of boron/poly(BAMO/NMMO) solid fuels (with 29% boron) burned in air at 1.034 MPa.

boron nitride was not found in the combustion residues from these tests. This implies that the nitrogen involved in the boron nitridation comes from the air but not from the nitrogen in the poly(BAMO/NMMO) under the testing condition. This may be explained by the fact that the release of N_2 from (BAMO/NMMO) copolymer begins at 130°C and ends at about 205°C. At these low temperatures, boron particles are not reactive with nitrogen. In principle, the gaseous nitrogen pyrolyzed from the copolymer could still react with boron in the high-temperature zones. Certain chemical reactions must occur to consume the gaseous nitrogen before reaching the high-temperature zones. Detailed chemical kinetic steps are required to understand this interesting observation.

IV. Summary and Conclusion

1) The steady-state combustion characteristics of boron/poly(BAMO/NMMO) fuel-rich solid propellants have been studied under various pressure conditions for compositions with different boron weight percentages. Thermochemical and thermoanalytical studies and strand-burner tests were conducted in a systematic fashion.

2) From the SFRJ performance point of view, there are both advantages and disadvantages of using BAMO/NMMO

copolymer-based fuels as compared to conventional HTPB-based fuels. The advantages are mainly due to its vigorous pyrolysis characteristics for dispersing boron particles from surface reaction zones into the main reaction zone. Therefore, high boron combustion efficiency can be expected. The second advantage can be attributed to its higher performance at lower air-to-fuel ratios, since it contains a certain fraction of oxygen and thus requires less ambient oxygen to burn. The disadvantages of BAMO/NMMO copolymer-based fuels are essentially due to their lower performance at normal SFRJ operating conditions. This lower performance is caused by their lower heats of reaction, resulting from lower hydrocarbon content, in comparison with conventional hydrocarbon fuels (such as HTPB), despite their high positive heats of formation.

3) Addition of boron particles in BAMO/NMMO copolymer fuels always increases the theoretical performance of solid fuels.

4) TGA results show that the pyrolysis characteristics of boron/poly(BAMO/NMMO) fuel-rich propellants are nearly unaffected by the percentage of boron content.

5) Formation of hexagonal crystalline boron nitride (BN) in the combustion residues of boron/poly(BAMO/NMMO) solid fuels was observed experimentally. Thermoequilibrium calculations show the existence of BN only at high equivalence ratios. Under these conditions, some performance gains can be obtained even though the heat of reaction in forming BN is less than one-half of that in forming B_2O_3 . This implies that boron nitridation could be important and deserves further study.

6) The burning rates of boron/poly(BAMO/NMMO) fuel-rich propellants were found to depend strongly upon boron weight percentage and pressure. Burning rate increases with boron percentage up to the vicinity of 20% and then decreases. An "energy sink" hypothesis has been proposed to explain this dependency. Thermocouple measurements of the maximum temperature of combustion products support this hypothesis. This hypothesis suggests that as the boron particle weight percentage exceeds a critical level, they absorb a significant amount of energy from the reaction zone and thereby reduce the energy feedback to the propellant surface. Also, boron particles under such high concentration conditions may not oxidize to form the second-stage vigorous combustion zone near the burning surface.

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