

Ignition and Combustion of Boron Particles and Clouds

Merrill K. King

Atlantic Research Corporation, Alexandria, Va.

Nomenclature

C_p	= heat capacity of the gases
C_{pB}	= boron heat capacity
$C_{p_{B_2O_3}}$	= oxide heat capacity
ΔH_H	= heat absorbed by reaction of B_2O_3 with H_2O
$\Delta H_{surf Rx}$	= heat absorption associated with surface reaction(s) (per unit mass of boron)
ΔH_{vap}	= heat of vaporization of B_2O_3
\dot{m}_{burn}	= particle burning mass flux
Q_{gas}	= heat release associated with gas-phase reaction(s) (per unit mass of oxygen)
Q_{Rx}	= heat release of $B + B_2O_3$ reaction
r_p, r_s	= particle radius
R_B	= molar rate of boron consumption
R_E	= molar evaporation rate of boric oxide
R_H	= molar rate of removal of B_2O_3 by water reaction
t	= time
T_p	= particle temperature
T_{RAD}	= effective surroundings radiation temperature
T_s	= particle surface temperature
T_∞	= ambient temperature
X	= oxide layer thickness
$X_{O_2, \infty}$	= ambient oxygen mass fraction
α_R	= surroundings absorptivity
ϵ	= particle emissivity
ρ_B	= boron density
$\rho_{B_2O_3}$	= boric oxide density
$\bar{\rho} \bar{D}$	= density-diffusivity product
σ	= Stefan-Boltzmann constant

Introduction

SYSTEMATIC advances in missile propulsion system technology have provided large increases in missile performance capabilities. Replacement of much of the solid propellant rocket oxidizer with freestream air, as in the ducted rocket concept, offers over a 5 to 1 increase in missile range capability, while the solid fuel ramjet concept, in which *no* internal oxidizer is carried along, with freestream air providing all the oxidizer for combustion, shows still greater potential range advantage. A useful figure of merit for ranking the potential of various candidate fuels for use in airbreathing rocket applications, particularly high-altitude cruise missions where operation can be carried out at high air/fuel ratios, is the heat of combustion. Values of this parameter for several possible fuels are presented in Table 1.

(Gravimetric heating values are of particular interest for weight-limited applications, while volumetric heating values are more appropriate for volume-limited missions.) As may be seen, the potential of boron relative to other fuels is quite impressive. Thus the use of boron as a ramjet or ducted rocket fuel ingredient potentially offers significant mission advantages, including increased range, reduced vehicle weight, higher intercept velocities, and/or lower time-to-target values.

In order for these advantages to be realized, however, the boron particles must ignite and burn completely within a very limited residence time. Since boron particles are generally initially coated with an oxide layer which inhibits combustion and since boron has an extremely high boiling point ($= 3930$ K) which necessitates surface burning subsequent to oxide removal, this can become difficult, particularly under adverse operating conditions. In the past, afterburning efficiency problems have been encountered with boron fuels, particularly at low afterburner pressure. Though considerable progress has been made in alleviating these problems, further improvements are desired.

Ramburner combustor design optimization is particularly critical, and definition of approaches to such optimization depends on good understanding of the phenomena involved in boron particle ignition and combustion. A reasonably accurate picture of the overall processes appears to have evolved from studies performed during the 1960s and 1970s, notably the flat-flame-burner work of Macek.^{1,2} A two-stage process appears to be involved in the burning of boron, the first stage being an ignition stage, during which a boron oxide coating is removed from the particle surface. This ignition phase is followed by a second stage, in which the clean boron particle burns vigorously. It seems likely, on the basis of experimental observation and thermodynamic considerations that this

Table 1 Heating values of various fuels^a

Fuel	Gravimetric heating value, cal/g	Volumetric heating value, cal/cm ³
JP5	10,150	8,230
Shelldyne-H	9,860	10,000
Carbon	7,830	17,700
Aluminum	7,420	20,000
(CH ₂) _n	10,400	9,600
Boron	13,800	32,200
Magnesium	5,910	10,300

^a Assuming H_2O (gas), CO_2 (gas), metal oxide (liquid) as products.

Merrill K. King is Chief Scientist for the Research and Technology Division of Atlantic Research Corporation. He has been working at Atlantic Research on fundamental aspects of solid propellant and airbreathing rocket combustion processes since 1964. Dr. King received his BS, MS, and PhD degrees in Chemical Engineering from Carnegie Institute of Technology. He is a member of the American Institute of Aeronautics and Astronautics and the Combustion Institute and is active in various JANNAF Working Group activities.

second stage (referred to subsequently as the full-fledged combustion stage) is a multistep process with the major heat release occurring in a vapor-phase reaction zone, some distance removed from the particle surface, where a suboxide produced at the surface is oxidized to final product. This full-fledged combustion stage appears to be diffusion controlled for large particles, but kinetics controlled for small particles, with transition in the general region of 15-30 μ diameter, the exact transition point depending upon pressure.

As mentioned above, afterburning efficiency of boron-loaded fuels has been observed to decrease with decreasing combustor pressure. According to the single particle ignition model of King^{3,4} (discussed later), critical surroundings temperature required for particle ignition and ignition delay time will both increase with decreasing pressure provided the particle is in such a flow environment that mass transfer coefficients are sufficiently high for evaporation kinetics rather than product oxide gas diffusion to control oxide coating removal rate. In addition, while much of the early experimental study of combustion times (subsequent to oxide layer removal) indicated diffusion-limited combustion (with burn time independent of total pressure) this work was unfortunately carried out with particles much larger than those used in airbreathing missile propellants. More recent work with smaller particles indicates a shift to kinetics-limited burning for particles in the size range of interest, with burn time consequently increasing with decreasing pressure. In light of these observations, it is not surprising that the low pressure afterburner operating conditions are most critical in terms of combustion efficiency.

An additional possible factor leading to nonattainment of the theoretical performance of boron-loaded fuels at high air/fuel ratios (where the products of boron combustion are thermodynamically predicted to be mostly condensed-phase oxide) is the kinetic trapping of boron combustion intermediate products in the gas state as either B_2O_3 (gas) or HBO_2 . Past work indicates that conversion of HBO_2 to B_2O_3 is particularly slow. Such trapping can potentially result in the loss of a significant fraction (up to about 25%) of the theoretical heating value of the boron.

Single Particle Ignition

As a result of recognition of the difficulty of igniting and burning boron particles of the sizes typically used in boron solid and slurry fuels (2-20 μ diameter) to completion in the limited residence times provided by typical ramburners (2-10 ms), considerable effort was expended in the 1960s and 1970s toward defining the mechanisms of boron particle ignition and combustion and quantifying the time requirements for these processes. Numerous studies aimed at identifying the ambient conditions required for single particle ignition (specifically, ambient temperature requirements) and ignition time delays were carried out. These included shock tube ignition studies (Uda,⁵ Chambers,⁶ Jones,⁷ Simmons and Bauman⁸), flat-flame-burner studies (Macek^{1,2}) and plasma generator product stream studies (Gurevich⁹). Macek observed in his studies that boron burning occurs in two stages. Following heatup to about 1800-2000 K, the boron particle becomes luminous, glows for a short period of time, fades out, and finally, provided the ambient temperature is sufficiently high, blossoms into a second stage of burning, which is much brighter and longer than the first stage. It is generally accepted today that the first stage is an ignition stage, during which the boron particle is coated by a molten boron oxide layer. Oxygen must diffuse through this layer to react with the boron, in order to provide reaction heat for vaporization of the oxide layer. Before the full-fledged combustion stage can occur, the oxide layer must be completely removed from the boron particle. This entire sequence may be broken up into three periods: the preheat time (time to bring the particle to point of first glow, associated with the onset of non-negligible

rate of reaction); the ignition time (time from first glow to beginning of the bright stage); and the combustion time (time from beginning of the second stage to burn out). (Some authors lump the first and second periods together and refer to the sum as the ignition time.)

Macek,^{1,2} Uda,⁵ Chambers,⁶ Jones,⁷ and Gurevich⁹ have all presented ignition temperature data. Unfortunately, the term "ignition temperature" as used by Macek refers to the particle temperature at the time of first glow rather than the more generally accepted definition of ignition temperature as the minimum ambient temperature required for particle ignition. However Macek did also make limited measurements of the latter parameter. These data, obtained at a total pressure of 1 atm and an ambient oxygen mole fraction of 0.20 indicate that in a dry atmosphere the critical temperature is nearly independent of particle diameter, ranging from 1980 K for 1- μ particles² to 1920-1930 K for 30-40- μ particles.¹ Gurevich,⁹ working with considerably larger particles, found a strong dependence of critical temperature on particle diameter, the value ranging from 2200 K at 70 μ to 1350 K at 250 μ in tests with $P=1$ atm, oxygen mole fraction = 0.15. In addition, he found the critical temperature to increase with decreasing oxygen content and with replacement of oxygen by water. (Macek, in limited testing, found the presence of water to decrease the critical temperature.) Uda,⁵ Chambers,⁶ and Jones,⁷ working with a shock tube, found the critical temperature for ignition to decrease strongly with decreasing diameter in the size range studied by Macek, in conflict with other results. However, careful examination of their work indicates that they were actually igniting clouds of particles rather than single particles. With clouds, as demonstrated by the models of Zolotko¹⁰⁻¹² (discussed later), ignition temperature would be expected to decrease with decreased particle size owing to associated increasing ratio of reaction surface area to cloud "surface" heat loss area. Thus these data can be discarded as regards single particle critical ignition temperatures. (Emphasizing the point that cloud ignition was actually being studied, the investigators themselves noted that their ignition temperatures decreased with increasing sample mass.) It should be noted in passing that most of the Macek data and all of the Gurevich data, while interesting, are for particles much larger than those of practical interest for airbreathing missile combustors.

An interesting (though not strictly comparable) study of boron ignition has been performed recently by Boussios.¹³⁻¹⁴ In this study, Boussios generates clean boron particles by grinding a pure boron rod into a nitrogen atmosphere with subsequent mixing with steam. When he injects this mixture into a cold (<300 K) airstream, he observes ignition of the boron particles with quite low injectant temperatures, the ignition/no-ignition boundary running from 1400 K at approximately 20% H_2O to 600 K at 35% H_2O . (It must be pointed out, however, that these are calculated temperatures assuming no reaction of steam with boron. Thermodynamically, this mixture is predicted to yield boroxine ($H_3B_3O_3$) in a fairly exothermic reaction. Thus the temperature of the injected mixture may be somewhat above the temperature quoted by Boussios and, moreover, the flammable boroxine may well aid in igniting the boron particles by its combustion yielding locally high temperatures around the particles.) Nonetheless, it seems likely that the presence of clean boron surfaces with adjacent H_2O available to tie up any B_2O_3 as HBO_2 is beneficial to the particle ignition process.

This question of the nature of the initial state of the particle surface is one that needs to be addressed further. It is not clear how quickly an "equilibrium" thickness of oxide is built up on an initially clean surface upon exposure to ambient temperature air, or what effect it has on particle ignition characteristics. Thus ignition tests with "clean" particles and particles exposed to air for various periods of time would seem to be of interest.

Table 2 Ignition time data

Gas temperature, K	Y_{O_2}	Y_{CO_2}	Y_{H_2O}	Ignition time, ms	
				$d_p = 35 \mu$	$d_p = 44 \mu$
2280	0.23	0.30	0	4.4	5.5
2430	0.20	0.33	0	4.8	5.7
2870	0.23	0.34	0	3.4	5.0
2450	0.37	0.34	0	2.1	3.3
2490	0.08	0.34	0	3.6	7.4
2240	0.19	0.11	0.16	4.0	7.2
2330	0.21	0.12	0.16	3.5	5.8
2430	0.19	0.13	0.19	3.8	6.1
2640	0.20	0.15	0.21	2.6	5.6

Typical ignition time data (defined here as the time from first glow to full brightness) obtained by Macek for 35- and 44- μ -diam particles are presented in Table 2. Additional data (particularly for smaller particle sizes which are much more relevant to actual applications) with systematic variations of such parameters as ambient temperature, pressure, and oxidizer type and mole fraction are needed for testing ignition models and postulated mechanisms behind them, as well as for a data base for the combustor designer.

Boron single particle ignition models have been developed by King,^{3,4} Mohan and Williams,¹⁵ Meese and Skifstad,¹⁶ Zolotar and Ozerov,¹⁷ Grigor'ev et al.,¹⁸⁻²⁰ Polishchuk et al.,²¹ Pen'kov and Sukhov,²² and Gaponenko et al.²³ All of these models have considerable similarities in that they are all based on the following general picture of events occurring during ignition, but as will be discussed later, there are significant variations between some of the detailed treatments. The processes occurring during the ignition of an initially oxide-coated boron particle in a hot gas stream are complex. First, there is a heatup stage during which the comparatively cold boron particle is heated solely by convective and/or radiative flux(es) from hotter surroundings. At sufficiently high particle temperature (approximately 1500-1800 K), non-negligible self-heating of the particle, by exothermic oxidation, begins to augment the convective and radiative fluxes. Since the particle is initially coated with an oxide layer, the oxygen required for this reaction must diffuse through the surface liquid oxide layer. As the oxidation of the boron particle continues, it causes the oxide layer to thicken, thereby increasing diffusional resistance. At the same time, as long as the particle temperature continues to rise, the viscosity of the oxide is decreased. This increases the rate of diffusion of oxygen to the boron surface. In addition, boron oxide is ejected from the particle surface by evaporation and diffuses away from the particle at a rate which depends upon the particle temperature. However, evaporation is an endothermic process, which tends to cool, or at least lower the rate of heating the particle. If the particle temperature rises above the surroundings temperature, the convective and radiative heat fluxes become negative and begin to cool the particle. As long as the sum of the self-heating terms and the convective/radiative heating terms are greater than the product of the oxide vaporization rate and the heat of vaporization, the particle temperature will continue to rise. Given a favorable balance, the oxide layer will become thin and a temperature runaway will occur. The particle will rapidly eject its remaining oxide (causing the aforementioned dark period), and full-fledged combustion will occur. If, on the other hand, the sum of the self-heating and convective/radiative terms drops below the vaporization heat demand before the surface is cleaned, the particle will not ignite. (The presence of H_2O gas in the particle surroundings adds at least one more parallel step to these processes, namely, the removal of condensed phase B_2O_3 from the

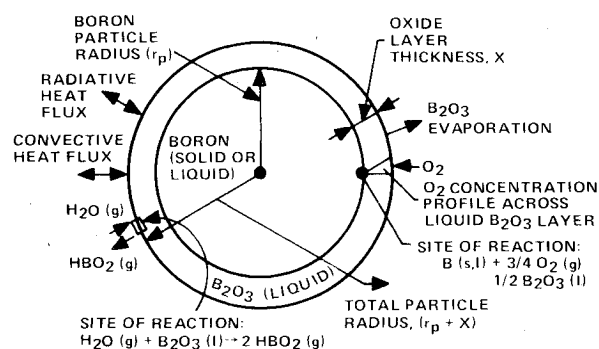


Fig. 1 Boron particle ignition model processes.

surface by an endothermic reaction to HBO_2 . Attempts have been made to include this affect in the ignition models of King,^{3,4} Meese and Skifstad,¹⁶ and Gaponenko et al.,²³ but the bulk of the modeling work has been aimed at dry atmospheres, and the following discussion will be concentrated on this situation.) A sketch depicting the modeled processes is given in Fig. 1. In all of the models, mass and enthalpy balances are used to obtain similar equations for the time rate of change of oxide thickness, boron radius, and particle temperature (although in many of the models the change of the boron radius during the ignition process is neglected, a reasonable approximation under most but not all conditions):

$$\frac{dr_p}{dt} = -\frac{R_B (MW)_B}{4\pi r_p^2 \rho_B} \quad (1)$$

$$\frac{dX}{dt} = \frac{(R_B/2 - R_E - R_H) (MW)_{B_2O_3}}{4\pi r_p^2 \rho_{B_2O_3}} \quad (2)$$

$$\begin{aligned} \frac{dT_p}{dt} = & \{ R_B Q_{RX} - R_E (\Delta H_{VAP}) - R_H \Delta H_H \\ & + 4\pi (r_p + X)^2 [h(T_\infty - T_p) + \sigma \epsilon_R (T_{RAD}^4 - T_p^4)] \} \\ & \cdot [(4/3)\pi r_p^3 \rho_B C_{PB} + 4\pi r_p^2 X \rho_{B_2O_3} C_{PB_2O_3}] \end{aligned} \quad (3)$$

[In the recent publication by Gaponenko,²³ a second possible water reaction is treated, as discussed later, with consequent addition of another reaction term in Eqs. (2) and (3).] In King's second model,⁴ the particle temperature equation is straightforwardly replaced by a similar equation describing the time rate of change of the fraction of the boron particle melted when the melting point of boron, 2450 K, is reached.

The major differences in the various models lie in the choice of expressions for the reaction rate terms R_B , R_E , and R_H , and in the subsequent mathematical treatment of the equation

set. (In addition, most of the Russian modelers ignore radiative heat transport, a poor assumption for particles as large as the ones they treat. Estimation of the sizes of radiation and conductive transfer terms for various points in the particle temperature-time history, particularly points near the critical runaway conditions, indicate that for cold radiation surroundings, one cannot safely neglect radiation for particle radii (in microns) greater than approximately three times the Nusselt number, while for radiation surroundings temperature equal to gas temperature, the factor rises to approximately 6.) Since, as mentioned earlier, most of the models do not include the treatment of H_2O gas effects on ignition, the R_H term will for the moment be ignored. With regard to the expression for the evaporation rate of boron (R_E), in King's first model³ and in the Meese and Skifstad model,¹⁶ this process is assumed to be limited by evaporation kinetics, while in the Mohan and Williams model¹⁵ and the Zolotar¹⁷ model it is assumed to be controlled by diffusion of the oxide vapor away from the particle. The later Russian studies appear to treat both possibilities individually. Only in King's second model⁴ are the evaporation kinetics and gas diffusion processes treated as series resistances, obviating the necessity for assumptions regarding which step is limiting.

With respect to the rate of boron conversion to boron oxide at their interface, there are several resistances to be considered: these include gas-phase diffusion of oxygen to the outer surface of the oxide layer, dissolution of oxygen into the liquid oxide at that interface, diffusion of oxygen across the molten oxide layer to the $B-B_2O_3$ interface, and reaction at that interface. In all of the published American modeling efforts, it has been assumed that diffusion of oxygen across the liquid oxide layer (with the concentration at the surface being determined by an equilibrium solubility law) is the limiting step. (This will obviously become invalid as the oxide thickness goes to zero, but numerical studies show that in general the thermal runaway leading to ignition takes off well before the oxide thickness reaches the point that the gas diffusion process is slow relative to the liquid diffusion process. However, it does prevent use of the model to treat the case of an initially clean or nearly clean surface.) In the early work of Zolotar and Ozerov,¹⁷ Polishchuk et al.,²¹ and Grigor'ev,¹⁸ on the other hand, the various processes are treated as series resistances (though in his later work, Grigor'ev treats the liquid diffusion step as limiting, without explanation for this change in approach). It should be noted, however, that in Ref. 17 the authors appear to assume that the mole fractions of oxygen on the two sides of the gas-liquid interface are equal, a particularly bad assumption leading to marked reduction in the resistance associated with transport across the oxide film. Grigor'ev appears to lump the solubility parameter into the diffusion coefficient for transport across the oxide layer, using the gas-side oxygen concentration as his driving force, while Polishchuk et al. explicitly employ an equilibrium solubility law. Extrapolating the Grigor'ev and Polishchuk²⁴ data for diffusion of oxygen in liquid boria (data taken at 700-1100 K and extrapolated to the 2000 K range) Grigor'ev compares the sizes of the resistances in Ref. 18. For the kinetic resistance he uses a rate expression based on an analysis of ignition data which appears to be suspect inasmuch as it depends on an assumption that the particle surface was clean under the experimental conditions employed (unlikely since the particle temperature was well below the boiling point of boron oxide). In addition, as discussed below, the diffusion expression that he uses does not appear to be consistent with the data of Ref. 24. At any rate, from this analysis he concludes that the kinetic resistance will be dominant for oxide thicknesses less than 2μ . If this conclusion is correct, models based on the diffusion of oxygen across the liquid oxide layer being the limiting step in the oxidation of an oxide-coated boron particle are obviously incorrect. As part of further examination of this question, a

comparison of the expression used by King^{3,4} to relate oxygen transport across the oxide film to temperature, film thickness and oxygen pressure on the gas side of the B_2O_3 -gas interface (based on Henry's law for solubility, the Wilke correlation for diffusion of dissolved gas through a liquid, and an Arrhenius viscosity-temperature law, with use of two data points obtained by Talley and Henderson²⁵ in the temperature regime of interest to fit two empirical constants) to the expression used by Grigor'ev¹⁸ has been made. At 2000 K the Grigor'ev expression was found to yield transport rates a factor of 100 higher than the King expression, with this ratio dropping to 40 at 2300 K (see Fig. 2). Next the King expression for the resistance through the liquid oxide layer was compared to the kinetic resistance postulated by Zolotar (even though it is suspect) and to the gas diffusion resistance. From this analysis, it was concluded that with the King expression the latter resistance should in general be negligible compared to the liquid diffusion resistance for oxide thickness/particle radius ratios greater than approximately 10^{-3} - 10^{-4} , while the surface reaction kinetic resistance need be included only for oxide thicknesses less than approximately 0.05μ . It is interesting to note that in most of the more recent Russian work, the liquid diffusion resistance is assumed to be the limiting step in the conversion of boron to oxide, without discussion of the dropping of the series resistance equations.

In a current model development effort being carried out by King,²⁶ gas diffusion, liquid diffusion, and kinetic resistances are all being considered in the calculation of R_B , since even though (as indicated above) the liquid diffusion resistance is dominant for most of the heatup-ignition life of the particle under particle size-pressure combinations of interest, the other resistances do become important for initially clean particles suddenly exposed to hot oxygen-laden atmospheres as well as for the "end-game" portion of the ignition event for all particles, where the oxide layer has thinned out markedly from its initial state. For consideration of these series resistances, the equation for the molar rate of boron oxidation at the boron-boric oxide interface is first written as

$$\begin{aligned} R_B/4\pi r_p^2 &= f_1(T_p) P_{O_2, \text{equivalent, B-B}_2O_3 \text{ interface}} \\ &= f_2(T_p) (P_{O_2, \text{gas, surface}} - P_{O_2, \text{equivalent, B-B}_2O_3 \text{ interface}}) / X \\ &= f_3(T_{\text{gas}}, r_p) (P_{O_2, \text{freestream}} - P_{O_2, \text{gas, surface}}) \end{aligned} \quad (4)$$

which may be rearranged with elimination of the two interface pressures to yield

$$R_B/4\pi r_p^2 = \frac{f_1 f_2 f_3 / X}{f_1 f_2 / X + f_2 f_3 / X + f_1 f_3} P_{O_2, \text{freestream}} \quad (5)$$

A reasonably accurate expression for f_3 can be easily developed, and estimates of f_1 based on the reaction kinetics of O_2 gas with solid boron as inferred from burn time data for clean boron particles in the kinetics-limited particle size regime (see later) are also straightforward. However, definition of an accurate expression for $f_2(T_p)$ is not nearly as straightforward. Estimates from several sources are collected in Fig. 2. As may be seen, the disagreements are rather large. The f_2 expression based on King's^{3,4} interpretation of the rather limited Talley and Henderson²⁵ data appears to be an outlier and is being replaced in the current analysis. (Fortunately, the disagreement with the other data is not particularly bad in the critical 2000-2500 K region and as a result preliminary calculations with the new model do not differ markedly from those made with the old one.) Similarly, the expression used by Grigor'ev et al. in Ref. 18, an expression which is supposedly based on the data of Ref. 24, appears to be considerably at variance with the other information (including the actual data of Ref. 24) and should probably be similarly disregarded. The data of Ref. 24 were obtained in a gravimetric experiment in which the weight

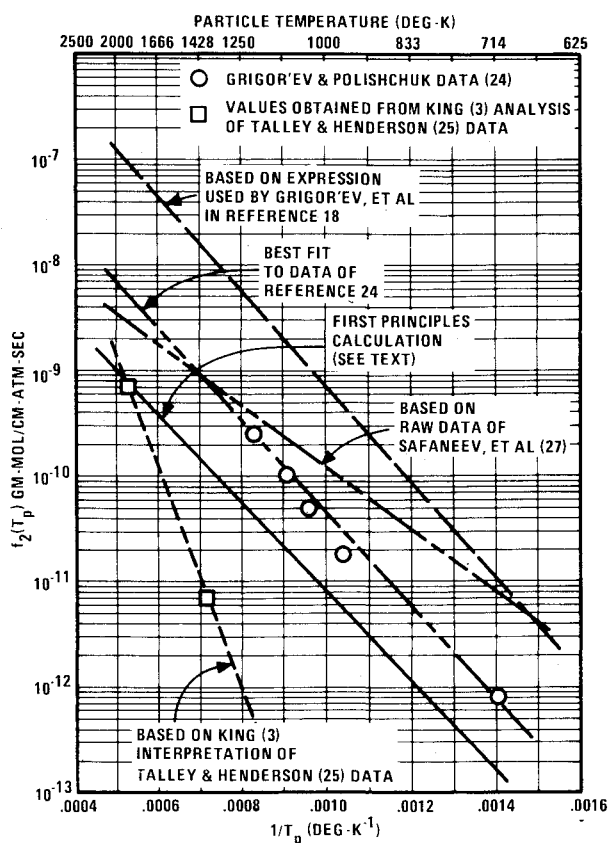


Fig. 2 Various estimates of the conductance of oxygen across a liquid boric oxide film as a function of film temperature.

change of boron particles exposed to an oxygen-containing atmosphere at a fixed temperature was measured as a function of time, and are in general probably fairly reliable. However, the highest temperature tested was 1200 K (considerably below the regime of interest) and even so the experimental data at the higher temperatures appears to have been partially compromised by gas-diffusion limitations. In the Safaneev work,²⁷ an electrothermal technique was employed in a rather sophisticated experiment in which the heat liberation rate accompanying the boron oxidation was measured. Unfortunately, there appears to be some problem in the data analysis, with results presented in Fig. 4 of Ref. 27 being inconsistent with the raw data of Fig. 3. The line representing Safaneev's work presented in Fig. 2 is based on the limited raw data presented in that paper. Finally, the solid line in Fig. 2 represents "first-principle" calculations of the liquid film conductance (inverse resistance) using various empirical correlations for solubility of gases in liquids, diffusion in liquids as a function of their viscosity, and viscosity of liquids as a function of temperature; it is somewhat encouraging (and surprising) that these calculations result in as good agreement with the limited data as they do. Limited calculations with a new ignition model (as yet unpublished) using the three middle lines of Fig. 2 to represent f_2 indicate that predicted ignition times and critical ambient conditions for ignition do not depend strongly on the choice between these three expressions.

The other area in which the various models differ is in their mathematical treatment of the equation set represented by Eqs. (1-3). In the works of King,^{3,4} Meese and Skifstad,¹⁶ and Zolotar,¹⁷ these equations are numerically integrated with the results being examined for thermal runaway, which will only occur under adequate environmental conditions. From this type of analysis, critical ambient conditions required for ignition can be obtained. In addition, a second very important parameter (since available residence times for ignition and

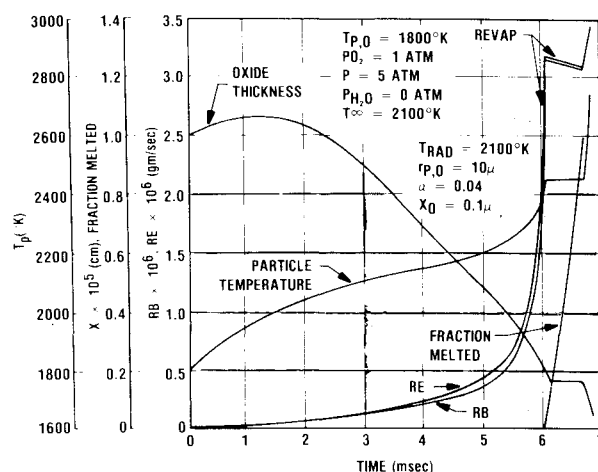


Fig. 3 Predicted time dependence of important variables for particle which ignites.

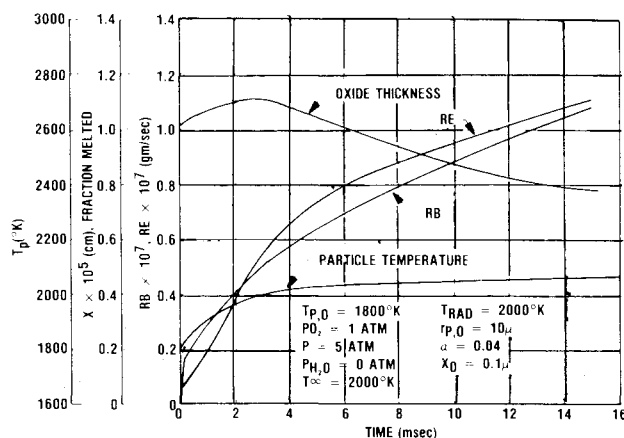


Fig. 4 Predicted time dependence of important variables for degenerate ignition case.

combustion in practical airbreathing combustors are rather short) of ignition delay time can be obtained. In the works of Mohan and Williams,¹⁵ Polishchuk et al.²¹ and several Russian papers dealing with conglomerate and cloud ignition (discussed later), a different type of analysis, commonly referred to as a stationary states analysis, is performed. In this approach [in which the change in particle radius is neglected, eliminating Eq. (1)], the derivatives of particle temperature and oxide thickness are set equal to zero and Eqs. (2) and (3) are then solved for quasisteady values of these parameters. The stability of this solution is then examined by linearized perturbation analysis around this quasisteady state with resultant derivation of a stability criterion which permits calculation of minimum ambient temperature required for ignition as a function of particle size and other environmental parameters. (Of course, no information regarding ignition time results.) One troubling aspect of this approach is that it involves an implicit assumption that no matter what the initial condition of oxide thickness and particle temperature, the path of these parameters plotted in a particle temperature-oxide thickness plane will be such that it will pass sufficiently close to the stationary state values for the stability analysis to apply.

King⁴ examined this problem briefly and concluded that, for the conditions examined (limited to 1 atm total pressure), the particle temperature vs oxide thickness history did indeed meet this criterion. However, it does appear that in other regions (higher total pressure for example) the stationary states analysis and full-up numerical integration of the differential equations gave different results for critical ambient

temperature required for ignition. For example, the stationary states analysis approach predicts that the minimum ambient temperature for ignition is independent of ambient oxygen mole fraction at a given total pressure. The numerical integration approach results in the same conclusion for $P_{\text{TOTAL}} = 0.1$ MPa (1 atm) but shows a significant dependence of minimum ambient temperature for ignition on oxygen mole fraction at $P_{\text{TOTAL}} = 2.0$ MPa (20 atm), the required temperature decreasing with increasing mole fraction. (See Fig. 8 of Ref. 4.)

A recent paper by Grigor'ev²⁰ (by far the most advanced of the Russian ignition models, but still neglecting radiative heat transfer) provides an excellent examination of this problem, explaining the above observations and confirming that *in general* the stationary states approach to determining critical ignition conditions should not be applied to the analysis of metals with volatile product films. However, as pointed out in the paper, if the ratio of the characteristic thermal relaxation time for the particle is much larger than the characteristic oxide buildup time, the approach will work. For boron ignition at low pressure, with the values of various constants (e.g., activation energies) which are used in King's model, this ratio is indeed large. However, careful examination of the equations used to estimate this ratio reveals that it decreases with increasing pressure resulting in breakdown of the stationary states approach at higher pressures.

It is particularly interesting to note the following implication of this ratio being high. With a high ratio of thermal relaxation time to oxide buildup time, the oxide thickness attained at each temperature as the particle temperature tracks out its history will be essentially equal to the asymptotic value achieved under isothermal conditions at that temperature. That is, oxide thickness becomes a unique function of instantaneous temperature, independent of history. Moreover, $dT_p/dt = 0$ under these conditions perforce implies $dX/dt = 0$. Thus the $X-T_p$ path is forced to pass through the critical stationary states pair of values independent of the initial values, and the stationary states analysis is valid.

Typical time-dependent behavior as predicted with King's⁴ second boron ignition model for a situation where a particle is predicted to ignite is shown in Fig. 3, while similar outputs for a no-ignition case are shown in Fig. 4. Note that the only difference in environmental conditions is a lowering of ambient temperature from 2100 to 2000 K. Detailed studies of the effects of various parameters on predicted critical ignition temperature and ignition times are presented in Ref. 4. A comparison of predicted and measured ignition times for the Macek¹ studies (recall, ignition time here is defined as time from first glow to the blossoming associated with completion of removal of the inhibiting oxide film and subsequent thermal runaway) is presented in Fig. 5—as may be seen, an evaporation coefficient of 0.04 provides reasonable agreement between theory and experiment. (Note, Blackburn²⁸ has measured a value of 0.03 ± 0.01 for the boric oxide evaporation coefficient.) Finally, predicted dependence of minimum ambient temperature required for ignition vs particle size is presented in Fig. 6. Two curves are presented: the upper one represents cases where the radiation temperature seen by the particle is 300 K, while the lower one is for $T_{\text{RADIATION}} = T_{\text{GAS}}$. For small radii, the curves are nearly identical, but for particle radii greater than about 10 μ , the differences become quite significant, indicating the necessity for treatment of radiation effects for the particle size regime (40–120- μ radius) examined by Zolotar,¹⁷ who neglected radiation losses in his modeling. For comparison with Macek's data, taken under conditions such that the effective surroundings radiation temperature is approximately 300 K, use of the upper curve is appropriate—accordingly, agreement of the theory and Macek's data are quite good. In the experimental study of Gurevich,⁹ mentioned earlier, critical temperature for ignition was found to decrease continuously with increasing particle radius up to radii of

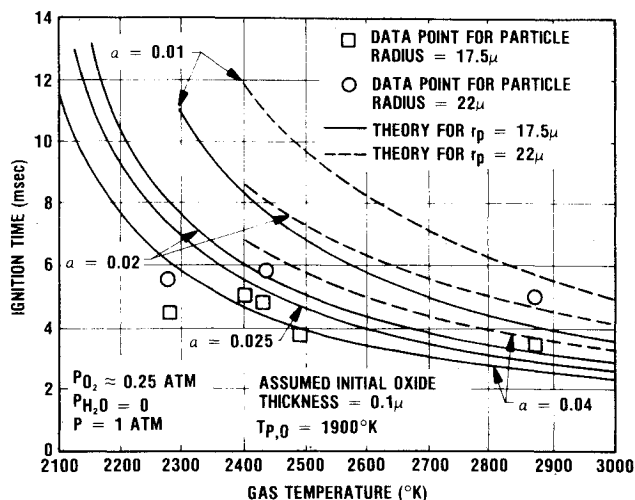


Fig. 5 Predicted and observed ignition times for boron particles studied experimentally by Macek (1969).

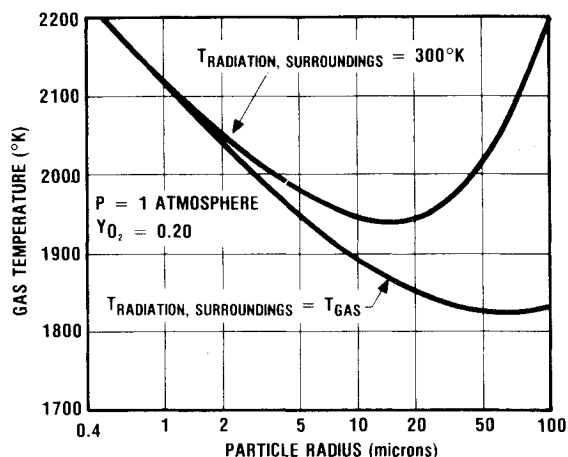


Fig. 6 Minimum gas temperature required to insure ignition.

approximately 130 μ : if in his experiments the effective surroundings radiation temperature was approximately equal to the gas temperature, the experimental and theoretical qualitative trends agree, although quantitative agreement is not particularly good. It is not made clear in the Gurevich paper what the effective surroundings radiation temperature was, but description of the hardware indicates that it should be quite high, closer to T_{GAS} than to 300 K.

As discussed in Ref. 4, for cases where the diffusion of boric oxide gas away from the particle controls the oxide removal rate, the effect of total pressure on ignition time and critical ignition temperature is predicted to be small, with total pressure increases making ignition more difficult for low oxidizer mole fractions and easier in the case of high oxidizer mole fractions. When evaporation kinetics control the oxide removal rate, however, as shown in Ref. 3 where diffusion resistance was neglected, ignition is enhanced (both in terms of critical temperature and time) by increased pressure. While the calculations of Ref. 4 indicated diffusional resistance to be dominant, it must be kept in mind that all of the calculations in that paper were done for a Nusselt number of 2 (no flow). In a motor environment, it can be expected that Nusselt numbers may be somewhat higher, perhaps resulting in a shift to evaporation kinetics control, thus resulting in decreased ignition difficulties with increased pressure.

In an attempt to treat the effects of water on boron particle ignition, King⁴ developed an expression for R_H assuming diffusion-limited reaction of water with $B_2O_3(l)$ to form HBO_2 at the coating outer surface—this attempt resulted in

overprediction of the effects of H_2O , indicating the need to include finite rate kinetics for this reaction. Meese and Skifstad¹⁶ found that they could achieve decent prediction of the effects of water on ignition by lowering the activation energy of the evaporation term by an amount proportional to the H_2O mole fraction; unfortunately this approach has no valid mechanistic basis.

In a very recent paper, Gaponenko et al.²³ have presented a somewhat more complete attempt at modeling the effects of water vapor on boron particle ignition. Their postulated processes for ignition in a mixed oxygen, water vapor atmosphere are depicted in Fig. 7. They propose that two water reactions are involved: first, a kinetics-limited surface reaction with liquid boric oxide at the outer surface to form HBO_2 ; second, an infinitely fast reaction between water and boron at the inner edge of the oxide layer to produce B_2O_3 and hydrogen. The hydrogen is then postulated to diffuse out to a point determined by H_2 - O_2 stoichiometry in the layer where it reacts with oxygen diffusing inward in an infinitesimally thin reaction zone to form water, which then diffuses back to the B- B_2O_3 interface for further reaction with the boron. In this picture, the net flow of H_2O from the outer surface to the H_2 - O_2 reaction radius is zero, as indicated by the constant H_2O concentration across that zone as shown in Fig. 7. In their analysis, Gaponenko et al. use a rate expression for the surface reaction between H_2O and B_2O_3 which they claim is based on the work of Vovchuk et al.,²⁹ who measured the gasification rate of boric anhydride droplets in a pure water atmosphere at several temperatures. However, analysis of the original Vovchuk data (a rather straightforward procedure) yields a somewhat different rate expression, with the rates exceeding those calculated using Gaponenko's expression by a factor of 10-20 (depending on temperature). This discrepancy is unexplained. In addition, Gaponenko assumes that the reaction between boric oxide and water yields HBO_2 at all temperatures: thermodynamic considerations indicate that the cyclic trimer, $H_3B_3O_6$, is the favored product below about 1700 K. Finally, the postulated reaction at the B- B_2O_3 interface appears somewhat questionable since thermodynamic considerations indicate that the reaction, $H_2O + (4/3)B + (1/3)B_2O_3 \rightarrow (2/3)H_3B_3O_3$ may well be preferred. An alternate possible scenario for the effects of water vapor on boron particle ignition (with oxygen reactions and evaporation processes omitted) is depicted in Fig. 8.

All in all, it appears that more effort in the area of boron particle ignition modeling is required, and that, most importantly, kinetic rate data and physical constant data for inclusion in this modeling are desperately needed. For example, data for the kinetics of the $B_2O_3(l) + H_2O$ reaction and the $B(s) + O_2$ reaction are needed. In addition, data regarding the solubility and diffusivity of oxygen and water vapor in liquid B_2O_3 at high temperatures are required.

Conglomerate Ignition

A subject of some importance, which to date has received little attention, is that of "conglomerate" ignition. First one must define just what a boron conglomerate is. In the combustion of boron slurry fuels, where each spray droplet may contain many individual boron particles, it is likely that the carrier will quickly vaporize in the combustor leaving the boron particles loosely grouped together like a cluster of grapes. This is one type of conglomerate, characterized by high porosity with ready access of virtually all interior surfaces to the ambient gas. Another type of conglomerate is likely to be produced by ball-milling of boron in preparation for casting in propellant grains or by pressing processes used in making compacted grains. This type of conglomerate more than likely behaves more like an individual particle, having very low porosity, with most of what pores there are being closed.

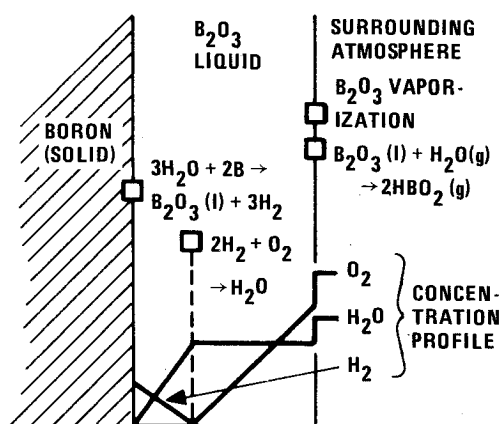


Fig. 7 Postulated ignition processes in the presence of an atmosphere containing water (Gaponenko et al.²³).

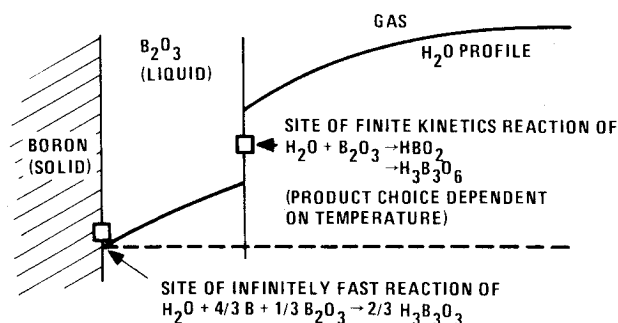


Fig. 8 Alternate possible scenario regarding the effects of water on boron particle ignition.

Shevchuk et al.³⁰ have developed a model for the ignition of the first type of conglomerate. In this model, they neglect evaporation of the oxide film and radiative heat transfer between the clump and its surroundings during the ignition process (tenuous assumptions). In addition, they assume that the pore-diffusion resistance to oxygen transport to the boron-boric oxide interface is negligible compared to other resistances. The specific reaction surface of the conglomerate is assumed to be given by

$$S_{sp} = (3/r_0) (\rho_c/\rho_m) \quad (6)$$

where r_0 is the radius of the unit particle in the clump, ρ_c is the overall conglomerate density, and ρ_m is the virgin boron density. With these assumptions, they derive equations for the time rates of change of oxide thickness and particle temperature and apply an analytical approach described in detail by Khaikin et al.³¹ for calculation of critical ignition conditions. (No ignition times are calculated in this model.) The equation used to describe the rate of conversion of boron to oxide at the film interface is that of King.^{3,4} With this model, they find that the critical surroundings temperature required for ignition increases with decreased conglomerate size for a given unit particle size and increases with increased unit particle size for a given clump size (not surprising when one considers the effects of these parameters on the ratio of internal reaction area to external heat exchange area). In addition, they find that the critical ignition temperature decreases with increasing oxygen partial pressure. As part of this effort, Schevchuk also conducted an experimental investigation of the effects of these parameters and found good agreement between theory and experiment. Critical ignition temperatures as low as 700 K were obtained.

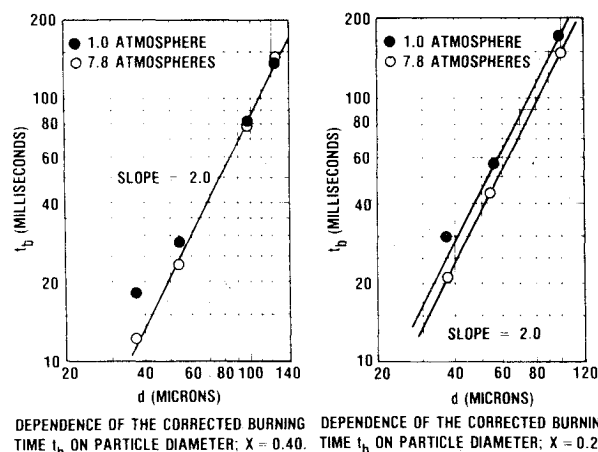
Cloud Ignition

In actual combustors, of course, one does not ignite individual isolated particles in all-gas surroundings: instead one ignites clouds of particles. Data obtained by Zolotko¹⁰ in experiments in which he puffs a cloud of particles into a heated reaction vessel indicate that, as would be expected, surroundings (reaction vessel wall) temperature requirements for ignition of boron clouds are somewhat less stringent than for single particles. Zolotko has also developed models for the ignition of clouds of boron particles,¹⁰ clouds of conglomerates,¹¹ and clouds of mixed metals¹² (boron and magnesium) in a vessel whose walls are held at constant temperature: in the interest of space, only the first model will be discussed here as the other two are somewhat similar. In this model, Zolotko writes equations for the time rate of change of oxide thickness and particle temperature similar to Eqs. (2) and (3). In addition, a third equation describing the time rate of change of the gas temperature is utilized. This equation includes terms for heat exchange between the gas and particles and between the gas and its container. Zolotko applies a stationary states analysis (setting the time derivatives equal to zero and solving for quasisteady values of gas temperature, particle temperature, and oxide thickness and then examining these for stability) to determine a critical surroundings (container) temperature required for ignition as a function of various parameters such as pressure, particle loading, and particle size. (Again, and even more so in this case, the use of the stationary states approach appears somewhat risky, as discussed in the section on single particle ignition. A numerical analysis treatment of these equations would be much safer and additionally would supply the ignition delay time, a value equally important as minimum critical ignition temperature.)

Meese and Skifstad¹⁶ have analytically examined a somewhat different cloud ignition problem. In their scenario, the cloud does not exchange heat with the surroundings. The particles are initially cold (298 K) and the gas is hot. They have developed two model variants, one in which the gas temperature is artificially held constant at its initial value and the other in which it is allowed to vary as dictated by heat exchange with the particles: only the latter case is of practical interest. They numerically integrate equations describing the time rate of change of particle temperature, gas temperature, and oxide thickness to determine whether for a given initial gas temperature the particles will ignite and, if so, how long it takes. They find that the minimum initial gas temperature required for ignition decreases with increasing pressure at fixed particle concentration (mainly due to the increased pressure causing the air mass per unit mass of boron to increase, resulting in less heat sink effect) and also decreases with increasing particle size over the size range studied (1-20 μ diameter). With respect to ignition delay time, they find that it decreases with increasing initial gas temperature, decreasing particle size, and decreasing cloud concentration (the last again being a heat sink effect).

Ignition Promotors

As a result of difficulties encountered in afterburning highly-boron-loaded, fuel-rich propellants at low ram burner pressures, Childs et al.³² embarked in the early 1970s on an effort to utilize chemical approaches to improving the ignition/combustion characteristics of boron. Improved efficiencies were achieved through incorporation of small amounts of magnesium/aluminum alloy in the propellant formulations. It was postulated that these additives functioned by producing a very intense radiation flux in the initial fuel-air mixing region, thus enhancing the boron ignition process, as predicted by King's ignition model.⁴ A second successful approach used by both Childs et al. and Flanigan et al.³³ involved coating the boron particles with a lithium fluoride coating, which was postulated to aid in the removal of boron oxide by formation of a low-boiling complex in-



DEPENDENCE OF THE CORRECTED BURNING TIME t_b ON PARTICLE DIAMETER: $X = 0.40$. DEPENDENCE OF THE CORRECTED BURNING TIME t_b ON PARTICLE DIAMETER: $X = 0.21$.

Fig. 9 Macek data from late 1960s showing dependence of boron particle burn time on particle diameter (d^2 law).

volving both compounds. Use of fluorinated oxidizers also resulted in increased afterburning efficiency, presumably via reaction of HF with B_2O_3 to form HBO_2 and BOF (both gaseous).

In studies of the supersonic combustion of boron slurry fuels in the early 1970s, Schmotolocha et al.³⁴ also found that magnesium and LiF coatings aided the ignition/combustion processes. The effectiveness of the lithium fluoride was found by these investigators mainly to influence the boron particle ignition times.

Zolotko¹² has addressed analytically the effects of magnesium loading on the ignition of a mixed boron-magnesium particle cloud. In this particular analysis, he interestingly abandoned the stationary states approach and performed numerical integration of the governing time-dependent equations to calculate critical temperature and ignition times. Replacement of 5, 10, and 15% of the boron was predicted (and observed in accompanying experimental work) to yield appreciable lowering of the critical surroundings temperature required for boron cloud ignition, along with markedly decreased ignition delay times. (As a sidelight, some of the detailed results presented in this study emphasize the importance of ignition delay time as opposed to minimum critical temperature. In experiments conducted with a reaction vessel wall temperature of 1565 K, ignition indeed can be achieved over a wide range of particle loadings and Mg/B ratios, but the ignition times involved are in many cases in the 50-200-ms range. Obviously, in a combustor with a 5-ms residence time the fact that the cloud will eventually ignite will not help efficiency very much with ignition delay times of this magnitude!)

Single Particle Combustion/Extinguishment

Considerable data on the effects of various parameters on boron particle combustion time, subsequent to removal of the oxide coating from the surface and melting of the boron ("full-fledged combustion")—combustion of a clean liquid boron droplet) have been obtained by Macek^{1,2,35,36} and Gurevich et al.⁹ among others. Unfortunately, the bulk of this data has been obtained for particle diameters of 35 μ or larger. In this size range, the observed dependence of burning time on particle size (d^2 law) indicates that combustion is diffusion limited. Macek data^{35,36} obtained in the late 1960s are presented in Figs. 9-11. As may be seen, the data fit a d^2 law very well, except at the lowest pressure-particle diameter combination. (More will be said about this exception later.) The near independence of total pressure observed in Fig. 10 is also characteristic of diffusion-limited combustion.

Accordingly, numerous diffusion-limited combustion analyses for the burning of clean-surface boron droplets have been developed, including those of Mohan and Williams,¹⁵

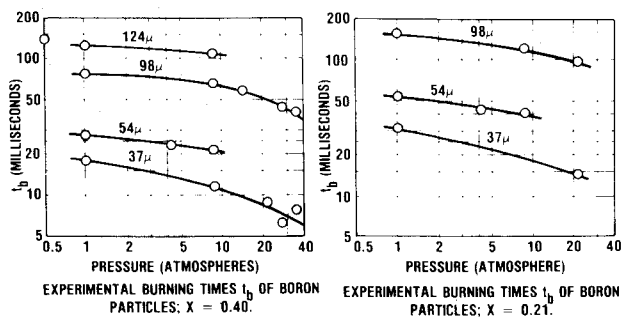


Fig. 10 Dependence of boron particle combustion time on pressure, as measured by Macek.

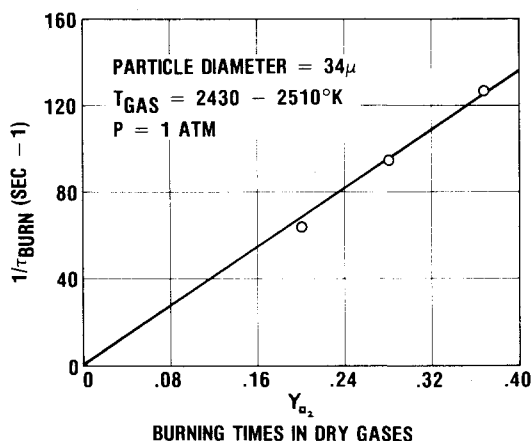


Fig. 11 Dependence of boron particle combustion time on oxygen mole fraction in surrounding gas, as measured by Macek.

King,²⁶ Coffin and Brokaw,³⁷ Knipe,³⁸ Vovchuk,³⁹ Derevyaga,⁴⁰ and Greymachkin.⁴¹ The Derevyaga approach is a vastly oversimplified transfer coefficient approach, while the Vovchuk model is greatly weakened by the neglect of convective fluxes in the transport equations.

Mohan and Williams¹⁵ draw an analogy between boron particle combustion and hydrocarbon droplet burning which results in the following equations for calculation of burning rate:

$$\dot{m}_{\text{burn}} = (\rho \bar{D}/r_s) \ell_n (1 + B) \quad (7)$$

$$B = \frac{Q_{\text{gas}} X_{\text{O}_2, \infty} + C_p (T_{\infty} - T_s)}{\Delta H_{\text{surf}} R_x} \quad (8)$$

with the surface temperature being arbitrarily chosen to be 2500 K. There appears to be a major problem associated with this analysis. Arbitrarily choosing the surface temperature to be 2500 K represents overspecification of the problem since alternate forms of the B equation resulting from heat transfer and mass transfer analysis permit solution for the surface temperature. When these alternative forms are properly employed, it is found that the surface temperature is strongly dependent on such parameters as ambient temperature and oxygen mass fraction in the freestream, with the consequent result that the dependence of B on these parameters is drastically different than that predicted by the analysis of Mohan and Williams. One unfortunate outcome of their analysis lies in their use of Eq. (8) to explain the existence of a limiting freestream oxygen concentration, freestream temperature boundary below which extinguishment occurs [calculated from Eq. (8) by setting $B=0$]. There is such a boundary but, as will be explained below, it results from the

surface temperature becoming sufficiently low at low combinations of $X_{\text{O}_2, \infty}$ and T_{∞} that B_2O_3 is predicted to condense out on the surface, thus blocking the path of O_2 to the boron.

The Coffin and Brokaw,³⁷ Knipe,³⁸ King,²⁶ and Greymachkin⁴¹ models are all quite comprehensive. Coffin and Brokaw, and Knipe all consider the effects of condensation of boron oxide away from the particle, while King and Greymachkin ignore this effect. The results of calculations by the former authors indicate that for ambient temperatures in the area of 300 K the condensation can have a slight augmenting effect on burning rate. It is anticipated, however, that in hot motor environments this condensation will occur so far away from the particle (if at all) as to have negligible effect on burning rate. Greymachkin⁴¹ actually develops two models, one for the burning of boron with oxide coexisting on the surface with boron, but not inhibiting the boron reaction in any way (unrealistic), and the other for a clean surface. The second analysis is virtually identical to that of King.²⁶ In these analyses, all reactions are assumed to be infinitely fast, with chemical equilibrium prevailing between the myriad boron-oxygen containing species (note that the analyses are thus far limited to burning of boron in oxygen-inert mixtures) at all radii. (Temperature of course varies with distance from the particle surface resulting in shifting equilibria.) Application of species and enthalpy transport equations, conservation equations for enthalpy and atoms, and equilibrium constant vs temperature relationships permits (with the assumption of unity Lewis numbers and no dependence of the density-diffusivity product on temperature) development of a set of algebraic equations which can be solved for (among other things) surface temperature, burning rate, and gas composition adjacent to the surface as a function of particle size and ambient (freestream) conditions. Careful examination of the results of such an analysis indicates that over a very wide range of variables the burning process may be reasonably well depicted as a reaction of B_2O_3 gas with boron at the particle surface to yield BO and B_2O_2 (the relative amounts being determined by the equilibrium constant for $2\text{BO} \rightleftharpoons \text{B}_2\text{O}_2$ at $T = T_{\text{surface}}$) followed by oxidation in the gas phase away from the particle surface of the $\text{BO}/\text{B}_2\text{O}_2$ intermediates to B_2O_3 gas. A particularly simple equation for the parameter B which results from such a picture closely approximates results from the detailed model:

$$\begin{aligned} B &= \frac{MW_{\text{B}_2\text{O}_3}}{MW_{\text{O}}(1.5MW_{\text{B}_2\text{O}_2}/MW_{\text{B}} - 1)} X_{\text{O}_2, \infty} \\ &= \frac{MW_{\text{B}}}{MW_{\text{O}}} X_{\text{O}_2, \infty} = 0.677 X_{\text{O}_2, \infty} \end{aligned} \quad (9)$$

Additional important outputs provided by the detailed model are the partial pressure of B_2O_3 gas adjacent to the particle surface and the surface temperature. Comparison of these values with a vapor pressure curve for B_2O_3 permits prediction of the critical ambient conditions at which B_2O_3 will be thermodynamically predicted to condense on the surface. At these conditions, the model breaks down. Physically, such conditions should be interpreted as extinguishment boundaries for the boron particle. Thus, for any given total pressure and freestream value of B_2O_3 gas mass fraction, one may use the detailed model to determine a curve of ambient oxygen mass fraction ($X_{\text{O}_2, \infty}$) vs ambient temperature (T_{∞}) separating a region in which Eq. (9) is valid from a region in which the particle will not burn. Such a plot is presented in Fig. 12. As may be seen, the boundary is predicted to rise with increasing values of total pressure or ambient B_2O_3 gas mass fraction. For fixed values of these parameters, the required $X_{\text{O}_2, \infty}$ decreases with increasing T_{∞} . Macek^{35,36} has observed in his laser-ignited boron combustion studies that at $P_{\text{TOT}} = 1$, $X_{\text{B}_2\text{O}_3, \infty} = 0$, $T_{\infty} = 300$ K, boron

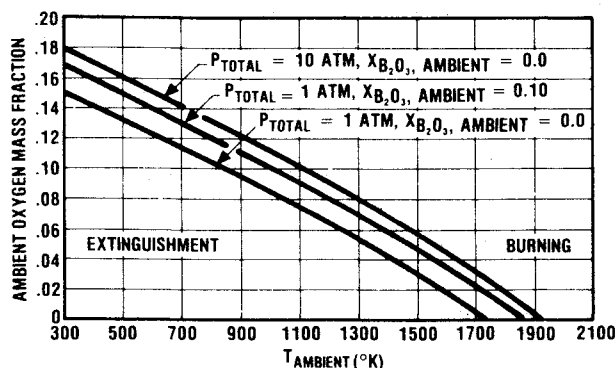


Fig. 12 Predicted burning-extinguishment boundaries for single boron particles.

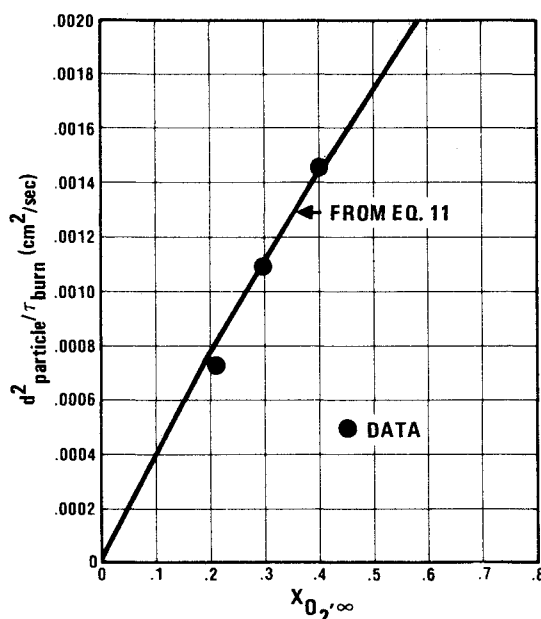


Fig. 13 Comparison of Macek burn-time data with calculations using Eq. (11).

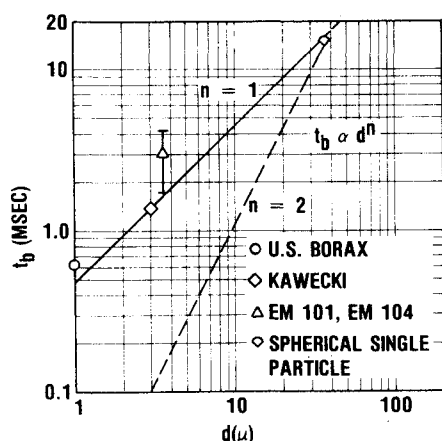


Fig. 14 Macek boron particle burn-time data for small particles, $T_{\text{gas}} = 2240 \text{ K}$, $X_{\text{O}_2} = 0.2$.

particles will burn for $X_{\text{O}_2, \infty} = 0.21$ but will not burn for $X_{\text{O}_2, \infty} = 0.10$, consistent with Fig. 9, which indicates a critical $X_{\text{O}_2, \infty}$ for these conditions of 0.15. (Actually Macek's numbers are mole fractions, but the difference is negligible.)

As mentioned earlier, Coffin and Brokaw³⁷ and Knipe³⁸ have briefly examined the effect of B_2O_3 condensation away from the particle on burning rate and found it to have some

influence (though not particularly large) on this parameter, for cold ambient temperatures. This may be the cause for the slight pressure dependence of burn time observed by Macek (Fig. 10) since increased pressure would be expected to decrease the radius at which condensate occurs.

It should be noted that combustion models of the type described above have apparently only been developed for burning of boron particles in oxygen. However, as long as the combustion remains diffusion limited, the same type of analyses may be performed for combustion of boron in CO_2 and H_2O . Since the reactions $\text{B}_2\text{O}_2 + \text{CO}_2 \rightarrow \text{B}_2\text{O}_3 + \text{CO}$ and $\text{B}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{B}_2\text{O}_3 + \text{H}_2$ are both thermodynamically favored in the temperature regimes of interest, it appears likely that the simple two-stage reaction analysis mentioned above will still apply and the resultant formula for B will be of the same form as Eq. (9), though with a different coefficient for the ambient oxidizer mole fraction, resulting from the different stoichiometry associated with these alternate oxidizers. Of course, the extinguishment limits can also be expected to shift (upward) owing to the considerably lower exothermicity of the reactions of boron with CO_2 and H_2O .

Equations (7) and (9) may be combined with a straightforward expression relating the time rate of change of particle radius to the mass burning flux:

$$\frac{dr_s}{dt} = -\frac{\dot{m}_{\text{burn}}}{\rho_B} \quad (10)$$

and integrated from the initial particle radius to burnout, assuming validity of the diffusion-limited model over this entire range (about which more will be said later) to yield the following d^2 law relating burn time to initial particle size:

$$\tau_{\text{burn}} = \frac{\rho_B}{8\rho_g \bar{D} \ln(1 + 0.677 X_{\text{O}_2, \infty})} d_{\text{INIT}}^2 \quad (11)$$

Since $\bar{\rho}_g \bar{D}$ is generally essentially independent of total pressure, τ_{burn} is also predicted to be independent of pressure in the diffusion-limited regime. It does, however, depend on ambient oxygen mass fraction through the logarithmic term and has a weak dependence on ambient temperature through the dependence of $\bar{\rho}_g \bar{D}$ on T , which is in turn dependent on T_{ambient} . In Fig. 13, the Macek data from Fig. 11 are replotted in the form of $d_{\text{particle}}^2 / \tau_{\text{burn}}$ vs $X_{\text{O}_2, \infty}$. Also plotted is a theoretical curve based on Eq. (11), with an assumed average temperature of 3500 K across the flame region and an average molecular weight of 35, leading to $\bar{\rho}_{\text{gas}} = 1.2 \times 10^{-3} \text{ g/cm}^3$, and with $\bar{D} = 15 \text{ cm}^2/\text{s}$ (based on extrapolation of $\text{O}_2 - \text{N}_2$ diffusivity data to 3500 K using a 1.8-power dependency on temperature). As may be seen, agreement between theory and experiment are excellent.

As pointed out by Bahn,⁴² however, use of a particle burning law based on diffusion-limited combustion must become erroneous for sufficiently small particle diameters, since the diffusional transport rates are predicted to approach infinity as particle size approaches zero, while kinetic process rates do not increase with decreasing particle size. Thus, at some finite diameter, the rate-limiting particle burning processes must become kinetic rather than diffusional, with a resultant shift from the burning mass flux being inversely proportional to particle radius to being independent of particle radius. This in turn will lead to a gradual transition from d^2 -law behavior ($\tau_{\text{burn}} \propto d_p^2$) to d^1 -law behavior ($\tau_{\text{burn}} \propto d_p^1$), with particles of sizes such that they spend a significant fraction of their life in both the diffusion-controlled and kinetics-controlled burning modes showing an intermediate dependence of burn time on initial size. It may easily be shown that the ratio of the burn time calculated allowing transition from diffusion control to kinetics control at $d = d_{\text{transition}}$ to the burn time calculated assuming diffusion-controlled burning all the way to burnout is

$$\frac{\tau_{\text{actual}}}{\tau_{\text{diffusion control}}} = \left(\frac{d_{\text{transition}}}{d_{\text{initial}}} \right)^2 + 1 \quad (12)$$

This indicates that as long as $d_{\text{transition}}/d_{\text{initial}}$ is less than about 0.4, the error involved in assuming diffusion-controlled behavior until burnout is small. It may be noted in Fig. 9 that the 1.0 atm, $X=0.40$, $d_p=35 \mu$ point deviates significantly from the d^2 -law line (≈ 50 -60% high); in line with Eq. (10), this suggests $[d_{\text{transition}}/35 \mu] = 0.8$ or $d_{\text{transition}} = 25 \mu$ for these conditions.

Thus far, only burn-time data taken by Macek in the late 1960s have been presented—additional, more recent data² are presented in Fig. 14. These data indicate an effective shift from d^2 law to d^1 law in the 30-40- μ particle diameter region, just on the lower border of the size ranges previously studied by Macek. Boron being utilized in airbreathing propulsion studies typically has a particle diameter of 3-5 μ , well within the kinetics-limited region. For such particles, burn-time equations based on diffusion-limited combustion models (or d^2 -law extrapolations) are useless. (These data, by the way, explain a dilemma which had been puzzling afterburner combustor designers: with the d^2 law, the particles were predicted to burn in ≈ 0.1 -0.3 ms, considerably less than typical combustor residence times, while the new data indicate a time requirement of 1.5-2.5 ms.) Other evidence for kinetics-controlled behavior taking over in the 20-40- μ -diam region is the observation by Macek that the burn time begins to show considerable pressure dependence in the subatmospheric (0.17 and 0.5 atm) region. (Lower pressure can be shown theoretically to cause the diameter at which transition from diffusion to kinetics control occurs to increase.)

There do not appear to be any existing complete models of boron combustion in the kinetics-limited regime, although Bahn⁴² did some preliminary examination of this problem many years ago. For proper development of such a model, reasonable reaction pathways will have to be identified and kinetic rate expressions for the limiting steps in these pathways will have to be developed. It seems likely that separate treatments for the reactions with O_2 , CO_2 , and H_2O will be required. A key part of the effort will almost certainly be definition of (and establishment of kinetics for) the surface step(s) leading to removal of boron atoms from the particle surface, the likely limiting step(s) in the overall combustion process.

Combustor Processes

In a typical ramburner configuration, there are recirculation regions which closely resemble an idealized perfectly stirred reactor (PSR), in which composition and temperature are nearly uniform. Of vital importance to the attainment of high afterburning efficiency is the high fractional conversion of boron to boron oxide in these regions. The designer requires information on the fractional conversion of boron in a dust cloud in a perfectly stirred reactor as a function of such parameters as pressure, temperature, oxidizer concentration and type, particle loading, and mean residence time, to properly design these regions in a ramburner and to predict ramburner efficiency. Such data are currently not available and an analytical procedure (which would need to include proper description of particle ignition and combustion mechanisms) for predicting such conversion efficiencies has not been developed.

There are also directed flow regions in the typical ramburner which closely resemble the idealized plug flow reactor (PFR). In order for flame to propagate between regions and fill the combustor, the turbulent flame speed, which depends directly on the laminar flame speed, must exceed the velocity of the PFR flow. In addition, laminar flame speed in the boron dust cloud is a parameter directly influencing flameholder blowoff velocity.^{43,44} Thus laminar flame speed data and predictive capability for boron dust clouds are of interest. Unfortunately, there is only an extremely limited

amount of data of this type,⁴⁵ with no systematic data on the influence of various parameters on boron dust cloud flame speeds. A rudimentary flame speed model has been developed by King.⁴⁶ However, this model does not treat the effects of H_2O on ignition, does not treat multiple oxidizers, is limited to unimodal boron, uses an oversimplified radiation treatment, and uses an empirical rather than mechanistic formula for burning rate during the "full-fledged combustion" interval. (Fortunately, at least, the empirical law used for burning rate in this model was based on kinetics-limited combustion rather than diffusion-limited combustion.)

A procedure for modeling combustor performance, which appears to have promise as a combustor design tool, is the zonal (connected-module) approach in which the combustor is broken into stirred reactor zones (recirculation zones) and directed flow zones, with shear layer analysis used to connect the zones (e.g., Edelman's modular model⁴⁷). This type of approach is particularly amenable to coupling in of proper analytical descriptions of particle ignition/combustion. To support this analytical procedure, knowledge of flame propagation in boron-oxidizer-inert gas dust clouds (as discussed above) is required for the directed flow modules, while information regarding the degree of conversion of boron to product oxide in perfectly stirred reactors of limited residence time, and data on stability of combustion in a perfectly stirred reactor (blowoff limits), are required for analysis of the stirred reactor modules.

Oxide Condensation

A potential problem area as regards full utilization of the heating value of boron involves the condensation of the oxide product, particularly in the presence of water vapor which may tend to kinetically trap the products of combustion in the form of HBO_2 and other oxyborohydrides. If the combustion products are not converted to condensed-phase oxide, up to 20-25% of the potential heating value of the boron can be lost. Thermodynamically, condensation should occur at approximately 1700-2000 K, depending on pressure and overall composition. However, there is a strong possibility that the kinetics of condensation are sufficiently slow at these temperatures to preclude condensation in the available dwell times. It is anticipated that the condensation process for HBO_2 will be considerably slower than that for B_2O_3 (gas) based on spectroscopic studies by Miller⁴⁸ which indicate that there must be a large number of complex sequential steps involved in converting HBO_2 to B_2O_3 .

Edelman et al.⁴⁹ have developed a model for B_2O_3 condensation based on classical homogeneous nucleation and cluster growth theory and used this to predict wall static pressure profiles through a nozzle for products of hydrogen-oxygen-boron combustion with test conditions such that condensation would thermodynamically be predicted in the nozzle—experimental results appear to agree well with predictions based on this model. However, it is not clear whether the applicability of this model to situations where considerable HBO_2 is formed in the combustion chamber has been thoroughly tested. In light of Miller's conclusion that there does not appear to be a simple pathway by which HBO_2 can be converted to B_2O_3 , it appears that further study of this potential problem is warranted.

Research Needs

From this review, it becomes apparent that there are numerous research needs associated with development of practical combustors utilizing particulate boron as a fuel. In the area of single particle ignition, upgrading of existing models is needed, with inclusion of treatment of the effects of water vapor on the ignition process. In support of this modeling, experimental information regarding the solubility and diffusivity of oxygen (and other possible oxidizers) in liquid B_2O_3 is needed, as are kinetic data for the reaction of water vapor with condensed oxide. Considerable extension of

the burning time and ignition time data bases into the small particle regime (less than 20 μ diameter) is needed, as is development of a kinetics-limited model for the "full-fledged" combustion stage of boron burning. For such modeling to be successful, experimental identification of reaction paths and determination of kinetic data for limiting reaction steps are required.

Definition of the nature of boron particles entering combustors should be addressed (single unit particles, loosely bound porous conglomerates, tightly bound low porosity conglomerates) and ignition/combustion models should be modified as needed to treat conglomerates as well as single particles. The mechanism(s) by which coatings affect particle ignition need to be experimentally defined and ignition models modified appropriately to treat these mechanisms. In addition, the effects of fluorine compounds in the gas phase on ignition should be experimentally and theoretically studied, as should the effects of external radiation flux.

With respect to ignition and combustion of boron dust clouds, improvement and extension of existing cloud ignition models to include prediction of ignition times as well as critical ignition conditions are needed. In addition, experimental definition of the dependence of critical conditions for ignition and of ignition delay times on such independent variables as pressure, temperature, and gas composition should be carried out. Experimental and modeling efforts defining fractional conversion of boron in dust clouds in a perfectly stirred reactor as a function of such parameters as residence time, particle loadings, pressure, temperature, particle size, and oxidizer type and concentration are also needed. The dust cloud flame speed model of King should be improved and extended to realistically treat radiation effects and handle multiple size particles and other oxidizers, and flame speed should be measured as a function of various independent variables.

Finally, further investigation of potential problems associated with conversion of B_2O_3 gas and, particularly, HBO_2 gas to condensed phase oxide appears to be needed.

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