Distribution in Swirling Flows from Mean Value Distributions," International Journal of Heat and Mass Transfer, Vol. 14, 1971,

p. 573.

15 Lavan, Z. and Rochino, A., "Analytical Investigations of Incompressible Turbulent Swirling Flow in Stationary Ducts," Transactions

of the ASME: Journal of Applied Mechanics, Vol. 36, 1969, p. 151.

16 Ragsdale, R. G., "Applicability of Mixing Length Theory and Turbulent Vortex Systems," TN D1051, 1961, NASA.

17 Damkohler, G., "Jahrbuch 939 die Deutschen Luftfahrtforschung,"

Zeitschrift fuer Electrochemie, Vol. 46, 1940, p. 601.

¹⁸ Corrsin, S. and Kistler, A. L., "Free Stream Boundaries of Turbulent Flows," Rept. 1244, 1955, NACA.

¹⁹ Stewart, R. W., "Irrotational Motion Associated with Free Turbulent Flows," Journal of Fluid Mechanics, Vol. 1, 1956, p. 593.

²⁰ Lewis, B. and Von Elbe, G., Combustion, Flames, and Explosion

of Gases, Academic Press, New York, 1961.

21 Reed, S. B., "Flame Stretch—A Connecting Principle for Blowoff Data," Combustion and Flame, Vol. 11, 1967, p. 177.

²² Ranz, W. E. and Gore, R. W., "Backflows in Rotating Fluids Moving Axially through Expanding Cross Sections," AIChE Journal, Vol. 10, 1964, p. 83.

²³ Thring, M. W. and Newby, M. P., "Combustion Length of Enclosed

Turbulent Jet Flames," 4th Combustion Symposium, Combustion Institute, Pittsburgh, Pa., 1953, pp. 789–796.

²⁴ Chigier, N. A. and Chervinsky, A., "Aerodynamic Study of Turbulent Boundary Free Jets with Swirl," 11th Combustion Symposium, Combustion Institute, Pittsburgh, Pa., 1967, p. 489.

²⁵ Rubel, A., "Some Effects of Swirl on Turbulent Mixing and Combustion," CR 1956, 1972, NASA.

²⁶ Hinze, J. O., Turbulence, McGraw-Hill, New York, 1959, Chap. 5,

p. 376.

27 Gosman, A., Pun, W. M., Runchel, A. K., and Spaulding, D. B.,

Runchel, A. K., and Spaulding, D. B.,

Runchel, A. K., and Spaulding, D. B., Heat and Mass Transfer in Recirculating Flows, Academic Press,

New York, 1972.

²⁸ Milne-Thompson, L. M., *Theoretical Hydrodynamics*, 3rd ed., Macmillan Co., New York, 1955, p. 525.

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Ignition and Global Combustion Models for Clouds of Boron Particles

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It is shown that the single particle ignition model proposed by Merrill King for the ignition of boron particles can be modified and extended to predict with reasonable accuracy the ignition delay times of single boron particles exposed to an oxidizing atmosphere. Provisions were also included to account for the effect of changes in system pressure, particle diameter, surrounding gas temperature, and the mole fraction of water vapor in the gas. The single particle ignition model is extended to clouds of particles by attempting to account for such factors as interparticle radiation and the finite amount of gas surrounding each particle. This model predicted ignition of particle clouds under certain conditions which would not favor the ignition of single particles. Finally, a global combustion rate is derived for a cloud of boron particles burning under steady-state conditions. This combustion rate was obtained from an analysis of the data obtained from a series of experimental runs performed in a one-dimensional flow reactor.

Nomenclature

= surface area, cm² = specific heat, cal/g-°K d^{c_p} = particle diameter, cm

= activation energy for evaporation = heat of fusion of boron, cal/g ΔH

 $\Delta H_{\rm vap}$ = heat of vaporization of boron oxide, cal/mole = convective heat-transfer coefficient, cal/cm²-sec-°K

= thermal conductivity, cal/cm-sec-°K

= molecular weight M

= mass, g

= pressure, atm

Pr= Prandtl number of the gas

= heat of combustion of boron with diatomic oxygen to form liquid B₂O₃, cal/mole; total energy, cal

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= molar rate of consumption of boron, g-mole/sec; gas constant

= molar rate of evaporation of boron oxide, gm-mole/sec

= Reynolds number based on particle diameter and relative

velocity between the gas and particle

= radius, cm

= oxide film thickness, $r_2 - r_1$, cm

T= temperature, °K

= time, sec

 particle cloud mass density, g/cm³ = mole fraction of H₂O present in the gas

= surrounding absorptivity (=1.0) = particle emissivity (=0.8) 3

= particle burning rate, cm/sec λ

= density, g/cm³

= Stefan-Boltzmann constant

Subscripts and Superscripts

= boil, burned

= final

= gas

= initial

= melt m = particle

RAD = radiation environment

= particle; first visible zone = particle + oxide layer; steady-state combustion zone

Introduction

THE combustion of boron in air augmented rockets and ramjets has been of interest for some time, particularly in the last ten years or so. Numerous investigations of the ignition and combustion of boron in the form of rods, single particles, and clouds of particles have been reported. A summary of these studies may be found in Ref. 1. The most recent theories for the ignition and combustion of single particles are those of King² and Mohan and Williams.³

The theory advanced in the following comprises a) a modified version of the ignition and combustion theory of King for single particles, b) an extension of that theory to describe the ignition of clouds of boron particles, and c) a model for the global combustion of clouds of boron particles. Comparisons with experimental data are presented where appropriate data exist.

Single Particle Ignition Model

It has been substantially accepted^{2,3} that the ignition stage in the oxidation of boron particles with diameters larger than about 1 μ involves diffusion of the oxidizer through a film of B_2O_3 on the particle at temperatures below the oxide boiling point. As inferred by the Glassman criterion,⁴ the oxidation of boron, at least in part, occurs on the particle surface. The results of Talley^{5,6} and Prentice⁷ support this description. Talley's results were employed by King in evaluating both the evaporation rate of the oxide and the molar consumption rate of boron as limited by diffusion through the oxide film.

King's² model for the oxidation of a spherical particle, including convective and radiative heat exchange with the surroundings, is represented by the equations;

$$(m_B c_{p_B} + m_{\rm B_2O_3} c_{p_{\rm B_2O_3}})(dT_p/dt) = RQ - R_E \Delta H_{vap} + 4\pi r_2^2 [h(T_g - T_p) + \sigma \alpha \varepsilon (T_{\rm RAD}^4 - T_p^4)]$$
(1)

$$dm_{R}/dt = -RM_{R} \tag{2}$$

$$dm_{\rm B_2O_2}/dt = (R/2 - R_E)M_{\rm B_2O_2}$$
 (3)

$$m_B = \frac{4}{3}\pi r_1^{\ 3} \rho_B \tag{4}$$

$$m_{\rm B,O_3} = \frac{4}{3}\pi (r_2^3 - r_1^3)\rho_{\rm B,O_3} \tag{5}$$

where R is the molar rate of consumption of B and R_E is the molar rate of evaporation of B_2O_3 .

The rates R and R_E represent the most significant unknowns. The forms of these relations employed by King are to be employed here, with minor adjustments, for the processes prior to boiling of the oxide. King² concluded that R_E would obey an Arrhenius-type relation. Mohan and Williams³ suggest a rate based on surface equilibrium conditions. While the latter model may have a more acceptable physical basis, the functional dependences are similar except for the pressure dependence. § This does not exhibit a strong influence, however, as noted in Ref. 3.

Although it is felt by the present authors that King's model substantially describes the phenomena, three factors have not been included. The first of these is minor, that the model was presumed to be in effect only after the particle had reached a temperature of 1800°K. The second factor was the neglect of the fact that the oxide boils off the particle surface when the particle reaches the oxide boiling temperature, thus invalidating the expression for R above this temperature. The third concerns the fact that the particle must melt at the melting point, thus causing the addition of an effective energy sink until the particle has completely melted. It is the inclusion of these effects along with other modifications of King's original work which forms the basis of the present model. Apart from the phase changes, the

present model accepts the relations (1–5) for conditions where phase changes do not occur, except for slight modifications of the rate expressions employed.

The following major assumptions are to be made in the derivation of the modified model for single particle ignition. 1) The boron particles are spherical with radius r_1 , and are initially coated with a uniform layer of B₂O₃ of outer radius r_2 . 2) The temperature of the particle including the oxide coating is uniform but may vary with time. 3) The temperature and composition of the surrounding gases remain constant and uniform. 4) The convective heat-transfer coefficient, h, is known. 5) Radiative exchange with the surroundings is treated as if the surroundings were perfectly black at a temperature T_{RAD} . 6) The reaction rate of boron is limited by the diffusion of oxygen through the boron oxide coating and the reaction forms only B₂O₃, prior to the complete removal of the oxide film. 7) The evaporation rate of boron oxide follows an Arrheniustype relation. 8) The temperature of the particle remains constant during the oxide boiling and particle melting processes. 9) Variations in convective heat-transfer rate, surface reaction rate, and oxide evaporation rate are neglected during the oxide boiling process. 10) The effect of the presence of water vapor is to reduce the activation energy of the oxide evaporation process. 11) The initial particle temperature is below both the oxide boiling point and the boron melting point. 12) The mass of B₂O₃ formed by combustion during the boiling process may be neglected in view of the relatively short time required for the B₂O₃ film to boil off. Several of these assumptions are discussed further as the various aspects of the model are developed in the following pages.

From the outset, it should be understood what is meant by the term "ignition." Instead of following the often used practice of linking the definition of ignition to the attainment of a particular temperature, in the present model, a particle is said to ignite if it reaches a state at which no energy barriers stand between that state and steady-state combustion. In this model, there are two such barriers to be overcome. One of these is the necessity that the oxide layer be removed from the particle surface and the other is that the particle must be melted. Oxide melting is of relatively minor importance. If the particle is able to pass these two barriers and still have an increasing temperature gradient, ignition is said to have occurred. The concept of passing energy barriers thus frees one from the impossible task of determining a particular ignition temperature for every combination of particle size, atmospheric temperature, pressure, and composition. It is this definition of ignition, the inclusion of oxide boiling and particle melting and the ability of the present model to allow the interchange of the order of these processes as the pressure increases which makes the present ignition model different from previous models.

The time required to boil away the liquid layer of B₂O₃ at the boiling point may be expressed as the ratio of the latent heat of evaporation divided by the rate of heat transfer, including the contribution due to combustion.

$$t_b = \frac{\rho_{\rm B_2O_3}({r_2}^3 - {r_1}^3)\Delta H_{\rm vap}}{3{r_2}^2[(R/A)Q + h(T_g - T_p) + \alpha\sigma\varepsilon(T_{\rm RAD}{}^4 - T_p{}^4)]M_{\rm B_2O_3}} \eqno(6)$$

Accumulation of B_2O_3 due to combustion during this relatively fast process is neglected in accord with assumption 12. The convective heat-transfer coefficient can hardly be expected to be represented by relations not accounting for the significant mass transfer, but this term will generally be small for most situations. The vapor pressure of boron oxide may be computed by means of the Clapeyron equation in conjunction with the latest thermochemical data concerning boron oxide as presented in the JANNAF tables.

Melting of the boron particle, by contrast, is a relatively slow process. Variations in the heat-transfer coefficient, surface reaction rate, and oxide evaporation rate are to be accounted for in the course of this process. Thus, if t_m is the time required to melt the particle, and ΔH_f is the heat of fusion of boron (5.39 kcal/mol at 2450°K)

[‡] There is an apparent typographical oversight in the equation corresponding to Eq. (1) in Ref. 2.

[§] The present work was substantially completed before publication of Ref. 3. Direct comparisons have not been made by the authors.

$$\Delta H_f m_B / M_B = \int_0^{t_m} \{ RQ - R_E \Delta H_{\text{vap}} + 4\pi r_1^2 [h(T_{\infty} - T_p) + \alpha \sigma \varepsilon (T_{\text{RAD}}^4 - T_p^4)] \} dt \qquad (7)$$

If the melting process occurs following the oxide boiling, the quantity $(RQ - R_E \Delta H_{\rm vap})$ is replaced by $R(Q - 0.5 \Delta H_{\rm vap})$.

The Ranz-Marshall equation⁸ employed in the computations for the convective heat-transfer coefficient between the particles and the gas

$$h = (1 + 0.296 Pr^{1/3} Re^{1/2})k_a/r$$
 (8)

has been employed by other investigators⁹ for small spheres.

The expressions for R and R_E originally presented by King were modified on the basis of recent observations by Macek¹⁰ and experience with the present model. The coefficient in the expression for R was increased in accord with Macek's recommendation and the exponent in the expression for R_E was reduced slightly to provide a better fit to the data of Macek and Semple.¹¹ The expressions employed in the computations were

$$R = (1/\Delta r) 2.0 \times 10^{-6} r_2^2 T_p P_{0_{2,p}} \exp(-22600/T_p)$$
 (9)

and

$$R_E = 1.225 \times 10^6 r_2^2 \exp\left(-42000/T_p\right) \tag{10}$$

As will be shown later, it was also found that if it is assumed that the effect of water vapor is to hydrolize the oxide layer and thus increase its volatility, reducing the activation energy of the evaporation process, it is possible to correlate the available data for such cases within reasonable limits if the activation energy is given by

$$(E/R)_{\text{wet}} = (E/R)_{\text{dry}} - 5000X_{\text{H,O}}$$
 (11)

where $X_{\rm H,O}$ is the mole fraction of water vapor present in the surrounding atmosphere. The linear form was chosen initially due to its simplicity and was not changed in light of the results obtained.

Equations (1-11) combine to form the present ignition model. The data chosen with which to compare the present model are those of Macek and Semple¹¹ because they comprise one of the few sets of data presently available for spontaneous ignition of a single particle exposed to an oxidizing atmosphere, and they were the best controlled of the experiments.

In their experiments, Macek and Semple injected a single boron particle coaxially into a stream of gases of known temperature and composition. The period between the first emission of visible radiation and the cessation of combustion was observed to be composed of two zones. The first zone, the " t_1 " zone in Macek's notation, was separated from the second, or " t_2 ," zone by a definite decrease in visible radiation; this was terminated by a sudden brightening of the particle track, which then persisted for the balance of the combustion process.

In the present model, when the fact that the oxide boils away as the particle reaches the oxide boiling temperature is taken into account, it is found that the oxide is completely removed very early in the t_1 zone. It has been found that the time required to melt the particle always comprises approximately 75% of the t_1 zone. It is thus the completion of particle melting that removes the last barrier and allows the onset of steady-state combustion. While there is obviously some type of combustion reaction occurring during the t_1 zone, the fact that one cannot guarantee that this reaction will be able to supply sufficient energy to completely melt the particle and thus allow the onset of steady-state combustion dictates the inclusion of this zone in the ignition stage.

The conclusion that the t_1 stage cannot be completely dominated by oxide removal is further supported by an analysis of Macek's data for this zone. For each size of particle studied, the length of this zone tended to decrease slightly with an

increase in gas temperature and was not affected by the addition of water vapor to the gas. If oxide removal were the controlling factor, the t_1 zone would surely be decreased significantly by the addition of water vapor since it has been established that water tends to significantly increase the volatility of the oxide layer.

Reiterating, the definition of ignition preferred by the authors is essentially that which occurs when both the oxide layer is removed and the particle has been melted.

A vital piece of information not presently available is the magnitude of the surface reaction rate following the oxide removal and prior to steady-state combustion. No information as to this value presently exists. In the present model, for lack of any other criteria, the surface reaction rate was fixed at the value obtained immediately prior to the onset of oxide boiling and it remained at this value throughout the boiling period and for all processes thereafter. This value was usually slightly below the values which have been presented for the steady-state combustion rate, ¹² and presumably represents a reasonable estimate of the actual rate.

The ignition time obtained by Macek with which to compare the present model was the time from particle injection until the onset of visible radiation plus the duration of the t_1 zone. Since only the distance traveled from injection to the beginning of the t_1 zone was measured, and since the particle was accelerated from the injection velocity to the freestream velocity, it was first necessary to convert this distance to a time in the flow. The equations employed to accomplish this were presented by Macek and Semple. The relative velocity between the gas and the particle found by this means was employed to determine Re in Eq. (8).

In correlating the experimental data, it was assumed that the initial particle temperature was 298°K and that the surroundings radiation temperature was also 298°K. (King later reported this radiation temperature in Macek's experiments was closer to 500°K based on the temperature of the container walls. However, it was found that this resulted in less than a 1% change in the computed ignition times.) An unknown factor was the initial oxide film thickness. Fortunately, it was found that for the

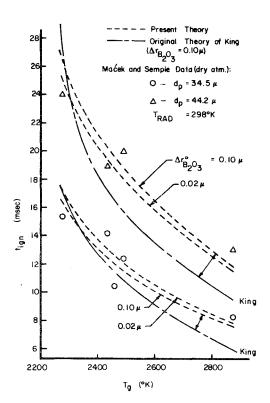


Fig. 1 Predicted ignition delay times compared with experimental data of Macek and Semple for dry atmospheres.

 $[\]P$ This does not necessarily explain the diminished emission observed, of course. Nonetheless, the surface properties of the oxide and the metal can be substantially different and the possible condensation of B_2O_3 in the region around the particle might alter the observed radiation as well.

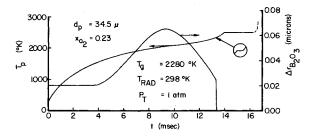


Fig. 2 A typical plot of particle temperature and oxide layer thickness vs time.

particle sizes considered the predicted ignition time is only a weak function of this initial thickness so that only an approximate knowledge of this value is sufficient.

The comparison between the experimental ignition delay times and those obtained from the present model for the same initial conditions in dry atmospheres is shown in Fig. 1. King's curves, adjusted for the initial heat up period, are also shown in the figure. It can be seen that the present model yields the proper magnitudes, trends, and particle size dependence. The effect of the initial oxide layer thickness is also shown. Figure 2 is a typical plot showing particle temperature and metal oxide layer thickness vs time. As the particle temperature reaches approximately 1500°K, the surface reaction rate becomes significant as indicated by the initial rise in the oxide layer thickness. At a temperature of approximately 1900°K, the oxide layer thickness peaks and begins to fall. At the same time, the particle temperature curve inflects upwards and the particle temperature begins to increase more rapidly. At the oxide boiling point, the particle temperature briefly stabilizes while the oxide is removed, as shown in the detail enlargement, followed by another period of rapidly increasing particle temperature. Finally, the particle temperature reaches the metal melting point, where it remains until the melting is complete. Once the particle has been melted, steadystate combustion can occur.

For the computations made with water vapor in the freestream gases the data could be correlated within reasonable limits if the activation energy was given by Eq. (11). The results are presented in Fig. 3. These results are not as satisfactory as the dry atmosphere results but are within about 15%. The limited amount of data available at this point simply did not justify any further attempts to refine Eq. (11).

The computed ignition delay times vs initial particle diameter for various gas temperatures are shown in Fig. 4. At relatively high gas temperatures, the ignition time is a monotonically increasing function of the particle size. At lower ambient temperatures, 2280°K for the example shown here, the ignition

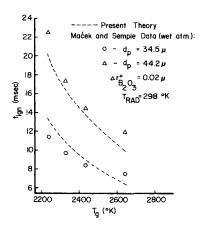


Fig. 3 Predicted ignition delay times compared with the experimental data of Macek and Semple for Atmospheres containing water vapor.

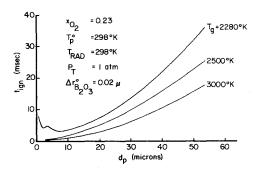


Fig. 4 Effect of initial particle diameter on the ignition delay time.

delay time initially decreases with decreasing particle diameter. However, below a particle diameter of about 8μ , the trend oscillates as the diameter approaches $1~\mu$ at which point, as will be shown later, the gas temperature falls below the minimum ambient temperature required to ignite a particle of this diameter. This "knee" in the ignition delay curve is a result of the complex interaction of the conductive and radiative heat transfer between the particle and the surroundings along with the time required to melt the particle. It should be kept in mind here that with $T_{\rm RAD}=298{\rm ^\circ K}$, the radiation is a loss term and the increased surface to volume ratio at lower particle sizes enhances its importance. No velocity lag between the particle and the gas was employed in these computations.

The effect of the system pressure on the ignition delay time is shown in Fig. 5. Increasing the system pressure from 0.5 to 5 atm causes a significant decrease in ignition time. Further increases in the system pressure have a decreasing influence on the ignition time with the magnitude of this influence decreasing with decreasing particle diameter. The fact that ignition is not predicted to occur below a pressure of about 0.5 atm, corresponding to an oxygen partial pressure of about 0.1 atm, might be compared with the reports of Prentice7 and Macek and Semple¹³ in which they stated that ignition did not occur in their experiments when the partial pressure of oxygen fell below about 0.09 and 0.07 atm, respectively. However, their experiments involved laser ignition in cold gases. The Mohan-Williams³ theory suggests lower flammability limits for the O2 concentration at elevated temperatures. In the absence of suitable experimental data the actual limit remains an open question.

Figure 6 shows the effect of the system pressure on the minimum ambient temperature required for ignition. The general trend that the minimum gas temperature required for ignition decreases with increasing system pressure, is in agreement with experimental data, but the data available are much too sparse to verify the actual shape of the predicted curves.

For the preceding studies, the initial particle temperature was assumed to be 298°K. Raising the initial particle temperature was found to decrease the ignition delay time. However, raising the initial particle temperature as high as 2200°K had no

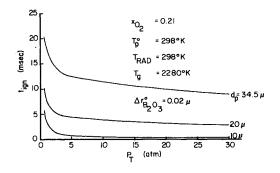


Fig. 5 Effect of gas pressure on the ignition delay time.

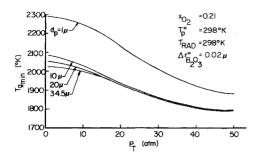


Fig. 6 Effect of gas pressure on the minimum ambient temperature required for particle ignition.

significant effect on the minimum ambient temperature required for ignition.

Cloud Ignition Model

The model suggested here for ignition of clouds of boron particles substantially simplifies the complex interactions present in real systems. The only two prominent aspects of the real problem represented in this model are the finite mass of gas surrounding each particle in the cloud and the radiative shielding provided by the cloud for interior particles. The radiative shielding is assumed complete; that is, no net radiative exchange occurs between a particle and the surrounding cloud. Of course, proper characterization of the radiative transfer would

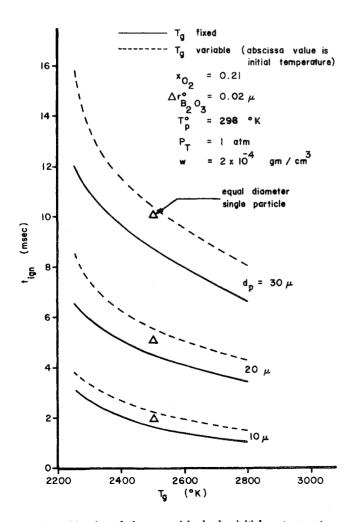


Fig. 7 Ignition time of a boron particle cloud vs initial gas temperature for both fixed and variable gas temperatures.

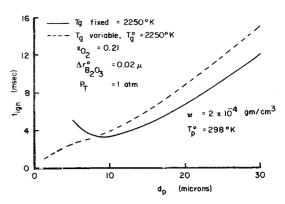


Fig. 8 Effect of initial particle diameter on the ignition delay time of a particle cloud for both fixed and variable gas temperatures.

be a difficult problem in itself, depending upon the particle size and number density, and the cloud geometry, among other factors. This would have to be examined for each situation of interest and is not within the scope of the present study. Rather, practical combustor arrangements may be well enough represented by the assumed conditions.

The particle cloud is taken to be a collection of identical particles subject to the assumptions listed in the previous section. All of the computations were made with air as the oxidizing medium. Two distinct cases were examined: the situation previously described where the mass of gas associated with each particle (well mixed, uniform temperature) exchanges heat and mass with the particle, and a rather artificial situation where the gas temperature is held constant. The latter differs from the single particle case only with respect to the radiative loss and depletion of oxygen in the gas surrounding the particle. Convective heat transfer was neglected in all of the computations.

The predicted ignition time vs initial gas temperature for various particle sizes is shown in Fig. 7. The solid line indicates the situation where the gas temperature remained fixed and the dashed line indicates computations for which the gas temperature was a variable. While the trends are the same as those predicted for the single particle studies, the magnitudes of t_{ign} are somewhat different. The predicted ignition time for the cases with constant gas temperature are below those predicted for a single particle of the same diameter for the indicated cloud concentrations. Since the gas temperature is fixed for these cases, the only major difference between these predictions and the single particle results is the radiant energy exchange between the particles. These results thus indicate the importance of this radiant exchange. On the other hand, for the cases with variable gas temperature, the times predicted are somewhat longer than the corresponding single particle ignition times. This indicates that it is possible for initially cold particles to cool the gas stream to such an extent that it more than compensates for the radiant energy exchange between the particles.**

One of the more interesting results of this study is illustrated in Fig. 8. This figure shows the predicted ignition time vs particle diameter for both fixed and variable gas temperatures. For the instances in which the gas temperature was fixed, the results are similar to those obtained with the single particle model; that is, as the particle diameter drops below about $10~\mu$ the ignition delay time begins to increase. However, when the gas temperature was allowed to vary, the ignition time continued to decrease with decreasing particle diameter. This phenomenon is a result of the heating of the gas above its initial temperature thus reducing the convective heat losses from the particle as the particle temperature increases toward ignition. These results thus indicate that it is possible for a cloud of small particles to

^{**} This, of course, depends on the pressure level (mass of gas) for a fixed particle density.

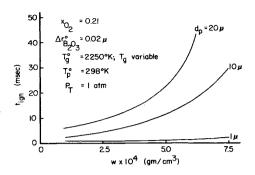


Fig. 9 Effect of cloud concentration on the ignition delay time.

ignite under conditions not favorable for the ignition of a single particle.

The effect of system pressure on the ignition time of a particle cloud was found to be generally the same as that shown for the single particle model except that the initial decrease in the ignition time with increasing pressure is slightly steeper in the cloud case. Whether or not the gas temperature is variable does not change the shape of this dependence. This is presumably because the mass of gas associated with the particle becomes large enough at the higher pressures so that it tends to remain isothermal.

The effect of the cloud concentration on the ignition delay time is shown in Fig. 9 for several particle sizes. The initial particle temperature was 298°K. For this study, the gas temperature was considered variable since the cloud concentration in the range considered has no effect when the gas temperature is held constant. As the particle diameter is increased, the effect of the concentration becomes much more pronounced. At a fixed concentration, the particle surface area per unit volume decreases as the particle diameter increases. This reduction in effective surface area correspondingly decreases the rate of heat transfer to the particles causing increased ignition times. As the concentration increases, there is a greater decrease in gas temperature, again decreasing the rate of heat transfer to the particles and thus increasing the predicted ignition times. These are some of the factors which combine to produce the indicated results. As the particle concentration approaches zero, the values tend toward a magnitude somewhat lower than those predicted by the single particle model due to the interparticle radiation. In reality, these values should exactly approach the single particle values, but do not in this case because of the dense cloud assumption which becomes invalid at low cloud concentration.

The minimum initial ambient temperature required for cloud ignition vs system pressure is given in Fig. 10. The curves presented are approximately correct for both the fixed and variable gas temperature cases with the variable gas temperature requirements generally lying slightly above the requirements for the fixed temperature situations. At pressures above about 10 atm the two types of temperature variations yield nearly the same results as indicated. However, at pressures below 10 atm, this determination is complicated by the fact that, for the variable gas temperatures, the particles approach a relatively unstable equilibrium from which, given a long enough period of time, ignition may be predicted. Comparing these predictions with the corresponding predictions for single particles the minimum initial temperature required for a cloud is slightly lower than that of a single particle of equal diameter, due mainly to the interparticle radiative heat transfer.

In all the computations it has been assumed that the particles were spherical. However, photographs of very small particles show them to be very irregular in shape generally resulting in a greater surface area than a corresponding sphere of equal mass. To determine what possible effect this shape irregularity may have on the predicted ignition times, a series of computations were performed in which the particle surface area upon which

reactions may take place was varied while keeping the initial particle mass and the initial oxide mass at fixed values. It was assumed that the surface irregularities were very fine so that, while the surface area upon which the reactions and evaporation take place varied, the effective surface area for convective and radiative heat transfer remained equal to the spherical surface area. For a particle with a diameter of approximately 1μ , the results indicate that increasing the surface area upon which reactions take place by a factor of four can cause a reduction in the predicted ignition time of approximately 80%.

The Global Combustion Model

The combustion model proposed here is of the global type; that is, the over-all rate of combustion of a boron dust cloud is found without attempting to specify what the intermediate steps in the physical reaction process are. While the knowledge of the complete reaction mechanism may be highly desirable, the determination of this mechanism is beyond the scope of this paper.

The experimental evidence on which this model is based was obtained with an apparatus designed to burn effluent from a small grain of solid propellant in a secondary air stream. The apparatus is described in Ref. 14 along with preliminary results. The solid propellant grain containing 51% boron was burned in a small combustor. Exhaust products from this combustor carrying the particulate boron were rapidly mixed with combustion heated air in a multiple jet mixing element in approximately stoichiometric proportions. This mixture subsequently flowed through a constant area duct, serving as a one-dimensional flow reactor, wherein the boron ignited and burned. Optical measurements revealed that 40-60% of the available boron ignited and burned within 11.5 in. from the point of injection. Auxiliary measurements indicate the boron particles in the combustor were of sizes in the 1 μ range.¹⁵ The initial particle temperature was computed to be in the neighborhood of 1800°K based on the primary combustor performance. Air entering the mixing element was nominally at 970°K. However, for the purposes here the effective gas temperature could probably be taken as that resulting from adiabatic combustion of residual hydrocarbons in the primary exhaust with the secondary air (approximately 1820°K). That is, the gas phase combustion may be presumed much faster than the ignition and combustion processes for boron. The average bulk velocity of the gas-particle mixture was 90 fps.

No attempt was made to determine the point where ignition occurred in the duct, but the evidence showed ignition occurred within a distance of 5.5 in. from the face of the injector. The length over which combustion took place, then, was between 5.5 and 11.5 in. Given the above initial conditions, the cloud ignition model did predict ignition to occur in times well within the time required for the flow to traverse the first 5.5 in. of the duct.

The burning of a single spherical particle may be described by the expression

$$d^n = d_i^n - \lambda t \tag{12}$$

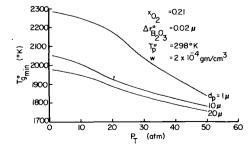


Fig. 10 Effect of gas pressure on the minimum initial ambient temperature required for cloud ignition.

where λ is an effective rate. It has been found generally that $n \leq 2$ for metal particles. The parameters n and λ are to be determined here for the combustion of boron particles in an environment representing that encountered in an air augmented rocket.

It has been shown that as a particle becomes small, it is to be expected that the burning rate would follow a "d" law. 16 In other words, while a particle may follow a "d" law, i.e., the burning rate is controlled by diffusion processes, at some given diameter, as that diameter is descreased below a certain value, the burning rate becomes kinetically controlled. In a recent study, 10 Macek has determined this critical diameter to be approximately 30 μ for boron. Therefore, since the maximum particle size entering the flow reactor in this study was less than $10~\mu$, well below the critical diameter, the value chosen for n was 1.

If d_f denotes the final diameter of a particle after a time increment Δt , then

$$\lambda = (d_i - d_c)/\Delta t \tag{13}$$

For the situation where half the particle mass is consumed, $d_f/d_i=0.794$. Employing a mean streamwise length for the combustion zone of 8.5 in., one has $\Delta t \sim 8$ msec. Then it is found that

$$\lambda = (2.5 + 1) \times 10^{-3}$$
 cm/sec

as a result of a careful analysis of the data (performing numerical integration along the combustor accounting for streamwise changes in the properties, as opposed to the "average" values previously quoted).

Discussion

The models for the ignition and combustion of boron particles described in the foregoing are entirely phenomenological and reflect substantial uncertainty as to the details of the ignition and combustion processes. This is particularly true for amorphous boron particles of irregular shape. Nonetheless, the models do appear to represent some aspects of the problem relatively well. There remains a need for more detailed experimental data and for data over a wider range of conditions to provide a basis for further refinement of the ignition and combustion models.

Most practical combustors involve schemes for mixing of the particle cloud with the secondary airstream. If the arrangement is to involve low flow losses there will be a region in which diffusion processes will be important as they affect the kinetics of the ignition and combustion of the particles. Models for these

processes have appeared in the literature; one incorporating the present ignition and combustion theory for boron has been developed at this laboratory.

References

¹ Meese, R. A., "Ignition and Global Combustion Models for Clouds of Boron Particles," Ph.D. Thesis, Aug. 1972, School of Mechanical Engineering, Purdue Univ., Lafayette, Ind.

² King, M. K., "Boron Ignition and Combustion in Air-Augmented Rocket Afterburners," Combustion Science and Technology, Vol. 5, No.

4, June 1972, pp. 155-164.

³ Mohan, G. and Williams, F. A., "Ignition and Combustion of Boron in O₂/Inert Atmospheres," *AIAA Journal*, Vol. 10, No. 6, June 1972, pp. 776–783.

⁴ Glassman, I., "Combustion of Metals," ARS Progress in Astronautics and Rocketry, Vol. 1: Solid Propellant Rocket Research, edited by Martin Summerfield, Academic Press, New York, 1960, pp. 253–258.

⁵ Talley, C. P. and Line, L. E., "Combustion of Elemental Boron," TM-838, June 1956, Quarterly Summary Report, March-May 1956, Experiment Incorporated, Richmond, Va.

⁶ Talley, C. P., "The Combustion of Elemental Boron," ARS Progress in Astronautics and Rocketry, Vol. 1: Solid Propellant Rocket Research, edited by Martin Summerfield, Academic Press, New York, 1960, pp. 279–286.

⁷ Prentice, J. L., ed., "Metal Particle Combustion Progress Report," July 1, 1965, May 1, 1967, TR NWC TP 4435, Aug. 1968, Naval Weapons Center, China Lake, Calif.

⁸ Ranz, W. E. and Marshall, W. R., "Evaporation from Drops," Chemical Engineering Progress, Vol. 48, 1952, pp. 141–146, 172–180.

⁹ Kuehl, D. K., "Ignition and Combustion of Aluminum and Beryllium," *AIAA Journal*, Vol. 3, No. 12, Dec. 1965, pp. 2239–2247.

¹⁶ Macek, A., personal communication, Atlantic Research Corp., Spring 1972, Alexandria, Va.

¹¹ Macek, A. and Semple, J. M., "Combustion of Boron Particles at Atmospheric Pressure," TR ARC-12-PU, Aug. 1969, Project SQUID, Purdue Univ., Lafayette, Ind.

¹² Kelley, C. M., Williams, R. E., and Takemoto, A., "Combustion Kinetics of Particulate Boron," TR DEN-1-PU, Sept. 1970, Project SOUID, Purdue Univ., Lafavette, Ind.

¹³ Macek, A. and Semple, J. M., "Combustion of Boron Particles at Elevated Pressures," TR ARC-13-PU, June 1970, Project SQUID, Purdue Univ., Lafavette, Ind.

¹⁴ Goede, P. J. and Skifstad, J. G., "Rate Processes in the Secondary Combustion of an Air-Augmented Solid Propellant," AIAA Paper 70-734, San Diego, Calif., 1970.

¹⁵ Mellor, A. M., "Particulate Matter in the Exhaust of a Boron-Loaded Solid Propellant," *AIAA Journal*, Vol. 9, No. 10, Oct. 1971, pp. 1944–1947.

¹⁶ Markstein, G. G., "Heterogeneous Reaction Processes in Metal Combustion," Univ. of Virginia TR CAL-92-PU, May 1966, Project SQUID, Purdue Univ., Lafayette, Ind.