PROJECT SQUID

TECHNICAL REPORT ARC-14-PU

COMBUSTION OF BORON PARTICLES: EXPERIMENT AND THEORY

BY

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PROJECT SQUID HEADQUARTERS
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LAFAYETTE, INDIANA

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13. ABSTRACT

The primary purpose of the work was measurement of burning times of single boron particles as functions of three experimental variables: particle diameter d from 37 to 124 μm, pressure P from 0.17 to 35.0 atm, and mole fraction of oxygen in gas X from 0.1 to 1.0. Limited studies were also made in fluorine-containing gases without oxygen. The experiments were done by a previously described laser-ignition technique. In oxygen-containing gases measurable pre-ignition delays were observed, except at low pressures; they were not observed in the absence of oxygen. The effect of convection in these free-fall experiments was found to be significant at large values of d and P, and had to be taken into account in interpretation of the data. When d, P, and X are sufficiently high, the burning times are found to be inversely proportional to X, directly proportional to d^2, and independent of P. At low values of these parameters, burning times deviate from these scaling laws. The flammability limit is between X = 0.10 and X = 0.21. Quantiative agreement with a gas-phase diffusion theory is good under conditions well removed from the flammability limit. Burning rates with fluorine as oxidant are lower than equivalent rates with oxygen, as expected from diffusion considerations.

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Burning rates						
Diffusion-Controlled combustion						

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I. INTRODUCTION

Combustion of boron particles has been studied in the past in several laboratories and by several experimental techniques, employing a gas burner[1], a shock-tube[2], and lasers[3,4]. There have also been theoretical studies[4,5,6,7]. Several points of agreement concerning the ignition and the subsequent self-sustanied combustion have emerged from these studies.

As in the case of some metals, thermal properties of the stable oxide, B_2O_3, play an important part in the processes leading to ignition of particles. It is now generally agreed that in the presence of oxygen chemical reactions responsible for ignition take place at temperatures between about 1500°K and the boiling point of B_2O_3 (2316°K at 1 atm). The relatively slow preignition processes are therefore dominated by the diffusion of oxidants (or conceivably of boron) through a liquid oxide coating. The subsequent rapid combustion takes place at higher particle temperatures, after removal of the oxide, and this process is dominated by the gas-phase diffusion of oxidants. In this paper we shall apply the term "combustion" exclusively to the second rapid stage. It now appears probable that combustion reactions take place in several steps involving volatile intermediates (BO, B_2O_2).

Despite these qualitative advances, quantitative information on boron particle burning rates has been extremely limited until now. The reason for this deficiency is that the accuracy and the range of physical conditions under which past measurements were done were quite inadequate for establishment of clear experimental trends. The important parameters are the gas properties

(temperature, pressure, and oxidant mole fraction), and especially the particle diameter. The purpose of the program described in this paper was the gathering of an accurate and extensive set of burning-time data on single boron particles, and a comparison of these data with theory. This was done by a laser-ignition technique. This technique, like most other laser or flash-heating techniques, is not suitable for quantitative ignition studies, and has the added disadvantage that the ambient gas in which particles are burned cannot be much above the room temperature; indeed, all our work was done at room temperature. However, the technique permits easy and arbitrary variations of gas composition and pressure, and is valid over a rather wide range of particle diameters. Thus it is very suitable for experimental determination of particle burning times, and hence burning rates, as functions of these three variables.

II. EXPERIMENT

1. Apparatus and Technique

Both the apparatus and the experimental technique were described earlier[3]. Very briefly, single boron particles were dropped directly into a focused laser beam in various oxidizing gases at room temperature. Gas compositions are given in Section II.3. In our previous work the pressure range was from 1.0 to 35.0 atm. We have now extended this range down to 0.17 atm. As each particle traverses the laser beam, its surface is rapidly (< 1 msec) heated to a temperature exceeding 2000°K. An induction period t_i follows, lasting up to 130 msec, depending on pressure, gas composition, particle diameter, and the detailed history of exposure to laser radiation. The subsequent burning time t_b was the most important quantity studied in this program. Both t_i and t_b were measured stroboscopically. Two photographs, each showing a cluster of boron

particles igniting and burning under somewhat different experimental conditions, are shown in Fig. 1. The significant difference in luminosity of particles as they emerge from the laser beam in these two photographs will be discussed in Section IV.

2. Particle Diameters

Careful definition of boron particle diameters was a very important part of this program. Whereas in our earlier work[3] only one sample of crystalline particles having irregular shapes with sharp edges was studied, the present work was done with particles which were nearly spherical. These had been prepared commercially from crystalline particles by the plasma-torch technique. The powder was then carefully screened into four monodisperse samples. A microphotograph of one sample is shown in Fig. 2. Particle diameters of all four samples were measured directly from such microphotographs. The measurement was then verified by two additional techniques. The two smaller samples were measured micromerographically, and the two larger ones by the weighing of a counted number of particles. The results are given in Table I. For the sake of uniformity only the microscopic measurements - 37, 54, 98, and 124μ respectively - were used in the analysis of results. Standard dispersions of measured diameters were only a few percent.

3. Gas Compositions and Pressures

An extensive series of experiments was performed with oxygen/nitrogen mixtures containing 10, 21 (air), 40, and 100 percent of oxygen over the entire pressure range from 0.17 to 35.0 atm. A much less extensive series was done with a mixture consisting of 20% nitrogen fluoride and 80% argon. The latter work was limited to pressures of 1.0 and 7.8 atm.

III. RESULTS

In O_2/N_2 atmospheres the two measured parameters - the induction period t_i and the subsequent burning time t_b - follow the same qualitative pattern as in the case of the previously reported results for crystalline boron[3]: the t_b values are reproducible (indeed, even more so in the case of narrowly screened spheroidized particles used in the current program), while the t_i values are quite scattered, especially at higher pressures. Combustion in fluorine-containing atmospheres presents a rather different picture (see Section III.2).

1. Oxygen-Nitrogen Mixtures

The body of t_i and t_b data in oxygen-containing atmospheres is now sufficiently extensive for a definition of quantitative trends. A value of each t_i and t_b was obtained as an average of about 50 individual readings from photographic tracks, such as those shown in Fig. 1, for each set of the three physical parameters: particle diameter d (37-124 μm), total pressure P (0.17 to 35 atm), and mole fraction of oxygen X (0.10 to 1.0). Thus the results presented in this section were obtained from measurements on several thousand individual particles.

Several qualitative observations can be made. When X and P are high the combustion is very bright while the luminosity during the pre-ignition stage is feeble, indicating widely different temperatures in the two regimes. As X and P decrease, the combustion temperature decreases and the pre-ignition temperature increases. This is readily accounted for by the thermal ignition theory[3]. Below a certain set of X and P values the two regimes become indistinguishable. For air (X = 0.21) this occurs near P = 1 atm. When X is further decreased, the limit of flammability is reached. We reported previously[3] that

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X = 0.07 is below the flammability limit. Now we have found that so is X = 0.10, regardless of pressure. Since no experiments were done with X values between 0.10 and 0.21, we do not know whether the limit depends on pressure.

Furthermore, there are indications that these trends depend somewhat on the particle diameter d. This fact is discussed briefly in Section III.1.c.

a. The Pre-Ignition Delay (t_i)

Average delays $\bar{t}_i$ for X = 0.40 and X = 0.21 are given in Tables II and III. As mentioned previously, no self-sustained combustion took place at X = 0.10. Several comments will now be made about these results.

First, it must be pointed out again that the scatter of individual t_i readings is often very large. Indeed, at high pressures the data sometimes appear to be essentially random. In such cases the probable deviation of individual values from the average $\bar{t}_i$ can be as much as ± 50%. It is probable that the scatter is caused by varying durations of exposure of particles to the laser beam, as suggested previously by Maček and Semple[3]. Nonetheless, inspection of the data reveals the trends quite clearly. The delays t_i generally decrease with decreasing d. They also decrease with decreasing P until the pressure is near 1 atm, at which point the trend appears to be reversed. It is interesting to note that the reversal occurs near the range of parameters X, d, and P where the distinction between t_i and t_b begins to disappear.

Second, a word of explanation is needed regarding the "No-Ignition" area in the lower right corner. The failure of particles to ignite in that range is probably due to the limitations of the experiment and not to any fundamental causes. As the particle diameter increases, both the heat capacity and the Reynolds number increase, while the residence time in the laser beam decreases because of increasing particle velocity. The Reynolds number also increases

with pressure. Thus at large d and P the balance of heat supply from the laser and heat losses (by convection to the gas and conduction into the interior of the particle) becomes such that the particle cannot ignite.

On the other hand, the fact that t_i becomes indistinguishable from t_b at low pressures (Table III) does appear characteristic of boron-particle combustion and independent of the details of the laser-ignition experiment. Quantitative data are given in Section III.1.c.

Finally, a limited study was made in oxygen (X = 1.0) at 1 atmosphere only. A clear distinction between t_i and t_b was observed. The values of $\bar{t}_i$ were found to be roughly 9 msec for $\bar{d}$ = 98 μm and 15 msec for $\bar{d}$ = 124 μm. No quantitative data were taken with smaller particles.

b. The Burning Time (t_b)

Burning times were measured over the same range of P, d, and X as pre-ignition times.

Data corresponding to X = 0.40 are collected in Table IV. It can be seen that the probable errors seldom exceed ± 10% and are generally ± 5%, or even less for large particles. The significance of the area in the table where ignition failed to take place has been discussed in Section III.1.a.

The data for X = 0.40 and X = 0.21 are plotted in Figs. 3 and 4. In addition, two values of t_b for X = 1.0 were obtained at P = 1 atm: $\bar{t}_b$ = 38 ± 2 msec for $\bar{d}$ = 98 μm, and $\bar{t}_b$ = 64 ± 3 msec for $\bar{d}$ = 124 μm.

The experimental dependence of t_b on X can now be obtained from these data. For any given particle size, the two log t_b vs. log P curves corresponding to X = 0.40 and X = 0.21 are about parallel, so that the ratio $R = \frac{t_b(X=0.21)}{t_b(X=0.40)}$ is almost independent of pressure. The numerical values of these ratios are: R = 1.7 for $\bar{d}$ = 37 μm; R = 1.9 for $\bar{d}$ = 54μ; and R = 2.0 for $\bar{d}$ = 98 μm. Since

$\frac{0.40}{0.21} = 1.9$, the t_b values between X = 0.21 and X = 0.40 are inversely proportional to X within reasonable accuracy. This is in agreement with our previously reported high-temperature data[1]. However, as X increases from 0.40 to 1.0, t_b does not decrease by a factor of 2.5, but only by a factor of slightly less than 2.

Figures 3 and 4 also allow determination of the effect of P and of d on t_b. Since, however, the particle Reynolds number is a strong function of both d and P, the burning times shown in these figures were recorded under substantially varying convective regimes. In order to obtain the true dependence of t_b on these two parameters, one must make the appropriate corrections. This will be done in Section IV.

It will be noted that Fig. 4 does not contain a curve corresponding to $\bar{d}$ = 124 μm. This is so, because only one value of t_b, 191 ± 6 msec at P = 1 atm, was measured. For P < 1 atm, there was no distinction between t_i and t_b. For P > 1 atm, these large particles failed to ignite, no doubt for the same reasons that they failed to ignite for X = 0.40 and P > 7.8 atm (see Section III.1.a.).

Finally, it is of interest to compare these data with the t_b data obtained previously with non-spherical crystalline particles[3]. The crystalline material had been screened between 62 and 88 μm and was therefore described as having average diameters of roughly 75 μm. However, the t_b values of that material agree more nearly with those corresponding to spherical diameters of about 55 μm. Microscopic measurement of random crystalline diameters gave 60 μm < $\bar{d}$ < 65 μm. These numbers show that non-spherical particles are not adequate for detailed quantitative studies of the particle-diameter effect.

c. The Low-Pressure Regime

As, for a given value of X, P is decreased below about 1 atm, particles continue to burn after a fashion, but apparently by a modified mechanism. Three qualitative observations can be made. First, there is no visible division of the total "burning" time into a t_i and a t_b. Second, the particle glow decreases in intensity with decreasing pressure; at 0.17 atm it is quite feeble. Third, the (one-stage) burning time increases considerably with decreasing pressure, indicating sharply decreased burning rates.

Burning-time data in air at reduced pressures are collected in Table V. In addition, a burning time of 371 msec was measured for $\bar{d}$ = 124 μm and X = 0.40 at 0.17 atm. According to this single datum, the low-pressure burning time is roughly inversely proportional to X. (For $\bar{d}$ = 124 μm and X = 0.40 at 0.50 atm the sum of t_i and t_b was found to be 180 msec - see Tables I and III). From these data it can be seen that the total burning time at 0.17 atm is always more than three times the value of t_b at 1 atm.

The sequence of transitions from the high-pressure regime (where t_i and t_b are distinguishable) first to the low-pressure regime and then to the flammability limit appears to depend both on d and on X. An indication of this is the behavior at 0.5 atm. The set of conditions d = 124 μm, X = 0.40 is in the "high-pressure" regime (Tables II and IV). When X is decreased to 0.21, a weak transition from t_i to t_b is still discernible (Table V). However, the distinction disappears entirely below d = 124 μm. Also, when d decreases to 37 μm at X = 0.21 and 0.17 atm the flammability limit has been crossed. We have no data for X = 0.40, P = 0.17 atm, d < 124 μm. Of course, the fact that the flammability limit depends strongly on X is clear from our work with X = 0.10.

2. Nitrogen Fluoride-Argon Mixture

A limited amount of work has been done with one sample of boron, $\bar{d}$ = 54 μm, in a gas mixture consisting of 20% NF_3 and 80% argon. Since nitrogen fluoride absorbs the 10.6 μm laser radiation, all the work was done at pressures of 7.8 atmospheres or lower. For the purpose of comparison, the pre-ignition and the burning times of the same boron sample were measured also in a mixture of 20% oxygen and 80% argon.

Boron combustion by NF_3 differs from combustion by oxygen in at least two aspects. First, there are no pre-ignition periods. Second, the particles burn more slowly in NF_3/argon (20/80) than in O_2/argon (20/80).

Sufficient measurements at atmospheric pressure were made in the fluorine-containing mixture for a quantitative definition of the burning time. The result is 76 ± 10 msec. In the oxygen-argon mixture the results are: t_i = 9.7 msec, t_b = 43.5 ± 2.5 msec. At 7.8 atm the qualitative results of combustion in NF_3/argon are similar to those at 1 atm, but no accurate measurements were made.

IV. DISCUSSION

1. Ignition

The experimental technique used in the present program is not suitable for a quantitative study of ignition parameters, because neither the radiant flux, nor the exposure time of the particle to that flux, nor the radiant absorptivity of the particle is known accurately. Our remarks, therefore, will be qualitative.

Theories of boron particle ignition in the presence of oxygen have recently been discussed by several workers. On the basis of the classical thermal theory Maček and Semple[3] concluded that in order to ignite, boron particles have to

be preheated by the laser beam to about T = 2200°K. The theories of King[7] and Mohan and Williams[4] are much more developed and more realistic, because in addition to thermal properties they consider also the processes of formation and removal of the liquid oxide layer which coats the surface of the particle. These theories apply mainly to situations where the ignition source for particles is a hot oxidizing gas. However, temperatures in the range of 2000 ± 300°K again are shown to be crucial for ignition.

One experimental aspect of the pre-ignition regime deserves attention. Photographs in Fig. 1 show clearly that the temperature during that regime is not constant; rather, it is quite high initially - especially in frame b of Fig. 1 where the initial stages of the pre-ignition regime appear almost as bright as the subsequent combustion - and then it decreases to an apparently steady value which persists up to the point of ignition*. The negative dT/dt transient cannot be explained by steady-state thermal theories which assume a uniform temperature distribution throughout the particle. The explanation probably lies in the fact that boron has a relatively low thermal conductivity[4]. Thus the surface of the particle is heated by the intense laser beam to a high temperature very rapidly, while the interior remains cool. Upon the emergence from the beam, the particle surface, which is the site of the exothermic reaction, loses heat not only to the cold gas, but also - and initially even more rapidly - to the cold interior. A realistic theoretical treatment of the laser-ignition experiment would have to include, in addition to heat exchange with the gas, both the transient heat transfer into the particle and the transient surface-layer behavior. Thus the existing models would have to be refined. Whatever the numerical results of such treatments, it appears clear that in cold environments the history of the surface temperature prior to ignition,

*The initial brightness can be virtually eliminated if the laser radiation intensity is decreased. Indeed, we worked mostly with beam intensities such that this feature was not very prominent; photographs in Fig. 1 were chosen expressly to underscore the point being made here.

and probably also the minimum surface temperatures needed for ignition, will depend on the rate of heating by the external energy source (laser, flash).

Since the pre-ignition periods t_i observed in the presence of oxygen are generally interpreted in terms of processes associated with a liquid layer of B_2O_3, the fact that such periods have not been observed in fluorine-containing gases in the absence of oxygen is not surprising. One would also expect the ignition temperatures with fluorine as oxidant to be lower than in the case of oxygen, but our laser-ignition experiments were inadequate to establish this as an experimental fact.

2. Combustion in Oxygen-Nitrogen Mixtures

a. The Convective Regime. Dependence of t_b on d and P

A correction of the measured times t_b (Section III.1.b.) will now be made on the assumption that the particle burning rate is controlled by the gas-phase diffusion of oxidant to the surface. The ratio η of the diffusive mass flux in a convective regime to the flux under stagnant conditions is [8]

$$\eta = \frac{\dot{m}}{\dot{m}_o} = 1 + 0.276\sqrt{Re}\ \sqrt[3]{Sc} \qquad (1)$$

where Re and Sc are are the Reynolds and the Schmidt number of the particle. To a very good approximation the Schmidt number can be replaced by the Prandtl number. For N_2/O_2 mixtures the Prandtl number decreases from about 0.75 to 0.62 as T increases from 300°K to flame temperatures. Thus $(Pr)^{1/3} = 0.9$ over the entire temperature range, and η is a function of the Reynolds number only:

$$\eta = 1 + 0.25\sqrt{Re} \qquad (1')$$

Now in free-fall, in the Stokes regime,

$$Re \propto udP \propto d^3P, \qquad (2)$$

where u is the limiting velocity. Numerically, evaluating the appropriate thermodynamic and transport properties at 1000°K - i.e., the logarithmic average

between 300° and 3000°K - we obtain Re = 0.017 for d = 37 μm at 1 atm and Re = 11 for d = 98 μm at 35.0 atm; these are the extreme experimental conditions for which t_b data are available. The corresponding values of η are 1.03 and 1.83 respectively. This means that a small (d = 37 μm) particle at atmospheric pressure burns under virtually stagnant conditions. On the other hand a large particle, especially at an elevated pressure, begins to burn at a rate substantially enhanced by convection; as the particle burns, $d \to 0$ and $\eta \to 1$. Hence, if the true dependence of the burning time on diameter is given by

$$t_b' = kd^n \quad , \tag{3}$$

then the burning time in a convective regime (e.g., measured burning time in free fall) will be

$$t_b = \frac{kd^n}{\bar{\eta}} \quad , \tag{4}$$

where $\bar{\eta}$ is the appropriate average of the parameter η over the burning time. If the uncorrected $\bar{t}_b$ data (Section III.1.b.) are used in Equ. 3, the numerical value of n so obtained will be spuriously low.

In view of the above discussion, all experimental values of t_b were reduced to a common basis corresponding to $\eta = 1$. Since no <u>a priori</u> burning-time law was assumed, the numerical correction had to be made stepwise. The corrected burning time for a 37 μm particle was taken to be $t_b'(37,0) = \frac{t_b(37,0)}{\bar{\eta}(37,0)}$, where $t_b(d_2,d_1)$ is the measured burning time from d_2 to d_1, and $\bar{\eta}(d_2,d_1)$ an average value over that range of diameters. The corrected burning time for a 54 μm particle is

$$t_b'(54,0) = t_b'(37,0) + t_b'(54,37)$$
$$= \frac{t_b(37,0)}{\bar{\eta}(37,0)} + \frac{t_b(54,0) - t_b(37,0)}{\bar{\eta}(54,37)} \quad ,$$

and similarly for $t_b'(98,0)$ and $t_b'(124,0)$. Since no single step in the correction was large, arithmetic averages $\bar{\eta}(d_2, d_1)$ were satisfactory.

The log t_b' vs log d plots for pressures of 1.0 and 7.8 atm are shown in Fig. 5 for X = 0.40. Three correlations concerning t_b' are evident. First, at P = 7.8 atm it is proportional to d^2. Second, for large particle diameters it is independent of pressure. Third, for small diameters at low pressures the value of exponent n decreases. The slope for low values of d at 1 atm is not known. The line corresponding to n = 1 is shown for orientation purposes only.

Analogous information for X = 0.21 is shown in Fig. 6. One difference from Fig. 5 is that t_b' increases with decreasing pressure even for large values of d.

We conclude that if d, P, and X are sufficiently high, the burning times of boron particles are: (a) inversely proportional to X (see Section III.1.b.); (b) directly proportional to d^2; and (c) independent of P. However, if any of these three parameters decreases below a certain value, the burning time increases beyond the value one would obtain by using these scaling laws.

b. Comparison with Theory

In the past we made very simple calculations of particle burning times on the assumption that the burning rate equals the gas-phase diffusion rate of the oxidant to the particle with a constant diffusion coefficient[1,9]. The above scaling laws agree qualitatively with this simple representation. However, since such calculations take no account of detailed flame structure, phase changes, shifting equilibria, etc., they can give only crude estimates. We shall now make a quantitative comparison of our experimental burning times (t_b') with the much better developed theory published recently by Mohan and Williams[4].

For P = 1 atm and X = 0.40, the theory[4] is in virtually complete agreement (about 10%) with the experiment in the range of large d values where $t_b' \propto d^2$

(Fig. 5). Since the theory predicts the d^2 dependence, it deviates continuously from the experiment as d decreases (40% deviation for d = 37 μm).

The theoretical dependence on X does not agree with the experiment, because the theory predicts more than a 3-fold increase of burning time as X is decreased by a factor of 1.9 (i.e., from 0.40 to 0.21). The discrepancy may perhaps be accounted for by the fact that the theory neglects condensation of products which will tend to maintain high burning rates as the limit of flammability is approached[10]. As it stands, the theory agrees with the experiment at small particle diameters for X = 0.21 (Fig. 6) and deviates from it as the diameter increases.

No theoretical calculations have been made for P other than 1 atm, so that only qualitative remarks can be made. The experiment shows no pressure effect on the burning rate (up to 7.8 atm) for X = 0.40, but an accelerating effect for X = 0.21. This appears reasonable in view of the fact that the effect of condensation will be felt more strongly at lower values of X. At reduced pressures the state of affairs remains clouded for two reasons. First, there are no theoretical calculations. Second, the experimental data must be interpreted with caution, because the total burning times given in Table V may be expected to vary somewhat with the details of the laser-beam interaction with the particle (see Section III.1.a. and Ref. 3). One thing which appears clear is that experimental burning rates decrease substantially as the flammability limit is approached; this is reasonable from the theoretical viewpoint.

From Ref. 4, the theoretical value of the flammability limit at 1 atm is X = 0.14; we bracketted it experimentally between X = 0.10 and X = 0.21. While the agreement is certainly gratifying, it may be fortuitous. The theory is aimed primarily at combustion of boron in hot gases. Further theoretical work

taking into account low-temperature processes would be useful. Here it is important to emphasize that the agreement of theory with experiment for combustion of particles in high-temperature gases is good. The relevant data are given in Table VI; the experimental values were obtained by the gas-burner technique described in Ref. 1.

In sum, the theory of Mohan and Williams[4] agrees well with the experimental results only in the range of high values of X and d if the surrounding gas is cold, but also down to X = 0.2, d = 37 μm if the gas is hot. (Although there are no experimental data, it appears reasonable to suppose that the theory would be valid at high temperatures for large values of X and d.) It will be noted that the agreement is good under conditions well removed from the flammability limit. The theory also accounts for the role of X in the approach toward the limit. The experiment shows an additional effect, namely deviation from linearity at low d in Figs. 5 and 6. There is indication that this behavior signals the approach to the flammability limit which in itself may be a function of d. Particle-diameter dependence of this sort is not predicted by the theory. Thus the cause of deviation from the $t_b \alpha d^2$ behavior is not clear. Decreased burning rates may be caused either by the marginal energy-balance as the flammability limit is approached, or possibly by the transition to the kinetically limited regime.

It is clear that the recent advances in experiment and theory have greatly improved our knowledge of boron-particle combustion with oxygen as oxidant. Two areas where additional studies would be most welcome are: (a) experiments with low values of d and X, below 30 μm and 0.2 respectively, in high-temperature gases; (b) theoretical work with variation of pressure and realistic inclusion of processes important at low ambient gas temperatures.

3. Combustion in Fluorine-Containing Atmospheres

Comparing the (one-stage) burning time of boron particles, $\bar{d}$ = 54 μm, in NF_3/A (20/80) with t_b measured in O_2/A (20/80), one is struck by the much slower burning rate in the former mixture (see Section III.2). However, the simple assumption that the burning rate equals the gas-phase diffusion rate of the oxidant shows that a substantial difference in burning rates should indeed exist. There are several effects.

First, if the combustion products are in thermodynamic equilibrium, the approximate stoichiometries of the overall combustion reactions are $B + NF_3 \rightarrow BF_3 + \frac{1}{2} N_2$ and $B + \frac{3}{4} O_2 \rightarrow \frac{1}{2} B_2O_3$. Thus boron requires one third more NF_3 than O_2 on the molar basis, and the burning time will increase accordingly. Second, the reaction with NF_3 forms three times the amount of gaseous products (even if no B_2O_3 condenses), the outbound diffusion of which will retard the inbound diffusion of the oxidant. Third, the diffusion coefficient of NF_3 should be lower than that of oxygen. A combination of these three factors may well account for the fact that the burning time in NF_3/A is 75% longer than that in O_2/A.

It is interesting to note that, according to this reasoning, the burning rate of boron in F_2 should also be lower than in O_2. Thus, while substitution of oxygen by fluorine may promote ignition of boron particles, it should not be expected to accelerate their combustion.

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Table I

Measured Particle Diameters of Spheroidized Boron
(microns)

Sample No.	Microscopy	Micromerography	Weighing
1	37	37	-
2	54	50*	-
3	98	-	102
4	124	-	132

* Approximate limit of instrument range

Table II

Average Pre-Ignition Delays ($\bar{t}_i$) of Boron Particles, X = 0.40
(Milliseconds)

$\bar{d}$(μm)	Pressure (atm)							
	0.50	1.0	4.4	7.8	14.6	21.4	28.3	35.0
37	-	5	-	2	-	8	22	43
54	-	5	2-3	2-3	-	-	-	-
98	-	24	-	31	54	-	78	104
124	41	44	-	54	----------No Ignition----------			

Table III

Average Pre-Ignition Delays ($\bar{t}_i$) of Boron Particles. X = 0.21.
(Milliseconds)

$\bar{d}$ (μm)	Pressure (atm)						
	0.17	0.50	1.0	4.4	7.8	14.6	21.4
37	N.C.*	No	12	-	15	-	16
54	distinction		13	10	9	-	-
98	between t_i		60	-	39	-	83
124	and t_b	112	90	-	-----No Ignition-----		

* No self-sustained combustion

Table IV

Burning Times ($\bar{t}_b$) of Boron Particles, X = 0.40
(Milliseconds)

$\bar{d}$ (μm)	Pressure (Atmospheres)							
	0.50	1.0	4.4	7.8	14.6	21.4	28.3	35.0
37	-	17.9±1.5	-	11.1±0.7	-	8.7±0.9	6.1±0.7	7.7±1.0
54	-	27±2	23±2	21±1.5	-	-	-	-
98	-	75±3	-	64±3	56±3	-	43±3	(40±10)
124	139±5	121±5	-	106±4	---------- No Ignition ----------			

Table V

Low-Pressure Burning Times in Air
(Milliseconds)

	Average Particle Diameter (μm)		
	37	98	124
0.17 atm	N.C.*	488	615
0.50 atm	62	249	384**

* No self-sustained combustion

** $\bar{t}_i$ = 112 msec, $\bar{t}_b$ = 272 msec

Table VI

Burning Times in High-Temperature Gases (msec)
d = 37μm, X = 0.23, P = 1 atm

Gas Temperature (°K)	Theory*	Experiment
2280	12.4	15.5 ± 1.5
2870	10.7	11.3 ± 0.9

*Ref. 4

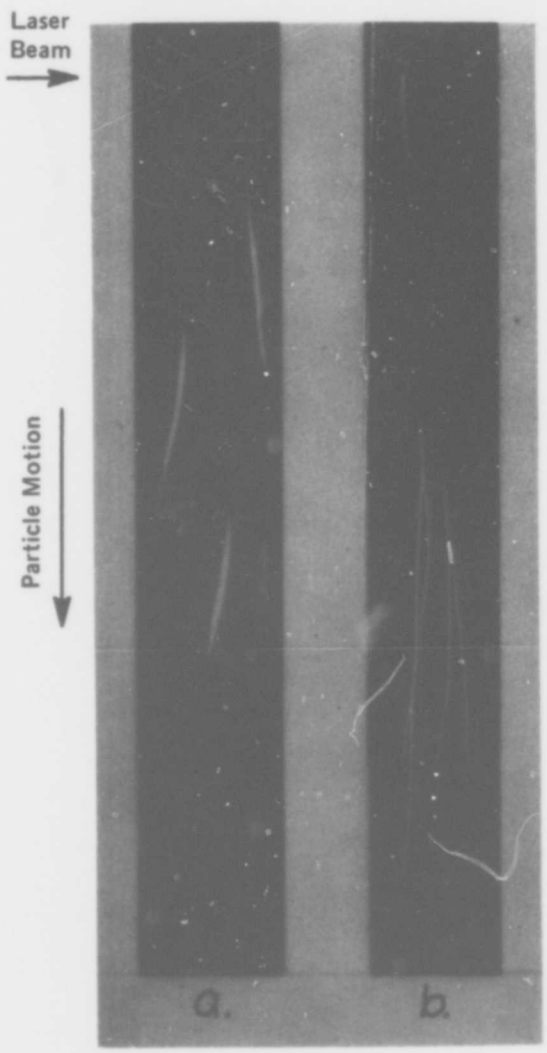

Figure 1. Photographs of Boron Particles Ignited by Laser at 21.4 atm. a. X = 0.40; b. X = 0.21

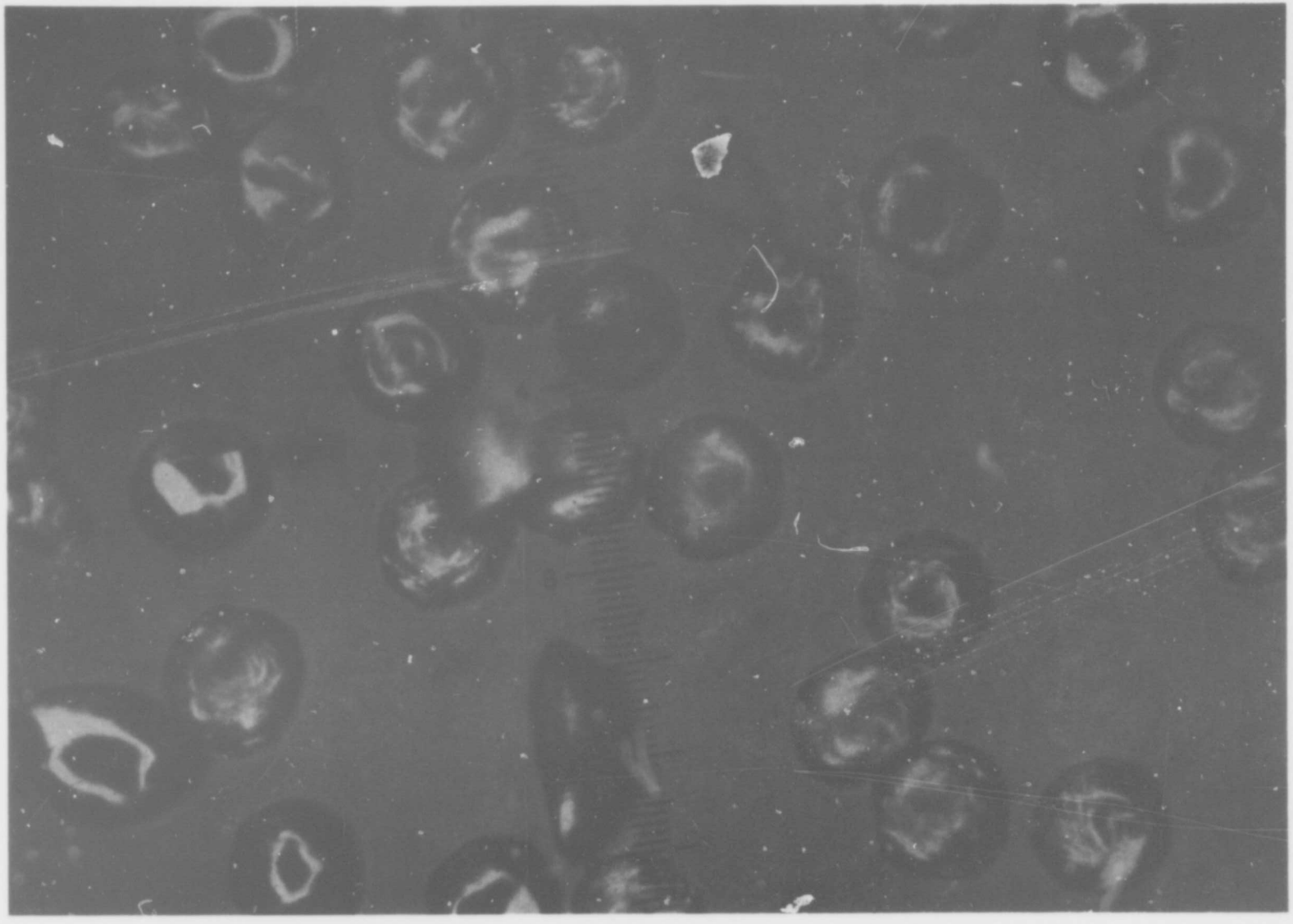

Figure 2. Microphotograph of Spheroidized Boron Powder; $\overline{d} = 37\,\mu m$.

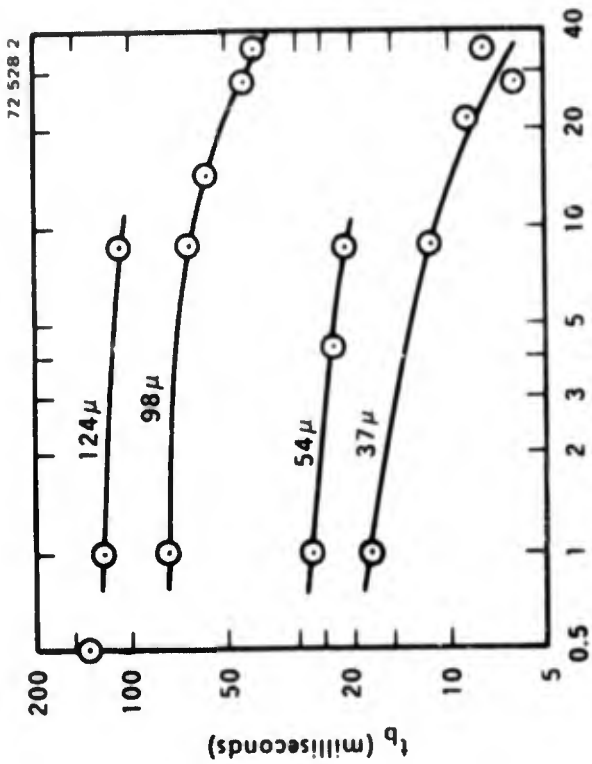

Figure 3. Experimental Burning Times t_b of Boron Particles; X = 0.40.

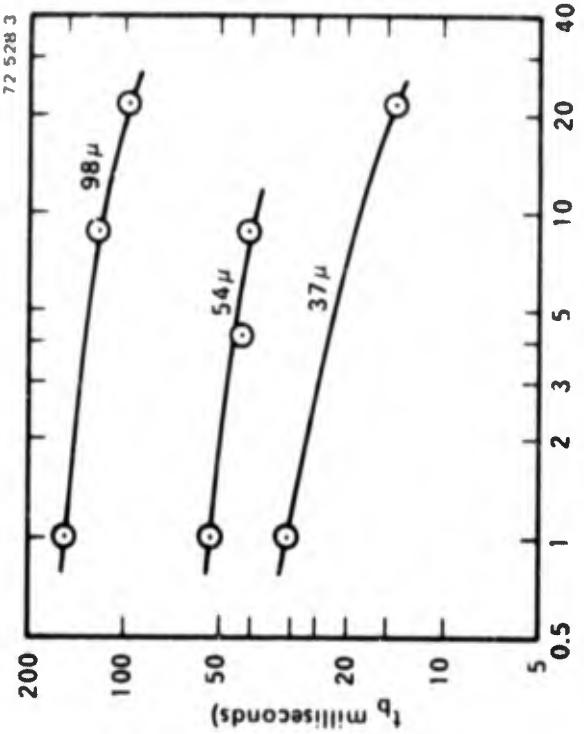

Figure 4. Experimental Burning Times $\bar{t}_b$ of Boron Particles; X = 0.21.

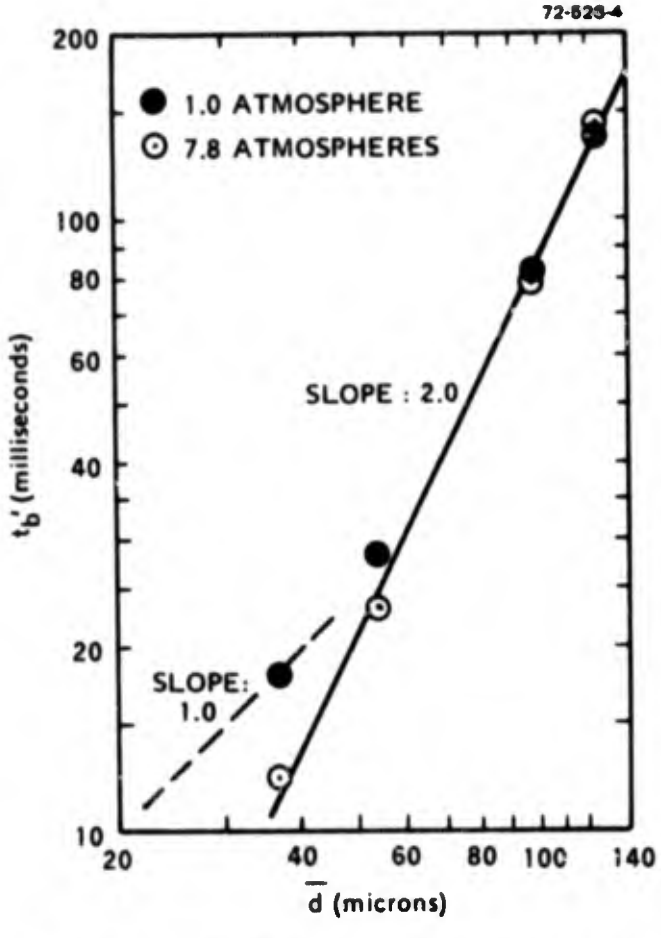

Figure 5. Dependence of the Corrected Burning Time $\bar{t}'_b$ on Particle Diameter; X = 0.40.

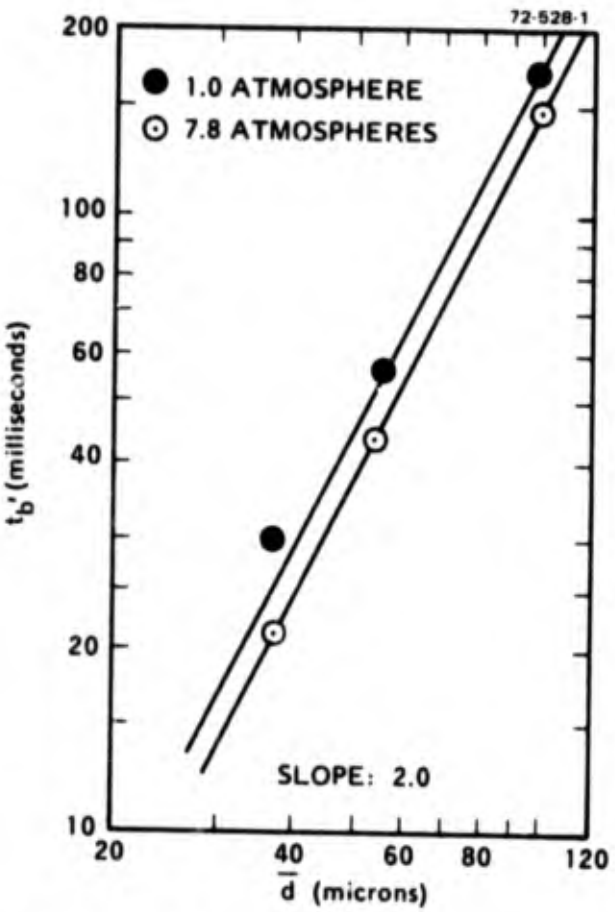

Figure 6. Dependence of the Corrected Burning Time t'_b on Particle Diameter; X = 0.21.