High Temperature Kinetics of Solid Boron Gasification by B_2O_3(g): Chemical Propulsion Implications

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New flow reactor measurements are reported of the intrinsic kinetics of the gasification of solid boron by each of these important vapors: B_2O_3(g), O_2(g), CO_2(g), and H_2O(g) at surface temperatures between 1330 and 2050 K. For illustrative purposes, our data for the remarkably efficient B_2O_3(g)/B(s) reaction and the O_2(g)/B(s) reaction are used to discuss the expected sequence of rate-controlling processes for the combustion of individual B(s) particles in air under typical ramjet conditions. A diagram of (log-) particle diameter vs (log-) chamber pressure is shown to be particularly useful for this purpose, as well as to display the onset of noncontinuum behavior and the locus of expected particle extinction due to passivation associated with the kinetically controlled onset of condensed B_2O_3 on the gas/solid interface. In this way we show that, whereas most previous boron particle combustion and extinction laboratory experiments have been performed in the regime of gas-phase diffusion control, under conditions of actual ramjet interest the gas/solid kinetics for the efficient B_2O_3(g)/B(s) reaction and the slower O_2(g)/B(s) reaction, as well as noncontinuum transport effects, become rate limiting.

I. Introduction

BECAUSE the combustion of boron in an oxygen-containing gas has an appreciable potential, considering all possible chemical elements in terms of gravimetric and especially volumetric energy density, it has been recognized as a potentially attractive fuel (see, e.g., Ref. 1). At typical anticipated operating conditions (temperature, pressure, gaseous environment) and based on its thermochemical properties, boron burns as a solid particle.[2,3] Because of the necessarily short combustor residence times, the required particle diameters are sufficiently small that the burning is expected to be kinetically limited during most, if not all, of the burning time.[3,4] Nevertheless, experimental and theoretical research in the late 1960s and early 1970s[5-7] concentrated on diffusion-controlled combustion, revealing only some of the features of boron particle combustion of the underlying semimetal. Indirect determination of some kinetic parameters during ignition appears in recent work.[8] Diffusion-controlled quasi-steady surface oxidation of boron (like carbon) is found to be a two-step process since ambient O_2 molecules can react in the gas phase with boron suboxides to form B_2O_3, i.e., O_2 does not necessarily reach the particle surface. In such cases the higher boron oxide vapor, B_2O_3(g), is the main surface gasifier, playing the same role as CO_2 in carbon gasification. However, as the particle gets smaller, this picture is expected to break down since the following new phenomena become involved: 1) kinetics (homogeneous and heterogeneous) begins to dominate over vapor phase diffusion, and 2) when the particle diameter becomes comparable to the gas mean free path, the individual particle flowfield is no longer continuum and, hence, the transfer of heat and mass to/from the particle exhibits new characteristics. B_2O_3 condensate may play an important role under these conditions also. Under kinetically controlled surface oxidation conditions, B_2O_3(c) may be present on the boron particle surface as a continuous submicroscopic layer or as patches, even at temperatures higher than the (equilibrium) condensation temperature. Only by experimentally studying the surface reaction kinetics (below) can we reliably determine the conditions leading to bare or covered surface behavior in such nonequilibrium cases.

Except for a qualitative understanding, until now a lack of experimental data, especially for the less predictable surface kinetics, has precluded accurate predictions of boron particle combustion behavior (via surface and gas phase kinetics/transport theoretical/numerical models) in the kinetically limited, and possibly noncontinuum, regime.

To appreciate the relative importance of the previously mentioned chemical reactions (homogeneous and heterogeneous) and transport processes we have summarized the preliminary calculations in Fig. 1. The diagonal straight lines on our

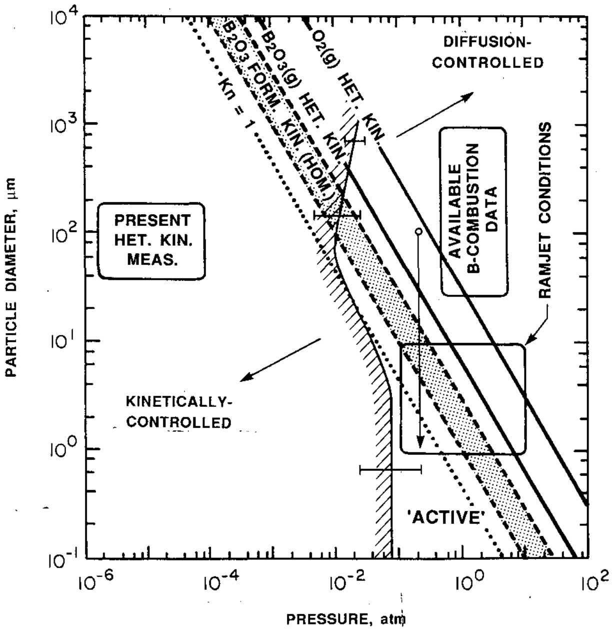

Fig. 1 Boron particle combustion map displaying expected: 1) diffusion-controlled or kinetically controlled regimes for B_2O_3(g) and O_2(g) reactions with the surface, 2) transition to noncontinuum behavior, and 3) extinction due to surface passivation.

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proposed (log) particle diameter vs (log) total pressure plane define loci of transition from the diffusion-controlled regime to the kinetically controlled regime for surface reactions of $B_2O_3(g)$ and $O_2(g)$ with solid boron and for the $B_2O_3(g)$ homogeneous formation reaction. Also shown is the Knudsen number locus $Kn=1$, i.e., approximately when the continuum approach fails. A knowledge of the relative position of these three locii gives a clearer picture of what are likely to be the important gaseous species and rate-controlling mechanisms in the history of a burning particle. In constructing this figure (see Sec. IV for details), we estimated the homogeneous kinetics and the $O_2(g)/B(s)$ kinetics based on previous fragmentary results. We deliberately assumed the upper limit surface reaction probability, $\epsilon=1$, for the $B_2O_3(g)/B(s)$ kinetics (which, remarkably, was found to be close to the measured reaction probabilities; see Sec. III) and concluded that this heterogeneous reaction would be important over more than one order of magnitude in particle diameter and, hence, three orders of magnitude in particle mass [the vertical segment from the O_2 kinetics locus, based on $\epsilon \approx 0.2$, where $B_2O_3(g)$ becomes the dominant species, until the homogeneous kinetics locus below which $B_2O_3(g)$ does not have adequate time to be formed]. Since ϵ for the $B_2O_3(g)/B(s)$ reaction turned out to be somewhat smaller, this interval would be even broader. Motivated, in part, by these initial estimates our objective was to study experimentally, under well-defined conditions, the intrinsic kinetics of the high-temperature surface reaction between solid boron and $B_2O_3(g)$ (structurally OBOBO, with a central B-O-B angle in the range 95–125 deg). For comparison purposes we also briefly examined the reagents $O_2(g)$, $CO_2(g)$, and $H_2O(g)$.

II. Experimental Techniques

Principles and experimental techniques for measuring the intrinsic kinetics of efficient gas/solid reactions at realistic reagent pressures without encountering external transport limitations have been developed at this laboratory and are discussed in detail elsewhere.[9,10] It was found that under conditions of small specimen size, high gas velocity, and subatmospheric pressure, a laboratory test environment appropriate for such kinetic measurements can be achieved. For monitoring the boron gasification rate we utilize a technique called microwave induced plasma emission spectroscopy (MIPES),[11-14] a sensitive yet simple chemical element detection technique capable of instantaneous measurements, together with high-temperature flow-reactor techniques developed earlier in our laboratory.[9,15-18]

Our experiments have been performed in a transonic, low-pressure (ca. 0.5 Torr), steady-flow chemical reactor (Fig. 2). We developed an electrically heated platinum boat source and obtained measurable amounts of $B_2O_3(g)$ effusing through a slit (0.5-mm width) at known conditions (ca. $T=1450$ K, at which the equilibrium vapor pressure is reported[19] to be about 0.2 Pa). Under equilibrium conditions it is known that $B_2O_3(l)$ vaporizes predominantly to $B_2O_3(g)$ with less than 0.1% boron suboxides simultaneously present.[19] The downstream boron filament specimen (obtained via AVCO Specialty Materials), of 0.142-mm diam, was electrically heated to the desired temperature (calculated from optical pyrometer measurements using a spectral emittance of 0.69, see Ref. 14 for details) and attacked by the selected gaseous reactant (B_2O_3,O_2,...) in crossflow using Ar as the carrier gas. The reaction product stream, collected through a skimmer immediately downstream of the central (uniform temperature) region of the filament, meets an opposed jet of argon metastable atoms Ar* generated by the microwave plasma discharge.[11] This leads to reaction product excitation and subsequent characteristic radiation emission. (In an earlier configuration,[12] we found that B_2O_3 condensed on the reactor walls was then removed by Ar* and diffused back into the central probe volume, thereby interfering with such measurements. Our modified counterflow geometry successfully eliminates this problem.) Emission of the strongest boron line, at 249.7 nm, coming from neutral boron atoms,[20] was focused by a 35-mm fl fused silica lens onto the slit of a 0.5-m monochromator (Jarrel-Ash, Model 84-110), with the signal collected into a photomultiplier tube (Hamamatsu, R212) and the output converted to a voltage signal by a picoammeter (Gencom, Model 1012). Since the reactant $B_2O_3(g)$ itself contains the element B, a signal is, of course, obtained even without surface reaction. Therefore, the change in signal over the reactant contribution, and over the boron filament sublimation signal, is the signal assigned to the surface reaction to form B-containing vapor products. A linear output vs boron element mass flow rate was obtained over ca. 4 decades of B-flow rate. Further details of the experimental procedure are given elsewhere.[14]

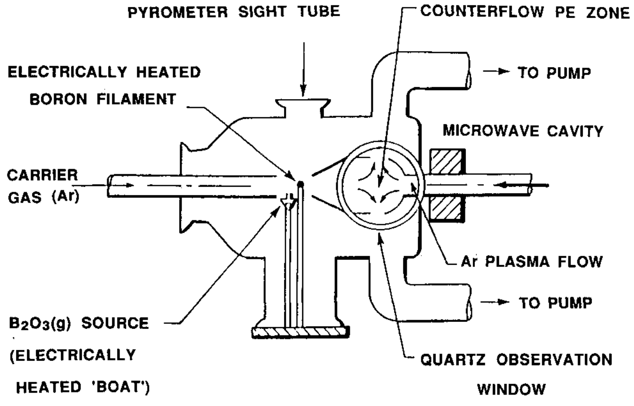

Fig. 2 Flow reactor configuration for kinetic studies of gas/solid reactions using product detection via microwave induced plasma emission spectroscopy (MIPES).

III. Experimental Results

In Fig. 3, we present our results for the surface reaction rate between solid boron and individual, important anticipated gaseous species as a function of the inverse of the solid surface temperature. Reaction rate results are shown in terms of a reaction probability ϵ, a nondimensional overall rate constant for the (nonelementary) surface reaction, defined as the ratio of the net flux of boron atoms, irrespective of speciation, emerging from the surface as a result of chemical reaction, to the arrival flux of the gaseous reactant B_2O_3, or O_2,... on the

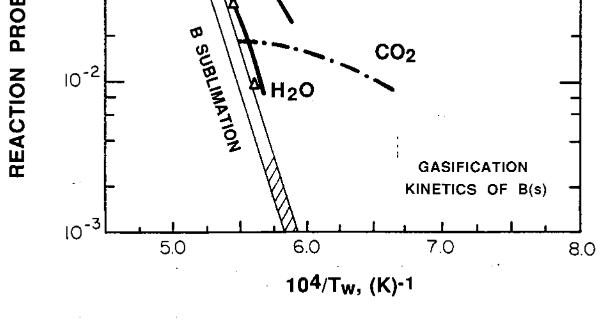

Fig. 3 Reaction probabilities for gasification of solid boron by $B_2O_3(g)$, $O_2(g)$, $H_2O(g)$, and $CO_2(g)$ at reactant pressure of the order of 10^{-2} Pa.

surface. Accordingly, this presentation is independent of the identity of the reaction products. The boron sublimation branch (ca. 132 Kcal/mole) shows what would be the contribution to the apparent reaction probability from the boron atom flux subliming into a vacuum (the left line pertains to the heavy reactant molecule B_2O_3 and the right line pertains to the lighter molecules O_2, H_2O). The O_2(g) and O(g) reactions on high temperature boron surfaces have been studied before using different experimental conditions and techniques.[15] We repeated a portion of the O_2(g)/B(s) reaction study using the present MIPES technique and found similar behavior.[21] In both cases, the reaction probability in the active regime (relatively insensitive to surface temperature) is ca. $\epsilon = 0.2$. Our new results for the B_2O_3(g)/B(s) reaction are presented here in greater detail, along with a discussion (Sec. IV) of their propulsion implications. This reaction probability was measured over a surface temperature range from 1330 to 2050 K at an estimated partial pressure of 10^{-2} Pa. Remarkably high reaction probabilities ($\epsilon = 0.5$) were inferred, exhibiting very low sensitivity to surface temperature over the range 1450–1800 K. Boron gasification by B_2O_3(g) is evidently more efficient than boron gasification by O_2(g), H_2O(g), or CO_2(g) and is comparable to that attained (over a narrower temperature interval) by atomic oxygen, O(g).[15] At still higher surface temperatures, the B_2O_3(g)/B(s) reaction probability rises to a maximum of $\epsilon = 0.9$ near 1950 K and then falls steeply. Below about 1450 K, we also observed a sharp reduction in reaction probability. The conditions at which this fall-off occurs (the so-called active-to-passive transition[18]) are of primary importance for predicting particle extinction, as discussed below. The slope of the Arrhenius curve (on the log ϵ vs $1/T$ plane) at each point gives the local overall activation energy of the surface reaction and provides valuable clues about the detailed surface processes.[14] In the aforementioned fall-off regime, this slope is found to correspond to about 60 Kcal/mole. Also shown are our MIPES estimates for B(s) gasification by measured gaseous fluxes of H_2O(g) or CO_2(g). It can be seen that H_2O contributes B atoms to the gaseous environment at about the same rate as boron sublimation at the measured temperatures, 1800–2000 K. The observed reaction probability for B(s) attacked by CO_2(g) is 0.01–0.02 in the temperature range 1500–1900 K, with much lower and T-dependent apparent activation energies.

In Fig. 4, we summarize our results for the active-to-passive transition locus of the B_2O_3(g)/B(s) reaction as inferred from experiments similar to the ones summarized in Fig. 3 but at different B_2O_3 pressures. The resulting transition condition establishes a locus that effectively divides the $p_{B_2O_3}$-T field into two qualitatively different regimes. The active regime is characterized by high reaction probabilities with low apparent activation energies. The passive regime is characterized by lower reaction probabilities and higher activation energy (the transition was found to be more abrupt as $p_{B_2O_3}$ is reduced). We have also estimated theoretically the active-to-passive transition locus based on a quasi-equilibrium approach[9,14,22] and obtained the same general trend: the expected transition temperature increases with B_2O_3 partial pressure. (However, the QE-predicted slope was slightly different from that observed; see Ref. 14 for further details.)

IV. Chemical Propulsion Implications

As pointed out previously, measurements of the true rates of these surface reactions (without diffusional falsification) enable us for the first time to estimate the relative importance of the reaction/diffusion processes during the burning history of boron particle in an oxygen-containing environment. In Fig. 1, we include four different kinds of information on the suggested logarithmic graph of particle diameter vs total pressure. A typical gas temperature of 2000 K was chosen for these calculations. The locus of unit Knudsen number (transition to noncontinuum behavior) at this temperature is also shown. Separated by the diffusion-to-kinetics transition loci, large particles at high pressures experience diffusion-controlled particle combustion and small particles at low pressures lead to kinetically controlled combustion, possibly in a free-molecular flowfield (on the scale of the individual particle diameter). The loci for the O_2(g)/B(s) and B_2O_3(g)/B(s) reactions, consistent with our gas/solid kinetic measurements (cf., Fig. 3) together with the B_2O_3(g) homogeneous formation [oxidation of the suboxides BO(g) and $(BO)_2$(g)] kinetics shown on this map, display an estimate of when the kinetics of each of these reactions is expected to become important compared to the relevant diffusional transfer of these species. While O_2 diffuses from the ambient toward the boron surface, if B_2O_3 forms in the gas phase near the surface its diffusion rate is enhanced by a calculable factor (F_{rxn}[23] here estimated to be about twofold), compared to simple diffusion in the absence of homogeneous reaction. The homogeneous kinetics band shown here covers the range of results from the highest possible bimolecular collision rate (left boundary) to an estimated overall formation rate of B_2O_3 from boron suboxides (right boundary). We based our nonelementary reaction rate estimate on fragmentary experimental measurements[24-26] and theoretical estimates summarized in Ref. 27 for selected gaseous elementary reactions between boron-containing species and oxygen-containing species; i.e., the rate of homogeneous B_2O_3(g) formation was estimated by deducing what would be the rate determining step from the possible rate constants appearing in Ref. 27. Homogeneous formation of atomic oxygen in the B,O system was predicted to be negligible compared to B_2O_3(g) formation in Ref. 27 and consequently is not considered further here. Since our measurements of the kinetics of the B_2O_3(g)/B(s) reaction indicated higher reaction probabilities than for the competing O_2(g)/B(s) surface reaction we conclude (i.e., based on the relative position of the locii) that B_2O_3(g) would be the main B(s) gasifier in the kinetic regime if it can be formed at an adequate rate in the gas phase diffusion boundary layer. Consequently, a boron particle of diminishing size at constant pressure (see the vertical path in Fig. 1) will exhibit a slower combustion rate under a critical size when homogeneous kinetics begins to limit the formation of B_2O_3(g) (thereby causing the direct O_2(g)/B(s) reaction to be the main surface reaction) even though conditions favor active kinetics for both surface reactions. Another important feature of these kinetically controlled combustion processes is possible extinction due to the transition from active to passive behavior for

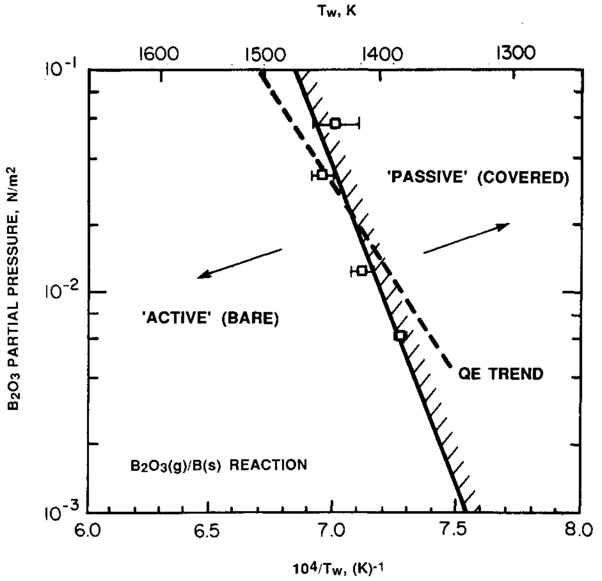

Fig. 4 Active-to-passive transition locus. Solid line: experimentally determined[14]; dashed line: inferred from quasi-equilibrium theory.

the surface oxidation reaction. Since the overall oxidation reaction is exoergic, when the reaction rate falls, less chemical energy is released and the particle surface temperature necessarily drops. This unidirectional process leads to a further reduction in the reaction rate and the particle surface temperature, ultimately causing extinction. We estimated the active-to-passive locus (the curved boundary on the graph) based on our rather preliminary active-to-passive transition data for the $O_2(g)/B(s)$ reaction [data similar to Fig. 4 for the $B_2O_3(g)/B(s)$ reaction]. Then using a quasisteady energy balance for an individual particle, assuming maximum radiation losses, we estimated particle temperatures as a function of particle diameter and total pressure (at $T_g = 2000$ K and $p_{O_2}/p \approx 0.20$) and the conditions under which passivation should occur due to the (temperature dependent) formation of a protective $B_2O_3(c)$ layer (i.e., Fig. 4). Although this locus is independent of particle diameter in the free-molecular regime, in the continuum kinetically controlled surface reaction regime the slope of the curve is determined by the solution of the energy balance and, therefore, is not known a priori. We find that, in the continuum regime, lower pressures are needed for extinction by passivation compared to the free-molecular regime. On the same graph we also present three rectangular domains of practical interest: 1) the domain of most previous experimental boron particle combustion research, which is essentially in the diffusion-controlled domain; 2) the domain of oxygen pressure and specimen size in which we have been measuring true gas/solid reaction kinetic data (not falsified by gaseous diffusion); and 3) the domain of principal ramjet interest, which falls between the domains of diffusion-controlled and kinetically controlled reaction and also between continuum to free-molecular flow domains. Thus, in such applications one cannot defend simplifying assumptions frequently made as to the rate-controlling steps and local flowfields.

V. Conclusions

Our experiments lead us to conclude that $B_2O_3(g)$ is a very efficient reactant for gasifying solid boron at high temperature—much more so than other possible stable reactants [$O_2(g)$, $H_2O(g)$, $CO_2(g)$] of chemical propulsion interest. Not only is $B_2O_3(g)$ found to be locally comparable to O(g) (cf. Refs. 15 and 17) but it is efficient over a much broader surface temperature range. It follows that, provided there is adequate residence time (in the gaseous boundary layer near a burning particle) to form $B_2O_3(g)$ by the vapor phase oxidation of boron suboxides [BO, $(BO)_2$,...], the $B_2O_3(g)/B(s)$ heterogeneous reaction will be the most important channel through which B(s) is gasified. We estimate that at atmospheric pressure boron particles under about 30-μm diam would undergo kinetically limited combustion and the surface attack would be governed by the $B_2O_3(g)/B(s)$ reaction until the particle diameter reached ca. 3 μm. This means that a particle of, say, 30-μm initial diameter would deliver as much as 99.9% of its mass and energy under conditions of $B_2O_3(g)/B(s)$ rate control, whereas, if we considered a particle of 10-μm initial diameter, 97.8% of its mass and energy would be delivered under the same conditions. Under ca. 3 μm particle diameter, we estimate that the particle surface would be attacked mainly by $O_2(g)$, thereby reducing the gasification rate by some 2-3 times. From the above arguments, we conclude that this transition to the $O_2(g)/B(s)$ surface reaction would not be important for initially large particles (say, 10-30 μm) since the relative amount of mass and energy released at this latter stage would be negligible. However, fine fuel particles (about 3-μm initial diameter or less) would undergo kinetically controlled surface reaction by the slower $O_2(g)/B(s)$ reaction with a correspondingly slower energy release rate. Furthermore, at about 1-μm diameter, the burning particle boundary layer can evidently no longer be considered a continuum. Thus, continuum-to-free molecular transition flow theories should be included in simulation calculations if an appreciable fraction of energy is expected to be released under such conditions. Our calculations also indicate that near atmospheric pressure a small solid boron particle undergoes heterogeneous reaction in the kinetically active regime and would be likely to remain in this regime through its entire burning time. This implies that a successfully ignited particle in the environments considered here should not extinguish due to a possible reduction of the surface gasification rate resulting from "surface passivation" by $B_2O_3(c)$.

With the help of experimental measurements for several important gas/solid reactions, we have shown that it is possible to identify the chemical kinetic and physical phenomena likely to play a dominant role at each stage in the combustion history of a solid boron fuel particle. These considerations should be included in future mathematical models. As is well known, in practice, hydrogen- and/or carbon-containing species may also be present and thus complicate the simple picture illustrated here for the B/O system. However, using the same general strategy, i.e., experimentally obtaining the missing necessary information (which in most cases today falls in the area of chemical kinetics of homogeneous and, especially, heterogeneous reactions: see, e.g., Ref. 28) under well-defined conditions, combined with environmentally specific transport calculations, one can identify the appropriate phenomena to include in a sufficiently comprehensive model of boron particle combustion in airbreathing propulsion systems.

Acknowledgments

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