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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Single particle boron ignition and combustion models developed in earlier phases of this program have been utilized and extended to treatment of boron cloud ignition, oxidizer depletion effects on cloud combustion time, laminar flame speeds in boron dust clouds, agglomerate ignition, and the effects of halogens, lithium fluoride coatings, and metal coatings on particle ignition. In addition, they have been utilized in a modular combustor model (well-stirred reactor followed by a two-dimensional mixing zone) of boron slurry combustion. Critical deficiencies in knowledge of processes of condensation of various boron oxides/hydroxides have been defined and an experiment to better quantify and understand these processes has been designed. An experimental program for definition of kinetics of boron oxide liquid plus water vapor (important to boron particle ignition) has been carried out. A comprehensive data base of ignition and combustion times for small (10 to 50 micron) boron particles in various wet and dry environments has been developed and a limited experimental study of the effects of LiF coatings on boron ignition performed (cont)			
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Dust Cloud Ignition  
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Cloud Combustion  
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19. ABSTRACT (Cont)

Finally, experiments aimed at characterizing dominant processes in boron solid-fuel ramjet combustion, utilizing a windowed slab burner, have been accomplished.

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**Report 41-5032-3**

**FUEL-RICH SOLID PROPELLANT BORON COMBUSTION**

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## I. RESEARCH OBJECTIVES

- (1) Modify the existing analytical model of boron ignition by King to include treatment of finite-rate kinetics for the reaction of water gas with surface oxide.
- (2) Develop a mechanistically accurate model for combustion of clean boron particles, with allowance for finite rate kinetic steps and multistage oxidation as necessary.
- (3) Upgrade an existing boron cloud ignition model to include a more detailed submodel of single particle ignition phenomena and to permit prediction of ignition delay times as well as critical conditions required for cloud ignition.
- (4) Modify the aforementioned single particle boron ignition model to treat effects of ignition modifiers.
- (5) Develop stirred reactor and directed-flow reactor models of combustion of boron dust clouds utilizing the unit ignition and combustion models developed in (1), (2) and (4).
- (6) Evaluate the feasibility of various approaches to determining the kinetics of the reactions of condensed-phase boron with various gaseous oxidizers and, if feasible, perform detailed design of such an experiment.
- (7) Critically analyze the literature regarding condensation of  $B_2O_3$  and  $HBO_2$  gases produced by the combustion of boron particles and define experiment(s) to quantitate this phenomenon.
- (8) Experimentally evaluate the kinetics of  $B_2O_3(l) + H_2O(g)$  using a flat-flame burner procedure.
- (9) Experimentally define the intermediates appearing in the combustion of boron.
- (10) Obtain ignition and burning time data for single boron particles in the 5 to 25 micron diameter size range using a flat-flame burner procedure.
- (11) Study the conversion of boron in a center toroidal recirculation zone reactor as a function of several independent variables.
- (12) Experimentally investigate the flame structure associated

with a consolidated boron grain burning in an air crossflow.

- (13) Experimentally evaluate the effects of such potential boron ignition promoters as magnesium, fluorine, and lithium fluoride on the ignition characteristics of boron particles.
- (14) Measure ignition delay times of boron dust clouds and critical conditions required for ignition of such clouds as a function of the important independent parameters.
- (15) Measure the flame propagation rates of boron dust clouds as a function of the important independent parameters.

**II. ACCOMPLISHMENTS AND PROGRESS DURING THE PAST YEAR  
(4/1/83 - 3/31/84)**

Several of the tasks listed in the previous section were completed during the first and second years of this program and are discussed in earlier annual reports (1 and 2). Progress made on other tasks (and an additional task, modeling of boron agglomerate ignition) during the past year is delineated herein. The first and second tasks were completed during the second year with final development of a unified single boron particle ignition/combustion/extinguishment model - a fairly extensive description of this work appears in References 3,4, and 7 listed in the Publications Section, and the work is also summarized in the first two annual reports.

While modeling of single particle boron ignition is important to interpretation of experiments aimed at defining and quantifying unit processes associated with such ignition, in practical applications boron particles are ignited in clouds. Accordingly, modeling of boron cloud ignition, which involves additional unit processes such as heating/cooling of the gases surrounding the particles and in which radiative heat transfer characteristics are considerably different than for the single particle case, is necessary for evaluation of whether or not a group (cloud) of particles will or will not ignite under a given set of ambient conditions and, if they will, how long the ignition delay time is. In Task 3, a model of ignition of boron dust clouds (with or without supplemental magnesium particles as ignition aids) which includes the unit process descriptions for generation and removal of the protective oxide coating from the boron particle used in the previous single particle modeling along with additional gas/solid and cloud/surroundings transport processes was developed.

General characteristics of this model include:

- (A) A spherical cloud with unimodal boron particles uniformly distributed through it is assumed.
- (B) Oxidizer depletion effects during ignition are neglected.
- (C) All particles are assumed to follow identical temperature-time histories (all start at the same temperature).
- (D) Allowance is included for unequal initial (and subsequent) boron, magnesium, and gas temperatures.
- (E) Transport property augmentation between gas and particles in the cloud due to relative motion between them is neglected.

- (F) Oxygen, water vapor, and halogens (HCl, HF, Cl<sub>2</sub>, F<sub>2</sub>) are considered as potential reactants.
- (G) In the absence of magnesium, radiative transport between the particles and the outside world is allowed, but such transport between the particles and gas within the cloud is neglected. With magnesium present, it is assumed that the MgO product and gas are in thermal equilibrium - in this case, radiative transport between the gas - MgO mixture (with effective emissivity equal to unity) and boron particles and radiative transport between the mixture and the surroundings are allowed subsequent to magnesium ignition, but radiative transport between boron and the surroundings is disallowed due to masking by the MgO - gas mixture.

Two possible scenarios are treated: in the first, the cloud is initially cold, with hot surroundings providing the energy to drive the ignition processes, while in the second case the initial cloud temperature is assumed to be equal to the surroundings temperature. Differential equations for the rate of change of boron particle size, oxide thickness, magnesium temperature, gas temperature, boron temperature, fraction of boron melted (if the melting point is reached) and magnesium particle size have been derived and are solved simultaneously using a Runge-Kutta procedure. A large number of cases have been calculated, with variation of numerous parameters which can affect cloud ignition, to yield minimum surroundings temperatures required for ignition and ignition times for conditions under which the clouds will ignite. An important result is that the minimum surroundings temperatures required for ignition are significantly lower for clouds than for corresponding single particles.

Additionally, in the area of boron dust cloud ignition/combustion, the effects of oxidizer depletion on combustion times of boron dust clouds have been examined for the general case where the combustion process may be partly diffusion-controlled and partly kinetics-controlled. (The two limiting cases have been previously examined by others - this analysis yields proper consistent limiting-condition results and permits handling of intermediate particle size cases where the user does not a priori know where he is relative to these two limiting conditions.)

There is considerable evidence that the very fine boron particles (less than 5 to 10 micron diameter) typically utilized in boron-loaded airbreathing propulsion fuels (slurries, ducted rocket formulations, solid-fuel ramjet formulations) generally undergo considerable agglomeration during the processes occurring prior to their appearance in the ignition/combustion zones of airbreather combustors. Since ignition time of the boron fuel is often of critical importance in determining whether or not the

high heating value of boron will be successfully utilized in typical low-residence-time combustors, it is important that the potential deleterious effects of this agglomeration (via increased ignition delay times) be evaluated. Accordingly, in addition to the tasks listed in the previous section, an agglomerate ignition model employing the same unit process descriptions for various resistances associated with generation and removal of the inhibiting oxide layer (whose time of removal is equated with ignition time) but also including consideration of increased surface area per unit mass for an agglomerate relative to a single particle of the same diameter and consideration of pore transport processes (resistance) for reactant and product gases has been developed.

Preliminary calculations indicated that assumption of constant temperature throughout the agglomerate (time-dependent, but independent of radial position) is reasonably accurate even with large variation in reaction rates with radial location - accordingly, this simplification has been employed. For cases where the product of reaction rate per unit surface area and available interface area per unit volume of pores plus solid divided by effective pore diffusivity is independent of radial location within the agglomerate, a relatively simple expression for distribution of reactant and product gas concentrations within the pores is available. Such a situation prevails for a large fraction of the ignition delay time, but is grossly in error as ignition is approached, with the oxide layer thinning at different rates at different radial locations. Accordingly, this approximation was relaxed for a number of cases and a more detailed description of the transport processes within the pores, involving a trial-and-error numerical analysis procedure nested within the simpler model was utilized to determine how much effect it had on predicted ignition times. As it developed, the effect was miniscule and the simpler (and much less costly) analysis was subsequently used for parametric studies.

Combining of equations for reaction resistances associated with kinetics steps, transport of oxygen and other reactive species across the oxide film, and partial pressure drop through the pore structure permitted calculation of oxide generation and removal rates as a function of instantaneous oxide thickness and particle temperature for a given set of ambient conditions and particle structure (agglomerate radius, unit particle radius). Substitution of these terms into equations for time rate of change of particle temperature and oxide thickness at various radial locations within the agglomerate then permitted calculation of the time history of particle temperature and oxide thickness versus radial location. Ignition was taken to occur at the time that any oxide thickness went to zero.

For comparison purposes, single particle ignition time calculations were performed using the single particle model for radii equal to the unit particle radius, the agglomerate radius, and an equivalent radius corresponding to the agglomerate mass



with zero porosity. Typically it was found that the agglomerate ignition times fell between those associated with the unit particle and the "equivalent radius" particle, being considerably closer to the latter values for high ambient temperature (non-marginal) conditions. However, the minimum ambient temperature required for ignition of the agglomerates was somewhat lower than for any of the comparable single particle cases.

A significant problem as regards use of boron as an ingredient in fuels for airbreathing propulsion systems is the non-negligible time required for igniting the boron particles: that is, the time required to completely remove an initial oxide coating which strongly inhibits the combustion of the metal. In many situations, this time is of the same order of magnitude as the available residence time of the particles in regions of the combustor amenable to boron particle ignition. Accordingly, several potential methods for enhancing the oxide removal have been examined on a theoretical basis, and experimental studies of one of these possible methods have also been carried out.

In the first of these studies, the possible effects of HCl, HF, F<sub>2</sub> and/or Cl<sub>2</sub> in the gases surrounding the particle have been analytically studied through extension of the previously referenced boron ignition model to allow for reactions of these species with the oxide layer to yield such gaseous products as BOCl, BOF, etc. Since detailed kinetic data for these reactions are not currently available, the studies have necessarily been parametric ones in which a range of likely activation energies for the reactions have been examined. Based on these studies, it appears that all of these halogen species will significantly lower the minimum critical ambient temperature required for ignition and for any given temperature will lower the ignition delay times, with the fluorine compounds being somewhat more effective than the chlorine species.

Next, possible effects of coating the boron particles with a layer of a second much more easily ignitable metal were examined. In this study, possible alloying reactions were neglected, with the effect of the outer metal layer being strictly thermal. Based on examination of thermodynamic considerations and ease of ignitability, two candidate metals, zirconium and titanium, were chosen for study. The following scenario was examined:

- (1) Particle heatup in hot gas surroundings without reaction until the outer metal ignition temperature is reached.
- (2) Combustion of the outer metal at a rate controlled by diffusion and/or the rate of reactive gas molecule collisions with the surface. Surface burning postulated, with retention of a non-protective outer metal oxide product and release of all reaction heat

to the particle.

(3) Two endgame possibilities, depending on the initial amount of outer metal:

- (a) If the particle temperature rises to the point where the vapor pressure of  $B_2O_3$  exceeds a specified multiple of total pressure (to allow for possible superheat requirements) before the outer metal is exhausted, the oxide and remaining outer-metal are explosively expelled at this point with subsequent clean particle combustion. (Ignition complete.)
- (b) If the outer metal is exhausted before such a temperature is reached, the particle temperature at this point is then used with the initial boron oxide thickness as input to the previously referenced boron ignition model and integration continued until the oxide layer is gone.

Parametric studies of the effects of various initial thicknesses of the outer metal (for various environments) on ignition time have been carried out: these calculations indicate that significant reductions in ignition time can be achieved through use of metal coatings at the 10-25 percent level.

Finally, the possible effects of lithium fluoride coatings on boron particles (over the oxide layer) have been examined, with the postulate that the LiF reacts with  $B_2O_3$  to form  $LiBO_2$  and BOF gases at a rate controlled by a combination of diffusion processes and equilibrium constant versus temperature relationship. Again, significant reductions in ignition time are predicted.

In a continuation of work on Task 5 (previous work on development of a perfectly stirred reactor model utilizing boron slurry fuel and of a zero-dimensional plug flow model for air addition downstream of the stirred reactor having been described in the first and second annual reports) a two-dimensional model, treating mixing and ignition/combustion processes, for prediction of fraction of boron burned in a boron slurry ramjet combustor has been developed. The configuration analyzed consists of an upstream centrally located perfectly-stirred-reactor (PSR) zone into which all of the fuel and a specified fraction of the air are fed, followed by a coaxial mixing region in which the products from the PSR are mixed with the remaining air, which flows coaxially around the PSR. In this analysis, the PSR zone is first analyzed (under the assumption that all of the liquid fuel carrier reacts in this region) to characterize the state of the effluent (temperature, composition, ignition/combustion status of the boron particles) leaving this region. In the PSR analysis, the boron ignition model and clean-particle combustion rate correlations based on the detailed combustion

model, both referenced earlier, are employed in combination with mass, species, and enthalpy conservation equations and equations for residence time distributions associated with perfectly stirred reactors as described in the second annual report.

Next, empirical correlations of coaxial mixing zone core length (and centerline velocity decay rate downstream of the axial location where the central core ends) are combined with assumed profile shapes (based on the literature) for velocity and temperature, and with conservation equations, for calculation of distributions of axial and radial velocities, atomic concentrations, enthalpy, and turbulent transport properties throughout the mixing region downstream of the PSR. Once these profiles have been established, they are utilized in a numerical analysis procedure for calculation of the boron particle ignition/combustion behavior in this region (under an assumption that the boron particles are sufficiently small that they will track with the turbulence eddies and thus undergo the same turbulent diffusive transport as the gases) involving marching down the combustor in the following manner. A two-dimensional radial-axial grid is first defined. At a given axial location, inputs to each radial element from its upstream end are known from the previous step in the marching analysis. In addition, the residence time associated with each element can be straightforwardly calculated. With these quantities established, the fraction of boron burned (or progress toward ignition, depending on the initial particle size) is calculated for each size cut of boron entering the element, using the previously mentioned boron ignition and combustion models. Summing over the various boron particle size cuts then yields the amount of boron oxide produced in each element. The previously established radial velocity and turbulent transport property distributions are then utilized in calculation of the radial transport of boron oxide into or out of the sides of each element, and species mass balances including the generation rate term calculated above are then used to calculate the oxide mass fraction at each radial location leaving the downstream end of the element as input to the next axial element. Finally, the previously established enthalpy and atomic mass fraction distributions are used to calculate other inputs (composition, temperature) for the succeeding axial element.

A final effort carried out under Task 5 during the third year was development of a model for prediction of laminar flame speeds in boron-oxygen-water vapor-carbon dioxide-nitrogen dust clouds, a model which should be of use in analysis of potential flameholding devices for boron dust clouds with various wet or dry gaseous species distributions. In this model, the equations developed for the single particle boron ignition model and correlation equations based on extensive calculations with the single particle boron combustion model are coupled with atom and enthalpy conservation equations through the flame structure, radiative transport equations, and a hierarchical selection method for molecular species (given the atom concentrations). A

preheat region final temperature (below which reaction rates are negligible) is specified and the mass burning flux and the oxygen mass fraction gradient at that location are guessed, permitting calculation of all species concentrations, temperatures, and spatial derivatives to be used as initial values for a Runge-Kutta integration of the equation set (first and second order differential equations plus ancillary algebraic relationships) through the ignition/combustion zones. Final temperature and composition values are then compared with those calculated from overall stoichiometry and thermodynamic considerations, and looping on the guessed mass burning flux and oxygen mass fraction gradient at the end of the preheat zone is continued (via a complex end-game procedure) until convergence on a flame speed is achieved. This model has only recently been completed and is currently being exercised parametrically for assessment of the effects of numerous independent variables on predicted flame speeds.

In Task 6, the feasibility of studying the kinetics of oxidation of solid boron with oxygen in the 2000 - 2400°K region (to provide needed information for the ignition and combustion models) in an apparatus where an oxygen-containing gas stream either flows through a nozzle throat made of boron or impinges supersonically on a boron target has been examined. It has been concluded that providing sufficiently high mass transfer coefficients to prevent the kinetics resistance from being overshadowed (and masked) by diffusional resistances is essentially impossible, given the expected approximate rate coefficients for the reaction(s). Accordingly, this approach has been abandoned. No other feasible direct approach to obtaining this kinetic information has been defined: accordingly an indirect approach in which parametric variations of kinetic constants in the models are used to search for optimum fits of single boron particle combustion time data has been resorted to by default.

With regard to Task 7, thermochemical calculations indicate that a considerable fraction of the total potential heating value associated with boron combustion will be lost if condensation of the product oxides to  $B_2O_3(l)$  does not take place. Review of the literature indicates that in dry atmospheres, condensation of gaseous  $B_2O_3$  to the liquid via homogeneous processes can be reasonably well predicted using classical theory. However, in the presence of hydrogen the situation is considerably complicated by the production of considerable quantities of  $HBO_2$  gas in the boron combustion processes, with the steps involved in conversion of  $HBO_2$  to  $B_2O_3(l)$  and hydrogen (thermodynamically predicted to occur as temperature decreases during expansion of the products through a nozzle or during mixing with excess relatively cold air in a combustor) being complex and poorly defined. In addition, no references to studies of the effect of seeding with extremely small refractory particles on condensation rates (and thus on tendency of actual condensation to track thermodynamically

predicted condensation during cooling) have been located. Accordingly, an experimental study to quantify and understand homogeneous and heterogeneous condensation of gaseous boron oxides (and hydroxides) in wet and dry systems has been defined. In this study, a long-residence-time, well-stirred combustor (with a long downstream burnout zone) burning carefully monitored amounts of hydrogen, oxygen, possible hydrocarbon fuels and either particulate boron or possibly a borane compound, along with nitrogen, is to be used to generate various product streams of well-defined total temperature and composition (particularly  $B_2O_3$  gas and  $HBO_2$  gas levels). A two-dimensional nozzle at the end of the combustor will control operating pressure and serve as the entrance to various two-dimensional expansion sections with various divergence angles (for control of temperature-time profiles for the expanding streams). Small optical accesses (windows) will be provided all along this expansion section to permit use of laser diagnostics for measurement of gaseous composition and particulate levels and sizes versus distance (and thus time) along the section. In addition, temperature and pressure are to be monitored along the expansion section. For a complete study, experiments should first be run with dry (no hydrogen) systems without seed nuclei, with subsequent extension to study of wet systems without seeding and finally to wet and dry systems with various levels and sizes of inert (e.g. zirconia) nuclei. From careful analysis of the progressively changing gas composition and particle nature (quantity and size) along the expansion section for various sets of initial conditions and expansion (cooling) rates, it should be possible to develop analytical models of the condensation processes for the various cases.

In Task 8, an experimental investigation of the reaction rate of boron oxide liquid with water vapor at elevated temperature has been conducted in order to provide crucial data for a model of the effects of water vapor on ignition of initially-oxide-coated boron particles. In this study, the transition region between diffusion control and kinetics control has been studied, with use of computer techniques to separate out the resistances when neither is negligible. The temperature range studied has been extended over that used in previous studies and the effects of variable oxygen and water-vapor partial pressures examined. While the experimental conditions were not directly representative of the combustion environment of an operational vehicle, they do come closer to being more realistic to the events which occur in the ignition and combustion of single boron particles in an oxidizing atmosphere. All work was performed in a flat-flame burner at one atmosphere, over a temperature range from approximately 1100 to 1900°K, with variable partial pressures of water vapor. A brief set of experiments was performed in a dry atmosphere (CO burned with  $O_2$ ) to provide reference data against which the water vapor experiments could be compared.

This study was conducted with boron-oxide beads mounted

on micro-thermocouples, and single beads mounted on platinum wires. The diameters of the beads were varied from a few hundred microns to as large as one and one half millimeters. The larger beads were more useful in determining diffusion-limited rates, but were oxidized completely to provide some data in the kinetics-limited regime. The beads were placed in the post-flame region of the flat flame burner, with and without flame-holders to modify the temperature environment of the bead, and were monitored with a variety of optical imaging techniques to establish the rate of change of radius with time. Bead internal temperatures were recorded using platinum/platinum - 10% rhodium thermocouples, bead surface temperatures were measured using a micro-optical pyrometer, and gas temperatures were determined from laser-induced fluorescence and heat-balance measurements.

The reaction rates and their dependence on temperature measured during the course of this study differ considerably from these previously measured by Russian investigators in experiments in which their results were somewhat confounded by uncorrected diffusional limitations. While the two data sets agree at about  $1000^{\circ}\text{K}$   $\text{B}_2\text{O}_3$  temperature, the activation energy obtained in these experiments is considerably higher (approximately 33 kcal) than that obtained by the Russian investigators (approximately 12 kcal) with our rates at  $1400\text{-}1500^{\circ}\text{K}$  (highest temperature obtained thus far) being approximately a factor of 50 higher than extrapolation of their data would indicate.

In Task 10, a comprehensive set of experiments for measurement of ignition delay times and combustion times of single boron particles has been carried out. The studies have been conducted in a combustion environment characterized by high (propane/oxygen) and low (carbon-monoxide/oxygen) water vapor concentrations. The nominal size range examined has included single particles in the 10 to 50 micron range and burner temperatures have been varied over the  $1900\text{-}2600\text{K}$  range. All work has been performed in a well-controlled flat flame burner operated at one atmosphere. The range of size parameters examined has permitted the very careful definition of the transition between diffusion-limited and kinetics limited combustion for single particle burning.

The two sets of experimental data collected (wet and dry flames) have utilized comparable diagnostic methods, in order to permit direct comparisons of the results. The primary diagnostic used was a stroboscopic still photograph taken with a combination of a single lens reflex 35mm camera and a high speed chopper (as utilized in lock-in amplifier applications). Additional data were obtained with high-speed macro-photography, a self-scanned diode-array electronic camera, laser doppler velocimetry, particle-size interferometry and laser-induced fluorescence measurements.

Ignition delay times have been determined by

stroboscopic imaging, high speed photography, diode-array imaging and a short series of experiments utilizing time resolved spectra of the oxide removal from the particles. For particles of ten to forty micron diameter, these delays varied from approximately six to twenty-four milliseconds in the high water vapor atmospheres, and from about two to twenty milliseconds in the dry flame environment. Free oxygen concentrations were varied over a range of from ten to forty-seven percent.

The determination of combustion times has been primarily derived from the conventional stroboscopic camera technique, but additional data have been obtained from a particle size interferometer utilizing the visibility concept of scattered laser light, in conjunction with intensity ratioing. These data show combustion times which vary from less than ten milliseconds for particles of the order of ten microns, to as much as fifty to sixty milliseconds at the larger end of the particle size distribution range for the wet atmospheres. The dry flame combustion results show combustion times which vary from about five milliseconds to over thirty-five milliseconds for comparable size ranges. The data define well the transition from diffusion to kinetics limited combustion, the effects of water vapor on the ignition delay times, and the importance of free-oxygen concentration. Significant differences in burning rate are noted in comparisons of the wet and dry flames.

A concept which offers potential for delivering maximum volumetric heating value for airbreathing propulsion systems is the highly-boron-loaded solid-fuel ramjet, in which air is blown across an ablating fuel slab, resulting in combustion of the boron particles emanating from the slab in the combustor port. Unfortunately, the physics of ejection of boron particles from the fuel surface and subsequent ignition and combustion of the boron in this environment are not well understood. One dominant view of the combustion of boron solid fuel ramjet grains in a high temperature air crossflow involves stabilization of a flame within a turbulent boundary layer formed above the ablating grain surface. Mechanisms fundamental to this view include grain surface ablation characteristics, ablated material physical properties and dynamics, radiation feed-back to the fuel surface from burning particles in the main stream and mean and fluctuating properties of the main stream and boundary layer regions. Modeling is an integral element in the understanding of such complex phenomena. However, adequate modeling of the complex interaction between kinetics and mixing limited phenomena is intractable without experimental data. Further, prior research has not employed diagnostics adequate for obtaining data essential for satisfactory modeling. Accordingly, Task 12 has been defined with the purpose of better defining mechanisms associated with boron solid fuel ramjet processes and providing inputs to models of such processes.

A unique combination of experiment design and diagnostics was assembled in this investigation to provide an

approach to acquiring the essential data on BSFRJ combustion. Laboratory-scale combustion testing was conducted in a two-dimensional windowed combustor, comprised of two facing slab grains designed to simulate essential radiative coupling. The laboratory-scale combustor consists of a series of bolt-together test sections to allow maximum experiment flexibility. Test sections include a high temperature air inlet and grain ignition section followed by a section for transition to square cross-section; flow straightener and turbulence generator sections precede the primary windowed-grain section which is followed by combustion mixing and nozzle sections. Instrumentation ports are provided throughout. The primary windowed grain section is designed to accept either 2-D facing boron grain slabs, or alternatively, to accept a single boron grain slab with an opposed optical access for a controllable radiation source. Optical access is provided through the side of the reaction chamber to allow use of both simple and advanced non-intrusive diagnostics. A unique element of the windowed 2-D combustor is the inclusion of air jets designed to assist in maintaining optical access. This feature proved instrumental to demonstrating the potential usefulness of this experimental approach. Diagnostics employed include standard ramburner pressure and temperature instrumentation. Grain regression/ablation features and fluid dynamics of the internal flow were examined using high framing rate (200 - 1000 f/s) color-photography, color video recording, a Reticon diode array camera and high response thermocouples embedded in the slab grains. Particle size distribution of the ablated grain material was recorded using particle size interferometry.

This experimental investigation has successfully demonstrated the potential for acquiring data essential to modeling and understanding boron SPRJ combustion phenomena. Consistent and repeatable criteria for 2-D flame stability were established for hydrocarbon and boron slab grains. Regression rates and combustor pressures representative of center-perforated test data were obtained. Definition of overall flow structure is possible by combining observed data from video, high framing rate photography, and Reticon recordings.

Available data allows observation of the time-dependent location of the ablating grain surface and dividing shear layer associated with sudden-dump recirculation zone formation. Observed boron grain surface ablation begins with break-off or ejection of fuel agglomerates from the surface, and an ignition delay preceding agglomerate rupture and rapid combustion. Multiple ignition centers of ablated grain material have been observed. Particle size interferometry measurements of ablated material resulted in a majority of recorded particle sizes falling at the upper end of the instrument dynamic range of 20  $\mu$  - 200  $\mu$  diameter. This is larger than anticipated and considerably larger than the virgin boron particle sizes of 1 - 2  $\mu$ . Experimental findings were encouraging and merit continued experimentation and analysis.



During this investigation period, in Task 13, an effort was made to examine the effects of additive coatings and material preparation on the ignitability of single boron particles. A standard particle size cut was established, and a uniform set of burner conditions determined which would be appropriate to assessing the effects of coatings. Tests were performed with a variety of techniques for the application of lithium fluoride as a coating on boron particles in the 46 to 53 micron diameter range. Data were obtained on the heat-up, ignition and total burn times for the various methods, and videotapes made of the particles as the burner temperature was dropped gradually to ignition cut-off. The use of tetrahydrofuran with lithium-fluoride dissolved in the liquid (as a coating technique) appears to have resulted in an enhancement (decrease) of ignition plus burn-time, and boron immersed in a water/lithium fluoride solution resulted in the shortest time to ignition. However, a significant effect noted was an increase (by a factor of two) in time-to-ignition of a LiF treated sample which had been stored for 45 days relative to a fresh sample. The data are being examined using statistical analysis, and temperature calibrations of the operating conditions are being made before final conclusions are drawn from the available data.

### III. PUBLICATIONS

- (1) King, M.K. "Ignition and Combustion of Boron Particles and Clouds", J Spacecraft and Rockets, 19, 4, July-August, 1982, p. 294.
- (2) King, M.K., "Boron Particle Ignition and Combustion," 1982 Eastern States Combustion Institute Meeting, Invited Paper, Atlantic City, N.J., December, 1982.
- (3) King, M.K., "Single Particle Boron Ignition Modeling," 19th JANNAF Combustion Meeting, Greenbelt, MD, CPIA Publication 366, Vol. II, p. 27, October, 1982.
- (4) King, M.K. "Modeling of Single Particle Boron Combustion," 19th JANNAF Combustion Meeting, Greenbelt, MD, CPIA Publication 366, Vol. II. p. 43, October 1982.
- (5) Komar, J.J. Taylor, G.L. and King, M.K., "Diagnostics of Single Particle Boron Combustion," AIAA Paper 83-0070, 21st Aerospace Sciences Meeting, Reno, Nevada, January, 1983.
- (6) Fry, R.S., and King, M.K., "Prediction of Boron Combustion Efficiency in a Slurry Ramjet Combustor," 20th JANNAF Combustion Meeting, Monterey, Cal, Oct., 1983, CPIA Publ. No. 383, Vol II, pp. 313-323.
- (7) King, M.K., "A Unified Model of Ignition, Burning, and Extinguishment of Single Boron Particles," 20th JANNAF Combustion Meeting, Monterey, CAL, Oct. 1983, CPIA Publ. No. 383, Vol. II, pp. 97-115.
- (8) King, M.K., "A Model of Boron Dust Cloud Ignition," Submitted to 21st JANNAF Combustion Meeting, Oct., 1984.
- (9) King, M.K., "A Model of Boron Agglomerate Ignition," Submitted to 21st JANNAF Combustion Meeting, Oct. 1984.
- (10) King, M.K., "Modeling of Effects of Various Aids (Halogens, Metal Coatings, LiF Coatings) on Boron Particle Ignition," Submitted to 21st JANNAF Combustion Meeting, Oct., 1984.
- (11) King, M.K., "Prediction of Boron Combustion in a Slurry Ramjet Combustor," Submitted to 21st JANNAF Combustion Meeting, Oct. 1984.
- (12) Komar, J. Taylor, J., and King, M.K., "Experimental Determination of Boron Oxide - Water Vapor Reaction Kinetics," Submitted to 21st JANNAF Combustion Meeting, Oct., 1984.
- (13) Komar, J., Taylor, J., and King, M.K., "Flat-Flame Burner Studies of Boron Particle Ignition and Combustion in Wet and Dry Atmospheres," Submitted to 21st JANNAF Combustion

Meeting, Oct., 1984.

- (14) Fry, R.S., Komar, J., and King, M.K., "An Experimental Investigation of the Mechanisms of Boron Solid Fuel Ramjet Combustion," Submitted to 21st JANNAF Combustion Meeting, Oct., 1984.
- (15) King, M.K., "A Unified Model of Boron Particle Burning", To be submitted to AIAA Journal
- (16) King, M.K., Technical Note: "Oxidizer Depletion Effects on Boron Dust Cloud Combustion Time," To be submitted to Combustion and Flame
- (17) King, M.K., "Boron Dust Cloud Flame Speed Model," To be submitted to 1984 Eastern States Combustion Institute Meeting (Dec. 1984) and possibly Combustion and Flame or Combustion Science and Technology
- (18) Komar, J., "Flame Visualization and Particle Diagnostics Using an Electronic Matrix Array Camera," Seventh Int. Conference on Lasers and Applications, San Francisco, Cal, Nov. 1984
- (19) Komar, J., and Taylor, J., "A Summary of Advanced Non-Intrusive Diagnostic Applications Applied to Particle Combustion Systems," To be Submitted to 1984 Eastern States Combustion Institute Meeting (Dec. 1984)

**IV. PROFESSIONAL PERSONNEL**

**Dr. Merrill K. King  
Dr. James Komar  
Mr. Ronald S. Fry**

## V. INTERACTION (COUPLING ACTIVITIES)

- (1) Atlantic Research has several advanced development contracts involving use of boron as a fuel. These include ducted rocket, slurry ramjet, and boron solid-fueled ramjet (BSFRJ) programs, funded by AFRPL, AFWAL, DARPA, and NWC. Dr. King, Dr. Komar, and Mr. Fry are all active in these programs, providing modeling and diagnostic support in the areas of boron particle ignition and combustion. As a specific example, Dr. King's ignition model is being incorporated in an analysis being used for design of a boron slurry ramjet combustor. In addition, output from the compacted boron solid fuel program for development of high energy advanced air-breathing propulsion system fuels is being used in this program and information developed on the slab grain phase of this program is being fed back into the fuel development area. Recently, Atlantic Research has been awarded a Boron Metalized Fuel Development Program from AFAPL (AFWAL/PORT): as part of this program, Drs. King and Fry will apply the single particle ignition and combustion models and parts of the stirred reactor and directed-flow reactor models of combustion of boron dust clouds to development of a modular model of boron-loaded solid-fuel ramjet combustors.
- (2) In March, 1983, Dr. King presented a seminar on boron ignition and combustion to personnel at Lawrence Laboratories, Livermore, CAL.
- (3) In January, 1984, Dr. King participated in a Swirl Combustor Workshop held in conjunction with the AIAA 22nd Aerospace Sciences Meeting, in which combustion of boron-loaded slurries was one of the topics considered.
- (4) In June, 1984, Dr. King will participate in a Workshop to define potential future directions of basic research in the area of boron ignition/combustion.
- (5) In June, 1984, Dr. King will participate in a Ducted Rocket Workshop to be held in conjunction with the AIAA 20th Joint Propulsion Conference - it is anticipated that boron-loaded gas generators may be considered in this workshop.