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13. ABSTRACT (Maximum 200 words)

A unified single boron particle ignition/combustion/extinguishment model capable of treating the effects of various oxidizers, Finite-rate kinetics, and time-dependent environmental conditions has been devloped and successfully checked against historyical data bases. In addition, parts of this model have been combined with enthalpy and species conservation equations for analysis of boron combustion efficiency in an idealized slurry ramjet combustor (perfectly stirred reactor followed by a series of incremental plug-flow reactors with arbitrary air addition as a function of operational and design parameters. Cibsuderabke subgke particle ignition/combustion data have been obtained over a wide range of particle sizes (5-70 Microns) in wet atmospheres with this experimental effort currently being extended to dry atmospheres. An experiment to determine the kinetics of the boron oxide-water reaction (crucial to ignition) is in progress. A laboratory apparatus for studying combustion of highly-boron-loaded solid fuel ramjet grains in hot air crossflow on a fundamental basis has been completed. Design of a well-stirred reactor for study of boron cloud and slurry combustion is complete and equipment

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FUEL-RICH SOLID PROPELLANT BORON COMBUSTION

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Annual Report Covering
4/1/82 - 3/31/83

Air Force Office of Scientific Research/NA
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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_xO_y 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 (4/1/82 - 3/31/83)

Several of the tasks listed in the previous section were completed during the past year, while considerable progress was made on additional tasks and work was initiated on others. In last year's report, progress on development of a single boron particle ignition model and of a quasi-steady-state combustion model was discussed, with delineation of the major factors considered and assumptions/approximations made. During the past year, work on these models was completed, with a resultant capability for prediction of ignition and combustion behavior of such particles in $O_2/CO_2/H_2O$/Inert atmospheres. Both the ignition and combustion models include treatment of finite-rate kinetics effects. In addition, the combustion model has been extended to treat transient effects as regards particle temperature, in particular treating the transition from completion of removal of the oxide coating to attainment of a slowly varying near-steady-state combustion condition in which the particle temperature tracks that predicted by the quasi-steady-state model quite well. Capability of predicting extinguishment has been built into the combustion model, and the models have been molded together into an integrated "birth-to-death" ignition/combustion/extinguishment model, consisting of two major sections. In the first section, the processes involved in removing the initial oxide coating from the boron surface in atmospheres of various compositions (wet or dry) and temperatures are modeled with the resulting differential equations describing the rate of change of particle size, temperature, and oxide thickness being integrated for a given set of environmental conditions (which can be varied with time, a particularly useful feature for analyzing a particle tracking through a variable environment in a combustor) until the oxide coating removal is complete (or until it becomes clear that the particle will not ignite). At the time of completion of removal of the oxide, the particle temperature, state (liquid or solid) and size are saved as initial conditions for the second section of the unified model.

In the second stage, the processes involved in burning of a clean-surface boron particle (including finite-rate kinetics, effects of oxidizers other than oxygen, and multistage oxidation consisting of initial oxidation by B_2O_3 and HBO_2 to suboxides at the particle surface followed by oxidation of the suboxides to final oxidized product away from the surface) are modeled. The resulting equation set, which includes a transient term in the enthalpy equation to allow for transient particle heating or cooling effects, is used to solve for the time rate of change of particle radius and temperature (or fraction melted) along with the composition at the particle surface for the particle temperature and size supplied from the end of the ignition phase and the specified environmental conditions (again allowed to vary with time). A small time step is then taken, with the $dT/d\theta$ and $dr_s/d\theta$ values being used to calculate the change in particle size and temperature over that time step and a resultant new particle size and temperature. This process is then repeated until the particle burns out or extinguishes (depending on environmental conditions), extinguishment being postulated to occur when the partial pressure of B_2O_3 adjacent to the particle surface exceeds the B_2O_3 vapor presure calculated at the surface temperature.

This unified model has been completed and successfully checked out against several ignition time and combustion time data bases developed by Macek in the 1970's. It is found to predict observed shifts from d^2-law to d^1-law burning behavior at low particle sizes, and to match observed dependencies of ignition and combustion times on environmental conditions reasonably well. Parametric studies aimed at mapping the effects of numerous independent variables on the ignition, combustion, and extinguishment of boron particles over a wide range of values are in progress. An important finding generated by these studies is the observation that careful tailoring of the environmental history seen by the particle as it tracks through a combustor can result in significant decreases in ignition/combustion times.

The detailed model of the ignition of initially-oxide-coated boron particles in wet and dry atmospheres and burn-rate correlations based on output of the detailed finite-kinetics boron combustion model have been combined with atom and enthalpy balances to yield a model for prediction of boron combustion efficiency in an idealized combustor consisting of a perfectly stirred ignition zone followed by downstream one-dimensional plug flow reactor segments with arbitrary air addition to each segment. This model has been used to examine the effects of various parameters on boron combustion efficiency in slurry ramjet combustors. Pressure, combustor loading (mass flow rate/combustor volume), and boron particle size are predicted to have major effects, efficiency increasing with decreasing particle size, increasing pressure, and decreasing combustor loading. The importance of internal tailoring of the air distribution in the combustor (fraction bypassing the ignition zone, distribution of bypass air along the secondary plug flow zones) is demonstrated, with control of air/fuel ratio in the ignition zone being shown to be especially important. In particular, tailoring the air split between the ignition zone and secondary zone so as to yield an ignition zone air/fuel ratio of about 6/1 - 7/1 (for the 60/10/30 B/Mg/HC fuel examined) appears to be quite important to attainment of high efficiencies.

Currently, several extensions of the modeling work described above are underway. These include:

(1) Development of an agglomerate ignition model. In this model, the unit processes treated in the single particle ignition model are included. In addition, effects of transport processes through pores in the agglomerates and effects of changed effective surface areas (differently defined for different processes) associated with agglomerate structure are included.

(2) Construction of a model of the effects of HCl and Cl_2, two gases commonly found in large quantities in the products of fuel-rich ducted rocket gas generators, on boron particle ignition. (These chlorine oxidizers can strongly effect ignition through reaction with the protective boron oxide coating to form low-boiling boron oxychlorides.)

(3) Analysis of the effects of various coatings (LiF, metals) on the boron surface on ignition. Several potential processes affecting ignition, including reaction of LiF with B_2O_3 to yield $LiBO_2$ and BOF, alloying reactions of the other metals with boron, and thermite reactions involving B_2O_3 and other metals will be treated.

(4) Modification of the slurry ramjet combustor model to include a coaxial-flow mixing analysis for the downstream regions following the perfectly-stirred-reactor ignition zone. In this model the mixing analysis will first be used to define temperature-composition profiles in the downstream regions in the absence of boron combustion. Particle tracking procedures (LaGrangian approach) will then be used to calculate boron consumption and heat release distribution with subsequent cycling back and forth beteen the mixing analysis and ignition/combustion analysis.

(5) Development of a first-order model of the combustion and transport proceses involved in the boron solid-fuel-ramjet concept, in which hot air is flowed over the surface of a highly-boron-loaded fuel slab.

During the second year's experimental effort, a laboratory scale combustion facility was established and made operational to support studies of boron ignition and combustion in combustor configurations involving: (1) a perfectly stirred reactor; and (2) a solid propellant grain exposed to a crossflow of high-temperature air. Design of the perfectly stirred reactor followed directly from parametric performance predictions made with the slurry combustor model described above. The reactor design includes features to allow variation in combustor pressure, combustor loading, fuel/air ratio and particle size distribution in the boron fuel flow. Additionally, the reactor incorporates head-end and aft-end swirl vanes to experimentally examine the influences of degree of mixing on ignition zone combustion compared with perfectly stirred reactor predictions. Hardware design has been finalized and components ordered. Future plans include experimental evaluation of the parametric influence of the key variables on the fraction of measured reacting boron. Tests will be performed in the Laboratory Scale Combustion Facility which has air flow capabilities for up to 3 lbm/sec at 1200^{o}R. Diagnostics include initial boron particle size distribution, combustor pressure and isokinetic exhaust sampling. Comparison of measured and predicted performance will be a key result of this task.

A second experimental task addressed during this year's effort is the study of the burning mechanisms of boron solid propellant grains exposed to a crossflow of high-temperature air. A special reaction chamber for study of the structure and governing mechanisms of a flame established within the recirculation zone and of the turbulent boundary layer zone of an ablating and burning boron grain has been designed, built, and tested. The hardware has been hydrostatically pressure checked for safety, and initial hot air flow tests performed. This hardware configuration will accomodate either cast or compacted propellant grains of variable formulation. Test sections comprising the reaction chamber include a high temperture air inlet and grain ignition section, common to all test hardware used in the LCF; this is 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. The turbulence generator section will accept generators of variable design, and the nozzle section will accept 2-D graphite nozzles of differing throat areas. The primary windowed grain section allows considerable experiment design flexibility by allowing evaluation of burning mechanisms of facing 2-D slab grains or a single slab grain with an opposed controlled external radiation source focused through a window which replaces the opposing grain located in the upper chamber wall. Optical access, provided through the side of the reaction chamber, is designed to allow use of both simple and advanced non-intrusive diagnostics developed under parallel experimental tasks. The reaction chamber window design includes a feature of gas-jet impingement on the surface exposed to hot gas flow for purposes of cooling and maintaining clarity of optical access.

The experiment design allows for observation of phenomena associated with three major processes involved in boron solid fuel ramjet operation: grain regression/ablation, combustion characteristics of ablated materials, and fluid dynamics of the combustor flow field. Fiber optics, heat flux gages, and thermocouples embedded in the grains, along with high-speed photographic, Schlieren, and Reticon photodiode array data will be used for characterization of grain regression/ablation behavior. The Reticon photodiode array data will also be used to characterize the structure of the thermal radiation field established above the grain. Particle size interferometry is to be added early in an attempt to characterize particle size distribution and velocity fields of the ablated material leaving the grain surface. Success will depend on the degree of control of the optical density in the regions of interest. LDV measurement will next be added to evaluate the mean and fluctuating velocity field. Finally, Raman scattering will be employed as resources permit to establish temporal and spatial distribution of the combustor temperature field.

Major experimental effort has been devoted during this past year to establishment of fundamental properties of single particle boron ignition and combustion, including development of a data base adequate for comprehensive testing of the boron ignition/combustion/extinguishment model discussed earlier. This effort has focused primarily over the last year on expansion of the data base for ignition and combustion times to particles in the 5 to 25 micron diameter size range, but also includes study of particles up to 60-70 microns in diameter (in an attempt to resolve discrepancies between past data obtained by Macek and Gurevich). This data set is now reasonably complete and attention is being shifted to ignition and combustion in dry atmospheres. Comparison of data and model predictions is just getting underway.

In addition, an experiment utilizing the uniform temperature/composition characteristics associated with the flat-flame burner for investigation of the kinetics of the reaction of liquid B_2O_3 with H_2O by measurement of the rate of change of size of a B_2O_3 droplet passing through "wet" flat-flame burner products has been designed and initiated. Difficulties have been encountered in that initial estimates regarding determination of rate of fractional change of size proved to be erroneous, necessitating resort to much smaller particles than originally planned. Once appropriate size cuts of B_2O_3 were obtained, it was soon determined that the measurement technique no longer yielded reliable results, in that the resulting light levels were significantly lower than those required for proper exposure of the fastest available film. Accordingly, an attempt was made to apply the Reticon diode array camera to the problem since reasonable success had been achieved with the 100 x 100 array during the investigtion of boron particle ignition and combustion. The low radiation intensity and small particle size of the B_2O_3 combined to defeat this approach to establishing reaction kinetics in that the size resolution of the 100 x 100 array was inadequate and the software used to establish grey-scale levels could not discriminate against the low radiation level changes.

The next approach entailed use of a higher resolution diode array camera (256 x 256): while some success has been achieved, it is only through the extreme preseverance of the programmer responsible for the data collection routines, in that Reticon does not support the software requirements of the 256 x 256 interface. Once it became clear that the electronic camera approach promised to entail an extensive development effort, a re-examination of available diagnostic options was initiated. A technique which shows promise for very small particle diameters was demonstrated briefly, to establish the feasibility of the measurement technique, and is now being implemented in the laboratory. This technique utilizes the visibility of scattered laser light from the liquid B_2O_3 droplet, and when combined with the expected light intensity level, is capable of very high reliability in detecting particle size. By collecting statistically significant numbers of data at several points within the temperature field, we anticipate being able to determine a reasonable value of the regression rate of the droplet diameters. This portion of the instrumentation is still in calibration.

III. PUBLICATIONS

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(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 Combusiton 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", AIAA/SAE/ASME 19th Joint Propulstion Conference, June 28, 1983, Seattle, Washington, AIAA Paper 83-1262.

(7) King, M.K., "A Unified Model of Ignition, Combustion, and Extinguishment of Single Boron Particles", Submitted to 20th JANNAF Combustion Meeting, October, 1983.

(8) Komar, J.J. and Taylor, GL., "Boron Oxidation Rates in Varying Ambient Atmospheres," paper submitted to 20th JANNAF Combustion Meeting. October, 1983.

(9) Komar, J.J. "Flame Visualization and Particle Diagnostics Using an Electronic Matrix Array Camera," paper submitted to 20th JANNAF Combusition Meeting, October, 1983.

IV PROFESIONAL PERSONNEL

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

V. INTERACTIONS (COUPLING ACTIVITIES)

1. Atlantic Research has several advanced development contracts involving use of born 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 will be fed back into the fuel development area.

(2) In March 1982, Dr. King presented a seminar on boron ignition and combustion to personnel at the Lawrence Livermore Laboratories, Livermore, California.