PARTICLE GENERATION AND EVOLUTION IN SILANE/ACETYLENE FLAMES IN MICROGRAVITY

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INTRODUCTION

The objective of this new experimental program is to advance the understanding of the formation of particles from gas phase combustion processes. The work will utilize the unique SiH_4 /C_2H_2 combustion system which generates particulate products ranging from high purity, white SiC to carbonaceous soot depending on equivalence ratio (Ref. 1). A key goal of this work is to identify gas phase or particle formation processes that provide the enthalpy release necessary to drive the combustion wave, and to locate the parts of the particle formation process that determine SiC stoichiometry and crystallinity. In a real sense, these SiH_4 /C_2H_2 flames act like "highly sooty" hydrocarbon flames, but with simpler chemistry. This simplification is expected to allow them to be used as surrogates to advance understanding of soot formation in such rich hydrocarbon flames. It is also expected that this improved understanding of SiC particle generation and evolution in these self-sustaining flames will advance the commercial potential of the flame process for the generation of high purity SiC powders.

BACKGROUND

We have previously investigated SiH_4/C_2H_2 flames in constant volume combustion experiments. In that work we found (Ref. 2) that SiH_4/C_2H_2 flames propagate over a wide range of stoichiometry ratios from 0.05 (acetylene-rich) to 2.5 (silane-rich). Burning velocities extracted from the pressure histories of combustion events exhibited an unusual dependence on the SiH_4/C_2H_2 reactant ratio as shown in Fig. 1. The major products of the combustion were hydrogen and fine powder containing most of the reactant mass of carbon and silicon. At the limits, this fine powder could be an atomic-level silicon-carbon mixture or a mixture of pure carbon and silicon particles. Either is consistent with the endothermic nature of the silane and acetylene reactants to decomposition to elemental silicon and carbon. Hence, over the range of stoichiometries observed to burn, a continuum of carbon-silicon compositions is produced. The homogeneity of the product must depend in part on the coupling between the silicon and carbon chemistries during the combustion and on the rates of elemental interdiffusion in nascent particles. For a very narrow range of SiH_4/C_2H_2 mixture ratios near 2.0 (equal silicon and carbon atomic concentrations), the powder product of the combustion was found to be stoichiometric nanocrystalline, cubic silicon carbide (SiC), consistent with intimate mixing on the atomic level. One possible mechanism to explain this would be parallel decomposition to carbon and silicon followed by rapid interatomic diffusion to produce stoichiometric SiC. We have presented evidence (Ref. 2) for coupling of the silicon and carbon chemistries, i.e., that the silicon-carbon bonds form early in the flame and have suggested that the such gas phase species determine the stoichiometry and crystallinity of the final product. There are problems with defining a suitable mechanism. Although a number of candidate small Si_xC_y species are known, they are high energy species which could present an significant energy barrier to the ultimate enthalpy-releasing process: formation of the condensed SiC phase. High molecular weight polyatomic silicon-carbon species are thermally unstable to dissociation, and unlikely

candidates for participating in particle formation. Insight into the mechanism of SiC formation may be gained through comparisons of flame data and the product properties for a series of related flames.
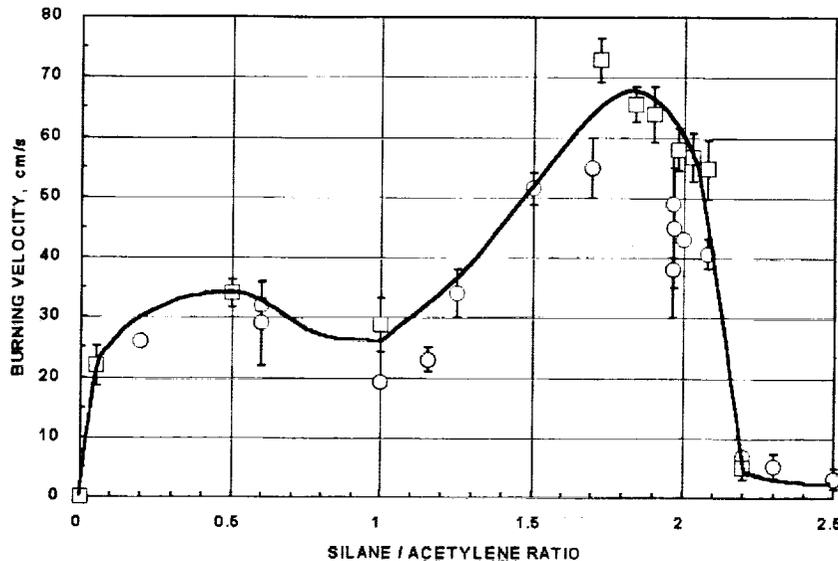
Figure 1 Experimental Silane/Acetylene Burning Velocities

It is difficult to obtain detailed flame structure information from constant volume combustion experiments like those described above. Instead, a steady-state, burner-supported flame is more suitable for accurate flame diagnostics. We previously established such constant pressure flames on a variety of burners in normal gravity, but found that laminar flames were extremely difficult to stabilize because of the interactions of buoyant product acceleration, settling and thermophoretic transport of the SiC powder product, and because of the apparent sensitivity of burning velocity to dilution and reactant mixture ratio. This sensitivity may arise from the close coupling of enthalpy release and particle formation that is unique to this combustion system. In the present microgravity studies, the complex effects of buoyancy, buoyancy induced mixing, and gravitational settling will be substantially reduced or eliminated. Less distorted and steadier flames that reflect the combustion chemistry and particle formation processes more than extraneous fluid transport effects are expected. It should be possible to obtain more accurate correlations among, e.g., reactant stoichiometry, added gases, burning velocities, flame temperatures, and the resultant powder properties. Several mechanistic questions will be addressed in this work: Are the enthalpy releasing particles formed from high energy small gas phase Si_xC_y species such as SiC(g) or large soot-like species? If the latter, at what stages in the particle formation are the one-to-one silicon to carbon ratio and the crystallinity developed? Based on the enthalpy release during particle formation, can the burning velocity be affected by increasing or decreasing the particle nucleation rate? This information will be used to improve our understanding of the heat release processes, and ultimately will provide an improved model picture of SiH_4/C_2H_2 flames to show whether and how a continuous burner process can produce high value SiC powder. The new understanding may help promote alternate approaches to commercial development of the synthesis flame process.

EXPERIMENTAL APPROACH

This program will focus on fundamental flame properties (burning velocity, particle and gas temperatures, flame species, and product characterizations). The key experimental challenges are to make reliable burning velocity measurements and to make useful measurements near the flame front to relate to the burning velocities of these particle-laden premixed flames. To make burning velocity measurements that reflect the adiabatic combustion chemistry, energy loss and thermophoretic transport to the burner must be minimized. Thus, multitubular burners are unsuitable for this purpose with these flames. In addition, flame front diagnostics require a geometry in which the pre-flame region is not obscured by the highly luminous particle cloud as with a Bunsen-type burner. A useful geometry that satisfies these requirements is that of inverted cone flame stabilized above a rod coaxial with the reactant flow, Fig. 2.
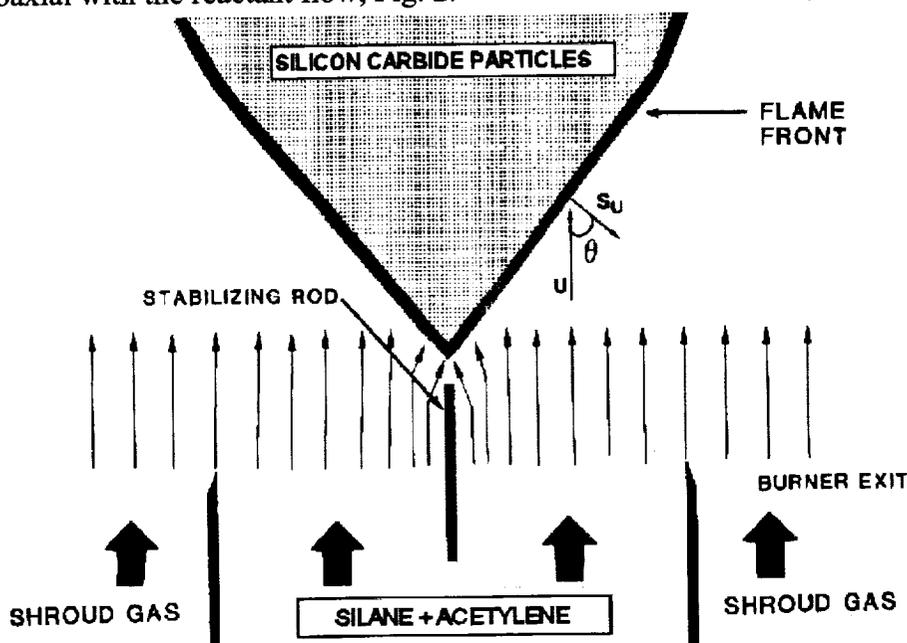
Figure 2 Inverted Flame Cone Geometry

The cone flame angle is related to the ratio of the flow velocity to the burning velocity. However, in normal gravity, the buoyant acceleration of the hot flame gases greatly distorts the cone angle. For the flames that will be investigated in this work, this normal gravity distortion would have a significant effect on a majority of the flames to be investigated and would dominate the lower velocity flames. These distortions would unpredictably affect each reactant mixture with its unique burning rate, flame products, and flame temperature, complicating the interpretation of measured differences among comparison flames. Therefore the microgravity environment is required to make burning velocity measurements suitable for flame comparisons and which predominantly reflect the fundamental flame chemistries and rates.

Measurements are planned to obtain overall structural information such as flame angle (measured from CCD camera images) to determine the burning velocity, preheat zone location (using schlieren imaging, thermocouples), particle temperatures (optical pyrometry), and particle volume fractions (laser extinction). The powder product from selected experiments will be collected and characterized as to particle size (N_2 surface area, TEM), material density (pycnometry), and

crystallinity (XRD, TEM). These properties will be compared to typical properties of powders produced in previous constant volume experiments and the comparisons interpreted in terms of differences in flame environments. Comparisons will also be made between the properties of SiH_4 /C_2H_2 flames that produce pure SiC (SiH_4/C_2H_2 ~ 2) and acetylene-rich (SiH_4/C_2H_2 < 0.1) flames that produce predominantly carbon soot. Dilution with inert gas will permit comparison of the two types of flames at the same burning velocity. The effects of additives that can affect particle nucleation (e.g., carbon black particles, electric fields, aromatic hydrocarbons) on burning velocity, flame properties, and/or product properties may be investigated. Additional diagnostics may be employed, including flame spectra (flame species information), gas sampling with microprobes for post drop analysis, thermophoretic particle sampling onto TEM grids for microscopic characterization, and thermocouple gas temperature measurements. All the data will be interpreted using thermochemical and kinetic estimates establish possible initial particle nucleation routes (e.g., carbon soot, silicon aerosol, low molecular weight Si-C species), and to improve the model of the synthesis flame.

PRESENT PLANS

The experimental system for the 2.2 second drop tower will be capable of quickly stabilizing inverted SiH_4/C_2H_2 cone flames (Fig. 2) suitable for burning velocity measurements. A completely contained system will be designed because of the pyrophoric properties of silane. The flame experiments require that we provide constant laminar flows with precisely controlled SiH_4 /C_2H_2 gas mixtures to the burner. To control the reactant mixture ratio, the (ignitable) mixture at about atmospheric pressure will be prepared (by partial pressures) in a resevoir. The resevoir will be designed to withstand the pressure of an accidental ignition. The reactant gas mixture will be fed at a constant rate to the burner by displacement using an inflatable internal bladder. The drop tower provides a limited time to establish a steady flame and record the flame measurements. For most planned and potential diagnostics, a sampling time on the order of one second will be adequate. Hence, the reactant flows must be stabilized and the flame ignited within a fraction of the first second of the drop. The burner (Fig. 2) will consist of a tube with flow straighteners at the reactant inlet and a converging nozzle to create a uniform velocity profile at the exit. The coaxial rod will act as a flame holder downstream of the burner exit. The flame will be supported in the sealed flame chamber in a stagnant or slowly flowing nitrogen atmosphere. In the short burning time the flame products are not expected to interfere with the flame or its observation with proper chamber size and geometry. The chamber pressure will be monitored with a pressure transducer.

ACKNOWLEDGMENTS

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