PRINCIPLES OF GAS PHASE PROCESSING OF CERAMICS

DURING COMBUSTION

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Introduction

In recent years, ceramic materials have found applications in an increasingly wider range of industrial processes, where their unique mechanical, electrical and optical properties are exploited [1]. Ceramics are especially useful for applications in high temperature, corrosive environments, which impose particularly stringent requirements on mechanical reliability. One approach to provide such materials is the manufacture of submicron (and more recently nanometer scale) particles, which may subsequently be sintered to produce a material with extremely high mechanical integrity. However, high quality ceramic materials can only be obtained if particles of known size, polydispersity, shape and chemical purity can be produced consistently, under well controlled conditions. These requirements are the fundamental driving force for the renewed interest in studying particle formation and growth of such materials.

Flames have most commonly been viewed as a means for generating energy; however, under some circumstances, they have also been used as an environment for chemical synthesis. The most notable industrial examples are the synthesis of carbon black, titanium dioxide and silica [2]. Some of the earliest work on the characterization of particle formation of refractories in flames was conducted by Ulrich [3]. Their work focused on the agglomeration processes following the formation of silica particles. More recently Calcote and his coworkers have used a generic novel halogen-alkali metal exchange reaction to generate a combustion environment in which the products are either a bare metal or a ceramic (and the halogen-alkali metal salt) [4].

For multi-component compounds where chemical stoichiometry is particularly important, aerosol decomposition is favored. Here, solutions containing the components are reacted within each aerosol droplet, precluding the necessity of controlling multi-component nucleation. Zachariah and Huzarewicz have shown that one can produce high Tc superconductors in a flame by this method [5].

The objective of this paper is not to review the field but to highlight from this authors prospective the most important areas features/factors affecting the growth of ceramic/semiconductor materials from the vapor. In this paper I will review the work on going at NIST on the vapor phase synthesis (gas phase chemistry/nucleation) of submicron and nano-phase particles from the prospective of the fundamental controlling factors and how they might be manipulated to obtain optimum properties.

Ideal Powder Characteristics for Advanced Ceramics

Based on current understanding the most important features in a powder are listed [6]:

-    Particle size below 1 μm diameter; nanophase powders < 100 nm.

-    Broad particle size distribution for greater packing density and less sintering shrinkage.

-    Equiaxed particle shape for highest packing density

-    Chemical and Phase purity/stability

-    No Powder defects (e.g. agglomerates)
        They negate all the above benefits!

From the prospective of "ideal" powder processing, agglomeration is the most serious issue which must be addressed in any synthesis process.

Model System Studies of Vapor Phase Synthesis in Combustion

In order to better understand the controlling factors underlying the vapor phase formation of ceramic compounds we have undertaken to study one model system in great detail. The system chosen was the formation of SiO_x particles. Here particles are formed from silane and silane like precursors in a counter propagating diffusion flame reactor, illustrated in Fig. 1. The details of the reactor geometry can be found elsewhere [7,8]. The two impinging jets create a classical stagnation plane, offset from which (on the oxidizer side) a flame can be stabilized. The flame acts as a heat and radical source to aid in the pyrolysis and oxidation of the precursor (added to the fuel stream). The advantage of this geometry, in a similar fashion to other more traditional combustion studies is that along the stagnation streamline the flow may be described as one dimensional, greatly simplifying the data analysis and modeling complexity.

Studies of the Particle Phase

In-situ light scattering studies in conjunction with aerosol dynamics modeling have been employed to characterize particle growth under a wide variety of process conditions (temperature, precursor concentration, strain rate, etc) [7,9].
The basic conclusions to be reached from these studies were that:

- Precursor concentration was the primary variable for controlling particle size.

- Under most operating conditions the particles formed are chained agglomerates composed of primary particles in the 10-30 nm regime.

- In-situ particle characterization based on light scattering showed average agglomerate sizes which ranged from as low as 50 nm up to 150 nm.

- Temperature was the primary variable for controlling particle morphology. Increasing flame temperature resulted in particle sintering and therefore more spherical shapes. At the highest flame temperatures used (T > 2500K) particles were completely coalesced with mean sized in the 50-100nm range. Sintering could be observed to occur from both light scattering and TEM studies.

- Modeling of particle growth employed both moment and sectional aerosol dynamics [10]. By using a temperature dependent source rate for the monomer (SiO_2) and applying a bi-collider kinetic scheme, one can without having to resort to classical nucleation theory adequately model the overall features of particle growth. Fig 2. shows a comparison of experiment and theory for both particle size and number density. It is clear that one can, using a kinetically constrained approach, model both the size and number density. The calculation also shows a good prediction of the onset of nucleation. Particle size distribution can be significantly perturbed from self-preserving during the early stages of particle growth when the monomer generation rate is high, but quickly evolves to the self-preserving distribution during the relevant flow times of most flames.

Studies of the Gas Phase

In any materials syntheses, morphology (size, shape) is only a part of the final characteristics that need to be controlled. Issues related to phase, chemical composition and crystallinity are also of interest. In order to address these issues it is necessary to develop or borrow methods for chemical characterization and modeling relevant to understanding the chemistry/nucleation that might occur. Characterization of the gas phase has been conducted using in-situ optical probes throughout the reactor during particle formation, for temperature (thermocouple, OH fluorescence), and gas phase/cluster species (laser induced fluorescence (LIF) and resonantly enhanced multi-photon ionization (REMPI)) [11-13].

These measurements have been made in conjunction with a chemical model, which includes gas phase hydrogen-oxygen chemistry, silane pyrolysis and oxidation chemistry (proposed). The gas phase portion of the mechanism contains at the present time 38 chemical species and 128 reversible chemical reactions. In addition, there are 31 nucleation reactions which remove species from the gas phase, through what amount to monomer reactions (e.g. $SiO_2 + SiO_2$ monomer). Added to this, 23 species undergo surface chemistry

directly from the gas phase onto the growing aerosol, via a CVD type mechanism (e.g. SiO_2 + surface) [14]. The chemical kinetics are solved in conjunction with a model for the counter flow geometry developed by Smooke et al [15]

Measurement of gas phase species made by either LIF or REMPI include Si, SiH3, SiO and OH [11,14]. As an example, we show in Fig. 3 concentration profiles for SiO made by LIF for various levels of silane loading. Also shown is the stagnation plane as defined by the steep decline in the scattered light from particles. To the right of the stagnation plane (ie where no particles are present) the SiO concentration is independent of the silane concentration initially used. This behavior is accounted for by considering that as the temperature is increasing for particles approaching the stagnation point, the equilibrium vapor pressure of SiO over a solid is also increasing. At the stagnation point, when all particulate surfaces are removed, the remaining gas phase SiO diffuses across the stagnation plane and is therefore independent of the silane concentration used. Of more interest to us is the region where SiO is sensitive to the amount of silane injected. This region also corresponds to the particle forming zone in the flow field. It is clear that the SiO concentration goes up with increased silane concentration. In addition, the appearance of SiO occurs later in the flow with increased addition of silane.

The mechanism has been tested against measurements of the OH radical made by LIF and allow us some confidence in the reliability of modeling the general features of the flame. The calculated SiO profiles are shown in Figure 4. The results show that the location and magnitude of the SiO concentration can be calculated quite well. The dominant channels (as determined from post-processing the simulation) for the chemistry are shown in Figure 5. The primary consumption route for silane is the unimolecular pyrolysis to silylene ($SiH_4 = SiH_2 + H_2$), which in turn may react with silane to form di, tri silanes. This process occurs under experimental conditions when silane is injected in the larger quantities (>0.25 mole %). It is also the manner in which silicon particles are observed to nucleate in silicon CVD reactors. On the oxidation side of our mechanism we know from our simulations that no molecular oxygen remains in the particle forming zone, having been consumed by the flame. Furthermore, we know from our OH measurement (not shown here) that OH is not in sufficient quantity in the particle zone to participate in significant oxidation. We are therefore left with concluding that H_2O is the primary donor of oxygen to silicon. The most likely candidate is SiH2. In order to address this point we have recently undertaken ab-initio molecular orbital (MO) calculations to show that water will insert to yield both the silicon analogues of methanol and formaldehyde (H3SiOH, H2SiO) [16]. RRKM analysis has been used to obtain rates from these calculations which indicate (see Fig 5) that these channels will be important. Once we have H2SiO, the large concentration of H atoms created in the flame and which have diffused into the particle forming zone successively dehydrogenate to produce SiO or alternatively undergo unimolecular decomposition to SiO and H2.

One of the interesting points regarding nucleation is that SiO2 is not formed in the gas phase and that solid formation must proceed through the polymerization of SiO, HSiOOH, and H3SiOH with subsequent oxidation in order to achieve full oxygenation. We have recently shown through MO calculation that the polymerization of SiO is highly exothermic and proceeds without an activation barrier, however subsequent oxidation to yield full oxidation is slow. This presents opportunity to make oxides with variable stoichiometry. It is this multicomponent nature of gas to particle conversion that is the key to controlled synthesis of nano-scale materials.

Another issue of importance is the dominant mode of particle growth. Based on the model calculation we can show that heterogeneous growth of gas phase species will play only a minor role in the growth of particles. This results from the fact that flame systems act as pulsed sources of monomer (due to the large gradients in temperature) which do not provide sufficient time for CVD growth to existing particles. This means that particle formation will always be dominated by new particle births in flames and will require greater emphasis on quenching to prevent agglomeration [17]

Studies of the Cluster Phase and Nano-Phase Materials

The bridge between gas phase species and the bulk solid is what is euphemistically termed clusters. What separates clusters from bulk species is that they have size dependent properties which can differ substantially from the corresponding property in the bulk. Depending on the property of interest (melting temperature, optical properties, coordination number, etc.) the critical cluster size to obtain bulk properties

will in general be different. One interesting aspect of this is that one has the potential to tailor make materials with a desired property, assuming one knows the size-property relationship and can control the formation/collection of these structures.

In order to understand the growth of this class of materials we have undertaken molecular dynamics studies of cluster growth processes [18]. The basic idea is to solve the classical equations of motion for an assembly of atoms based on known interaction potentials. Because the interaction potential surface is quite well known for silicon, our studies to date have been limited to pure silicon clusters.

A representative example result of these calculations are presented in Fig 6. for the case of two 15 atom silicon clusters (equilibrated with an internal temperature of 1850 K) colliding with a relative velocity of 2400 K. The oscillation of the relative velocity of the cluster results from the two body attractive and three body repulsive parts of the interaction potential producing the initial stages of an **agglomerate**. The potential energy curve shows the time evolution of the newly formed 30 atom cluster from the agglomerate through to the coalesced sphere. The potential well at 0.2 ps corresponds to an agglomerate of the two clusters. By climbing an energy barrier the clusters gain a tremendous amount of configuration stabilization and thus much lower potential energy.The temperature profile is essentially a mirror image of the potential curve, showing the large self-heating of the cluster as the cluster finds a more stable configuration.

The relevance to nano-scale materials processing become clear when one realizes that the primary objectives are to make small structures that have little or no agglomeration. This can be accomplishes by either, (for very small particles) forcing particles to cross over the barrier or (for larger particles) trapping them in the agglomerate potential well by rapid cooling.

Potential for Microgravity Processing

Microgravity combustion environments provide the possibility to:

1. Increase residence time
2. Decrease the extent of thermal mixing

These two characteristics have the potential for providing processing conditions not easily achieved on the ground and which in principle at least can be considered to provide an opportunity for further development.

Increased residence time could be applied to the problem of growth of very large particles (microns) which have importance in catalysis. One of the problems encountered in the growth of large particles is the requirement of large residence times in order to vapor deposit onto the existing particle rather than continuously forming new particles via homogeneous nucleation. The increased residence time will allow for extended periods where heterogeneous chemistry CVD can take place under slow chemistry conditions.

The decrease in thermal mixing rates due to the lack of buoyancy driven flows has some potential in the formation of extremely fine particles (nanometer scale). As revealed from the experimental and molecular dynamics models previously discussed, temperature plays a key role in the kinetics of agglomerate formation/coalescence. Increasing temperature can cause complete or partial sintering given sufficient time. Therefore with a judicious choice of time-temperature history, nanophase particles could be made to form and then quickly quenched so that the agglomerates that are made are only weakly bound. Because of the absence of buoyancy, thermal boundary layers can be maintained with steeper gradients for longer times, allowing particles in a flame to be transported by electrophoretic or thermophoretic transport to a much colder quench layer. In this way one can separate nucleation from agglomeration.

Conclusions

Combustion synthesis has established its credentials as a practical method for the synthesis of fine ceramic particles. Its future contribution will be determined by the ability to develop strategies for the formation of particles with specific requirements for size, morphology and chemical composition.

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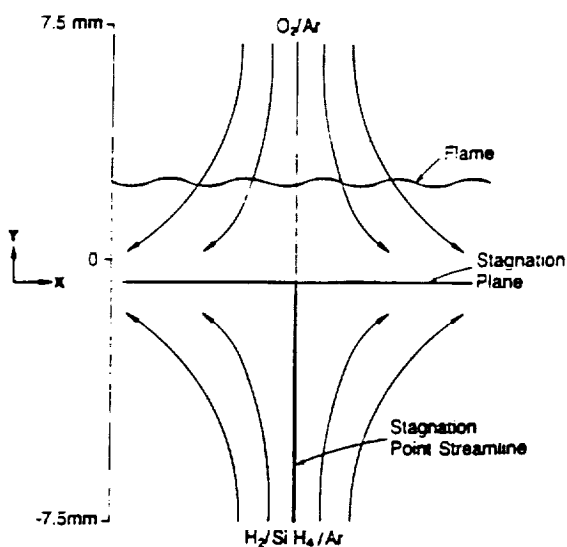18. Blaisten-Barojas, E., and Zachariah, M.R., Phys. Rev. B., **45**, 4403, (1992)

Figure 1. Schematic of counter flow diffusion flow field; Particles formed below stagnation plane. Laser diagnostics along stagnation streamline.
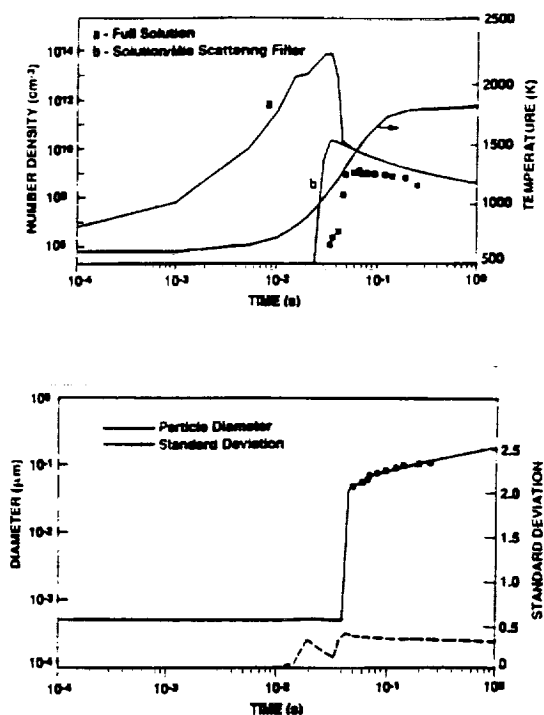

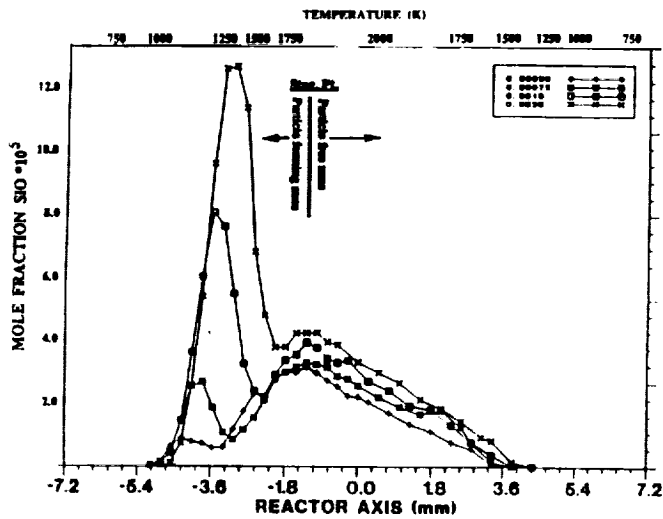Figure 2. Comparison of model and experiment of SiO2 particle formation in a flame.

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Figure 3. LIF concentration measurement of SiO as a function SIH4 mole fraction. Particles form to the left of the stagnation plane.
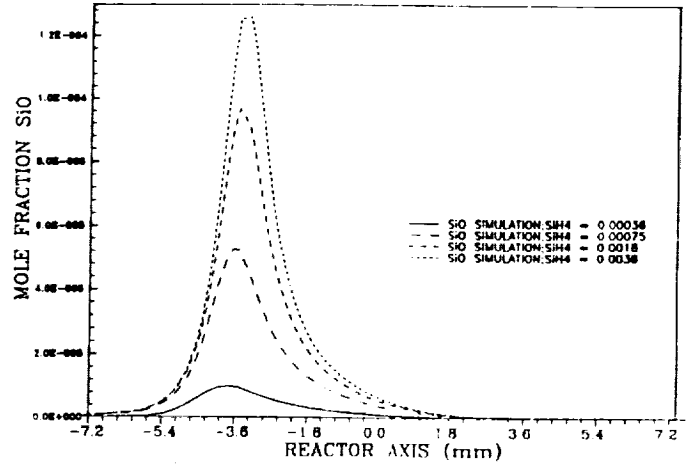

Figure 4. Model predictions of SiO concentration.

DOMINANT GAS PHASE CHEMICAL PATHWAYS FOR
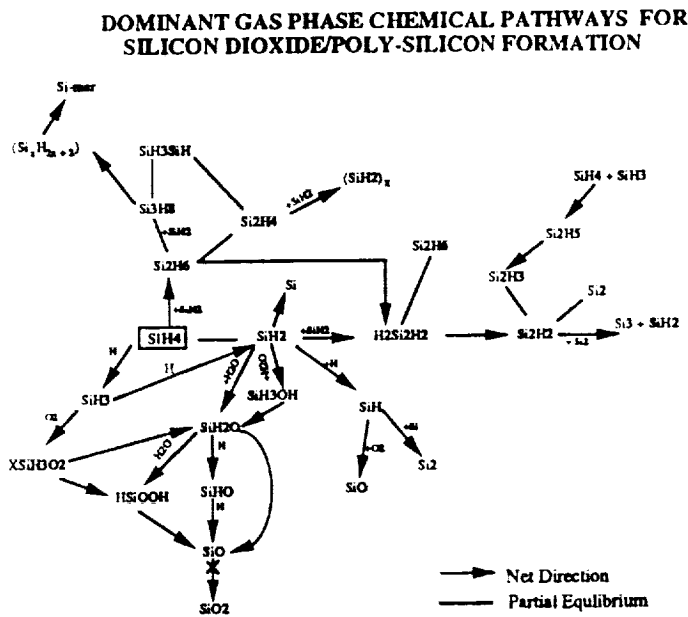SILICON DIOXIDE/POLY-SILICON FORMATION

Figure 5. Dominant pathways computed from model
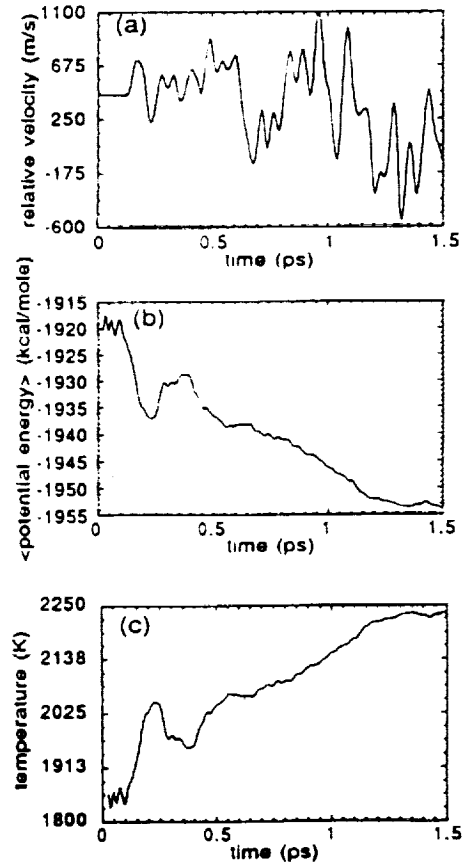calculations for silane oxidation/pyrolysis

Figure 6. Results from molecular dynamics computation for the collision
of two 15 atom silicon clusters for the relative (center of mass) velocity,
potential energy and temperature.

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COMMENTS

Question (Michael Frenklach, Penn State University): In addition to combustion synthesis in "regular" flames (like laminar premixed or diffusion flames), one can employ a "combined" flame environment. For example, using a microwave-assisted combustion, we were able to synthesize diamond particles in the gas phase.

Answer: I would agree completely that augmented flames can provide a more flexible environment for synthesis. Your diamond synthesis is a fine example of that principle. However, we should not lose sight of the one great advantage "regular" flames provide over other synthesis schemes -- "simplicity" -- which translates into cost-effectiveness, the driver for most process development. As we move to augmented flames through addition of energy (laser, RF, etc.) we transgress into a much more complicated synthesis environment, and into direct competition with the myriad of other processing techniques that may provide a similar result at comparable or lower cost.

SESSION C - Diffusion Flames and Diagnostics

(Chair, Robert Santoro)

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