

**PROJECT TITLE:** *Combustion Aerosol Synthesis of Crystalline Ceramic Nanoscale Materials*

Advanced ceramic materials consolidated from nanometer scale ceramics have the potential to provide improved mechanical, optical, and electronic behavior over their larger-grained counterparts. Potential applications include barrier coatings, catalysts, structural materials, and the core of superconducting wires. It has been suggested that nanoscale ceramic alloys or nonequilibrium phases could be developed because of the ability to control composition at the nanometer scale. This promise remains largely untapped, however, because of incomplete understanding of the relationship between composition and mechanical properties, and difficulties in producing low cost, chemically complex nanoscale materials.

In this project, we are exploring the development of combustion aerosol synthesis, a novel and promising route for producing chemically complex nanoscale ceramic materials. In combustion aerosol synthesis, ceramic precursors are dissolved or dispersed in a combustible carrier solution. When this solution is atomized into a high temperature flame, each droplet becomes a micro-reactor for nanoscale ceramic particle synthesis. The high temperature exothermic droplet combustion reactions enable the generation of crystalline materials *in-situ* without need for further heat treatment. The high temperatures, as well as the intimate precursor mixing afforded by the droplets, also permit the production of chemically complex materials. By controlling chemistry at the droplet level through manipulation of the precursor concentration, product of high chemical and phase purity can be produced. Nanoscale materials formation occurs either through nucleation within the exothermically reacting carrier droplet, or in the vapor phase as the result of vaporization and nucleation. The use of reactive, combusting droplets as micro synthesis reactors makes this approach unique.

One of the most challenging aspects of producing nanoscale ceramic materials is the need to understand and control particle growth by sintering. Sintering (or coalescence) rates affect the formation of particle aggregates; they are also important in determining densification of a ceramic body prepared from nanoscale powders. Sintering in these systems is particularly complex; depending upon the material, at high flame temperatures viscous flow may dominate, whereas at ceramic processing conditions a combination of solid-state diffusional mechanisms will contribute. In this project, we propose to conduct a fundamental examination of particle coalescence and

sintering for nanoscale ceramic particles, both as an aerosol and as a ceramic compact. This will be accomplished by using nanoscale (i.e. <50nm) yttria-stabilized zirconia synthesized in the Helble laboratory through combustion aerosol process. Yttria concentrations of 0-15% are being produced to permit us to examine fully and partially stabilized materials. The homogeneity of phase distributions in these samples is to be compared to those obtained in conventional coarser grained materials.

As part of this effort, we propose a detailed study of particle sintering and coalescence. This will be carried out as follows:

(1) Conducting experimental research to assess the importance of coalescence as a rate controlling step in the growth of coagulating combustion-derived nanoscale aerosols. Chemically homogeneous and heterogeneous systems will be studied to separate effects of particle surface composition from bulk composition on coalescence.

(2) Exploring the mechanisms of particle formation and growth by modeling the particle formation step, using kinetic approach (cluster addition), modeling the aerosol growth process, using existing aerosol general dynamic equation solving codes as the framework, modeling the coalescence process by analogy to sintering, and then modifying aerosol growth models to account for coalescence limited growth

(3) Studying sintering and grain growth in ceramic compacts formed from selected nanoscale powders.

One major objective of this project is an assessment of coalescence as a growth rate-limiting phenomenon in chemically complex systems. Thermophoretic sampling and light scattering will provide some information, but will be difficult to interpret in this context because of the need to isolate coalescence from collision and condensation. Our detailed examination of coalescence will therefore be conducted with a dilute aerosol stream in a tube furnace to maintain the isothermal conditions needed to derive diffusion coefficient data.

By varying particle composition (e.g. fraction of yttria used as a stabilizing agent) as well as compositional stratification (e.g. yttria on the surface vs. yttria intimately intermixed), we should be able to determine the compositionally dependent rate of coalescence. From these measurements

and a model of diffusion-limited coalescence, the diffusion coefficient for the diffusing species can be extracted.

The experimental data generated under this program will be used to evaluate existing coalescence models. As a starting point we will consider the viscous flow model of Frenkel and its modifications recently published by our group (Garabedian and Helble, 2001); the lattice diffusion model of Kuczynski; the exponential long-time viscous flow model will also be examined. Depending upon the results of this exercise, other models may be considered. Bonevich and Marks recently studied sintering of 50 nm alumina clusters and concluded that surface diffusion dominates for particles of this size. Because of the mobility of surface atoms in surface-diffusion controlled processes, they speculated that trace impurities would significantly increase the diffusivity and the sintering (coalescence) rate. Lattice diffusion was expected to become dominant for larger (order 1  $\mu\text{m}$ ) particles, but no information on the transition region important to combustion-derived aerosols was provided. Volume diffusion coalescence times scale as  $x^7/r_0^3$  or, for  $x$  approaching  $r$ , as  $r^4$ . The dependence on physical properties scales the same for both lattice and surface diffusion mechanisms. *Relative* coalescence time differences among materials should therefore remain the same under diffusion control regardless of the mechanism; this is something we will explore in examination of our data.