TAILORED NANO-STRUCTURED COATINGS *via* LII-CONTROLLED FLAME SYNTHESIS FOLLOWED BY 'RESONANT IMPACTION'

NSF Functional Nanostructures Grant 9871885

D. E. Rosner(PI), **J. Fernandez de la Mora**, **M.B. Long**, and **W. Tong**
Yale University, Departments of Chemical and Mechanical Engineering; NSF Grant CTS-9871885

The premise of this pilot NSF program is that *aggregation* in high-yield flame synthesis nano-particle reactors is no impediment to ultimately forming useful (dense, nano-structured) coatings, so long as flame conditions are controlled to preclude strong inter-spherule bonds. We believe that this *can* be accomplished, and such "weakly bonded" aggregates can be gas-dynamically accelerated and broken up upon high velocity impact. Toward this end, our program has focused on obtaining the requisite fundamental understanding in 4 key areas, briefly summarized below:

1. Aggregation and Sintering in Well-Defined Inorganic Nano-Particle Synthesis Flames (D.E. Rosner)

We have obtained, and are currently exploiting, a rather complete set of data on *alumina* nano-aggregate population evolution using a "seeded" counterflow laminar diffusion flame reactor with laser-based optical- as well as TEM grid thermophoretic sampling (Xing *et al*., 1999). Currently, we are developing tractable simulation tools to predict this population evolution both using presently available rate/transport laws (for aggregate coagulation frequency, thermophoresis and sintering (in terms of the state variables: particle volume, v and surface area, a), as well as rational improvements, currently under development). Our bivariate simulation methods (Rosner and Pyykonen, 2001), the simplest of which is equivalent to a 9-moment method, will also lend itself to future parameter estimation; *eg.,* inferring a "best-fit" activation energy for alumina nano-particle sintering by, say, surface-diffusion (see, *eg.,*Xing and Rosner,1999).Variants/extensions of these simulation techniques should also enable incorporation into, say, full *PDF*-methods for *turbulent* synthesis reactors of industrial interest.

2. Use of LII and LLS for Real-Time *In-situ* Suspended Nano-Aggregate Characterization (M. B. Long, A. Schaffer, A. Filippov and D.E. Rosner)

While angle-dependent "elastic" laser light scattering (LLS) provides local, *in situ* information on the state of nano-particle *aggregation* in well-defined flame environments (Xing, *et.al*.,1999), it is now clear that, when combined with *time-resolved laser-induced incandescence* (LII), it is also possible to obtain *spherule sizes* in atmospheric pressure flames. This has been demonstrated using 532 nm Nd-YAG pulses of *ca*. 8 ns duration to size absorbing spherules in the *ca*. 20 nm diam. range, provided the dispersity of the spherule population is sufficiently narrow (Schaffer *et.al*.,2001). Adequately narrow distributions of alumina spherules *have* been observed in our counterflow laminar diffusion flame experiments, but since alumina is only weakly absorbing at 532 nm, we have been optically and thermophoretically probing *iron oxide* nano-aggregates in flat premixed flames at temperatures below 1600K. In a promising recent development, it appears that it may not only be possible to do time-resolved LII spherule *sizing* at low laser fluences (say, below 0.02 J/cm^2), but that there is simultaneous LLS-evidence for *laser-induced aggregate break-up* (LIABU) at somewhat higher laser fluences (but well below the apparent spherule vaporization threshold). These observations may provide us with an additional (on-line "optical") way to characterize the apparent *interspherule bonding* in such flame-produced nano-aggregate structures (*cf.* Section 3, below). The

interpretation of further LIABU measurements will be initiated in the remaining 7 months of the present NSF program.

3. Threshold Conditions for Impact-Breakup of Well-defined Aggregates
(J. Fernandez de la Mora)
This task involves: (a) developing techniques to produce well-defined aggregates, (b) studying their collision against a surface at controlled velocities, and (c) EM analysis of the impact products. Task (a) has been completed. Available mono-disperse nano-spheres of a desired material are suspended in a highly conducting liquid and electro-sprayed into drops of predetermined size, containing 1, 2,..., n, suspended spheres. The liquid and salt in the drops evaporates, leaving compact aggregates. While the *spherule* diameter is thereby fixed, spraying produces a distribution of *cluster* sizes. Figure 1a shows a DMA-derived *mobility distribution* of such clusters. Since multiple charges have been eliminated by neutralization, the measured mobility is simply related to aggregate size, with the left-most peak corresponding to one sphere (here the protein lysozyme), etc., so that the n^{th} peak is known unambiguously to contain n primary spheres (or globules). While individual peaks cannot be distinguished beyond *ca*. n=12 (due to the finite size-spread of the starting spheres) a simple relation between aggregate mobility and n (*cf* Fig 1b) allows selecting larger clusters with known n-values (with essentially no upper limit). This procedure applies to other proteins, with molecular masses, M, from 14 to 44 kDa, and other materials, including: chain polymers (*eg.,* poly-ethylene glycol (4<M<120 kDa), and multi-branched spheroidal polymers ("dendrimers"; 3.3 <M< 28 kDa). We will investigate as many sphere types as monodisperse samples become available.
Task (b) is currently being carried out using a *hypersonic impactor*. Here the jet formed by expansion of a carrier gas accelerates the mobility-selected aggregates, whose impact velocity can be controlled up to *ca*. 1 km/s. A new impactor was installed/calibrated in Fall 2000 for diameters down to 16 nm. We are currently extending the calibration down to *ca.* 4 nm, and will start impacting some of the clusters described. Our first candidates will be dendrimers (with intra-sphere bonds much stronger than the interspherule forces).

4. Characterization of "Nanostructured Coatings" (C. Xie (GRA) and W. Tong)
This task is concerned with developing new methodologies to characterize nano-scale film coatings, including fracture strength and strength of the coating-substrate interface. A reliable and consistent measurement of these properties is critical to control/improve thin film coating processing technologies. Essential aspects of our methodology include (a) *in-situ* tensile testing of plastically deformed coated substrate under an optical microscope, SEM and AFM, and (b) a nonlinear finite-element analysis of such coating-substrate systems. As an illustration, we have successfully studied nano-scale anodic oxide coatings (10-300 nm)) on aluminum alloy substrates, with results presented at the *Int. Conf. Metallurgical Coatings and Thin Films* (April10-14, 2000, San Diego,CA) and the *SEM IX Int. Congress Exp. Mechanics* (June 5-8, 2000, Orlando, FL). A paper: "Fracture of Nano-structured Thin Film Coatings" is being prepared for *Acta Materialia.* This sub-Task includes developing experimental capabilities for characterization, internal stress measurement, and annealing of nano-particle- and nano-structured coatings. With the help of two NSF equipment grants we have added to our materials research lab:(a) a Phillips XL30 SEM with energy dispersive chemical analysis(EDS), crystal orientation imaging microscopy (OIM) and micro-tensile test capabilities; and (b) dual X-ray diffractometers (Shimadzu XRD-6000, and Bede D1). A preliminary study of the effects of annealing of initially amorphous nano-scale oxide films on a Si substrate on their crystallization kinetics is currently underway.

References Cited

Filippov, A.V., Zurita,M. and Rosner, D. E.,"Fractal-like Aggregates: Relation Between Morphology and Physical Properties", *J. Colloid Interface Sci*., **229**, 261-273 (Sept. 2000); see, also: "Drag and Torque on Clusters of N Arbitrary Spheres at Low Reynolds Number ", *ibid.*., **229**, 184-195 (Sept,. 2000)

Fernández de la Mora,J. de Juan, L. , Eichler,T. and Rosell, J. "Differential Mobility Analysis of Molecular Ions and Nanometer Particles",*Trends in Anal. Chem.*, **17**, 328-339, (1998)

Fernández de la Mora, J., Hering, S.V.,. Rao, N. and McMurry, P. "Hypersonic Impaction of Ultrafine particles", *J. Aerosol Sci*., **21**, 169-187 (1990).

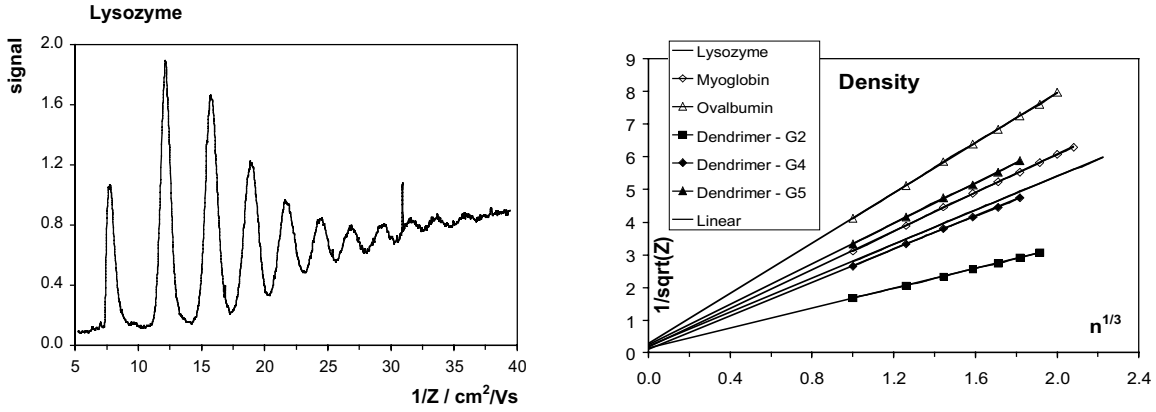
Gamero-Castaño, M. and Fernández de la Mora, J. "Mechanisms of electrospray ionization of singly and Multiply Charged Salt Clusters", *Analytica Chimica Acta*, **406**, 67-91, (2000)

Rosner, D.E. and Pyykonen, J.J., "Bi-variate Moment Method Simulation and Measurement of Populations of Coagulating and Sintering Nano-particles in Laminar Diffusion Flames", *AIChE J.* (to be submitted, Feb.2001; see, also: Rosner, D.E,*et.al*.: "Relevant 'Mixed'-Moments for the Calculation of Deposition, Vapor Scavenging, and Optical Properties for Populations of Non-spherical Suspended Particles", Paper #10g in *Proc. AIChE 2000/Fourth Internat. Particle Technology Forum*,(CD format), November 2000

Rosner, D.E.: ***Transport Processes in Chemically Reacting Flow Systems***, Dover Publications, Mineola NY, September 2000; ISBN/Dover # 0-486-41182-6

Schaffer,A.,Long, M.B., Filippov,A.V. and Rosner D.E., "Nano-particle Sizing in Atmospheric Pressure Flames Using Time-Resolved LII", (in preparation, Feb. 2001)

Xing, Y., U.O. Köylü, and D.E.Rosner. "*In situ* Light-Scattering Measurements of Morphologically Evolving Flame-synthesized Oxide Nano-aggregates", *Applied Optics* **38**, 2686-2697 (1999); see,also: Xing, Y. and D.E. Rosner, "Prediction of Spherule Size in Gas Phase Nanoparticle Synthesis". *J. Nanoparticle Res*. **1**,1-15 (1999)



Part 2; Figure 1: Mobility spectra of aggregates from 1 to 12 lysozime globules (left), and relation between mobility and degree n of clustering for the various aggregate types investigated (right).

Prepared for *Proc.* ***Jan 29-30, 2001 NSF Nanotech Grantee Conference:*** *'Partnership in Nanotechnology'* (Arlington,VA)