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Chapter 7

Conclusions and Recommendations

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Flame synthesis is a very attractive route for industrial production of nanophase materials. However, contamination and agglomeration of the starting particles are serious drawbacks for this technique. These problems are addressed in this work by using the particle encapsulation method originally proposed by Axelbaum, et al.[26] The basic approach of the particle encapsulation process is to allow the nucleation and growth of the primary particles to proceed normally but then coat these particles, with an appropriate material, when they have grown to the required size and before they begin to agglomerate, thus producing encapsulated particles. These particles will agglomerate, but the primary particles within them will not. When the coating is later removed, the resulting powder will contain only weakly agglomerated particles. During subsequent handling, the encapsulation protects air-sensitive nanophase particles like W and Ti from oxidation or contamination.

This work has demonstrated the use of the encapsulation method by synthesizing unagglomerated nonoxide tungsten (W) and tungsten titanium (W-Ti) nanosized particles in a sodium/halide flame. This work also has provided substantial insight into understanding the encapsulation process by numerically simulating the dynamics of particle formation in combustion aerosols through the Markov-MC method developed in this work as well. The Markov-MC method is a general technique to simulate particle dynamics in two-component aerosol subject to simultaneous nucleation, condensation, and coagulation. A summary of the main conclusions obtained during the development of this work follows.

1. Synthesis of nanosized W, Ti, and W-Ti particles by flame synthesis

High-quality nanosized W, Ti, and W-Ti nanoparticulates were produced and consolidated to demonstrate the applicability of the flame synthesis process to produce nanosized materials and of the encapsulation method to control purity and agglomeration of nanosized particles.

Nanoparticulates of W, Ti, and W-Ti were synthesized by a gas-phase combustion process employing exchange reactions between sodium and metal chlorides. The sodium/halide

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chemistry is exothermic and has thermodynamic yields of 100% for T < 1250°C. To minimize agglomeration and protect the particles from contamination during subsequent exposure to atmosphere, the NaCl by-product was condensed onto the particles within the flame. Gaseous reactants were introduced into an open atmosphere burner forming a coflow diffusion-flame. Several runs were made to optimize the characteristics of the produced powder.

The collected powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). XRD was used for phase identification of bulk powder samples and to obtain information about the size of the nano-crystallites using the X-ray line broadening method (i.e., the Scherrer formula). SEM and TEM studies of the powders were carried out to determine particle size. Elemental composition was determined by energy disperse X-ray analysis (EDAX). Powders were exposed to atmosphere and XRD characterization studies were performed in open atmosphere.

Nanocrystalline W particles were produced by reacting Na and WCl_6. The W particles appear unagglomerated, cubic and hexagonal in shape, and have an average size of ca. 30 nm. XRD results indicate the presence of only α-W, β-W, and NaCl. No contamination is detected even after extended exposure to atmospheric conditions. Vacuum heat treatment of the powders at 800°C results in effective removal of NaCl with no detectable change in particle size. The heat treatment also transforms the β-W phase to α-W.

A nanopowder consisting of W-Ti was also produced via $Na/WCl_6/TiCl_4$ chemistry. XRD spectra of as-produced powders show only W and NaCl. EDAX indicates the presence of Ti, and analysis of lattice parameters suggests that part, not all, of the Ti is in solid solution. Particles are unagglomerated, cubic in shape, with an average size of ca. 30 nm. Heat treating the sample at 850°C increases average particle size to ca. 40 nm. When the amount of Ti is increased to 22 wt%, XRD spectra of as-produced powders show small peaks of α-Ti and β-Ti, in addition to W and NaCl.

The nanocrystalline W and W-Ti powders were successfully consolidated into pellets of 6 mm diameter and 6–8 mm long. Densities as high as 97% were achieved by hot pressing and hipping at temperatures of $0.42T_m$ to $0.48T_m$. Microstructures of the consolidates consist of nanometer-sized grains (40 nm). Hardness measurements indicate hardness values 4 times that of conventional tungsten.

To investigate the effectiveness of different methods of removing the NaCl from the as-produced samples, heat-treated and water-wash samples were analyzed for Na and Cl. Na was determined by ICP-atomic emission spectroscopy and Cl by ion chromatography. When the sample was heat treated at 850°C for 10 h, results showed 0.025 wt% residual Na and 0.02 wt% residual Cl, indicating that the salt encapsulation can be effectively removed. Similar elemental analysis tests have shown the effectiveness of the NaCl encapsulation method protecting the powder from contamination. AlN was synthesized with an 0_2 content <0.8 wt %, while traditional methods offer AlN with oxygen content >5 wt%.

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2. Monte Carlo simulation of two-component aerosol processes

To gain insight into the understanding of the particle encapsulation method, a code to simulate particle formation in two-component aerosols has been developed. The simulation is carried out using a Monte Carlo technique. This approach allows for the combination of probabilistic and deterministic events. Thus, the nonlinear terms of the general dynamic equation (GDE) were Monte Carlo simulated, and the other more workable terms were solved analytically and incorporated into the model. To simulate coagulation, a uniform mixture was assumed and only collisions were simulated, not in the physical sense but as a transition in a Markov chain. The model includes nucleation, condensation, coagulation, sources, and sinks for two-component aerosol processes. The Kelvin effect and particle heating due to condensation have been included in the model as well.

The code is general and does not suffer from problems associated with numerical dispersion, mass conservation, and approximations on particle composition. It has been validated for the case of constant temperature, constant collision frequency, and initially monodisperse aerosols where only coagulation is important and where there is an analytical solution to the GDE. Table l compares the Markov-Monte Carlo (Markov-MC) method with the sectional method. From here it can be concluded that the Markov-MC method offers important advantages and is an attractive tool to study particle dynamics in two-component aerosols.

Method	Markov-MC	Sectional
Solution	Probabilistic Simulate collisions as a transition is a Markov chain. Nucleation and condensation are solved analytically and couple with coagulation through time.	Deterministic Solve m ODEs, where m is the number of sections
Assumptions	Within a size-composition section, particles assume same dynamic mean size and same dynamic mean composition	Within a size section, particles have same constant size and constant composition
Best application	Very short timescales Combustion aerosols	Very large timescales Atmospheric aerosols
Relative Advantages	• Higher resolution in size and time • Easy to incorporate new phenomena	• Deterministic solution
Weaknesses	• Probabilistic approach	• Numerical diffusion • Problems associated with mass conservation • Problems handling simultaneous condensation and coagulation

Table 1. Comparison of the Markov-MC and Sectional numerical methods.

3. Numerical simulation of the particle encapsulation process

The Markov-MC method was applied to M/NaCl/Ar combustion aerosols to study the particle encapsulation process. This type of aerosol is formed during the production of nanosized powders in sodium/halide flames and is composed of M, NaCl, and Ar, where M is a metal or ceramic. The aerosol is characterized by very high particle concentrations (~10^{18} particles/m^3) and high temperatures (>1000°C). Furthermore, the M/NaCl/Ar aerosol is a two-component aerosol, since both M and NaCl are condensable phases.

Particle formation in flames is affected by many factors that make a complete analysis of this process extremely complicated. Particle dynamics, chemical kinetics, heat and mass transfer fields are some of the factors that affect the final product. Despite these complications, considerable insight was gained by focusing attention on aerosol dynamics alone and considering the burner as an idealized plug flow reactor in which the relevant gas-phase chemistry and transport are decoupled from the particle dynamics. This can be done since the characteristics of the final particles, for example, size distribution and morphology, are primarily affected by coagulation and condensation, i.e., by aerosol dynamics.

Particle dynamics in M/NaCl/Ar aerosols involves the formation and growth of M and NaCl particles by nucleation, condensation, and coagulation. Since NaCl is the more volatile material, encapsulation of M particles occurs, either directly when the NaCl vapor condenses onto the M particles producing NaCl-coated M particles, or indirectly when uncoated particles coagulate with the coated particles. Since the encapsulation process is not directly affected by nucleation of M, it was assumed that nucleation and condensation of M has been completed before the onset of NaCl condensation. An initial size distribution for M was assumed, and the evolution of the aerosol subject to coagulation and condensation was modeled. The modeling reduced to solving the governing equation through the Markov-MC model under appropriate assumptions and conditions. The main assumptions and conditions are about the morphology of the particles, the effect of temperature during the condensation process, and the working regime.

3.1. Particle spheroidicity

Particle sintering is a strong function of particles size and temperature. It was found that for 800°C < T < 1400°C, Ti and W particles smaller than ~50 nm in radii sinter within a period of time much shorter than the shortest scale in the process. Then sintering can be assumed instantaneous and particles spheroidicity at any time during the simulation. Based on this results, particles were assumed to be made of a M core coated with NaCl.

3.2. Constant temperature during condensation

A heat transfer model was developed to evaluate the increase in particle temperature and gas-phase temperature due to latent heat release during NaCl condensation. It was shown that for the CR the increase in particle temperature is negligible, but in the FMR it is substantial. For NaCl condensation at 1100°C it was found that the increase in temperature is upto ~37°C for

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S = 1.5. Furthermore, it was found that the rate of condensation when particle heating effects are included is about 4 times less than when particle temperature is assumed constant. These heating effects were included in the model.

3.3. Working regime

For typical experimental conditions of M/NaCl/Ar aerosols, 0.01 < Kn < 10.0. Therefore, the well-known Fuchs-Sutugin correction factor for condensation and coagulation in the transition regime was included. Implementation of more accurate correlation of more accurate correlation is straightforward.

This study was intended to allow for an understanding of the dominant mechanism involved in the nano-encapsulation process and to demonstrate the usefulness of the model in studying two-component aerosols. Two cases were considered: constant temperature and constant heat loss. The constant temperature case was considered to introduce the salient features of nano-encapsulation, nonetheless, heat loss which is intrinsic to most flame systems, was shown to be of fundamental importance in controlling nano-encapsulation.

The results were not expected to yield quantitative agreement with experiments because the flame has a complex 2D structure and the aerosol was assumed to be uniform and evolving with time. Nonetheless, we expect the model to elucidate the essential features of nano-encapsulation. The system of Ti through the Na/Cl/Ti/Ar chemistry was used as a case study.

3.3.1. Encapsulation at constant temperature

The constant temperature condition applies to very diluted aerosols or to systems where the rate of latent heat release can be dissipated as it is generated. As an initial study, a case where a sudden encapsulation occurs in the preexisting aerosol was considered. The aerosol is subjected to a step change in saturation ratio as might be experienced in flames, expansion shock waves, mixing, or sudden drops in temperature. The main characteristic of the evolution of the aerosol is that because of the high number density, condensation is extremely fast and only a small fraction of the tail of the size distribution is coated. Since r* grows as S decreases, the largest particles receive most of the subsequent coating and smaller particles remain uncoated, until they collide with coated particles. Better conditions for encapsulating the particles are obtained when both the time prior to the onset of heterogeneous condensation and the drop temperature are maximized. Maximizing the time prior to condensation, coagulation ensures larger particles and lower particle concentration. Maximizing the drop in temperature, the mass vapor available for encapsulation increases. The combined conditions seek to maximize the mass of condensable material per particle in the aerosol. The upper limits for these time and drop in temperature are the onset of formation of agglomerated structures and the onset of homogeneous nucleation, respectively. However, the extremely high number densities in flames (N~1O^{18} particles/m^3) make this process impractical because the timescale for coating is microseconds. Thus, the step change in T would have to occur on a submicro-second timescale.

Another drawback of this encapsulation alternative is that it only uses a small fraction (100(S-1)%) of the entire mass of the condensable material to encapsulate the particles. Since for condensation to occur, S = l is the lowest value of S, in constant temperature aerosols, most of the condensable material remains indefinitely as vapor, i.e., S = l at the flame temperature gives the lowest possible vapor pressure. The total mass of the condensable material can be used to encapsulate the particles by controlling the rate of cooling of the aerosol such that only heterogeneous condensation occurs during the entire process.

3.3.2. Encapsulation at constant heat loss

In practice, the environment downstream the flame zone is not at constant temperature. Radiative and convective heat loss can result in substantial heat loss from the aerosol. Heat loss is quite beneficial to nano-encapsulation as can be understood by considering the two concerns discussed above when temperature is constant. First with heat loss, r* reduces as temperature reduces. This allows more particles to be directly coated. Second, with the resulting decrease in temperature, virtually all the condensable vapor eventually condense out. Several outputs from pure coagulation were taken as the initial conditions just prior to condensation, and the evolution of the aerosol subject to heat loss was observed. A rate of heat loss of 10^{-6} W/m^3 was used. Heat loss of 10^{-6} W/m^3 is high but reasonable for these heavily particle-laden flames. The results show that by cooling the aerosol, a fraction of the particles in the aerosol are initially coated and a small fraction of these particles contain most of the condensable material. For a given mass of aerosol and a given heat loss rate, the number of particles initially coated is maximized by decreasing N. When N decreases, particle size increases but the surface area for condensation is smaller. Since the latent heat release is the same, the number of particles initially coated is approximately the same. However, the percentage of the particles being coated increases. For any desired value of $r_{m,}$ ~80% of the particles are initially coated by controlling the concentration of the reactants such that N~10^{14} particles/m^3 for the chosen r_m. However, this alternative limits the production rate and requires high levels of reactant dilution for small core particle size. Greater percentage of coated particles can be obtained by increasing the rate of heat loss. This alternative, however, has physical constrains, and therefore is not feasible.

When the condensable vapor has been depleted, condensation ceases, and coagulation after condensation is the dominant process. During this time period, indirect encapsulation of the particles occurs via coagulation of the coated particles with the uncoated particles. The results from previous runs were taken as initial conditions, and the evolution of the aerosols was observed. Temperature was held constant at 800°C. Results show that the number of particles being encapsulated as a function of time has an exponential behavior with 90% of the particles being encapsulated within the first ~400 ms. This shows that coagulation after condensation ensures that most of the particles are encapsulated within a time period comparable to the typical experimental residence times(>1 s).

Results for M/NaCl/Ar aerosols under typical experimental conditions showed ~10^{14} particles/m^3 of total size r~300 nm. Assuming that the particles within the NaCl matrix collide and sinter, as expected in the case of Ti, the core size obtained was r~45 nm. These results are in qualitative

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agreement with experimental results where it was obtained particles of total size r~150 nm with single cores of size r~35 nm. On the other hand, assuming that the particles within the NaCl matrix remain separate, the number of cores within the NaCl matrix depends on the particle mean size prior to condensation. For example, if the mean size is r~20 nm, every particle contains ~10 cores. This again is in qualitative agreement with experimental results for the case of AlN, where ~10 AlN particles of ~24 nm per NaCl particle have been observed. Similar agreement was found for the case of TiB_2, where it hundreds of Ti cores within every NaCl particle have been observed.

Only qualitative agreement has been found between the Markov-MC simulations and the experimental results due to the strong simplifications made, and the lack of accurate temperature and species concentrations profiles in sodium/halide flames. The main simplifications were introduced when a 1D problem was assumed and particle dynamics decoupled from chemistry and flow field. The results presented have shown the ability of the Markov-MC model to simulate particle dynamics in two-component aerosols and have provided insight into the understanding of the particle encapsulation process by exploring the different alternatives where the encapsulation process is feasible and the alternatives to optimize it.

4. Recommendations

Further work is required to address the following issues:

- W and W-Ti production rates.

A laboratory-scale laminar sodium/halide flame was used here to synthesize W and W-Ti nanoparticles. The production rates were ~2g/h. Further work is required to increase this production rate up to ~20 kg/h. This can be done by operating the reactor in turbulent regime. Operating in turbulent regime, the turbulence mixes the reactants uniformly and therefore the amount of excess Na required in laminar flames to ensure 100% yields can be reduced. Besides optimizing the use of raw materials, this approach will reduce the presence of Na in the products, and consequently the possibility of contamination of the primary particles. Na reacts with the water in the atmosphere to produce sodium hydroxide (NaOH), which dissolves the NaCl protective coating, leaving the primary particles directly exposed to atmospheric conditions. Furthermore, the flame temperature will be higher since the reactants are in proportions closer to stoichiometry. With higher temperatures, primary particles have longer times for coagulation prior to the onset of condensation, and therefore N will be smaller. This condition favors the number of particles being coated during the condensation process. Other potential advantages of this approach are the lower energy required per gram of primary material produced, and the presence of more uniform aerosols. However, since the high of turbulent flames is larger the laminar ones, it is required to protect the particles at the exit of the burner from atmospheric entrainment with long heated extensions. It is also advisable to operate the burner upside-down to alleviate the clogging at the exit of the burner.

- Mechanical properties of the W and W-Ti consolidates.

A complete evaluation of the mechanical properties – both at static and at high rates of deformation – are required. The results of this characterization will lead to optimizing the different steps during the production of these materials, and thus their properties. The mechanical properties at high strain rates of the consolidates can potentially be improved by using starting powder of smaller size. It is believed that when the grain size approaches 1O nm in diameter,the material reaches its maximum strength. In addition, the idea of mixing pure nanosized W with pure nanosized Ti in the right proportions instead of simply consolidating W-Ti nanosized powder could be explored. With this approach, during consolidation Ti will constitute the desired soft matrix for the embedded W nanosized grains. Ti will diffuse into the W grains forming a shell of W-Ti in the outside of the W grains. This structure seems to be better that having the Ti in solid solution uniformly within the W grains.

- Alternative to demonstrating the effectiveness of the NaCl coating.

During this work, the particle encapsulation process was proven to be effective in controlling agglomeration and protecting the nanosized powder from contamination. Another alternative to demonstrate the benefits of the encapsulation process is to produce, under the same conditions, a given material with and without NaCl encapsulation. This can be done by reacting the respective halide with hydrogen to produce HCl gas. Besides providing a base for comparison, this experiment will be illuminating about the morphology of the particles. For example, the size of the particles prior to agglomeration will be observed. It has been postulated that the size of the particles in agglomerated structures depends only on the physical properties of the material and not on the synthesis process. Furthermore, the effect of the encapsulation over the particle size distribution will also be observed.

- Interactions of the condensable material with the core material.

The effect of the interactions of the condensable material with the core material on the rate of condensation requires further studies. Situations where, for example, a metal is encapsulated within another metal or a ceramic could have very different behaviors to that described here for NaCl and Ti.

- Re-evaporation.

The Markov-MC mode1 requires to inc1ude evaporation processes. Even though this is a straightforward step, it has not been included yet. The rate of decrease in particle size during evaporation is given by [98]:

$$\frac{dr}{dt} = \frac{4DM}{Rr\rho}\left(\frac{P_\infty}{T_\infty} - \frac{P}{T}\right)\left(\frac{\lambda + r}{2r + 5.33\left(\frac{\lambda^2}{2r}\right) + 3.42\lambda}\right) \tag{1}$$

where r is the size of the partic1e, the subscript ∞ refers to conditions removed from the partic1e and the other variables are evaluated at the particle surface. The 1ast factor in Equation 1

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corrects for diffusion in the transition regime. For vo1atile particles such as water or alcohol, a correction must be included for the cooling of the droplet due to rapid evaporation. This se1f-cooling effect reduces the drop1et temperature and, consequently the partial pressure at the drop1et surface. Equation 1 also needs to be corrected to inc1ude the Ke1vin effect. It is anticipated that inc1uding re-evaporation processes, the results obtained during the deve1opment of this work would not be substantially different. The number of partic1es being coated during condensation will decrease and the coated partic1es will have heavier coatings.

- Prob1em associated with condensation.

As already observed, during condensation at constant heat loss, a 4-modal distribution was obtained. The presence of these four modes was attributed to the change in the rate of bulk condensation or to artifacts of the Markov-MC model. The issue remained unresolved even when the same results were obtained for higher reso1utions and denser grids. Since the particle ordering principle as discussed earlier is followed by most of the combustion aerosols, a moving grid will resolve this issue. The advantages of the Markov-MC model will still prevail and the implementation of the moving grid for condensation coupled to the Monte Carlo simulation of coagulation is straightforward.

- Compatibility of the Markov-MC model with other codes.

The Markov-MC model has the potential of being incorporated into time step marching codes that model the fluid-dynamics and the chemistry of flames. The possibility of producing general (universal) solutions to the evolution of aerosols subject to coagulation and condensation needs to be explored, since this type of solution will greatly simplify the modeling of aerosols where the flow field, chemistry, and particle dynamics are simultaneously important.

- Application of the Markov-MC model to other aerosol problems.

During this work, the Markov-MC model has been applied to combustion aerosols, which are characterized by high number densities, high temperatures, and high rates of condensation. However, the Markov-MC model is general and can be used to study other aerosol problems. For example, the modeling of atmospheric aerosols is an important application where the model can be exploited.

- Optimization of the code.

Relatively little effort has been put into optimizing the Markov-MC code. Several subroutines can be improved to reduce the computational time. Furthermore, a methodology to improve the code efficiency can be generated, where coarse solutions are produced first and finer solutions later. This methodology provides an additional mechanism to ensure that the grid and statistics used during the simulation are enough for accurate solutions.

- Markov-MC simulation of particle encapsulation process.

Experimental validation of the results obtained by Markov-MC simulating the evolution of M/NaCl/Ar aerosols and the particle encapsulation process is required. This step has several complications because of the nature of the sodium/halide flames. The presence of sodium limits

the use of the typical experimental optical tools to study flames. The high temperatures and the very high number densities in sodium/halide flames make the information obtained through the use of thermocouples and aerosol samplers of little relevance. Furthermore, the numerical results were obtained for the equivalent 1D plug flow reactor, while the laminar sodium/halide flame has complicated 2D flow field. However, a qualitative validation can be obtained by exploring extreme conditions. For example, maintaining the aerosol at constant high temperature for very long periods of time will provide information about the effect of NaCl coating on the particle size distribution and particle morphology. Having a very diluted aerosol will provide information about the effect of the number density on the fraction of particles that can be encapsulated.

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