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Introduction

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1. Nanophase materials

More than 30 years ago, Nobel Prize–winning physicist Richard P. Feynman mused that in the future, when scientists have learned how to control the arrangement of matter on a very small scale, they would see materials take on an enormously richer variety of properties. [1] In recent years, considerable attention was focused on the production of these materials, so-called *nanophase materials*. These materials, also referred to as nanostructured, nanocrystalline, or nanometer-sized crystalline solids, are single-phase or multiphase polycrystals, with dimensions of the order of 1–100 nm. [1] They can be classified according to the number of dimensions of the grain in the nanometer range as shown in Table 1. A general review of nanophase materials is found in References 2 and 3.

Dimensionality	Designation	Typical method of synthesis
3D	Crystallites (equiaxed)	Gas condensation
2D	Filamentary	Chemical vapor deposition
1D	Layered (lamellar)	Electrodeposition

Table 1. Classification of nanophase materials.

Compared to conventional materials, nanophase materials possess unique advantages with respect to properties and processing. [4] As grain size decreases down to the nanometer-size range, nanophase metals generally get stronger and harder, while nanophase ceramics show ductility, even superplasticity, at lower temperatures than conventional brittle ceramics. For example, 1000% increase in fracture stress, 2000% increase in magnetic susceptibility, 25% decrease in density, and 165% improvement in critical temperature for superconductivity have been observed in nanophase metals. [5] As an example, Figure 1 shows the stress–strain curve for a) nanophase (14 nm) Pd sample compared with that for a coarse-grained (50 μm) Pd sample and b) nanophase (25 nm) Cu sample compared with that for a coarse-grained (50 μm)

Cu sample. [6] It shows that the yield stress for nanophase materials for these two materials is higher than the conventional material.

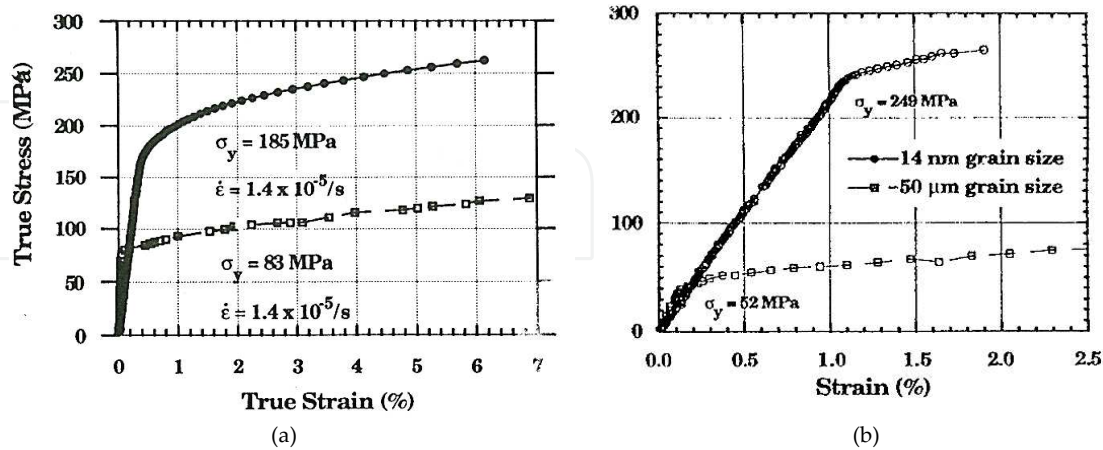


Figure 1. Stress–strain curve for a) nanophase (14 nm) Pd sample compared with that for a coarse-grained (50 μm) Pd sample, and b) nanophase (25 nm) Cu sample compared with that for a coarse-grained (50 μm) Cu sample. [6]

These unique properties arise because of the dramatic grain refinement and the novel characteristic of grain boundaries. Nanophase materials contain a high concentration of grain boundaries with random orientation, and consequently a substantial fraction of atoms lies in the interfaces. For example, when grain size is about 5 nm, there are approximately 10^{19} boundaries/ cm^3 with random orientation and 50% volume fraction of atoms at the interfaces. The volume fraction decreases to about 30% for 10 nm grains and to about 3% for 100 nm grains. Figure 2 is a schematic representation of a nanophase metal. [7]

The increase in strength of nanophase materials stems from the smaller grain sizes, which cause a change in the fundamental mechanism of plastic deformation. In conventional metals, the fundamental mechanism is dislocation migration, [8] where rows of missing atoms within the lattice (dislocations) migrate in the direction opposite of an applied stress. The result of this migration is that dislocations pile up on one side of the grain, and thus the grains themselves are deformed. The ease of migration of these dislocation lines is related to the length of the dislocation line; longer lines migrate more readily than shorter lines. [9, 10]

In conventional metals where grain sizes are large, these dislocation lines are very long and consequently can migrate readily. In nanocrystalline materials where grain sizes are very small, the dislocation lines are very short, and do not migrate readily. Dislocation migration is then effectively shut down as a mechanism of plastic deformation in nanocrystalline materials. Grain boundary sliding becomes the active mechanism of deformation in nanocrystalline materials. This mechanism of plastic deformation does not cause deformation of the individual grains. It is a higher-energy mechanism of deformation, yielding increased strength in nanocrystalline metals, and for nanophase ceramics it provides a mechanism for plastic deformation that formerly was not present. The increased ductility in ceramics can be attributed to grain boundary sliding and the higher rates of atomic diffusion in the less dense grain boundaries as compared to the crystalline grains.

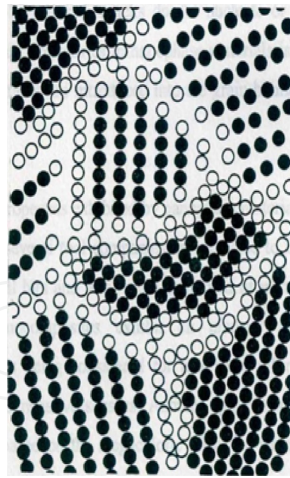


Figure 2. Schematic representation of an equiaxed nanocrystalline metal distinguishing between the atoms associated with the individual crystal grains (filled circles) and those constituting the boundary network (open circles). [11]

The improved fracture toughness of nanophase materials is related to the increased grain boundary fraction. Fracture toughness is defined as the ability of a material to resist cracking. Cracks nucleate in areas of stress concentration, which includes areas where dislocations pile up. If stress concentration sites can be relieved, cracks do not nucleate or propagate. The advantage of the increased number of grain boundaries in nanophase materials is that the stress concentrations are relieved because dislocations are introduced into the grain boundaries more quickly, and therefore they do not pile up.

The high-performance properties exhibited by nanophase materials have important implications for industry. For example, several tool companies are expected to introduce stronger, tougher, long-lasting cutting tools, drill bits, and wear parts composed of ultrafine grain cobalt/tungsten carbide composites. Some nanocomposites exhibit an unusual magnetic behavior called “giant magnetoresistance,” which is being considered for read/write information in storage devices and to make improved magnetoresistive sensors. Another application under consideration is solid-state magnetic refrigerators based on the magnetocaloric effect by which heat is reversibly absorbed and discharged when small ferromagnetic particles are aligned by magnetic fields. In addition, unusual magneto-optical characteristics of nanostructured iron oxide are expected to be applicable for high definition color copiers. [12] Production of nanophase materials typically involves two steps: powder preparation and powder consolidation. To better appreciate the required specifications of the starting powders, we will consider powder consolidation first.

2. Consolidation

Advanced materials are processed in a manner similar to traditional ceramics, i.e., by compacting and firing powders as illustrated in Figure 3. The process that often follows powder

preparation involves dispersing the powders in solution by adding organic polymers or surfactants. These highly concentrated suspensions are called slurries, or slips.

The final shape of the material is given when the slurry is either poured in a form (slip casting), spread onto a smooth surface (tape casting), or coated on a support. It is currently recognized that powder packing, which occurs during this stage, determines the structures that develop during sintering. After drying, the material (called “green” before firing) is sintered at a temperature and pressure that depends on particle size, composition, and sintering aids. Nanophase materials must be compacted and sintered at temperatures low enough to prevent grain growth and at the same time high enough so that sufficient sintering occurs to form dense, uniform polycrystalline materials. Typically, nanophase powders are consolidated by vacuum hot pressing or hot isotactic pressing at 600–1400°C and 70–210 MPa for 1–4 h. [13, 14] Figure 3 summarizes the evolution of the structure from the powder state to the sintered material.

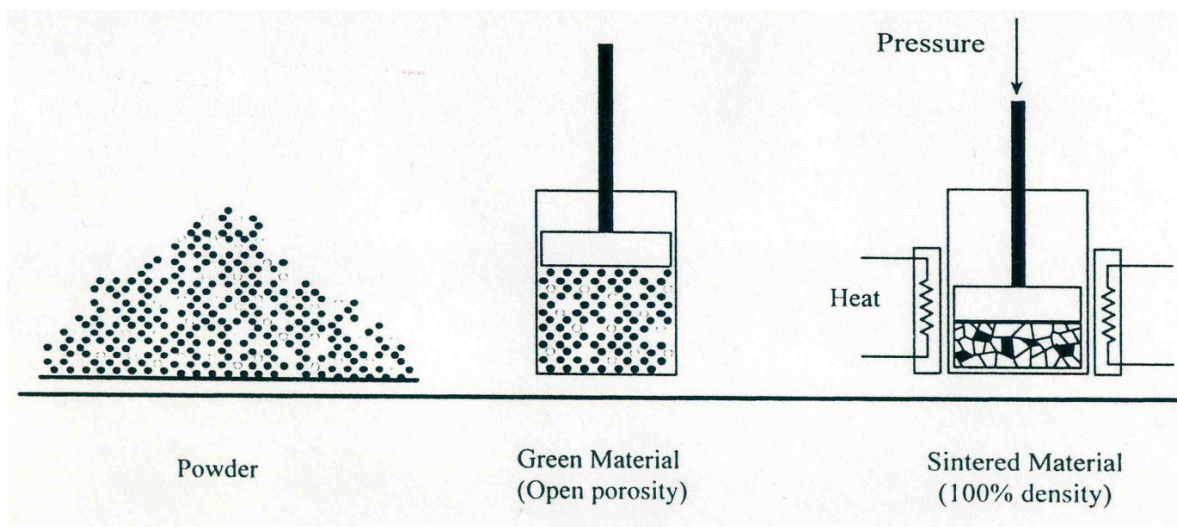


Figure 3. Consolidation process of nanophase powders.

Depending on the method of synthesis a variety of nanocomposites of the type shown in Figure 4 can be produced. [15] Nanocomposites are made by dispersing nanometer-scale particles of one material either inside the grains of a second material or between the grains. Combinations in which both phases are equally fine (nano–nano composites) are possible. The advantages of, for example, nanosize-reinforced metal–matrix composites include a combination of high strength, high elastic modulus, high toughness and impact properties, low sensitivity to temperature changes or thermal shock, high surface durability, and low sensitivity to flaws.

Defects that destroy the properties of the bulk nanophase material can nearly always be attributed to some specific event in the processing history. Strength-limiting effects can often be avoided if careful control is exercised over all aspects of processing, the most critical being the characteristics of the starting powder. The ideal characteristics of the starting powder for advanced materials are: [16]

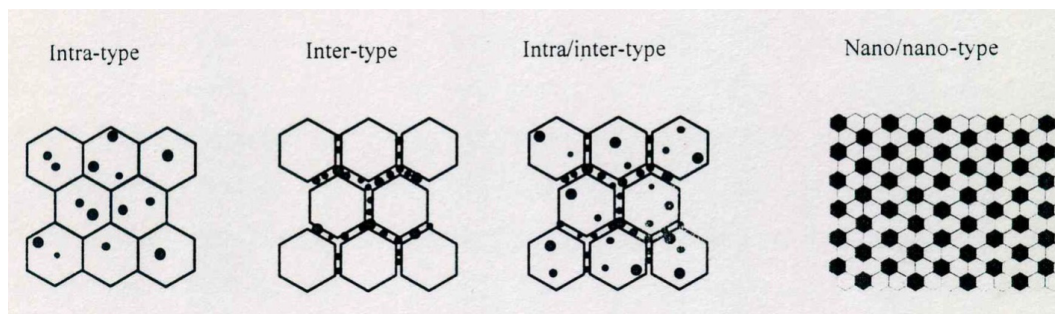


Figure 4. Types of nano-composites possible by nanophase material synthesis methods. [15]

- Spherical shape (to improve packing)
- Particle size below 100 nm in diameter
- A narrow size distribution (to improve packing, avoid grain growth and maximize grain – density)
- Freedom from agglomeration (to improve packing and minimize void fraction)
- Highly controlled purity

Contamination and the presence of hard agglomerates are the major limiting effects, and are probably the most difficult properties to control during the powder preparation process, as will be discussed in the next section. Highly controlled purity is important because the quality of the bulk nanophase material depends directly on the purity of the starting powders. However, nanophase materials usually are very susceptible to contamination. For example, tungsten in nanosize phase – in contrast to conventional tungsten – is highly pyrophoric.

Freedom from agglomeration is important to improve stability of the structure and to significantly reduce sintering time and temperature. Hard agglomerates must be avoided since their presence gives rise to the formation of pores and flaws during sintering. The pores slow down the sintering process, limit densification, and reduce the strength of the material by acting as crack formation sites. Hard agglomerates are distinguished from weak agglomerates by necking (bridging) that occurs between particles. This necking is due to surface reactivity, surface growth, or sintering. It is the hard agglomerate, not the weak agglomerate that is undesirable. For example, to produce optimum parts from fine ceramics particles, the powder must be compacted to low void fractions such that near-net-shape parts are obtained after sintering. The poor packing characteristics of hard agglomerates make them of little use to the ceramic industry. [17]

3. Powder preparation by aerosol processes

The methods shown in Table 2 have been used with different levels of success to produce ultrafine particles. Only gas-to-particle conversion processes are described here because of

their widespread use and potential for large-scale production of materials. See References 18, 19, 20, and 21 for a general review.

Gas-to-particle conversion processes refer to production of particles from individual atoms or molecules in the gas phase. The processes constituting the overall process are well understood qualitatively and are shown in Figure 5. By using any high-energy source such as a flame, joule (resistive) heating, plasma, sputtering, ion, electron or laser beams, or a hot wall reactor, condensable product atoms or molecules are formed. Depending upon the kinetics, thermodynamics, reactor design, and operating conditions, the product atoms/molecules self-nucleate and form molecular clusters. Over a very short period of time, a high concentration of clusters is formed.

Production Methods of Nanosized Structures			
Method		Description	Characteristics
Aerosol methods	Mechanical grinding (Ball milling)	Repeated welding, fracturing, and rewelding of powders in a high-energy ball charge	Control of impurity content is difficult
	Gas-to-particle	Flame reactor Furnace reactor Gas condensation Plasma reactor Laser ablation Sputtering	Narrow size distribution, high purity, spherical and solid particles. Formation of hard agglomerates
	Spray pyrolysis		High purity. Appropriate for multicomponent materials Solubility problems can exist. Low production rates
	Film generation	Droplet deposition Chemical vapor deposition Solid participle deposition	Produces layered structures
	Solution phase methods	Reactants are diluted in an appropriate solvent, mixed together and particles are obtained by homogeneous precipitation	Extreme uniformity can be achieved. Applicable to limited range of compositions
	Solid phase methods	Achieved by mixing the reactants powders together and heating of ignited to high temperatures	Starting materials may be synthesized in pure forms

Table 2. Production methods of nanosized structures.

The newly formed clusters grow by condensation of atoms/molecules or by coagulation with other clusters. Early in the process, particles possess very high surface energy. Therefore, the rate of particle sintering is extremely fast and colliding particles rapidly assume a spherical shape. As particles grow further, surface energy decreases substantially, the rate of particle sintering becomes slow and collisions among particles result in irregularly shaped particles (agglomerates). Figure 6 illustrates the typical agglomerated structures obtained.

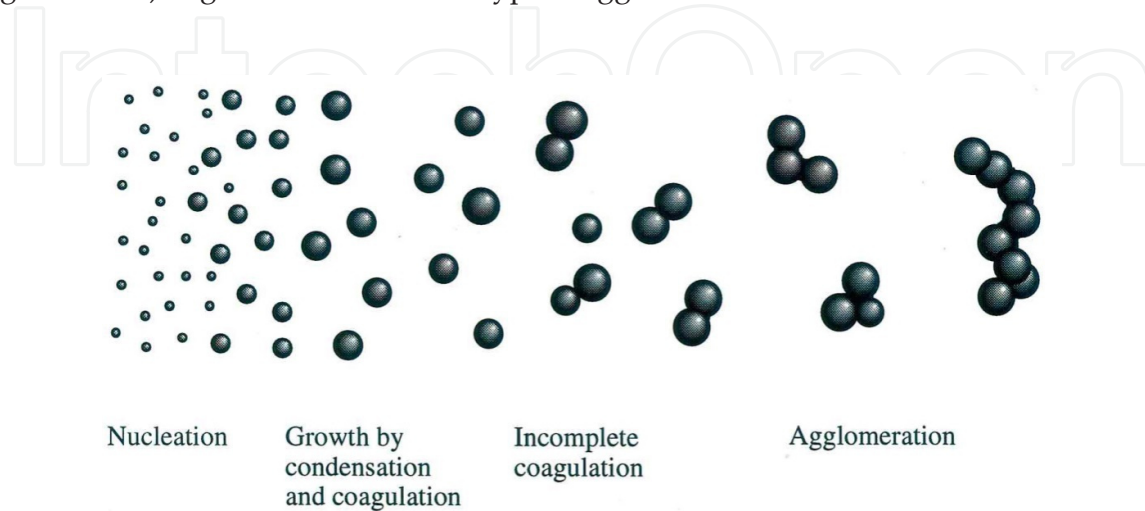


Figure 5. Processes occurring during powder production from aerosol processes.

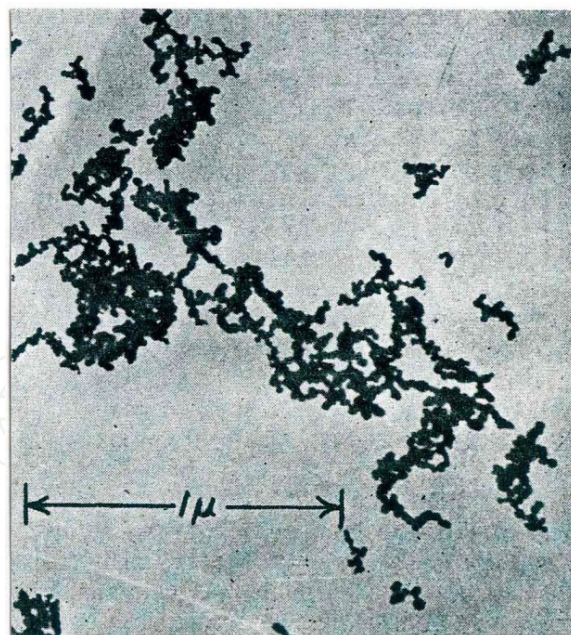


Figure 6. Long agglomerates formed during synthesis of nanosize tungsten by flame synthesis. [22]

The primary advantages of gas-to-particle routes are small particle size, narrow size distribution, nearby spherical solid particles, and high purity. The disadvantages for most aerosol methods include low production rates, chemical inhomogeneities for multicomponent

materials, high energy costs, and problems associated with hazardous gaseous reactants and by-products. A critical disadvantage is the formation of hard agglomerates in the gas phase when number densities are high.

Unlike other aerosol processes, flames have high production rates and low energy costs, and the potential for scale-up is well established. [23] Figure 7 illustrates the process of particle formation by flame synthesis. Reactants are brought to a high temperature reactor either premixed or separately (nonpremixed) in a coflow configuration. When the reactants reach the flame front, reaction takes place. The products of the reaction process are the desired materials are often a gas-phase by-product. The desired material follows the gas-to-particle route described above, yielding nanosized particles. However, due to the high particle number densities and steep temperature gradients present during the entire process, hard agglomerates are usually formed, and flames traditionally offer poor control over particle size and morphology.

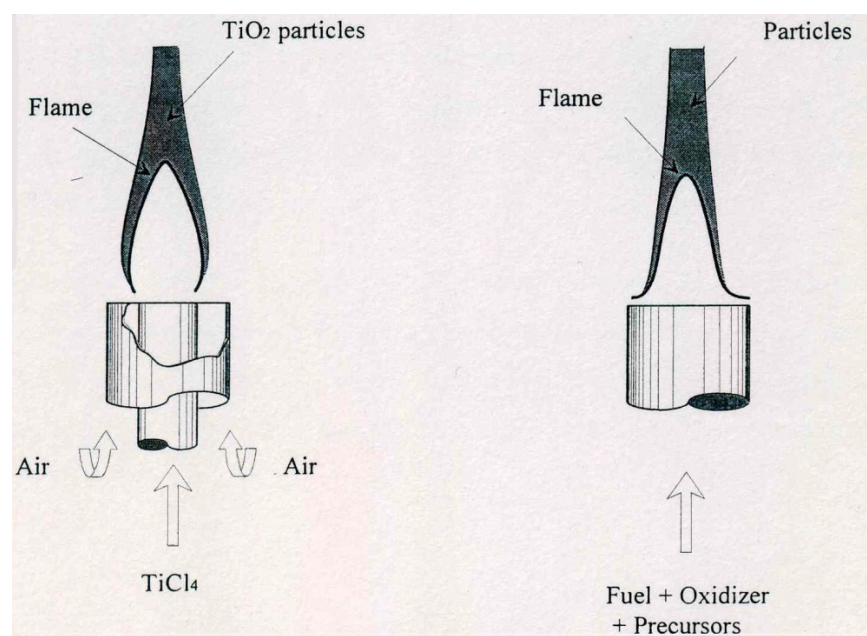


Figure 7. Illustration of the flame synthesis methods to produce nanosized materials.

4. Description of the problem

Some work has been performed to establish conditions to minimize agglomerate formation. Flagan and Wu [24] proposed controlling agglomeration in an aerosol reactor by maintaining a sufficiently low number concentration of primary nuclei and varying temperature along the reactor such that coagulation is minimized while condensation is maximized within the residence time of particles in the reactor. Zachariah and Dimitriou [25] noted that agglomerates are almost exclusively constructed from 10-30 nm primary particles and proposed controlling agglomeration by limiting the homogeneous nucleation rate in such a way that the 10-30 nm

primary particles can grow by heterogeneous condensation. Thus, they developed a set of criteria for determining the onset of runaway nucleation as the criteria to control agglomeration. These methods have not been demonstrated experimentally and are not applicable to high number density, high production rate methods of synthesis such as flame synthesis.

Recently, Axelbaum et al. [26] successfully demonstrated control of agglomeration in flames with a novel particle encapsulation approach. Figure 8 illustrates this process. The basic approach is to allow the nucleation and growth of the primary particles to proceed normally but then encapsulate 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 particle within them will not. When the encapsulation is later removed, the resulting powder will contain only weakly agglomerated particles. Encapsulation is accomplished by either encapsulating the particles with a byproduct of the combustion process or with an additive chosen for this purpose.

The encapsulation process is triggered to occur thermodynamically, kinetically or through mixing. The encapsulating material must be chosen such that it can be completely removed by, for example, heat treating or washing. Another important advantage of the encapsulation method is that it could protect air sensitive nanophase particles from oxidation or contamination during subsequent handling.

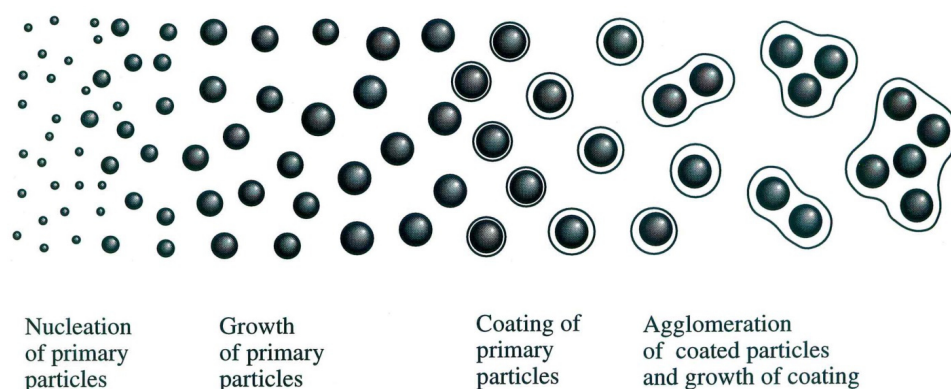


Figure 8. Illustration of the particle coating method to control agglomeration during gas-to-particle formation process.

5. Objectives

In previous sections it was stated that: 1) among the different methods of synthesizing nanosized powders, flame synthesis has by far the highest possible production rate, and it is the only method in which scale-up to high production rates has been demonstrated, 2) hard agglomerates are usually formed during aerosol processes, particularly in flames, because of the high number densities and steep temperature gradients, 3) nanophase materials are very susceptible to contamination, 4) contamination and the presence of agglomerates destroys the properties of the nanophase bulk material, and 5) the encapsulation process could be an

effective solution to control agglomeration, and to protect the primary particles from contamination.

The objectives of this work are to:

1. Demonstrate the applicability of the particle encapsulation method to the production of high purity, unagglomerated nano-particulates of tungsten (W) and tungsten titanium alloys (W-Ti) by flame synthesis.
2. Develop a Monte Carlo method to model particle dynamics in multi-component aerosols.
3. Apply the Monte Carlo method to study the processes occurring in two-component aerosols in order to understand the encapsulation process and evaluate approaches to optimize the encapsulation process as a solution to the particle contamination and agglomeration problems during the formation of nanosized powders in flames.

Specific objectives

In order to accomplish these objectives, several specific tasks must be performed:

- Apply the particle encapsulation methodology to produce high-purity, unagglomerated nanoparticles of W, Ti, and W-Ti by flame synthesis. This step requires:
 - Selecting the appropriate reactants for the production of W
 - Adapting the existing burner for the production of W
 - Producing ~20 g of nanosized W and W-Ti powder of optimal quality
 - Consolidating produced powder into bulk cylindrical pellets
- Identify and describe the variables and mechanisms controlling the encapsulation process.
- Formulate the mathematical equations that govern the physical processes occurring in flames and in multi-component aerosols. These processes include nucleation, condensation, and coagulation.
- Establish an appropriate methodology to solve the mathematical model in terms of the variables of interest: particle size distribution and composition.
- Validate the method of solution by comparing with analytical and experimental results available for simplified conditions.
- Apply the mathematical model to a simplified flame configuration, where the general equations reduce to their simplest form. The simplified configuration is equivalent to steady state systems where gas-phase precursors react in 1D flame.
- Describe the process of encapsulation under different conditions.
- Identify the conditions that will inhibit or promote effective encapsulation.
- Prescribe optimum operating conditions for the production of unagglomerated nanosized particles.

6. Outline

This document is organized in seven chapters with three appendices. Chapter 2 describes the production of high-purity, unagglomerated nanoparticulate of W, Ti, and W-Ti by flame synthesis. Chapter 3 contains the formulation of the model that describes the physical processes involved in multicomponent aerosols and the different methods that are available to solve the governing equations. Monte Carlo simulation is identified as the appropriate solution method for modeling multicomponent aerosol processes. Chapter 4 describes the Monte Carlo method developed to simulate coagulation. Chapter 5 describes the methodology used to model condensation processes and the coupling of coagulation and condensation. Chapter 6 provides a detailed description of the encapsulation process and explains the physics under which encapsulation occurs. Finally, Chapter 7 contains conclusions and recommendations for future work. Appendix A contains a heat transfer model to predict particle heating during condensation. Appendix B is a literature review about particle sintering, and Appendix C is a description of particle dynamics in colloidal systems.

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