ADVANCED
MATERIALS

Generation of Complex Metal Oxides by Aerosol Processes: Superconducting Ceramic Particles and Films

Aerosol Decomposition
Superconducting Films
Oxygen Diffusion
Ferroelectric Ceramics
Ferrimagnetic Ceramics
Powder Generation

By Toivo T. Kodas*

Complex metal oxides, including ferroelectric, ferrimagnetic and superconducting ceramics, have a variety of technologically useful properties that can be exploited for a number of applications. Fabrication of complex metal oxide ceramics with specific properties requires high-purity powders with controlled chemical compositions, size distributions, and morphologies. Powders with these characteristics can be produced by aerosol processes in which fine particles are generated in gaseous flow systems. The particles can also be deposited from the gas phase onto surfaces to form films. This paper will discuss the use of aerosol processes for the generation of complex metal oxide powders. A review of aerosol processes will be presented first, followed by a discussion of the methods used for the generation of superconducting ceramic powders. Examples include the production of $YBa_2Cu_3O_7$, $La_{1.85}Sr_{0.15}CuO_4$, and Tl-Ca-Ba-Cu-O powders and films. Emphasis will be placed on defining the conditions required for the generation of chemically homogeneous particles with controlled morphologies.

1. Introduction

The fabrication of complex metal oxides with specific electrical, magnetic, optical and superconductor properties begins with molecular precursors which must be transformed into the product film or part. A versatile class of methods for accomplishing this transformation is aerosol processes. The term aerosol process is used here to describe systems in which particles are formed in the gas phase as the result of chemical or physical processes and systems in which particles or droplets are deposited from the gas phase onto surfaces to form films. For this discussion, the terms particle and droplet will include clusters, collections of a small number of atoms or molecules in which an appreciable fraction of the atoms or molecules are at the surface.[1, 2] Table 1 lists the major types of aerosol processes that have been used for the generation of metal oxide particles and films. Systems such as laser-heated reactors[3] which have been used primarily for non-oxide ceramics are not included.

The processes in Table 1 can be grouped into gas to particle conversion, intraparticle reaction, and hybrid processes. In gas to particle conversion processes (Fig. 1) a supersaturated vapor of a condensable gaseous species is formed either as the result of chemical reactions which create new molecules[4, 5] or physical processes such as cooling which reduce the vapor pressure of the condensable species.[6] At a sufficiently high supersaturation, new particle formation occurs by homogeneous nucleation. Nucleation is followed by particle growth, and for sufficiently high particle concentrations, by coagulation and agglomeration. Gas to particle conversion processes can be coupled with particle deposition from the gas phase to provide methods for film fabrication.[7] Particle deposition from the gas phase onto surfaces can take place by mechanisms including impaction, thermophoresis, and diffusion.[8-10]

In intraparticle reaction processes, often called spray pyrolysis, evaporative decomposition, spray roasting or aero-

Table 1. Aerosol processes for the generation of metal oxide powders and films.

Films	Powders
1. Gas to particle conversion	
1.1 Physically induced processes	
Ionized cluster beam [75–82]	Supercritical fluid expansion [83, 84]
Supercritical fluid expansion [83, 84]	Condensation processes [85–87]
1.2 Chemical Reaction Processes	
Laser evaporation/deposition [88–91]	Flame reactors [92–96]
Heated-wall reactors [12]	Heated-wall reactors [97–102]
Plasma spraying [103–105]	Plasma reactors [106–108]
2. Intraparticle Reaction	
Spray pyrolysis or pyrosol process [55, 56, 109–130]	Spray pyrolysis, evaporative decomposition, spray roasting or aerosol decomposition [43–48, 51–54, 61, 62, 131–139]
3. Hybrid processes	
	Condensation/intraparticle reaction [50, 140–145]

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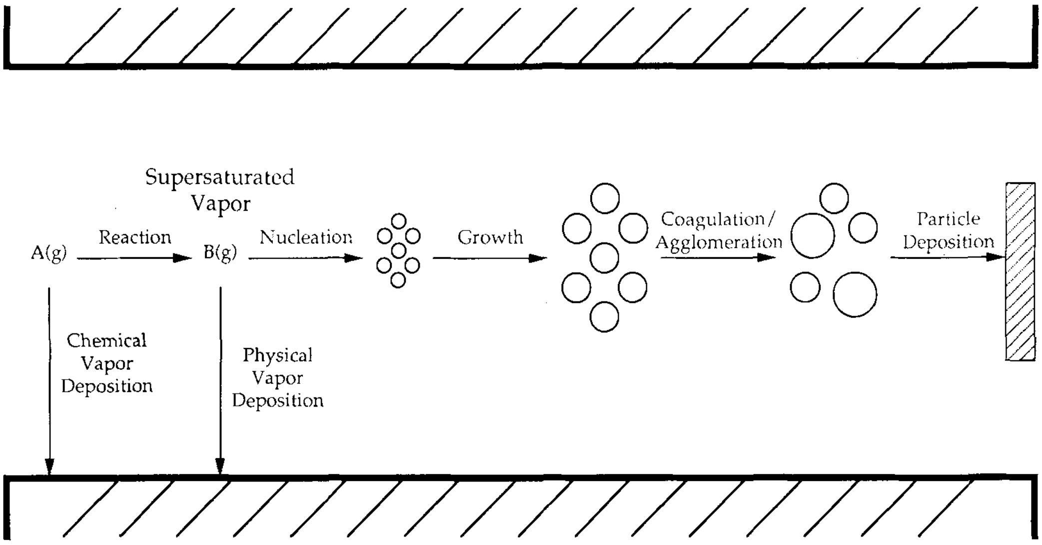

Fig. 1. Particle generation by gas to particle conversion.

sol decomposition, particles containing precursors are formed mechanically using a droplet or particle generator (Fig. 2a). The precursors in each particle are then reacted with a gaseous species or are pyrolyzed in the particulate phase to form the product. A modification of the aerosol decomposition process, spray pyrolysis (the same name as for the powder generation process), or the pyrosol process, can be used for film generation. The liquid droplets are deposited onto a heated substrate where the precursors decompose, and further heating results in the formation of the product film. One variation of this process is to first form solid particles in the gas phase, deposit them onto a substrate, and sinter them to form the solid ceramic film.[11] Another variation (Fig. 2b) is to use volatile reactants which evaporate into the gas phase and deposit materials by chemical vapor deposition. Although gas to particle conversion processes and intraparticle reaction processes provide convenient groups for classifying aerosol processes, some methods incorporate elements of both processes. For example, in the hybrid process cited in Table 1, droplets of an organometallic species can be formed by nucleation and condensational growth and then be converted to a ceramic species by intraparticle chemical reaction.

Aerosol methods have been used to produce a wide variety of metal oxide ceramics as shown in Table 2. These studies have shown that aerosol processes allow the generation of particles with a unique combination of properties that in many cases cannot be obtained by other processes. Typical properties include:

- high purity
- single-crystal or polycrystalline
- multicomponent materials
- coated/multilayer or chemically homogeneous
- porous or non-porous
- size from clusters to 5 μm
- unagglomerated, soft or hard agglomerates

An example of a process which can produce complex metal oxide powders with these characteristics, aerosol decomposition, will be discussed later.

The advantages of aerosol deposition for film fabrication include:

- high purity
- multicomponent materials
- high deposition rates

One of the best examples of a process which exploits these advantages for film formation is optical fiber production in which high-purity SiO_2 is deposited at high rates onto the inside surface of a tube which is eventually filled in and drawn into an optical waveguide.[12]

Aerosol processes for the generation of metal oxide ceramics have been used primarily for simple metal oxides and to a lesser extent for complex metal oxides containing two metallic or semiconducting species (Table 2). A smaller number of studies have examined the generation of powders containing three or more of these species. However, rapidly advancing technologies in areas such as superconductivity, electronics, solar cells, optics, and high-tech ceramics for structural applications are requiring increasingly complex materials which often contain three or more metallic or semiconducting species in addition to oxygen, nitrogen and other nonmetallic species. Examples of such materials are given in Table 3. Both powders and films with controlled chemical compositions and microstructures are required.

This paper will discuss the use of aerosol processing for the fabrication of complex metal oxide ceramic powders and films. Emphasis will be placed on the aerosol decomposition process for powder and film generation (see Tables 1 and 2) since it is the only aerosol technique that has demonstrated the ability to produce complex metal oxides. The present status of research in this area will be discussed first. Superconducting ceramic powder generation by intraparticle reac-

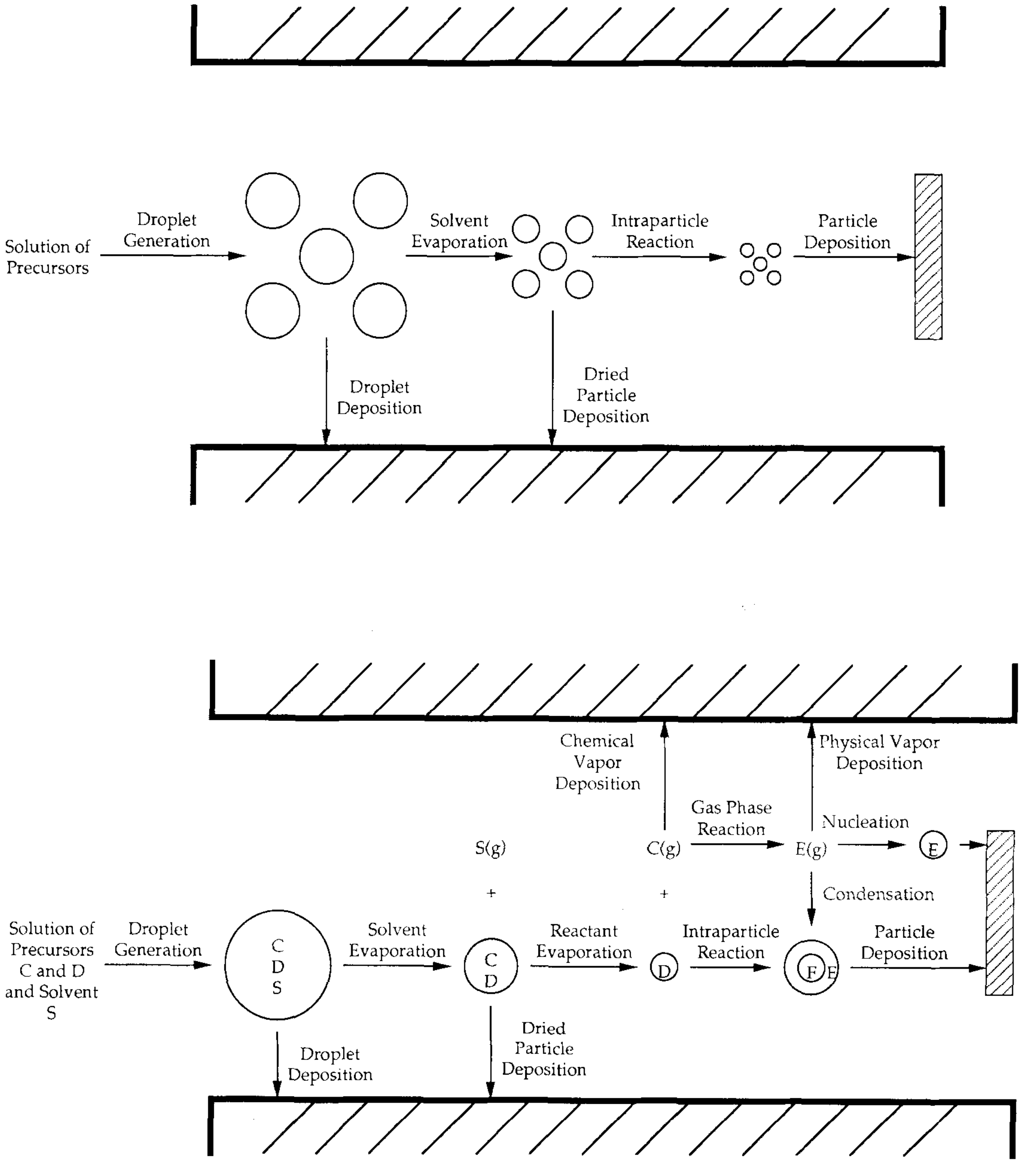

Fig. 2. Particle generation by aerosol decomposition. a) Pure intraparticle reaction and b) combined intraparticle reaction and gas to particle conversion.

tion and a combination of gas to particle conversion and intraparticle reaction will be discussed along with deposition of the particles onto surfaces to form films. New results will be presented with a review of previous work. Emphasis will be placed on describing the physical and chemical processes which control the chemical composition and morphology of complex metal oxide particles and films produced by aerosol decomposition. A goal of the paper is to identify the problems which must be solved in order to increase the range and number of applications of aerosol processes for the generation of powders and films.

2. Present Status of Research on Aerosol Processing of Complex Metal Oxides

2.1. Theory

Gas to particle conversion and intraparticle reaction methods for powder generation can involve a variety of physicochemical processes (see Figs. 1, 2a and b). These processes include:

- gas-phase chemical reactions
- single-particle chemical processes such as surface and intraparticle chemical reactions

Table 2. Examples of metal oxides synthesized by aerosol processes.

Complex metal oxides	
Superconductors	
$YBa_2Cu_3O_7$	films [11, 74, 88–91, 116–118, 146–148] powders [11, 37–41]
Bi-Sr-Ca-Cu-O	films [57, 119, 120] powders [11]
Tl-Ca-Ba-Cu-O	powders [11]
La-Sr-Cu-O	powders [11]
Magnetic materials	
$M_xM_yFe_{3-(x+y)}O_4$	where M = Bi, Zn, Mg, Ni, Mn, films [77, 78, 109] powders [43, 52, 136]
Assorted	
$NiMn_2O_4$	powders [52]
$NiMgO_2$	powders [43]
$MgCr_2O_4$	powders [43]
$CoCr_2O_4$	powders [43]
$CaAl_2O_4$	powders [138]
$MgAl_2O_4$	powders [54]
$Gd_3Fe_5O_{12}$	films [121]
Simple metal oxides	
Al_2O_3	films [81, 111, 126, 149–151] powders [45, 53, 86, 93,96, 107, 108, 131, 138, 141, 142, 144, 145]
BeO	films [75]
CaO	powders [86]
CeO_2	powders [86]
Cr_2O_3	films [111, 115] powders [43]
Fe_2O_3	films [110, 113, 115, 122, 125, 127, 129, 130] powders [52, 96, 98, 134, 135]
Ga_2O_3	films [152]
GeO_2	films [84] powders [84, 96]
In_2O_3	films [111, 115, 123]
La_2O_3	powders [48]
MgO	powders [46, 51, 85, 86, 97, 107]
NiO	powders [52]
SiO_2	films [12, 76, 83, 84] powders [84, 86, 92, 107, 140, 145]
SnO_2	films [111, 115, 123, 128]
TiO_2	films [80, 111] powders [92, 94, 96, 101, 143, 145]
VO_x	films [96, 111, 115]
Y_2O_3	films [111]
Yb_2O_3	films [105]
ZnO	films [79, 112, 114] powders [47, 52, 62, 85]
ZrO_2	films [105, 111] powders [48, 86, 96, 100, 107, 133]

Table 3. Examples of complex metal oxides of technological importance.

Superconducting ceramics [66, 153,154]	
$M_wM_xM_yM_zO_u$ where M = Cu, Tl, Bi, Ca, Sr, Ba, Pb, Sb, Y, etc.	
Examples	
$YBa_2Cu_3O_7$	power transmission, magnets
Bi-Pb-Sr-Ca-Cu-O	electronic devices
Tl-Pb-Ca-Ba-Cu-O	
Ferroelectric ceramics [155, 156]	
$(M_wM_xM_yM_z)O_3$ where M_i = K, Zn, Nb, Fe, W, Pb, Ba, Ni, Zr, Ti, Li, Ca, Sr, Sn, Ta, etc.	
Examples	
$(Sr_{1-x}Ca_x)[(Li_{1/4}Nb_{3/4})]_{1-y}Ti_yO_3$	electric resonators
$K(Ta_xNb_{1-x})O_3$	optical oscillators
Ferrimagnetic ceramics [157]	
$M_xM_yFe_{3-x-y}O_4$ where M = Mg, Zn, Mn, Ni, etc.	
Examples	
$Mg_{1-x}Zn_xFe_2O_4$	circuit elements
Sialon ceramics [158]	
$M_x(Si, Al)_{12}(O, N)_{16}$ where M = Li, Mg, Ca, Y or rare earths	

- single-particle physical processes such as nucleation, evaporation and condensation
- multi-particle physical processes such as coagulation and agglomeration
- mass transport including diffusion and deposition of gases and particles
- heat and momentum transport leading to nonuniform velocity and temperature fields
- effects associated with plasmas, photons, electric fields, supercritical fluids, and other complicating features

The processes which occur depend on the mode of aerosol reactor operation. One of the simplest cases, aerosol decomposition, can involve only intraparticle chemical reactions for particles in nonuniform temperature and velocity fields (Fig. 2a). Gas to particle conversion processes can, however, involve many of the processes mentioned above (Fig. 1). Similarly, aerosol decomposition processes with one or more volatile species (Fig. 2b) can involve many of these processes. Because of this variety of processes that can occur, a complete understanding of aerosol methods for film and particle generation will only be obtained by an interdisciplinary approach.

A large number of studies have theoretically examined the behavior of aerosol processes for film and particle generation. However, few have studied the behavior of multicomponent systems. Fortunately, many of the results from single-component systems can be used to understand qualitatively the behavior of the more complicated multicomponent systems. Models for single-component systems incorporating gas phase reaction, particle formation and growth, nonuniform velocity profiles and diffusion of gaseous reactants and products in flow systems have been developed.[13–23] The added complexities of coagulation and transport of particles have also been added to these models.[24–25] The aerosol dynamics in well-mixed systems (continuously stirred tank reactor) with exponential residence time distributions have been examined,[26, 27] and the roles of particle nucleation, growth and coagulation in determining particle characteristics have been studied in detail.[28–35, 99] These and other studies have provided a basis for the understanding of the aerosol dynamics in a variety of systems for powder and film generation.

2.2. Experimental Results

The only aerosol method that has demonstrated the ability to produce chemically homogeneous complex metal oxides, including superconducting ceramics,[11, 36–41] is aerosol decomposition. The powder generation process begins by passing a solution of precursors through an aerosol generator to form fine droplets.[42] The droplets are then passed through a furnace where chemical reactions convert the precursors to the product powder which is then collected on a filter.

This process has several advantages over gas to particle conversion processes for the generation of multicomponent materials. Particles with a uniform chemical composition can be produced in many cases since the precursors are present in the correct stoichiometry in each droplet produced by the aerosol generator. Volatile precursors are not required; thus, a wide variety of reactants can be used while avoiding the need for carbon-containing precursors. Gas to particle conversion or nucleation processes have not been successful in producing multicomponent materials due primarily to difficulties in controlling the nucleation process when several species are involved (see section 3.2.2). In contrast, aerosol decomposition processes can produce multicomponent materials. The generation of multicomponent ceramic powders can be carried out on an industrial scale using only a few unit operations; the ability to scale up these systems for production of ton-quantities of conventional ceramic oxide powders has already been demonstrated.[43, 44]

The morphology of particles produced by aerosol decomposition strongly influences the properties of ceramics produced by sintering the particles. The primary difficulty with the intraparticle reaction route for powder generation has been that in most cases porous polycrystalline particles have been formed.[43-48] This morphology can lead to difficulties in sintering to near-theoretical density, a crucial problem for superconducting ceramics where porosity can lead to degraded superconductor and mechanical properties.

The morphology of the particles depends on a variety of physicochemical processes including reactant crystallization in the particle during solvent evaporation, chemical reaction in the particles, and transport of gaseous reactants and products into and out of the particles. Few studies have examined how solvent evaporation influences the final particle morphology. Conditions leading to solid particles during evaporation are believed to be a nuclei-free system, high solute solubility, low drying rates and low relative humidities.[49] The rate of intraparticle reaction of water vapor with metal alkoxide droplets has been measured optically, but little information about particle morphology was reported.[50]

A variety of precursors have been used for the generation of ceramic powders by aerosol decomposition. They include chlorides, oxalates, lactates, citrates, nitrates, acetates, alkoxides, sulfates and acetylacetonates (Table 2). However, only a few studies have examined the role of the precursors in determining the morphology of particles produced by spray pyrolysis. The difference between using nitrate, chloride and acetate salts of Mg as precursors for MgO generation has been examined.[46, 51] The acetate gave dispersed particles while the nitrate and chloride gave large aggregates. A similar study was carried out for ZnO, NiO, $NiMn_2O_4$, $ZnFe_2O_3$, and Fe_2O_3 generation from the nitrate and acetate salts. The acetates gave powders ranging from hard aggregates to fine unagglomerated particles while the nitrates gave hard agglomerates under all conditions.[52] However, unagglomerated $YBa_2Cu_3O_7$ particles have been obtained by aerosol decomposition using the nitrates.[36-41] Little information is available for other precursors.

The processing of powders produced by aerosol decomposition has been investigated only in a few studies. Examples include processing of Al_2O_3 to form 96% dense ceramic[45, 53] and $MgAl_2O_4$ to form 93% dense material.[54] The processing of most other powders produced by aerosol techniques (see Table 2) has not been investigated. Further work is required to characterize the powders and to study the fabrication of ceramics using these powders.

Films of many materials have been deposited by spray pyrolysis (see reviews[55, 56] and Table 2). The gas phase processes occurring during film generation are similar to those occurring during powder generation by spray pyrolysis (Figs. 2a and b). As for powder generation, few studies have used modern aerosol techniques to determine how the properties of the films can be improved by controlling the droplet size distribution, reactor design and operating conditions. Instead, the large majority of these studies have concentrated on characterizing the electrical, optical, and magnetic properties of simple metal oxide films.

Deposition of particles from the gas phase onto surfaces followed by sintering has been used for many years for the fabrication of optical waveguides.[12] However, this process has only recently been exploited for the generation of films of materials other than SiO_2. An example is the formation of thick films of superconducting ceramics by the deposition of superconducting ceramic particles formed by aerosol decomposition[11] (see section 3.5). Advantages of the process include in situ formation of films while minimizing exposure to contaminants, adaptability to different chemical systems, and the integration of materials synthesis and processing steps. A modification of this process has been used to produce Bi-Sr-Ca-Cu-O films.[57] Amorphous particles generated by a non-aerosol process were entrained in a carrier gas to form an aerosol and then deposited from the gas phase onto heated surfaces to form crystalline films. Films have also been generated by simultaneous deposition of particles and vapor from the gas phase. Deposition rates were orders of magnitude higher than those achieved by conventional chemical vapor deposition processes.[7]

3. Generation of Superconducting Ceramics by Aerosol Decomposition

Typical superconducting ceramics contain three or more metallic species and oxygen. Examples include Bi-Pb-Sr-Ca-Cu-O, Tl-Pb-Ca-Ba-Cu-O and Y-Ba-Cu-O. The motivation behind using aerosol processes for superconducting powder generation is the need for high-purity multi-component powder composed of unagglomerated particles with a uniform chemical composition and controlled size distribution,[58-60] characteristics which can only be obtained by aerosol decomposition. No other aerosol methods have demonstrated the ability to produce complex metal oxide powders with these characteristics. A further motivation for studies of these materials is that, because of the large number and variety of species involved, they are excellent model systems for studies of the generation of other ceramic powders by aerosol processes (Table 3).

3.1. Experimental

Powders were generated by the following method. Metal-containing species were dissolved in a solvent and passed through an aerosol droplet generator to form micron-sized solution droplets. Aqueous solutions of the nitrate salts of the metals are used to minimize carbon contamination from either the solvent or precursors. The droplets were then passed through a furnace where chemical reaction took place to convert the reactants to the product powder. Average residence times were typically 1 to 25 seconds with temperatures of 800–1200 °C. The powders were collected on silver-membrane filters to minimize contamination. Powders based on the $YBa_2Cu_3O_7$, $La_{2-x}Sr_xCuO_4$, Bi-Sr-Ca-Cu-O, and Tl-Ca-Ba-Cu-O systems have been generated by this technique.[11, 36-41]

3.2. Mechanism of Particle Formation

The process of forming ceramic particles by aerosol decomposition can be viewed in the simplest case as the drying of droplets followed by solid and liquid phase chemical reactions in a microreactor (the particle) suspended in a gas to form the product. However, the actual behavior of the system is in many cases more complicated. The microreactor can exhibit two types of behavior which are determined by the nature of the species transported into the gas phase. If only nonmetallic species (O_2, CO, CO_2, NO, NO_2) are transported across the particle/gas interface, only intraparticle and surface reactions occur, and the product stoichiometry can be precisely controlled during mixing of the precursor solution (Fig. 2a). As will be shown, samples of $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ formed from the metal nitrates exhibit this type of behavior. If metal-containing species are exchanged across the interface, gas phase, surface and intraparticle chemical reactions can occur. In this case, control of the stoichiometry and phase purity becomes far more difficult than for the case of a purely intraparticle reaction. An example of a system exhibiting this type of behavior is the formation of Tl-Ca-Ba-Cu-O from the metal nitrates where volatile Tl-containing species are transported across the particle/gas interface.

3.2.1. Intraparticle Reaction: $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$

In the purely intraparticle reaction mode where only gaseous species are transported across the particle/gas interface (Fig. 2a) the solvent evaporates from the droplets formed by the aerosol generator followed by nucleation of the metal salts in the particle to form one or more solid phases. This is followed at higher temperatures by decomposition of the metal salts in the particles to form reaction intermediates. As the reaction proceeds, these intermediates diffuse together and react to form the final product. Since no metal-containing species leave the particles, the spread of the particle size distribution is limited by the spread of the size distribution of the droplets formed by the aerosol generator. Thus, nearly monodispersed particles can be produced by using ultrasonic droplet generators.[38, 40, 41]

The intraparticle reaction mode occurs during formation of $YBa_2Cu_3O_7$ by decomposition of metal nitrates. The melting points of the oxides of Cu, Y, and Ba (1326–2410 °C) are far above the typical reactor operating temperature (900–1000 °C); thus, evaporation of the oxides does not occur. Similarly, no evidence of evaporation of any of the nitrate species or reaction intermediates was found by examination of the powders by transmission electron microscopy (TEM) electron diffraction, X-ray diffraction, and wet chemical analysis of the composition of the powders. Since the Y, Ba, and Cu are confined to the particles, it is possible to form $YBa_2Cu_3O_7$ particles (Fig. 3) with the following characteristics:[36, 37]

- Completely reacted (thermogravimetric analysis (TGA))
- Single phase (X-ray diffraction (XRD))
- Superconducting with $T_c > 90$ K (magnetic susceptibility)

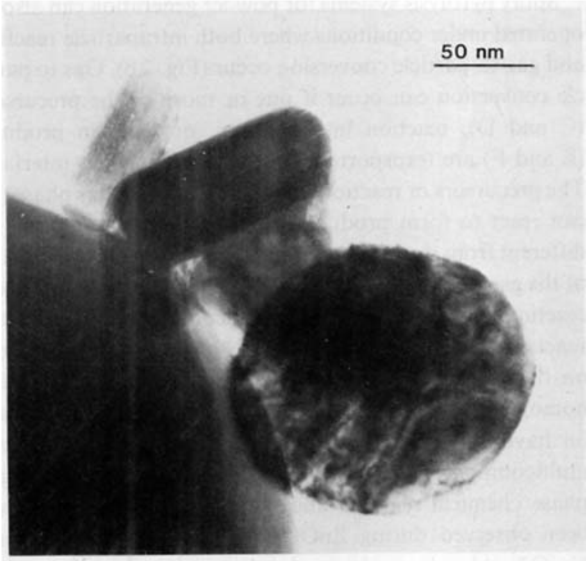

Fig. 3. Single-crystal $YBa_2Cu_3O_7$ particles generated by aerosol decomposition at 1000 °C.

- Single-crystal particles (electron diffraction)
- Uniform composition from particle to particle (energy dispersive spectroscopy (EDS))
- Solid particles (TEM and Brunauer, Emmett, Teller (BET) surface area measurements)
- Fully oxygenated (iodometric titration)
- 1:2:3 ratio of Y:Ba:Cu (wet chemical analysis)
- Equiaxed and spherical shapes

Similar results were obtained for the $La_{1.85}Sr_{0.15}CuO_4$ system. The X-ray diffraction pattern for the powder generated by aerosol decomposition of the nitrates at 1100 °C is shown in Figure 4. TGA showed that the material was fully reacted. Sintered and annealed material had a T_c at approximately 35 K.

Although $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ particles with a uniform chemical composition can be formed, cases exist where intraparticle reaction leads to chemically nonuniform particles. One example is the formation of $YFeO_3$ and Fe_2O_3 instead of yttrium-iron garnet ($Y_3Fe_5O_{12}$) during intraparticle reaction of the sulfates of yttrium and iron at 1000 °C. The preferential formation of the $YFeO_3$ and Fe_2O_3 was attributed to fast nucleation of the $YFeO_3$ phase.[61] Another example of the formation of multiphase materials by aerosol decomposition is the generation of Bi-Sr-Ca-Cu-O powders by reaction of the nitrates. Experiments under conditions which produced single phase $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ produced only multiphase Bi-Sr-Ca-Cu-O particles. In this case, both thermodynamic and kinetic limitations may have been responsible for the multiphase material.

3.2.2. Combined Intraparticle Reaction and Gas to Particle Conversion: Tl-Ca-Ba-Cu-O

Spray pyrolysis systems for powder generation can also be operated under conditions where both intraparticle reaction and gas-to-particle conversion occur (Fig. 2b). Gas to particle conversion can occur if one or more of the precursors (C and D), reaction intermediates, or reaction products (E and F) are transported across the particle/gas interface. The precursors or reaction intermediates in the gas phase (C) can react to form products which may be the same as or different from the products of intraparticle reaction (E). Any of the gaseous species, either after being formed by chemical reaction in the gas phase or during cooling while exiting the reactor, may condense on the walls of the system, condense on the particles from which they evaporated, or nucleate homogeneously to form new particles. These types of behavior have been observed during the operation of single and multicomponent systems. Zinc acetate evaporation, gas phase chemical reaction and nucleation to form ZnO has been observed during ZnO particle formation,[47, 62] and Na_2O loss has been observed during generation of powders containing Na, Mg and Al by spray pyrolysis.[53]

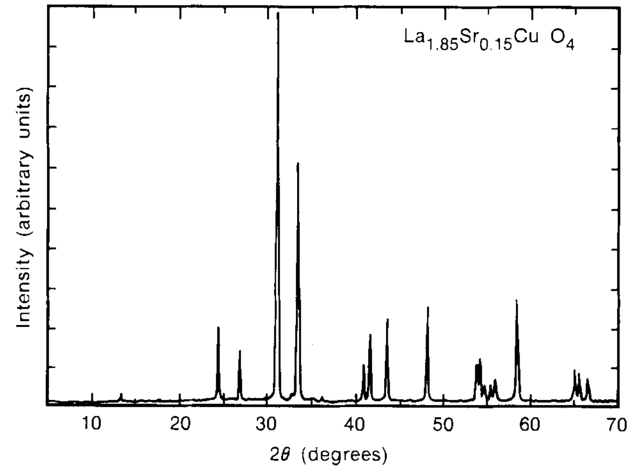

Fig. 4. X-Ray diffraction pattern for $La_{1.85}Sr_{0.15}CuO_4$ generated by aerosol decomposition at 1100 °C showing single-phase material.

The physicochemical processes shown in Figure 2b influence the properties of the product powders and hence the properties of ceramics produced from the powders. Total condensation onto the existing particles (particles of F coated with E) restores the initial stoichiometry, but only in a volume average sense; the particles are no longer chemically homogeneous and consist of a multicomponent core covered by a single-component layer of the condensed material. Homogeneous nucleation to form new particles (E) without condensation on the walls again conserves the composition of the powders averaged over the total particle volume. However, the powder consists of fine particles of one material (E) mixed with larger particles of E and F which are now depleted in the volatile species (E). Condensation on the walls results in a change in the volume average composition of the powder. Since the fraction of the volatile species remaining in the particles is difficult to control, this situation is usually the least desirable of the possibilities. Fortunately, wall losses can be eliminated by appropriate design and operation of the reactor. Studies of gas to particle conversion in tubular flow reactors suggest that rapid cooling rates which lead to high saturation ratios will result in new particle formation.[13-21] Slow cooling rates allow condensation on the particles and walls since the saturation ratio can be kept below the critical value for particle formation. The relative amounts of condensation on the walls and particles are controlled mainly by the surface area of the preexisting particles and the reactor radius. Larger aerosol surface areas and larger reactors favor condensation onto existing particles.

Experiments at a variety of temperatures and reactor residence times showed that aerosol decomposition of the Tl, Ca, Ba, and Cu nitrates resulted in particle generation by a combination of intraparticle reaction and evaporation/condensation. X-ray diffraction of collected powders showed only peaks corresponding to Tl_2O_3 (Fig. 5). TEM, EDS and electron diffraction analysis of the powders, however, showed that the Ca, Ba and Cu were present mainly in an

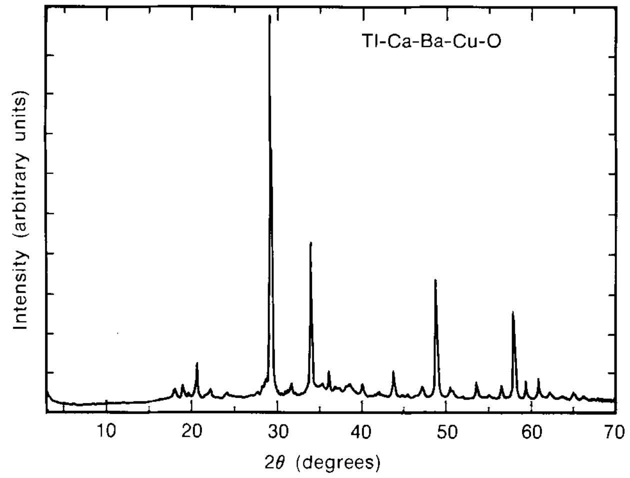

Fig. 5. X-Ray diffraction pattern corresponding to Tl_2O_3 for powder generated by aerosol decomposition of Tl, Ca, Ba, and Cu nitrates. Ba, Ca and Cu are present mainly as amorphous material.

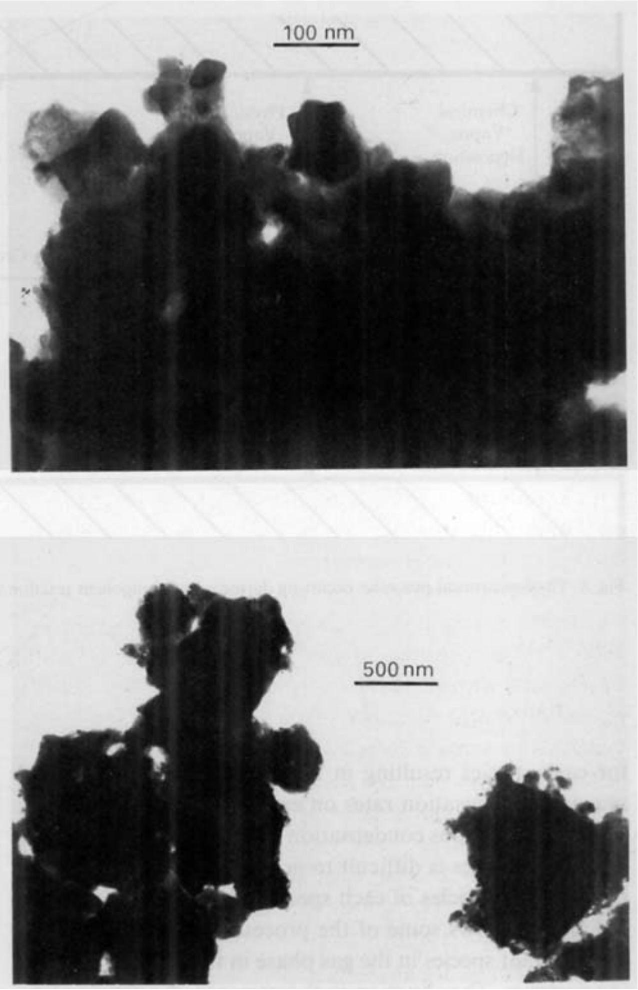

Fig. 6. Powder generated by aerosol decomposition of Tl, Ca, Ba, and Cu in 2:2:2:3 ratio. Energy dispersive spectroscopy showed the presence of Tl-containing crystallites on the surface of the particles.

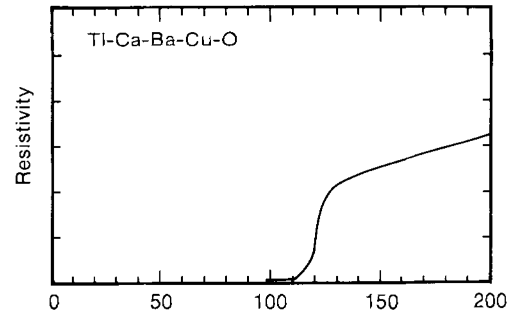

Fig. 7. Resistivity as function of temperature for sample generated by sintering aerosol powder with Tl:Ca:Ba:Cu ratio of 1:2:2:3.

amorphous form with the Tl present in a crystalline oxide form on the surfaces of the particles (Fig. 6). Wet chemical analysis of collected powders showed that all the species were present in the appropriate ratios, except for Tl whose concentration was reduced by up to 50%. The observed Tl loss from the particles was consistent with the observation of a coating on the walls of the system. The coated particles (depleted of Tl by 50%) could be sintered to produce Tl-Ca-Ba-Cu-O ceramics showing zero resistance at 110 K (onset at 125 K) (Fig. 7).

These results can be explained by the high volatility of the Tl-containing species. Under typical conditions, Tl nitrates, Tl_2O_3 and Tl_2O evaporate into the gas phase resulting in loss of Tl from the particles. Because of the high vapor pressure of the Tl_2O (roughly 500 Torr at 1000 °C),[63] the Tl exists mainly in the gas phase until cooling while exiting the reactor where the Tl-containing species condense and coat the existing particles. The particles are not superconducting as produced since the Tl was not in contact with the Ba, Ca and Cu at the temperature required for formation of any of the superconducting phases. However, EDS analysis suggested that the Ca, Ba and Cu in each particle were well-mixed. Since the mobilities of Tl species are high at typical processing temperatures, Tl-coated Bi-Sr-Ca-O particles may provide a beneficial route for formation of this particular class of superconducting ceramics.

In the case where two or more species enter the gas phase, a multicomponent nucleation/condensation problem can occur. This may take place for superconductors containing Tl and Pb[64] in which two components have significant vapor pressures under typical operating conditions (approximately 1 Torr for PbO and 500 Torr for Tl_2O at 1000 °C)[63] or for systems in which two or more precursors have significant vapor pressures under the operating conditions. This type of system has not been studied extensively, but useful information can be obtained from studies of the behavior of single-component aerosol flow reactors relying on gas-to-particle conversion.[13-35] This work and that by other investigators has shown that the aerosol dynamics depend strongly on the rate of formation, surface energy, and vapor pressure of the condensing species. These parameters are usually different

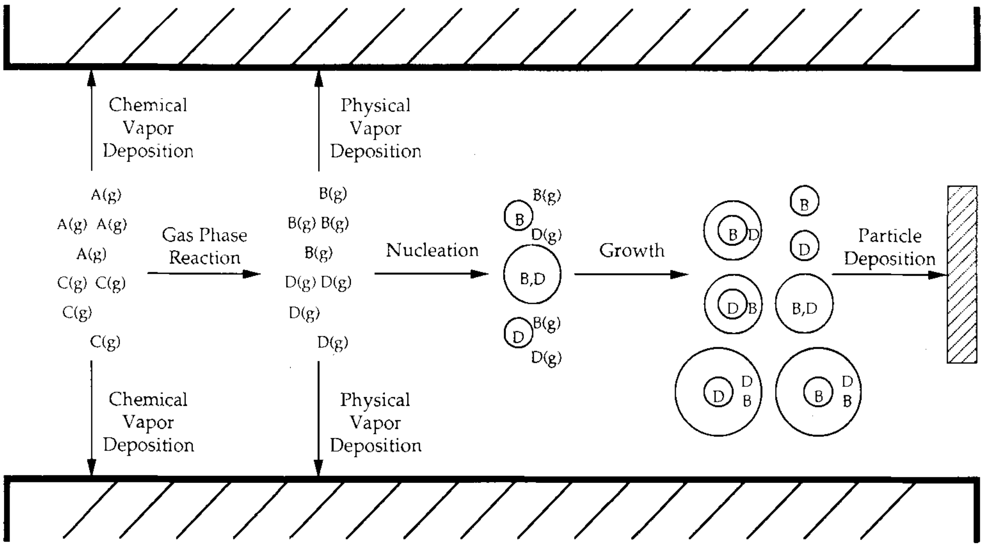

Fig. 8. Physicochemical processes occurring during a two component reaction/nucleation/condensation process.

for each species resulting in unequal nucleation rates and unequal condensation rates on existing particles and walls. Thus, simultaneous condensation to form chemically homogeneous particles is difficult to achieve. Instead, nucleation of separate particles of each species can occur.

Figure 8 shows some of the processes that can occur for two reactant species in the gas phase in the absence of existing particles. The situation in the presence of existing particles, as would be the case for aerosol decomposition, is even more complicated. Particles of one product (B), the other product (D) and a mixture of both products (B and D) may be formed by homogeneous nucleation. These species may grow by addition of B and D from the vapor phase. Many particle compositions and morphologies are possible: uniform mixtures of B and D, pure B, pure D, B coated with D, D coated with B, and other combinations.

The result of the processes outlined above is particles with a broad size distribution, a nonuniform distribution of chemical species with respect to particle size, and a nonuniform chemical composition within each particle. The spread of the size distribution and the distribution of the various chemical species with respect to particle size strongly influence the properties of superconducting ceramics obtained by processing the powders. Broad particle size distributions can lead to difficulties in obtaining high density material. Nonuniform chemical composition within a particle and from particle to particle leads to inhomogeneous material resulting in degraded superconductor properties. Thus, research is required to determine if the nucleation process can be controlled to provide particles with predetermined compositions: for example, a uniform mixture of B and D or particles of one species coated with the other species.

3.2.3. Implications For Other Systems

Although the previous sections discussed superconducting ceramic powder generation by intraparticle chemical reaction and a combination of intraparticle chemical reaction and gas to particle conversion, the results have implications for other systems where particles containing superconducting ceramics or their precursors are formed or suspended in a gas at high temperatures. Examples (Table 1) of such processes include plasma spraying, flame spraying and spray pyrolysis systems for film generation and plasma reactors, flame reactors, and electrohydrodynamic atomization[65] for powder production.

Because of the small particle dimensions involved, transport processes for individual particles in the gas phase can occur extremely rapidly. In general, transport of a reactant, intermediate or product to or from the interior of an aerosol particle consists of three steps, gas phase transport, interfacial processes including adsorption and chemical reaction and transport in the particle.[8-10] The time needed for the gas phase concentration profile around an aerosol particle to achieve a steady state for typical conditions is in the order of microseconds or less for a 1 μm particle. The time to reach interfacial equilibrium is a function of the operating conditions, but can be rapid compared to the characteristic time for solid state diffusion.[8] Thus, the time required for a volatile species to evaporate from a particle or for a species such as oxygen to diffuse into a particle can be controlled by the rate of diffusion in the solid or liquid particle. Further generalizations are difficult, however, because diffusion coefficients in liquids and solids vary tremendously with changes in temperature and composition.

An estimate of the time required for complete evaporation of a species from a particle can be made for the Tl-containing ceramics. If gase phase transport and interfacial processes are rapid, the time depends on the diffusion coefficient of the Tl-containing species in the particle. A diffusion coefficient of 10^{-8} cm^2/sec will allow complete evaporation in roughly 1 second for a 1 μm particle. Thus, if the particle's residence time at the elevated temperatures is greater than 1 second, complete evaporation can occur. In the case of plasma spray or flame spray processes, the heating of Tl-containing particles may result in the loss of Tl from the particles and subsequent segregation of Tl from the other species. A similar situation may occur during spray pyrolysis for film generation. As a droplet is transported to the substrate it is heated, and Tl-containing species may evaporate into the gas phase. Since deposition rates for particles and gaseous species can differ greatly,[22] this mechanism can lead to the incorrect stoichiometry in the deposited films.

3.3. Control of Particle Morphology and Phase Purity

Although most previous studies of particle formation from the nitrates have produced porous particles,[45-48] single-crystal $YBa_2Cu_3O_7$ particles (Fig. 3) can be formed from the nitrates by aerosol decomposition at temperatures near 1000 °C.[39] Single-crystal particle formation is favored by operating at reactor temperatures near the melting point of the material being formed. Thus, operation at lower temperatures can result in porous polycrystalline particles.[39] Other conditions that favor single-crystal particle formation include long residence times and small particle diameters which allow diffusion and reaction in each particle to form solid particles.

Particle formation proceeds as follows. Water droplets containing the nitrate salts of the metals enter the heated reactor where the water evaporates to form porous particles. As the temperature increases, the metal salts decompose to yield porous particles composed of the metal oxides. As the particles are heated further, the metal oxides react and nucleate to form a crystallite of the superconducting phase at a temperature near its metling point. Because of the high temperature relative to the melting point and the short diffusion distances involved, diffusion of the species in the particle to the crystallite results in a collapse of the porous particle to form a solid particle and complete mixing of the various species to form the product. Alternatively, the particle may start as a polycrystalline entity and the preferential growth of one crystallite at the expense of the other crystallites may lead to single-crystal particles.

Materials generation by chemical reaction in a microreactor (each particle) has one major advantage over bulk solid state chemical reaction. In bulk solid state reaction processes, liquid phases that form can percolate through the material resulting in macroscopic segregation. Further heating results only in further aggregation. In contrast, any liquid phases formed during reaction in a particle suspended in a gas are confined to the particle. Since the liquid phase cannot leave the micron-sized particle, macroscopic aggregation of species cannot occur. Thus, the thermodynamically favored product can eventually be formed even when prior melting of the reactants, intermediates or products has occurred.

3.4. Oxygen Diffusion in Single-Crystal $YBa_2Cu_3O_7$ Aerosol Particles

Intraparticle mass transport processes play a critical role in determining the properties of superconducting ceramics. As discussed earlier for the Tl-Ca-Ba-Cu-O system, these processes determine whether or not chemically homogeneous material is obtained. These transport processes can also control the oxygen content of superconducting ceramics. $YBa_2Cu_3O_{7-x}$ formed at temperatures of 900–1000 °C is not a superconductor and must be annealed in oxygen at temperatures of the order of 500 °C to allow the oxygen to diffuse into the material and convert it to the superconductor.[66] Previous methods for the measurement of oxygen diffusion coefficients in $YBa_2Cu_3O_{7-x}$ have examined sintered and annealed material.[67-70] In general, diffusion in sintered ceramics can proceed by several mechanisms including bulk, surface and grain boundary diffusion. Thus, the apparent diffusion coefficient depends in a complicated way on the concentration and distribution of impurities, the structure of grain boundaries and the density of the sintered ceramic part. The relative importance of these different diffusion mechanisms could be sorted out if bulk diffusion coefficients were available.

Bulk diffusion coefficients for oxygen in $YBa_2Cu_3O_{7-x}$ can be obtained by measuring the time required to oxygenate equiaxed single-crystal aerosol particles of known size suspended in oxygen. A temperature-averaged diffusion coefficient was obtained from experiments in which the size of the particles, their oxygen content after being cooled to roughly 100 °C, and the temperature/time history of the particles were measured.[71] Titration measurements[72] gave an oxygen content of $7.04 \pm .03$ for the $YBa_2Cu_3O_{7-x}$ powder indicating that the particles were fully oxygenated. XRD and TGA also showed that the powder was fully oxygenated. Oxygenation of the powder is limited by the time needed for oxygen to diffuse into the largest particles. This time is of the order of r_p^2/D where r_p is the radius of the largest particles and D is the diffusion coefficient of oxygen in $YBa_2Cu_3O_{7-x}$ averaged over the temperature range where diffusion took place.[73] The largest particle radius observed was roughly 1 μm. The time the particles spent cooling from 1000 °C to 100 °C was less than 10 seconds. Thus, the temperature averaged diffusion coefficient was roughly 10^{-9} cm^2/sec. The primary advantage of this method is the ability to measure diffusion coefficients for single crystals in the absence of grain boundary effects and impurities. Further work is necessary to obtain diffusion coefficients as a function of temperature.

3.5. Thick Film Formation by Aerosol Deposition

Aerosol deposition has been used extensively for the generation of optical waveguides.[12] The formation of thick films of other materials has been investigated only in a few cases. This section will discuss recent results for the formation of thick $YBa_2Cu_3O_7$ films by aerosol deposition.

The fabrication of superconductor/metal wires and tapes with high critical current densities is complicated by difficulties in eliminating impurities such as carbon and obtaining the correct oxygen content in the superconductor. These problems can be minimized by producing high-purity $YBa_2Cu_3O_7$ particles in a gaseous flow system as described earlier, depositing the particles directly from the gas phase onto surfaces by thermophoresis, and then sintering and annealing the deposited particulate films in an oxygen flow to form thick superconducting coatings.[11] Copper tubes with uniform, adherent coatings on their inside surfaces were produced. The coatings showed sharp superconducting transitions above 91 K and critical current densities (J_c) of roughly 100 A cm^{-2}. Advantages of the process include the ease of obtaining the correct oxygen content in the superconductor (since oxygen can be passed through the center of the tube) and the ability to fabricate wires and tapes with arbitrary shapes. A similar process has been used to produce thick Bi-Sr-Ca-Cu-O films with J_c of 8000 A cm^{-2}.[74] Further work is necessary to improve the J_c values and to investigate the formation of thick films on other types of substrates.

4. Summary and Conclusions

The most successful aerosol process for generation of complex metal oxides is aerosol decomposition without transport of metal-containing species across the particle/gas interface. This process has demonstrated the ability to produce $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ particles with the following properties:

- Single-crystal
- Fully oxygenated
- Single phase
- Superconducting as produced with $T_c > 90$ K
- Equiaxed and spherical shape
- Uniform chemical composition

An advantage of carrying out materials synthesis in a micron-sized reactor (an aerosol particle) is that segregation is minimized since any liquid phases formed cannot leave the particle. This can be contrasted with bulk processes where macroscopic segregation of species can occur when liquid phases are formed.

Aerosol decomposition can also be carried out under conditions for which metal-containing species can be transported across the particle/gas interface. This can result in the formation of new particles, vapor wall losses, and condensation on existing particles. An example of this mode of reactor operation for superconducting ceramics is generation of Tl-containing powders. In this case, Tl-Ca-Ba-Cu-O particles with a nonuniform chemical composition and a nonuniform distribution of Tl with respect to particle size are obtained. In addition, the particles are not superconducting as produced. However, the particles which consist of a core containing Ca, Ba, and Cu coated with Tl oxides can be processed to produce bulk superconducting ceramics. Thus, the Tl-coated particles provide a useful starting point for the fabrication of bulk ceramics.

Superconducting ceramic aerosol particles can also be exploited for measurements of properties as a function of particle size and for film formation. Oxygen diffusion coefficients can be measured in single-crystal aerosol particles to provide values of bulk diffusion coefficients in the absence of the effects of grain boundary diffusion. Thick superconducting ceramic films can be formed by depositing particles directly from the gas phase onto surfaces.

5. Future Trends

With respect to the general problem of forming complex metal oxides, including superconductors and ferroelectric and ferrimagnetic materials, some of the open questions are as follows:

- For aerosol scientists: How do evaporation, reaction, condensation and nucleation of volatile precursors, reaction intermediates and reaction products influence the chemical composition and morphology of the particles and films?
- For chemists: How can the chemical composition and morphology of particles of existing materials be improved by developing novel precursors? What new materials can be generated using novel precursors?
- For chemical engineers: How do transport processes on a micron-scale such as solvent evaporation, intraparticle transport and intraparticle chemical reaction and heat and mass transport on a reactor-scale influence the morphology and chemical composition of the particles?
- For materials scientists and physicists: What changes in the properties of the powders must be made to

improve the properties of ceramics formed by processing the powders?

The possibility of producing high quality $YBa_2Cu_3O_7$ has been demonstrated. Powders of other materials with similar characteristics are required for a number of processing schemes for the generation of superconducting ceramic parts and films. Several areas need to be explored in order to increase the number and variety of applications of powders produced by aerosol processes:

- Tl-Pb-Ca-Ba-Cu-O, Bi-Pb-Sr-Ca-Cu-O, and Sb-containing powders produced by aerosol processes may have characteristics that cannot be obtained by other processes. For example, coated and non-equiaxed particles may be useful for the fabrication of bulk ceramics.
- Deposition of superconducting ceramic aerosol particles to form films at higher rates and purities than is currently possible may be feasible.
- The fabrication of bulk superconducting ceramics needs to be studied in conjunction with powder generation by aerosol processes in order to determine the optimum powder generation and processing conditions.

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