Aerosol Processing of Materials

AEROSOL PROCESSING OF MATERIALS

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PREFACE

There is currently considerable commercial and scientific interest in the production of powders and the deposition of films employing aerosol-based methods. Existing applications that employ aerosol techniques range from the production of highly dispersed metal oxide powders for use in the pigment industry to the deposition of thin films of materials, which modify the optical characteristics of glass windows and display screens.

This book describes the principles and practice of aerosol science and engineering along with the relevant aspects of materials science and engineering. The book is organized in the following manner: the early chapters deal with the basic principles of aerosols. After a general introduction in Chapter 1, Chapters 2–7 describe the fundamental aspects of aerosols such as particle size, transport, growth, evaporation, and collision and coalescence. Chapter 8 describes the chemistry relevant to aerosol processes to materials and Chapter 9 describes the characteristics of nanostructured materials because aerosol methods are among the best synthetic routes to prepare this class of materials. This is followed by a discussion of the overall qualitative behavior and technology of gas-to-particle conversion; liquid-to-solid, and solid-to-solid conversion; and film formation in Chapters 10–15. These chapters combine the principles described in Chapters 1–9 to better understand the practicalities of these systems. Equipment that can be used to produce materials by aerosol methods is found in Chapter 16 and Chapter 17 describes the measurement techniques that have been used to characterize materials produced by aerosol methods.

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NOMENCLATURE

A	total particle surface area per volume of gas, cm^2/cm^3
a	surface area of agglomerates or particles, cm^2
A_A	Avogadro's number, number/mole
a'	interatomic distance, cm
a_a	water activity in solution droplet, dimensionless
A_c	constant
a_c and a_{sol}	solute activity, dimensionless
a_o	monomer surface area, cm^2
A_r	rate constant
A_s	substrate surface area or heated area over which deposition takes place, cm^2
a_s	surface area of sphere, cm^2
b	number of moles of solid required for reaction with one mole of gaseous reactant
B_1, B_2, B_3, etc.	constants
b_{th}	deposition efficiency, dimensionless
C	concentration, moles/cm^3 or molecules/cm^3
$\mathbf{c}$	velocity vector, cm/sec
C_{A_g}	concentration of species A in gas, moles/cm^3
C_b	percentage of atoms in grain boundary, dimensionless
C_c	Cunningham correction factor, dimensionless
C_D	drag coefficient, dimensionless
C_L	concentration of reactant in liquid, g/cm^3 or moles/cm^3
C_o	concentration of solute at center of drop, mole/cm^3; or solubility over a flat surface, g/cm^3
C_p	heat capacity at constant pressure, erg/K mol
C_{pa}	heat capacity of wet air, erg/K mol
C_r	molar concentration of gaseous reactant, moles/cm^3
C_s	concentration at surface of particle or immediately above substrate, moles or molecules/cm^3
C_{sat}	saturation concentration, moles/cm^3 or molecules/cm^3
C_T	pre-exponential for temperature-dependent form of precursor vapor pressure, moles/cm^3
c_x	velocity in x-direction, cm/sec

$\dot{C}_\infty$	vapor concentration far from droplet, moles/cm^3 or molecules/cm^3
$\bar{c}$	mean molecular velocity, cm/sec
D	particle diffusion coefficient or diffusivity of gas or vapor, cm^2/sec
D_{cr}	effective diffusivity of vapor in crust, cm^2/sec
D_e	effective diffusion coefficient in film or porous layer, cm^2/sec
d_e	equivalent volume diameter, diameter of sphere corresponding to same volume as irregular particle, cm
D_f	mass fractal dimension, dimensionless
D_g	diffusion coefficient in gas phase, cm^2/sec
d_g	average particle diameter for a lognormal distribution, cm
d_{gm}	geometric mass average diameter, cm
d_{gn}	geometric number average diameter, cm
d_{gr}	average grain diameter, cm
D_L or D_l	liquid phase diffusion coefficient of solute, cm^2/sec
D_o	diffusion coefficient at reference conditions, cm^2/sec
d_o	diameter of primary particle, cm
d_p, d_{p1}, d_{p2}	droplet or particle diameter, cm
d_p^*	critical particle diameter, cm
d_{pi}, d_{pj}	particle diameter, cm
d_{pm}	mass average diameter, cm
d_{pn}	number (count) average diameter, cm
d_{po}	initial particle diameter, cm
d_{pp}	average primary particle diameter, cm
d_{ps}	equivalent sphere diameter of completely dried droplet, cm
$d_{p\overline{m}}$	diameter of particle with average mass, cm
D_s	surface fractal dimension, dimensionless
d_s	Sauter diameter, cm
d_t	tube or pipe diameter, cm
D_v	vapor diffusion coefficient in air, cm^2/sec
$d_{\overline{m}}$	mass mean diameter, cm
E	electric field
e	charge of an electron, statcoulomb
E_I	efficiency of impaction, dimensionless
E_A	activation energy, erg/mol K
E_d	deposition efficiency, fraction of particles entering that deposit inside tube or other channel or body, dimensionless
E_L	surface field strength for spontaneous emission of electrons or ions, statvolt/cm
F	rate at which molecules enter gas phase by diffusion from single droplet, molecules/sec
f	Fanning friction factor, dimensionless

f_0	fraction of material A in mixture, dimensionless
F_1, F_2	Fuchs–Sutugin correction factor, dimensionless
F_a	air molar flow rate, moles/sec
F_E	electrophoretic force exerted on particle, dyne
F_G	force of gravity, dyne
F_i	force acting on a particle, dyne
$F_{i,j}$	free energy, erg/cm^3
F_R	gas drag, dyne
F_r	feed rate of reactant, moles/sec
F_S	gravitational force exerted on particle, dyne
f_t	transducer frequency, 1/sec
F_{th}	thermophoretic force exerted on particle, dyne
G	particle growth law, cm^3/sec
g	acceleration due to gravity, cm/sec^2
G_c	constant, cm^2/sec
H	Henry's constant
h_g	heat transfer coefficient in gas surrounding particle, erg/cm^2 sec K
H_L	latent heat of water evaporation, erg/mol
H_r	heat of reaction, erg/mol
h_s	heat transfer coefficient around droplet, erg/cm^2 sec K
h_w	heat transfer coefficient at reactor wall, erg/cm^2 sec K
I	nucleation rate or particle current in volume space, molecules/cm^3 sec
i^*	number of monomer units in particle of critical size, dimensionless
i	number of monomer units in particle, dimensionless
J	particle flux, number/cm^2 sec
J_m	molecular flux, moles/cm^2 sec
K or K_{th}	thermophoretic coefficient, dimensionless
k	thermal conductivity, erg/cm sec K
K'	volume compressibility coefficient
k^*	number of monomers in critical-size particle, dimensionless
k_1	first-order reaction rate constant, 1/sec
k_B	Boltzmann's constant, erg/molecule, K
K_C	coagulation coefficient in continuum regime, cm^3/sec
K_{eq}	equilibrium constant, dimensionless
K_F	coagulation coefficient in free molecule regime, cm$^{5/2}$/sec
k_g	mass transfer coefficient, cm/sec
k_H	Hall–Petch intensity parameter, units vary with definition [see Equation (9.14)]
k_L	first-order reaction rate constant in particle, 1/sec
k_m	vapor mass transfer coefficient for laminar tube flow
Kn	Knudsen number, dimensionless
k_o	pre-exponential constant, cm/sec
k_p	thermal conductivity of particle

k_s	surface reaction rate constant, cm/sec
K_T	turbulent coagulation coefficient, cm^2/sec
L	dimension of system, cross section of flow, characteristic length, substrate diameter, tube length, thickness of coating, or thickness of concentration boundary layer, cm
L_f	latent heat of fusion, erg/mol
L_v	latent heat of vaporization, erg/g or erg/mol
M	molecular weight, g/mole
m'	exponent that depends on sintering mechanism, dimensionless
$M(d_p)$	cumulative mass distribution function with respect to diameter, g/cm^3
$m(d_p)$	continuous mass distribution function with respect to diameter, g/cm^4
M_0, M_1, M_2	moments of particle size distribution [see Equation (2.16)]
M_1	molecular weight, g/mole
m_1	mass of a molecule or atom, g
m_d	mass concentration of solvent at droplet surface, g/cm^3
m_g	mass concentration of solvent far from particle, g/cm^3
M_i	mass of particles within an interval, g
$M_i(d_{pi})$	discrete mass size distribution [see Equation (2.6)]
M_j	jth moment of distribution [see Equation (2.16)]
M_m	atomic weight of depositing species, g/mole
m_m	solution molality
m_p	particle mass, g
M_s	solute molecular weight, g/mole
M_s'	saturation magnetization, emu/g
M_∞	total mass concentration, g/cm^3
$\overline{m}$	average mass of a particle, g
N, N_1, or N_2	number concentration of aggregate, number/cm^3
$N(d_p)$	cumulative number distribution function with respect to diameter, number/cm^3
$n(d_p)$	continuous number distribution with respect to diameter, number/cm^4
$n(s)$	particle size distribution function with respect to surface area, number/cm^5
$n(v)$	particle size distribution with respect to volume, number/cm^6
n, n_1, n_g	atomic or molecular concentration, molecules/cm^3
n_{1s}	reactant concentration in gas phase at particle surface, molecules/cm^3
N_A	Avogadro's number, moles/molecule
N_f	number of primary particles, dimensionless
N_i	number of particles in an interval in an agglomerate, dimensionless

n_i	particle concentration for discrete size i, number/cm^3
$N_i(d_{pi})$	number discrete size distribution [see Equation (2.6)]
n_{in}	particle concentration entering bend, number/cm^3
n_l	lognormal distribution, number/cm^4
n_{out}	particle concentration exiting bend, number/cm^3
N_o	initial or inlet particle concentration, number/cm^3
n_p	number of primary particles in an aggregate, dimensionless
n_s	saturation concentration of monomer, molecules/cm^3
Nu_M	Nusselt number for mass transport, dimensionless
n_w	vapor concentration at reactor wall, molecules/cm^3
N_∞	total particle or aggregate concentration, number/cm^3
p	gas pressure, dyne/cm^2 or cm Hg
p_1	partial pressure of species 1, dyne/cm^2
p_{1s}	reactant partial pressure at particle surface, dyne/cm^2
P_d	aerosol penetration, dimensionless
p_d	vapor or partial pressure at particle surface, dyne/cm^2
p_{ds}	solvent vapor pressure at droplet surface, dyne/cm^2
Pe	Peclet number, dimensionless
p_e	equilibrium vapor pressure over flat surface, dyne/cm^2
p_i	partial pressure of species i corresponding to complete evaporation, dyne/cm^2
p_o	total pressure at reference conditions, dyne/cm^2
Pr	Prandtl number, dimensionless
p_r	reactant partial pressure outside concentration boundary, dyne/cm^2
p_s	vapor pressure at droplet surface at T_s, dyne/cm^2
p_{sat}	vapor pressure for pure solvent, dyne/cm^2
p_s^o	equilibrium water vapor pressure at T_o, dyne/cm^2
p_∞	partial pressure of solvent far from droplet, dyne/cm^2
Q	aerosol or gas flow rate, cm^3/sec
q	number of charges on a particle
q_{rms}	rms charge on a particle
r	radial coordinate, cm
R, R_G, R_g	gas constant, cm^3 atm/mol K
r_1 or r_2	monomer radius or radius of curvature, cm
R_a	characteristic length of aggregate, cm
R_c	collision radius, cm
Re	Reynolds number, dimensionless
Re_j	jet Reynolds number, dimensionless
Re_L	Reynolds number based on length L, dimensionless
Re_p	Reynolds number based on particle diameter, dimensionless
Re_t	tube Reynolds number, dimensionless
r_i, r_j	particle radius, cm
R_p	droplet or particle radius, cm

r_p	radius of primary particle, cm
R_r	reaction rate, molecules/cm^3 sec
r_s	surface reaction rate, molecules/cm^2 sec
R_t	tube radius, cm
r_v	rate of reaction per unit volume, moles/cm^3 sec
S	saturation ratio, dimensionless
S	stopping distance, cm
s	surface area of a particle, cm^2
S^*	critical saturation ratio, dimensionless
S_1 or S_2	surface area, cm^2
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
St	Stokes number, dimensionless
T	temperature, K or °C
t	time, sec
T_c	Curie temperature, K
T_d	droplet temperature, K or °C
T_e	temperature at entrance or far from surface, K or °C
T_g	gas temperature at entrance or far from surface, K or °C
T_o	reference temperature for gas above substrate or inlet temperature, K
T_p	temperature of particle, K or °C
T_{pre}	preheater temperature, K or °C
T_s	droplet temperature, K or °C
T_w	temperature at surface or wall, K or °C
T_∞	temperature far from particle, K or °C
U	average gas velocity, cm/sec
u	particle velocity, cm/sec
U_o or u_e	velocity of gas far from surface (free-stream velocity), cm/sec
V	total aerosol volume, cm^3/cm^3
V_1 and V_2	volumes of particles and coating on particle, respectively, cm^3
v and v'	particle volume, cm^3
$\mathbf{v}$	gas velocity vector, cm/sec
v^*	critical particle size, cm
v_0	monomer volume, cm^3
v_1	molecular volume, cm^3
v_a	atomic volume, cm^3
V_{dif}	diffusion velocity, cm/sec
V_e	electrical migration velocity, cm/sec
v_g	geometric mean volume, cm^3
v_i and v_j	particle volume, cm^3
V_M	particle deposition velocity, cm^3

v_m	volume of deposited species, cm^3
v_p	volume of a primary particle, cm^3
V_s	sedimentation settling velocity, cm
V_t	total or terminal velocity, cm/sec
V_{th}	thermophoretic velocity, cm/sec
v_{tr}	thermophoretic velocity in radial direction, cm/sec
v_{tz}	thermophoretic velocity in z direction, cm/sec
v_x	gas velocity in x direction, cm/sec
$\bar{v}$	average particle volume, cm^3
$\bar{v}$	variable of integration, cm^3
W	spread of the particle size distribution, dimensionless
W_{ij}	factor for coagulation, dimensionless
X	residence time, dimensionless
x	reactor axial coordinate, cm
x_A	mole fraction in liquid, dimensionless
x_{rms}	root mean square diffusion distance, cm
x_s	mole fraction of solvent, dimensionless
y_i	concentrations of particles of size i, dimensionless
Y_k	concentrations of particles in sections k, dimensionless
y_w	water vapor mole fraction in air, dimensionless
Z	number of charges per particle, dimensionless
$\bar{Z}$	average number of charges per particle, dimensionless
z	coordinate in axial direction, cm
z_i	number of charges on particle, dimensionless
$Z_{s,\max}$	maximum number of acquired charges, dimensionless

GREEK

α	thermophoretic coefficient, dimensionless
α_c	ratio of characteristic times for collision and fusion, dimensionless
α_g	thermal diffusivity of gas, cm^2/sec
α_p	thermal diffusivity of particle, cm^2/sec
α_s	sticking coefficient, dimensionless
β_C	collision frequency in continuum regime, cm^3/sec
β_{Ch}	collision frequency function for charged particles, cm^3/sec
β_F	collision frequency in free-molecule regime, cm^3/sec
β_{FA}	coagulation frequency function of agglomerates, cm^3/sec
$\beta_{i,j}$	collision frequency function, cm^3/sec
β_T	collision frequency for turbulent coagulation, cm^3/sec
$\beta(v, v')$	collision frequency of particles of size v and v', cm^3/sec
γ	surface tension, erg/cm^2
γ_A	activity coefficient, dimensionless

$\gamma_{i,j}$	dimensionless function
γ_s	activity coefficient of solution, dimensionless
γ_{sol} and γ_c	activity coefficient of solute, dimensionless
ΔH_{vap}	enthalpy of evaporation of precursor, erg/mole K
δ	delta function, dimensionless
δ_c	crust thickness, cm
ε	dielectric constant, dimensionless
ε_c	rate of gas molecule collisions, 1/sec
ε_d	rate of energy dissipation, cm^2/sec^2
ϵ	total number of collisions with particle surface per unit time, number/sec
ϵ_p	prefactor, dimensionless
η	particle volume, dimensionless
η_r	size of smallest eddies, cm
θ	reaction time, dimensionless
θ_1	characteristic time for reaction, dimensionless
θ_2	numerical coefficient, dimensionless
θ^*	temperature, dimensionless
κ	mass transfer coefficient (or deposition velocity) by turbulent diffusion, cm/sec
λ	gas mean free path, cm
λ_p	heat of phase transition, erg/cm^3
μ	gas viscosity, g/cm sec
ν	kinematic viscosity of gas, cm^2/sec
ρ	density, g/cm^3
ρ_1	droplet density, g/cm^3
ρ_b	molar density, $mole/cm^3$
ρ_f	gas density, g/cm^3
ρ_L	density of pure water, g/cm^3
ρ_{liq}	density of liquid, g/cm^3
ρ_p	particle density, g/cm^3
ρ_s	solute density, g/cm^3
ρ_{sol}	density of solid, g/cm^3
σ	surface tension, erg/cm^2
σ_d	hard-sphere molecular diameter, cm
σ_g or σ_{gs}	geometric standard deviation of size distribution, dimensionless
σ_s	surface energy of TiO_2, dyne/cm or erg/cm^2
σ_{ys}	yield strength, $dyne/cm^2$
τ_{as}	characteristic time for reaction in particle when ash diffusion controls, sec
τ_C	characteristic time for particle collisions, sec
τ_{CC}	characteristic time for coagulation in continuum regime, sec

τ_{CF}	characteristic time for coagulation in free-molecule regime, sec
τ_D	characteristic time for diffusion in particles, sec
τ_{dg}	characteristic time for concentration profile to achieve steady state, sec
τ_e	evaporation time, sec
τ_f	characteristic time for sintering or fusion, sec
τ_{fs}	coagulation parameter, dimensionless
τ_{GC}	characteristic time for particle growth in continuum regime, sec
τ_{GF}	characteristic time for particle growth in free-molecule regime, sec
τ_{gs}	characteristic time for reaction in particle when gas phase transport controls, sec
τ_{GSR}	characteristic time for particle growth by surface reaction, sec
τ_{GV}	characteristic time for particle growth by volume reaction, sec
τ_L	characteristic time for diffusion in coating, sec
τ_p	characteristic time for particle formation, sec
τ_{pd}	time between particle collisions with same region on surface, sec
τ_r	reactor residence time, sec
τ_{rs}	characteristic time for reaction in particle when chemical reaction controls, sec
τ_S	time needed for an aerosol to reach a self-preserving distribution, sec
τ_s	settling time, sec
τ_{sat}	characteristic time to saturate gas with vapor from evaporating droplets, sec
τ_{SC}	time needed to reach self-preserving distribution in continuum regime, sec
τ_{SF}	time needed to reach self-preserving distribution in free-molecule regime, sec
τ_{Tg}	characteristic time for heat transfer in gas phase around a particle, sec
τ_{th}	time for particle transport by thermophoresis, sec
τ_{Tp}	characteristic time for heat transfer in solid particle or droplet, sec
ϕ	water osmotic coefficient
χ	dynamic shape factor, dimensionless
ψ	normalized charge $= q/q_{rms}$
$\psi(\eta)$	self-preserving size distribution, dimensionless

ACRONYMS

AACVD	aerosol-assisted chemical vapor deposition
AES	Auger electron spectroscopy
BET	Brauner–Emmett–Teller
CSTAR	continuous stirred tank aerosol reactor
CVD	chemical vapor deposition
DTA	differential thermal analysis
FTIR	Fourier transform infrared
GDE	general dynamic equation
LFAR	laminar-flow aerosol reactor
MLCC	multilayer ceramic capacitor
NMR	nuclear magnetic resonance
PCB	printed circuit board
PE	plasma enhanced
PFAR	plug-flow aerosol reactor
PSD	particle size distribution
RF	radio frequency
SEM	scanning electron microscope
SPSD	self-preserving size distribution, dimensionless
SSA	specific surface area
TEM	transmission electron microscope
TGA	thermogravimetric analysis
TMEDA	tetramethylethylenediamine
UHV	ultrahigh vacuum

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