Control of Size, Morphology and Phase of Nanoparticles Using Laser Irradiation in Flame Aerosol Synthesis

Donggeun Lee

School of Mechanical and Aerospace Engineering Seoul National University, Korea

Abstract

Nanoparticles and nanophase materials may have significantly different and improved properties compared with compacts composed of coarser grained powders. Size, morphology, and crystalline phase of nanoparticles determine the properties of nanostructured materials. Therefore, the mastery of controlling properties ultimately requires the control of size, morphology and phase of nanoparticles. In many cases, more uniform, smaller, and unagglomerated particles are highly desirable for compacting and subsequent sintering processes to synthesize high quality nanophase materials. From various aerosol methods, highly pure nanoparticles can be produced, however, agglomeration has been considered as almost unavoidable when high concentration is necessary for a practical application. Efforts to control agglomeration have had only limited success. Here this work reports that the enhancement of coalescence of nanoparticles using laser beam irradiation on aggregates formed in flames can solve this problem and successfully control the size, morphology, and crystalline phase of high concentration nanoparticles.

The present control strategy has been successfully applied to silica and titania

particles during flame aerosol synthesis. This method is based on the fact that morphology and size of any flame-made particles are determined by the competition between collision and coalescence of particles. When a strong laser beam irradiates on small aggregates that exist at the early particle-forming stage in a flame, aggregates are transformed into volume-equivalent spheres which have much smaller collision cross sections than the former. Correspondingly, the growth of particles could be retarded maintaining their spherical shape.

First, this method was applied to control size and morphology of silica particles generated due to hydrolysis and oxidation of SiCl₄ in an oxy-hydrogen diffusion flame. TEM image analysis of locally captured particles and light scattering measurement revealed that three different mechanisms took place depending on the irradiation heights. At the low irradiation height in a flame, the particle generation effect becomes dominant due to the absorption of laser power by gases. This results in the increase of Ar-ion light scattering intensity and the particle generations are confirmed from TEM observation. At the intermediate height of laser irradiation, the effect of coalescence of aggregates due to the irradiation of CO₂ laser beam was observed. As a result, smaller and more uniform spherical particles are produced as laser power increased. Higher carrier gas flow rate case even showed the change of non-spherical particles into smaller spherical particles as laser power increased. Number density and volume fraction of non-absorbing spherical particles have been estimated from measured volumetric scattering coefficient with determining particle sizes from TEM image analysis. As a result, the coalescence effect was demonstrated to play a dominant role in the decrease of particle size at relatively low laser powers. For higher laser powers, even though evaporation occurs, the coalescence effect as well as the evaporation effect contributes to the reduction of particle size.

Secondly, this method was also applied to control crystalline titania particles generated

in a flame. Two flame conditions such as high- and low-temperature flames were employed to control size, morphology and crystalline phase of titania particles. As laser powers increase, particles have been transformed from large aggregates to much smaller sized (20 nm) spheres. Surprisingly, rutile titania particles are transformed into anatase phase having excellent thermal stability. The possible reasons of the transformation to anatase phase with excellent thermal stability were discussed via Raman scattering analysis and Fourier analysis of XRD profiles in terms of oxygen-deficient defect structure and microstrains in the samples. In addition, bulk titania with high density near the theoretical value with very fine grains (~70nm) were obtained using 20nm titania particles synthesized from the present method under pressureless simple sintering condition.

Keywords: laser irradiation, coalescence (sintering), control, size, morphology, phase, anatase, rutile, silica, titania

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Nomenclature

а	radius of isolated-spherical particles [m]
A(L)	Fourier cosine coefficients
A_a	projected area of aggregates from TEM image [nm ²]
$A^{D}(L)$	Fourier distortion coefficients
$A^{S}(L)$	Fourier size coefficients
B(L)	Fourier sine coefficients
c	speed of light in vacuum (=2.9979x10 ⁸ m/s)
c _p	specific heat of particles [J/g/K]
C_{vv}	differential scattering cross section of isolated-spherical particles [m ²]
$C^{p}_{\ abs}$	absorption cross section of primary particles [m ²]
$C^{p}_{\ vv}$	differential scattering cross section of primary particles [m ²]
$C^{a}_{\ abs}$	absorption cross section of aggregates [m ²]
$C^a_{\ vv}$	differential scattering cross section of aggregates [m ²]
c _t	average thermal speed of surrounding gas molecules [m/s]
d	diameter of CO_2 laser beam at the burner center $[m^2]$
D	effective crystallite size [nm]
D ₃₀	generalized volume mean diameter [nm]
da	projected-area-equivalent diameter of aggregates (= $(4A_a/\pi)^{1/2}$) [nm]
d _{avg} ,	number mean diameter of isolated-spherical particles [nm]
dg	geometric mean diameter of isolated-spherical particles [nm]
d_p	primary or isolated-spherical particle diameter [nm]
d_{pm}	mean diameter of primary particles [nm]
D_{f}	fractal dimension of aggregates

$f(d_p)$	probability density function of isolated-spherical particle size
f(L)	probability density function of column length L
f(N _p)	probability density function of aggregate size
f(V _p)	probability density function of isolated-spherical particle volume
\mathbf{f}_{v}	volume fraction of particles [cc/cc]
h_L	height of CO ₂ laser beam from the burner surface [mm]
\mathbf{h}_{p}	height of Ar ion laser beam and local sampling probe from the burner surface
	[mm]
h _d	height of deposition tube from the burner surface [mm]
k _b	Boltzmann coefficient (1.38x10 ⁻²³ J/K)
kg	fractal prefactor based on radius of gyration of aggregates
k _L	fractal prefactor based on maximum length of aggregates
Κ	Sherrer constant
ID	inner diameter [mm]
Ia	the strongest anatase peak (101) intensity [cps]
I_i	incident laser beam intensity [W/cm ²]
$I_{i,vv} \\$	vertically-polarized incident laser beam intensity [W/cm ²]
I _r	the strongest rutile peak (110) intensity [cps]
L	column length normal to the reflection plane [nm]
L ^a	maximum length of aggregate [nm]
m	complex refractive index of particles (n+ik) where n is refractive index and \boldsymbol{k}
	is extinction coefficient
m _p	particle mass [g]
Na	number density of aggregates [#/cc]
N_{g}	geometric mean number of primary particles per an aggregate

N _p	number of primary particles per an aggregate
\mathbf{N}_{pm}	mean number of primary particles per an aggregate [#/cc]
N _s	number density of isolated-spherical particles
OD	outer diameter [mm]
Р	CO ₂ laser power [W]
pg	gas pressure [Pa]
q	modulus of scattering vector (= $4\pi/\lambda_i \sin(\theta/2)$)
$Q_{\rm vv}$	volumetric differential scattering coefficient of particles [cm ⁻¹]
r	radial position [mm]
R _g	radius of gyration of aggregates [nm]
S	magnitude of the diffraction vector (= $2\sin\theta/\lambda_i$)
s ₀	s value at Bragg angle.
SR	system response for calibration of optics for light scattering measurement
STD	standard deviation [nm]
\mathbf{S}_{vv}	scattering intensity [a.u]
Tg	temperature of the surrounding gas molecules [K]
T _p	temperature of the heated particles [K]
t	time [s]
V	average volume of the aggregate
V_p	volume of isolated-spherical particles
$\mathbf{X}_{\mathbf{p}}$	optical size parameter $(=\pi d_p/\lambda_i)$
Z	height from the burner surface [mm]

Greek symbols

 α dispersion (STD/d_{avg})

α_{E}	thermal(or energy) accommodation coefficient
α_r	rutile weight fraction in TiO ₂ samples
β	full angular width at half-maximum intensity on the 2θ scales in radians
γ	a constant depending on D _f
ΔV	measuring volume [cm ³]
$\Delta \Omega$	solid angle of the collection optics [sr]
θ	scattering angle
$ ho_p$	density of particles [kg/m ³]
$\sigma_{\rm g}$	geometric standard deviation of isolated-spherical particle size or primary
	particle number per aggregate
η	the efficiency of the optical system (lens, filter, polarizer and PMT)
λ_i	wavelength of the incident laser beam [m]
τ	the characteristic heating or cooling time [s]
$\tau_{\rm c}$	the characteristic collision time of particles [s]
$\tau_{\rm f}$	the characteristic coalescence time of particles [s]
φ	volume loading or volume fraction of particles
$< \epsilon_L^2 >^{1/2}$	root-mean-square strain in the crystallite

Subscript

V	vertical polarization state
m	mean value over a population

Superscript

- p primary particle property
- a aggregate property
- mean value over a population

Chapter 1

Introduction

Flame aerosol synthesis has been widely used for large-scale production of various ultra fine particles such as ceramic, metal and composite powders, and also thin films and fibers such as planar and circular optical waveguides because this flame synthesis can produce highly pure particles continuously without further subsequent process, for example, drying and calcination in the wet chemical process. The sizes of flame-made particles range from a few to several hundred nanometers in diameter depending on process conditions.

Nanoparticles and nanophase materials have significantly different and improved properties compared with compacts composed of coarser grained powders. Size, morphology, and crystalline phase of nanoparticles determine the properties of nanostructured materials. Therefore, the mastery of controlling properties ultimately requires the control of size, morphology and phase of nanoparticles. In many cases, more uniform, smaller, and unagglomerated particles are highly desirable for compacting and subsequent sintering processes to synthesize high quality nanophase materials.

From various control methods proposed previously, highly pure nanoparticles can be produced, however, agglomeration has been considered as almost unavoidable when high concentration is necessary for a practical application. Efforts to control agglomeration have had only limited success, and presently no method has been shown to be viable for large-scale production. Here the author reports that the enhancement of coalescence of nanoparticles using laser beam irradiation on aggregates formed in flames can solve this problem and successfully control the size, morphology, and crystalline phase of high concentration nanoparticles.

Our method relies on controlling the characteristic time for coalescence of nanoparticles by irradiation of CO_2 laser beam on the early stage aggregates formed in a flame. The coalescence characteristic time depends strongly on particle temperature following the exponential decay as an Arrhenius form. Therefore, the coalescence

characteristic time can be controlled nearly independently of Brownian collision by heating aggregates rapidly. When early-stage aggregates formed in a flame are irradiated by a high power CW CO_2 laser beam to rapidly coalesce and become more spherical particles. Since spherical particles have much smaller collision cross-sections than volume equivalent aggregates, much slower growth of nanoparticles can be achieved. Therefore, smaller, at the same time, spherical nanoparticles can be successfully produced at high concentrations.

The present control strategy will be explained in detail and the effect will be confirmed experimentally for silica particles in Chapter 2. TEM images of locallycaptured particles and light scattering measurement tell that three different mechanisms can occur dominantly according to the laser beam irradiation heights: at the low irradiation height, the particle generation effect becomes dominant due to the gas absorption of laser power. At the intermediate height of laser irradiation, the effect of coalescence of aggregates was observed and resulted in smaller spherical particles as laser power increased. At the high irradiation height, particle evaporation or ablation effect is dominant. For more quantitative confirmation of the coalescence effect, number density and volume fraction of silica particles are estimated via Mie scattering and TEM image analysis. As a result, the coalescence effect solely causes the significant reduction of spherical particle sizes at relatively low laser powers, while further reduction of the particle sizes at high laser powers is due to both the coalescence effect and the evaporation effect. Another objective of Chapter 2 is a confirmation of the availability of the present control method at high precursor concentration. Three times higher precursor concentration case showed the change of non-spherical particles into smaller spherical particles as laser power increased.

In Chapter 3, the effects of laser irradiation on the size, morphology and crystallinity

of titania particles are investigated in detail by virtue of light scattering, TEM observation, Raman scattering and X-ray diffraction. Large aggregates in the absence of the laser irradiation becomes progressively transformed into more spherical particles and finally, 29 nm sized spheres are produced at high concentration condition. We could obtain 20nm sized spherical particles via some optimization processes for systematic parameters. Moreover, the present method is capable of even controlling the crystalline phase of nanoparticles. Surprisingly, stable rutile titania particles have been transformed into metastable anatase nanoparticles and the weight percent of each phase could be controllable. The possible reasons of the stabilization of anatase phase under the laser irradiation condition will be discussed via Raman scattering analysis and Fourier analysis of XRD profiles in terms of oxygen-deficient defect structure and microstrains in the samples. In addition, it will be discussed in this chapter to produce bulk titania with high density near the theoretical value and much fine grains (~70nm) under pressureless sintering condition.

Finally, Chapter 4 summarizes this work and suggests the industrial fields could be promisingly applied by the present control method.

Chapter 2

Coalescence Enhanced Synthesis of Silica Nanoparticles

2.1 Introduction

Flame aerosol processes have been widely used for production of various ultra fine particles such as ceramic, metal, and composite powders, and also thin films and fibers such as planar and circular optical waveguides (Wooldridge, 1998). The sizes of flame-made particles range from a few to several hundred nanometers in diameter depending on process conditions. Nanosized particles are known to display highly desirable traits such as enhanced catalytic activity, lower sintering temperatures and higher density (Pratsinis, 1998). Additionally, the properties of materials made from particles depend on the size, morphology and chemical composition of particles. Therefore, there is a great need controlling the size and morphology of the particles as well as generating high concentration aerosols (Pratsinis, 1998).

The morphology of particles formed in flames is determined by the competition between particle collision and coalescence (Windeler et al., 1997). The formation of aggregates is due to the collision occurring faster than the particles coalesce. In the opposite case (fast coalescence case), particles become nearly spherical. Recently, various control methods have been proposed and the main idea has been focused on the reduction of collision rate (Pratsinis, 1998). Pratsinis et al. (1996) demonstrated that different flame configurations could drastically alter the size and specific surface area of titania particles by changing the injection location of the fuel and oxidizer. Under the condition of longer flame lengths and higher flame temperatures, particles easily coalesced and became larger and more spherical due to the increased residence time and flame temperature. Under the opposite conditions, aggregates composed of many nanosized primary particles appeared. This may correspond to a passive control via the control of process condition. Electric charging offers a tool for an active control of the characteristics of flame-made particles. Vemury and Pratsinis (1995, 1996) and Vemury et al.(1997) found that sizes of aggregates and primary particles generated in flames decreased proportionally to the applied electric field. This was attributed to the decrease in particle residence time (due to thinner flame zone) and a reduced particle collision frequency (due to electrostatic dispersion). However, formation of aggregates could not be avoided. The laser-chemical vapor precipitation (L-CVP) for Si₃N₄ powders was studied utilizing reactant gases absorption of the CO₂ laser beam and resulting chemical reactions and particle formation (Cannon et al. 1982; Bauer et al., 1989). Control of primary particle size and chemical composition was successful. However, aggregates were also formed due to high nucleation rate caused by the rapid heating of reactant gases and subsequent quenching by cool surrounding gas.

The coalescence characteristic time depends strongly on temperature and follows an Arrhenius expression (Kingery et al., 1976), that is, exponential decay of the coalescence characteristic time as particle temperature increases while the collision characteristic time for the free molecular regime decays according to $T_p^{-1/2}$. Therefore, the coalescence characteristic time can be controlled nearly independently of the collision time through heating aggregate particles rapidly. An attempt is made in the present study to control the coalescence characteristic time using CO_2 laser irradiation on aggregate particles generated in a flame. CO_2 laser irradiation on aggregates to more spherical particles. The aggregates irradiated by a high power CW CO_2 laser beam may be heated up to high temperature and can then be coalescent to become more sphere-like particles due to enhanced coalescence rate. Since spherical particles have much smaller collision cross sections than volume-equivalent aggregates (Pratsinis, 1998), much slower growth of particles due to CO_2 laser irradiation should become smaller than that of aggregates which

existed originally in a flame. The above control method is illustrated with Figure 2.1. In this way, the synthesis of smaller and, at the same time, spherical particles could be successfully made using laser irradiation on aggregates formed in a flame.

A coflow oxy-hydrogen diffusion flame burner was used for hydrolysis of SiCl₄ to produce silica particles. TEM image analysis with local thermophoretic sampling and a light scattering technique were utilized to study the effect of laser irradiation in a flame on the change of size and morphology of the particles. Both the measurements of the scattered intensity with Ar-ion laser light and observation of TEM photographs reveals that the present control strategy of the coalescence characteristic time using CO_2 laser irradiation in a co-flow diffusion flame is successful.

2.2 Experiments

2.2.1 Experimental appratus

Figure 2.2 shows the experimental setup which consists of a burner, two laser optical systems for heating particle and light scattering measurement, and a local thermophoretic sampling device. The burner is composed of six concentric stainless steel tubes as shown in Fig. 2.3. The carrier gas passed through a bubbler containing SiCl₄ liquid is injected through the center nozzle of the burner, and shield gas N_2 is injected through eight circumferential holes adjacent to the center nozzle to prevent deposition of formed particles on the nozzle surface. Hydrogen and oxygen are injected through the next two concentric annuli in that order. Dry air flows through the outer tube (25.4mm ID and 53mm OD) which contains a honeycomb with 100 openings cm⁻² and three fine meshes in

order to stabilize the flame. The center nozzle was lowered by 3mm from the burner surface. This arrangement is effective to prevent the clogging of particle.

A bubbler containing SiCl₄ liquid is maintained at 26° C for all experiments. The carrier gas N₂ passed through the bubbler is nearly saturated with SiCl₄ vapor in the present study. The flow rate of SiCl₄ vapor can be calculated under the saturated condition. Therefore, maintaining the constant speed of gas injected through the center nozzle for different carrier gas flow rates would require the additional gas (N₂) dilution before entering the center nozzle. The flow rates of all gases are shown in Table 2.1 and are controlled by mass flow controllers (MKS Instruments).

The burner was mounted on a two-axis traverse system with the precision of 0.01mm, which allowed different parts of the flame to be studied without moving the optical system. An industrial 2800W continuous wave (CW) CO₂ laser (Bystronic, BTL 2800), radiating at a wavelength of 10.6 μ m was used to rapidly heat up silica particles. The infrared spectra of silica particle reveal that SiO₂ has a broad absorption band between 800 and 1100 cm⁻¹ due to Si-O-Si vibration(Edahiro et al., 1980). The used power density profile of the laser beam showed a donut-like ring structure (TEM01^{*} mode). The laser beam was partially focused with a ZnSe lens (focal length, 150mm) to a beam of 3.6mm in diameter that covered the orthogonal upward stream of chemical mixture and oxy-hydrogen flame-generated silica particles at the height of h_L from the burner surface as shown in Fig. 2.1. CO₂ laser powers used in this study ranged from 250 to 2500W.

A 0.5W Ar-ion laser was employed as a light source for light scattering measurements. The beam chopped at 1200Hz was focused into the test region with a 500mm focal length lens to provide a beam waist of 0.2mm in the test region. The scattered light at 75° angle was focused into the entrance pinhole aperture of a photo multiplier tube (PMT, Hamamatsu R928). The entrance pinhole aperture and the size of the laser beam waist defined the measuring volume. A polarizer was used to reject possible cross-polarization effects and a narrow bandpass filter (1nm FWHM, peaks at 514.5nm) was placed in front of the PMT. Signals from the PMT were fed into a lock-in amplifier (Stanford Research Systems Inc., SR830) for amplifying only the chopped light signals and canceling other noise components. The Ar-ion laser beam travels at the height of h_p located 5mm higher than the CO₂ laser irradiation height (h_L). The reason is that the local thermophoretic sampling for examining size and morphology could not be made at the position where CO₂ laser beam was irradiated. Ar-ion light scattering measurement and local sampling should be done at the same position (h_p) as shown in Fig. 2.1. Signals digitized from the lock-in amplifier were transmitted to a PC via GPIB interface.

Sizes and shapes of silica particles were measured by TEM image processing after the local sampling of particles was made. To compare the result of light scattering with that of the sampling, particles in the same volume of light scattering should be captured, correspondingly, a local sampling is necessary. The local sampling device consists of a sampling probe holding a TEM grid, a shield covering the TEM grid, two air cylinders and three timers to control the insertion times of the probe and the shield independently, (Cho, 1999; Cho and Choi, 2000). Detail illustration is shown in Fig. 2.4. The shield covers the probe to prevent deposition of particles on the grid when the probe was inserted into the desired local point in a flame and pulled out of the flame. The shield has been designed to retract and expose the grid during the sampling duration only after the probe is located at the desired local position within the flame. The sampling area of the grid is confined by 1.5mm diameter hole and exposed to flames for about 70 ms.

A B type (Pt/6%Rh-Pt/30%Rh) thermocouple with a ceramic insulator was used to measure flame temperatures. The average bead diameter was 0.56 mm and the output data were digitized with an A/D converter (Keithley Instruments Inc. DAS-8) and recorded in a

PC. Flame temperatures were measured without feeding $SiCl_4$ and thermocouple stayed in a flame for sufficient times to obtain steady data. The measured flame temperatures were corrected for radiative heat loss (Chung and Katz, 1985).

2.2.2 Experimental method

Since silica particles are transparent at the visible region, the traditional extinction/scattering technique cannot be used, therefore, one cannot obtain the number density and volume fraction of silica particles only with light scattering measurement. Fortunately, our group presented a new method for estimation of number density and volume fraction of non-absorbing particles in a flame (see Cho and Choi (2000)). By virtue of this method, we can estimate the number density and volume fraction of silica particles in the flame as follows.

The scattering intensity of Ar ion laser light, $S_{vv}(\theta)$, can be expressed as follows (van de Hulst, 1981).

$$S_{\nu\nu}(\theta) = Q_{\nu\nu}(\theta) \eta \Delta V \Delta \Omega I_{i,\nu\nu} = Q_{\nu\nu}(\theta) SR$$
(2.1)

where η , ΔV , $\Delta \Omega$, and $I_{i,vv}$ are the efficiency of the optical system, the measuring volume, the solid angle of the collection optics, and the incident beam intensity, respectively, and the double subscript vv indicates that both the incident and scattered light are vertically polarized to the scattering plane. SR is the system response independent of the scattering angle, θ and the volumetric differential scattering coefficient, Q_{vv} , can then be determined by calibrating SR using nitrogen gas with known scattering cross section (Cho, 1999). For spherical particles, the mean volumetric differential scattering coefficient of polydisperse spheres, Q_{vv} , is found by intergrating over all spheres size, as follows.

$$Q_{\nu\nu}(\vartheta) = N_s \int C_{\nu\nu}(X_p, \vartheta) f(d_p) dd_p$$
(2.2)

where $C_{vv}(X_p,\theta)$ is the differential scattering cross section of a spherical particle calculated by Mie theory, and X_p is the optical size parameter (defined as $\pi d_p/\lambda_I$). The probability density function of spherical particle size, $f(d_p)$, is determined from TEM image analysis and is approximately log-normal (this approximation will be proved right later). In this case, $f(d_p)$ is written as:

$$f(d_p) = \frac{1}{\sqrt{2\pi}d_p Ln(\sigma_g)} exp[-\frac{(Ln(d_p) - Ln(d_g))^2}{2Ln(\sigma_g)^2}]$$
(2.3)

where d_g is the geometric mean diameter of spherical particles and σ_g is the geometric standard deviation of the particle size.

From Eq. 2.2, one can easily calculate the number density of spherical particle, N_s with known Q_{vv} , $f(d_p)$ and C_{vv} . The volume fraction, f_v , is also calculated from following equation:

$$f_{\nu} = N_s \frac{\pi}{6} \int d_p^{3} f(d_p) dd_p = N_s \frac{\pi}{6} D_{30}^{3}$$
(2.4)

where D_{30} is the generalized volume mean diameter of particles.

2.3 Basic theory

To expect the behavior of the particles within the CO_2 laser beam, the absorption process of the laser beam by particles should be examined. Therefore, we explained in detail the possible process that happen in the laser beam as follows.

Since sizes of spherical particles observed in this study range from 20 to 120 nm, both the scattering and absorbing processes of CO_2 laser beam (10.6 µm) correspond to Rayleigh regime. In Rayleigh regime, absorption and differential scattering cross sections for a spherical particle are given by the following relations (Bohren and Huffman, 1983):

$$C_{abs}^{p} = \frac{4\pi x_{p}^{3} E(m)}{k^{2}}, \qquad C_{vv}^{p} = \frac{x_{p}^{6} F(m)}{k^{2}} (2.5)$$

where $x_p = 2\pi a/\lambda$, $k = 2\pi/\lambda$, $E(m) = -Im((m^2-1)/(m^2+2))$, $F(m) = /(m^2-1)/(m^2+2)|^2$, *a* is the particle radius and m is the complex refractive index of the particle. Scattering of CO₂ laser beam becomes negligible compared to absorption even for the largest particle observed in this study (see Eq. 2.5). Non-spherical particles such as aggregates exhibit neither Rayleigh nor Mie scattering behavior. When primary particle sizes are within Rayleigh regime and |m-1| is less than one, Rayleigh-Debye-Gans/Fractal-Aggregate (RDG-FA) theory could be utilized under the assumption that aggregates are mass-fractal objects (Farias et al., 1995; Dobbins and Megaridis, 1991). According to Farias et al. (1995), the absorption process of the laser beam by non-spherical particles is not affected by aggregation of particles, that is, the absorption amounts of CO₂ laser beam by the aggregates could be differed only with the primary particle size. Thus, although Eq. 2.5 is derived for a spherical particle, we could use this equation for estimation of the temperature increment of the irradiated aggregates.

When a particle is irradiated by a high-power laser beam, its absorption of

electromagnetic energy results in a sharp increase of its temperature. During and after the absorption process, the particle is cooled by different physical mechanisms such as heat conduction loss through collisions with the surrounding gas molecules, evaporation loss of material from the particle surface if ablation occurs and loss due to thermal radiation. Since the latter two effects are generally small compared to the molecular heat conduction and can be neglected up to particle temperatures lower than the evaporation temperature of the particles (Roth and Filippov, 1996). As a result, the simplified version of energy balance equation for a spherical particle can be described as:

$$m_{p}c_{p}\frac{dT_{p}}{dt} = C_{abs}^{p}I_{i} - 2\pi a^{2}p_{g}c_{t}\alpha_{E}(\frac{T_{p}}{T_{g}} - 1)$$
(2.6)

where m_p is the particle mass, c_p is the specific heat of the particle, T_p is the particle temperature, T_g is the surrounding gas temperature, I_i is the incident beam intensity, p_g is the gas pressure, α_E is the thermal accommodation coefficient and c_t is the average thermal velocity of gas molecules. The first term on the right-hand side in Eq. 2.6 designates the term due to the energy absorption by a particle per unit time and is proportional to particle volume in the Rayleigh limit. The second term describes the heat conduction to a surrounding gas in a free-molecular regime (Williams and Loyalka, 1991). Assuming constant gas temperature (Roth and Filippov, 1996), time dependent particle temperature can be obtained:

$$T_p(t) = T_g + \frac{4\pi a T_g}{\lambda_i p_g \alpha_E c_t} E(m) I_i (1 - exp(-t/\tau))$$
(2.7)

where τ is equal to $2a\rho_p c_p T_g/3p_g c_t \alpha_E$.

In Eq. 2.7, the time t can be considered as the passing time of particle through the CO_2

laser beam (3.6 mm in diameter) in this study and is in the order of about 1 ms taking account of particle velocity. On the other hand, τ is the characteristic cooling time due to collisions with gas molecules and appears to be less than 1 µs in this study. Thus, while passing within the laser beam, particles are rapidly heated up to high temperature and soon reaches a steady-state temperature. The particle passed through the laser beam is rapidly cooled down to thermal equilibrium temperature. It should be noted that the steady-state temperature is proportional to particle radius *a* in Eq. 2.7, which means the temperature increment of large particle becomes larger than that of small particle for the same laser power.

2.4 Present control strategy

As described in the Introduction part, the most important factors determining size and morphology of particles are the characteristic times of collision and sintering. The characteristic time for collisions of aggregates with the radius of primary particle *a* in the free molecular regime is expressed as (Windeler et al., 1997):

$$\tau_c = 2v^{3/2 - 2/D_f} \left(\frac{6k_b T_p}{\rho_p}\right)^{-1/2} \left(\frac{3}{4\pi}\right)^{1/2 - 2/D_f} a^{6/D_f - 2} (\gamma \phi)^{-1}$$
(2.8)

where v is the average volume of the aggregate, k_b is the Boltzmann constant, ρ_p is the particle density, D_f is the fractal dimension, γ is a constant depending on D_f , ϕ is the volume fraction of the particles. For completely coalesced particles, D_f equals 3 and Eq. 2.8 reduces to the classical theory for spherical particles. The characteristic time for coalescence or sintering is varied for different sintering mechanisms. Viscous flow mechanism has been applied for silica particles and Kingery et al. (1976) gives the characteristic time for coalescence as:

$$\tau_f = 1.3 \times 10^{-14} a \exp(8.3 \times 10^4 / T_p)$$
(2.9)

where *a*, in cm, is the primary particle radius. It is noted that the coalescence time depends strongly (exponentially) on particle temperature, as evidenced by the above Arrhenius expression. Small aggregates with nanosized primary particles are formed at the early stage of the particle growth in a flame. The aggregates irradiated by a high power CW CO_2 laser beam are heated up to high temperatures and then are rapidly coalesced to become sphere-like particles due to enhanced coalescence rate. Since collision rate of spheres is much lower than that of aggregates (Pratsinis, 1998), the growth of the transformed sphere-like particles due to the irradiation of CO_2 laser should become smaller than that of aggregates that exist originally in a flame. The present control strategy utilizes the significant enhancement of the coalescence of particles generated in a flame by CW CO_2 laser irradiation for the synthesis of spherical and, at the same time, smaller nanosized particles.

2.5 Results and discussion

2.5.1 Measurement of flame temperature

Since flame temperatures are known to have a dominant effect on particle growth,

measurements of flame temperature distribution have been done to interpret the evolution of the size and morphology of flame-formed particles. Figure 2.5 shows the radial distributions of flame temperature measured at various heights above the burner exit in the absence of SiCl₄, however, keeping the total flow rate of 225 cc/min through the center nozzle as constant (see condition A in Table 2.1). The horizontal axis denotes the radial position, r. The radial distributions of flame temperature near the burner surface, e.g., z = 5, 8 and 11 mm, show that the maximum temperature occurs away from the centerline. As flames move upward, the peak point shifts to the centerline. For z equal to 17, 20 and 23 mm, the peaks occur now near the center. This characteristic is typical for co-flow flames and attributed to the initial generation of flame away from the centerline and the diffusion of combustion products to the centerline. It is also noted that slight asymmetry of the flame could be seen. Distributions of size and concentration of flame-generated silica particles may be similar to those of flame temperature because the chemical reaction of SiCl₄ vapor depends strongly on temperature, which could be confirmed by light scattering measurement and observation of TEM images as discussed later.

2.5.2 Effect of CO₂ laser irradiation on light scattering

As mentioned earlier, to protect the TEM grid, the local sampling and the measurements of light scattering were made at the height of h_p while CO₂ laser irradiates at the lower height h_L (5 mm below). Figure 2.6 shows variations of scattered intensity along the centerline of the burner for different CO₂ laser powers and different carrier gas flow rates. Figures 2.6 (a), (b) and (c) correspond to experimental conditions B, C and D in Table 2.1, respectively, and describe the effect of SiCl₄ concentrations. The horizontal

axis denotes the height, h_p , where the scattered intensities are measured and the vertical axis denotes the scattered intensity in arbitrary units.

Without CO_2 laser irradiation (P = 0 W in Fig. 2.6), the rapid increase of scattered intensity up to about 16 mm height results from particle generation due to flame hydrolysis and oxidation of SiCl₄ and rapid coagulation of particles. As particles move further downstream, the particles undergo collisional growth combined with sintering and thus the scattered intensity increases slowly. When CO_2 laser beam irradiates through the flame, the variations of scattered intensity become significantly different from the case without the irradiation. As laser power increases, the scattered intensity increases at low flame heights of CO₂ laser irradiation (h_p less than 12 mm for Fig. 2.6 (a), which corresponds to CO₂ laser irradiation heights h_L less than 7 mm). On the other hand, the scattered intensity decreases at high locations of CO₂ laser irradiation. For example, the scattered intensity at $h_p = 18 \text{ mm}$ ($h_L = 13 \text{ mm}$) decreases up to three order of magnitude from the values without CO₂ laser irradiation as laser power increases. Thus, depending on the flame height where CO_2 laser beam irradiates, the trend of change of scattered intensity may be opposite. This phenomenon is true for all three different carrier gas flow rates even if the flame height where the reversion of the change occurs may be different. At low flame heights of irradiation, e.g., h_p less than 12 mm ($h_L \le 7$ mm), the observed increase of scattered intensity of Ar-ion laser beam would be due to the particle generation effect caused by the gas absorption of CO₂ laser beam. Up to 7 mm above the burner exit, gas-phase SiO and unreacted SiCl₄ vapor are likely to exist (Tezaki et al., 1994) near the centerline of flame due to incomplete reactions. This can be seen from a TEM photo even at z = 12 mm (See Fig. 2.7 (a)). Moreover, SiO is known to be a strong absorber of CO₂ laser beam (10.6 µm) (Emel'yanov et al., 1989; Palik, 1985). Thus, if the CO₂ laser beam irradiates at this low height, silica particles can be generated from gas absorption of the

laser beam even though the direct absorption of CO_2 laser beam by $SiCl_4$ vapor may be negligible (Bauer et al., 1989). Correspondingly, the scattering intensity measured at 5mm above the CO_2 laser irradiation height, increases with increasing CO_2 laser power. This effect of particle generation due to the gas absorption of CO_2 laser beam at low flame heights was confirmed from TEM photographs (discussed later).

On the other hand, if CO_2 laser irradiates at high flame heights, the significant decrease of Ar-ion light scattering intensity is observed. As will be confirmed later from TEM photographs, the reason is that the irradiation of CO_2 laser causes the enhancement of sintering of aggregate particles formed at the same flame heights, which results in more-spherical particles with smaller collisional cross sections than the aggregate of the same volume. At 5 mm higher location above CO₂ laser irradiation position, smaller spherical particles could be evolved than those in the absence of CO₂ laser irradiation. Therefore, smaller sizes cause the significant decrease of the Ar-ion light scattering intensity. This sintering effect can be pronounced when CO₂ laser irradiates on aggregates. As can be seen in Fig. 2.7 which is the case without CO_2 laser irradiation, aggregates form up to z equal to 16 mm, however, at z = 18 mm, fully coalesced spherical particles of about 100 nm were observed. If CO_2 laser beam irradiates on these spherical particles, the effect of sintering could not be expected, but, the increased diameter may result in higher particle temperature due to the more effective absorption of CO₂ laser beam as inferred from Eq. 2.7. Therefore, if sufficient laser power is applied, the particles may be easily evaporated. Thus, depending on the laser irradiation location in a flame, the effect of particle generation due to gas absorption of CO_2 laser beam or the effect of sintering of aggregates or the effect of ablation of 100 nm order grown spherical particles can be expected in separate or combined manners. If the laser power is fixed and the irradiation height is increased (any curves except P = 0 W in Fig. 2.6), the increase of scattered

intensity at low flame heights indicates the effect of particle generation due to gas absorption while the decrease of scattered intensity beyond the certain height reflects the enhancement of sintering.

Figures 2.6 (b) and (c) show a similar fashion to that of low carrier gas flow rate shown in Fig. 2.6 (a). However, the characteristic points such as peak points of scattered intensity are found to move further downstream of the flame with increasing carrier gas flow rate, which would be explained by the increase of gas momentum. Even though the exit velocity of gases through the center nozzle is maintained by introducing the additional dilution gas when increasing the carrier gas flow rate, larger amount of SiCl₄ vapor means larger momentum of gas since SiCl₄ is heavier than the dilution gas N₂. This increase of gas momentum would inhibit the diffusion of water vapor into the center region of the flame. The resulting effect should be the delay of particle formation even without CO_2 laser irradiation (Allendorf et al., 1989).

2.5.3 TEM observation to confirm laser irradiation effects

To find out morphological changes of particles in an oxy-hydrogen flame, particles were locally captured at various heights along the centerline in the absence of CO_2 laser irradiation and the corresponding TEM photos were shown in Fig. 2.7. Figure 2.7 obviously shows the fast evolution of silica particles from the forming stage to fully sintered spheres along the centerline of the flame.

To confirm the above-mentioned effects of laser irradiation, CO_2 laser beam with various powers were irradiated at h_L equal to 6 mm, 12 mm and 18 mm above the burner surface and particles were captured simultaneously at h_p equal to 11 mm, 17 mm and 23
mm, respectively. Figures 2.8, 2.9 and 2.10 show the corresponding TEM photos, respectively, for low carrier gas flow rate of 50 cc/min.

As shown in Fig. 2.8 that corresponds to the low irradiation height, the particlegeneration effect is obvious as CO_2 laser power increases; for example, from the clear difference between cases of P = 0 and 760W. In addition, primary particle size was found to increase and the fraction of nearly unagglomerated particles tends to increase with increasing CO_2 laser power (see Fig. 2.8(c)). The latter part would be attributed to enhanced particle generation and co-existing sintering effect. The increasing trend of scattered intensity is consistent with morphological changes observed from TEM photographs as the laser power increases.

Figure 2.9 shows the effect of laser irradiation on particles irradiated at $h_L = 12 \text{ mm}$ by CO₂ laser beam and captured at $h_p = 17 \text{ mm}$. From Figs. 2.7 (a) and (b), small aggregates would exist in the region from z = 12 mm to z = 14 mm without CO₂ laser irradiation. It is also noted that the radius of CO₂ laser beam is 1.8 mm, therefore, the laser beam would irradiate small aggregates. When the laser irradiates at this intermediate height, the originally existing aggregates in a flame can be heated up to high temperatures that may be less than the evaporation temperature, but high enough to enhance sintering. Thus, aggregates could be converted into more sphere-like particles. Consequently, the size of particles captured 5 mm higher can be reduced maintaining spherical shape due to much lower collisional cross section of spheres than that of the volume-equivalent aggregates as described in the section of present control strategy. As the laser power increases, the average diameter of spherical particles evidently decreases to about 60 % of the size of the case without CO₂ laser irradiation (about 20 % in volume) as can be seen in Fig. 2.9. Thus, the control strategy adopted in the present study, which is the control of the sintering characteristic time, seems to be promising for the flame synthesis of more spherical and

smaller particles. Later, it will be shown that the use of CO_2 laser irradiation in a flame can alter non-spherical particles to spherical particles. Beyond the laser power of 1170 W, aggregates composed of a few nanometer sized primary particles also appeared together with about 40 nm spherical particles. The higher the laser power, the more aggregates appeared. For extremely high power such as 2500W, all observed particles were composed of only aggregates (not shown), which could be explained as a result of evaporation and recondensation. Table 2.2 shows that both mean diameter (d_{avg}) and standard deviation (STD) of particles decrease monotonically with increasing CO_2 laser power. All statistical data in the Table were obtained by averaging 2000 – 3000 particles each case and the sensitivity of sample numbers of particles for a proper averaging was also checked. Table 2.2 also shows that the dispersion α defined by STD/d_{avg} decreases up to approximately 0.2. This indicates the size distribution to become more uniform one. Cai et al. (1998) noted that nearly mono-disperse distribution could be assumed when Fuch's criterion α was smaller than 0.2.

Figure 2.10 shows TEM photographs of particles irradiated at $h_L = 18$ mm by CO₂ laser beam and captured at $h_p = 23$ mm. At the flame height of $h_L = 18$ mm, particles exist as fully sintered spherical particles even without CO₂ laser irradiation as seen in Fig. 2.7 (d). Therefore, the effect of sintering could not be seen apparently even if CO₂ laser irradiation is applied. Figure 2.10 also confirms this as showing nearly similar spherical particles for P = 0 and 760 W cases. However, the case of P = 1808 W revealed the coexistence of large spherical particles and aggregates composed of a few nanometer primary particles. The fraction of the aggregates was found to increase with further increasing the laser beam, which is believed to be attributed to the evaporation of particles due to the strong absorption of high power CO₂ laser beam by relatively large 100 nanometer range spherical particles and recondensation after passing the laser beam of 3.6

mm diameter.

Figure 2.11 shows TEM photographs for high carrier gas flow rate of 150 cc/min in which particles are captured at $h_p = 20$ mm and CO₂ laser is irradiated at $h_L = 15$ mm. Flow rates of gases correspond to the condition D in Table 2.1. Without CO₂ laser irradiation, the increased volume loading of SiCl₄ results in non-spherical particles (see Fig. 2.11(a)) as contrasted to the case of low carrier gas flow rate in which spherical particles are evolved even up to z = 18 mm as shown in Fig. 2.7(d). It is notable that nonspherical particles change into spherical particles due to the sintering effect even for low laser power such as 259 W (refer to Fig. 2.11(b)). The major trend is similar to the previous experiment shown in Fig. 2.9. Table 2.3 shows that mean diameter (davg) and standard deviation (STD) of particles decrease monotonically with increasing CO2 laser power. For the case without CO_2 laser irradiation, a projected-area-equivalent diameter was presented because particles appeared as non-spherical particles. As the laser power increases, particles become smaller due to the sintering effect occurred at the irradiation location (lower by 5 mm than the particle capturing location), and at the same time, particles have a narrower size distribution. In view of production rate, this result may suggest a promising possibility, that is, the synthesis of smaller nanosized, and at the same time, spherical particles under the high volume loading condition needed for large production rate.

2.5.4 Radial distribution of scattered intensity and change of particle Morphology

Radial distributions of scattered intensity were also measured at two heights of 11 mm

and 17 mm when CO_2 laser was irradiated at the heights of 6 mm and 12 mm, respectively for low carrier gas flow rate of 50 cc/min (case B in Table 2.1).

At the low irradiation height, the particle generation effect becomes dominant near the flame centerline, whereas the sintering effect becomes dominant in off-center region as shown in Fig. 2.12 (a). The radial distribution of scattered intensity without CO₂ laser irradiation is similar to that of flame temperature near the burner exit as shown in Fig. 2.5. Donut-like radial distribution of scattering intensity reflects the distribution of gas-toparticle conversion depending on flame temperature at this low height. At the height of 6mm, gas-to-particle conversion occurred incompletely near the centerline of flame, while aggregates could already exist away from the centerline due to high temperature. The laser beam could sinter aggregates that reside off-center while gas absorption of laser beam near the centerline might produce particles. To confirm this, TEM photos of particles captured at r = 0 and -2.5mm for various laser powers are compared in Fig. 2.13. Comparison between Figs. 2.13 (a1) and 2.13 (b1) evidently reveals that aggregates may exist offcenter while particle formation is incomplete at the centerline for the case without CO_2 laser irradiation. Along the centerline, the effect of particle generation due to gas absorption of laser power can be seen from Figs. 2.13 (a1), 2.13 (a2) and 2.13 (a3). Figure 2.13 (a3) even shows the effect of sintering. The sintering effect is more pronounced away from the centerline. Aggregates observed for the case without CO₂ laser irradiation now turn into spherical particles as laser power increases (see Figs. 2.13 (b1), 2.13 (b2) and 2.13 (b3)). The results of radial distribution of scattering intensity are consistent with the changes observed from TEM photographs. It is emphasized that the localized sampling technique mentioned earlier (Cho, 1999; Cho and Choi, 2000) enabled the sampling of particles at the desired local position(r, z) in a flame.

In contrast, at higher height of laser irradiation ($h_L = 12$ mm), small aggregates could

exist at almost all radial positions even without CO_2 laser irradiation. When CO_2 laser is irradiated at this height, particle sizes could begin to decrease maintaining spherical shapes with increasing the laser power. Thus, scattered intensities decrease at all radial positions as shown in Fig. 2.12 (b). Morphological changes of particles were also confirmed by Fig. 2.14 which shows TEM photographs of particles captured at two different radial positions (r = 0 and -2.5 mm) and at $h_p = 17$ mm. The decrease of particle sizes are evident due to the sintering effect occurred at the laser irradiation location, $h_L = 12$ mm. Figure 2.14 (b3) also shows the effect of evaporation and recondensation of particles off-center for P = 1138 W.

2.5.5 Coalescence and evaporation of aggregates within the laser beam

For more quantitative confirmation of the coalescence effect, number density and volume fraction of silica particles are estimated via Mie scattering and TEM image analysis. Figure 2.15 shows the evolution of silica nanoparticles along the flame height under the condition E in Table 2.1 without CO₂ laser beam irradiation (a1, a2, a3, a4 and b1) and the changes of spherical particle sizes depending on the laser powers (b1, b2, b3 and b4). At low height (13 mm, see Fig. 2.15 (a1)), particle-like condensed phase exists and is regarded as SiOH, which was confirmed by measuring FT-IR spectra. As particles go upward, aggregates with more fine primary particles are formed from the condensed phase and then sintered into more spherical particles (see Fig. 2.15 (a3), (a4) and (b1)). Note in Fig. 2.15 (b1) that some of particles still have non-spherical shape. Aggregates composed of small primary particles begin to form at about 14-15 mm from the burner

surface (Figs. 2.15 (a2) and (a3)). When CO_2 laser beam (3.3 mm in diameter) irradiates at 14 mm height with various laser powers, the size of the particles captured at 19 mm is monotonically decreased maintaining their spherical shape with increasing the laser power as shown in Fig. 2.15 (b).

Figure 2.16 (a) again confirms the considerable reduction of particle mean diameter from about 90 nm to less than 50 nm. At the same time, the volumetric scattering coefficient Q_{vv} of particles at 19 mm decreases substantially with CO₂ laser power; Q_{vv} decreases up to about 1 % of the original value of the case without CO₂ laser irradiation. From TEM image analysis, the size distributions of particles shown in Figs. 2.15 (b1), (b2), (b3) and (b4) are found to be well approximated by log-normal distributions (see Fig. 2.16 (b). The corresponding geometric standard deviations are also found to decrease monotonically from 1.4 (P = 0 W) to 1.2 (P = 1107 W), which indicates the synthesis of more uniform particles. This is clearly proved in Fig. 2.16 (b) where the probability density distribution of spherical particle volume becomes narrower with increasing the laser powers.

The volume fraction and number density of silica particles are evaluated by using MIE scattering theory and log-normal distributions (see Eqs. 2.2, 2.3 and 2.4), as shown in Fig. 2.17. For low CO₂ laser powers until P = 257 W, the number density rapidly increases up to 3 times the original value without the irradiation while volume fraction of particles remains almost the same. The substantial reduction of collision cross-sections for volume equivalent spherical particles transformed from early stage aggregates at 14 mm can increase number density and at the same time, decrease the sizes of particles captured at 19 mm. Volume fraction should be nearly the same since coalescence and collision of particles can not alter the total volume fraction of particles. Above 257 W, both volume fraction and number density are decreased with the laser power, which implies that

evaporation or thermal dissociation of silica particles occurs (Emel'yanov et al, 1989; Bailar et al., 1973). But, it should be noted that the number density at the highest laser power is comparable to the original one (at P = 0 W). In other words, because the number of particles can be increased only by the coalescence effect, both the coalescence effect and the evaporation effect contribute to the reduction of particle size even at considerably high laser power. This again demonstrates that the present control method works well.

The radially-averaged volume fraction of particles in a flame has been calculated theoretically under the assumption that: (1) the particles follows the host fluid closely (2) there are no further source or sinks of particles (3) the ratio of gas phase density and volume fraction of particles is conserved at any residence time (see Xing et al., 1996). The volume fraction measured at 19 mm is 2.06×10^{-6} without CO₂ laser irradiation, which is indeed consistent with the theoretical average value (2.45×10^{-6}). This agreement proves that the measured volume fraction and number density of silica particles would be correct.

Experimental errors for estimating number density and volume fraction are mostly resulted from the accuracy of the fitted size distribution. Because scattered intensity is strongly affected by larger particles rather than smaller ones, slight difference of the large-side tail in log-normal size distribution can lead to considerable uncertainty. In this case, maximum uncertainty is calculated to be 19% (95% confidence).

2.6 Conclusions

A new approach for control of size and morphology of flame-generated particles using laser irradiation was proposed and the effects of laser irradiation in flame synthesis of nano particles were confirmed by measurements of light scattering and the observation of TEM photos of locally-captured particles. Depending on the irradiation height of CO_2 laser beam in a flame, significantly different mechanisms were found. At the low irradiation height in a flame, the particle generation effect becomes dominant due to the gas absorption of laser power. This results in the increase of Ar-ion light scattering intensity and is confirmed from TEM observation. At the intermediate height of laser irradiation, the effect of coalescence of aggregates was observed and resulted in smaller spherical particles as laser power increased. Higher carrier gas flow rate case even showed the change of non-spherical particles into smaller spherical particles as laser power increased. Higher carrier gas flow rate case as laser power increased. This proposed method controlling the coalescence characteristic time using CO_2 laser irradiation in a flame seems to be promising to produce smaller nanosized and, at the same time, spherical particles even for high carrier gas flow rate. The radial distributions of scattering intensity and morphological change were also studied. The measured number density and volume fraction of particles proves that this coalescence control method is successfully applied to the significant size reduction of spherical silica particles at high concentration.

experimental condition	А	В	С	D	Е
carrier gas N ₂ [cc/min]	0	50	100	150	75
dilution gas N2 [cc/min]	225	150	76	2	113
SiCl ₄ vapor [cc/min]	0	25	49	73	37
Q _{total} [cc/min]	225	225	225	225	225
Shield gas N ₂ [cc/min]	400	400	400	400	400
H ₂ [l/min]	2.5	2.5	2.5	2.5	2.5
O ₂ [l/min]	5.0	5.0	5.0	5.0	5.0
Dry air [l/min]	70	70	70	70	70
Mole rate of SiCl ₄ vapor	0	9.9x10 ⁻⁴	2.0×10^{-3}	2.9×10^{-3}	1.5×10^{-3}
[mol/min]					

Table 2.1. Gas flow rates used in this study at the standard condition.

The bubbler containing SiCl₄ liquid is maintained at 26° C and the above flow rate of SiCl₄ vapor is estimated by the assumption that the carrier gas N₂ passed through the bubbler is saturated with SiCl₄ vapor. Q_{total} is total flow rate of mixed gas injected through the center nozzle of the burner.

Table 2.2. Variations of statistical data of particles for different CO_2 laser powers at low carrier gas flow rate of 50 cc/min; $h_L = 12$ mm, $h_p = 17$ mm.

	P = 0 W	P = 271 W	P = 556 W	P = 1170 W
d _{avg} [nm]	69.6	52.6	47.3	42.4
STD[nm]	21.0	15.3	13.2	10.1
STD/d _{avg}	0.30	0.29	0.28	0.24

 d_{avg} denotes number mean diameter obtained by averaging 1500 or more particles. STD denotes standard deviation and dispersion α (defined by STD/ d_{avg}) is a criterion for determining a degree of poly-dispersity of the size distribution, i.e., $\alpha < 0.2$ implies the distribution is well approximated to be monodisperse.

Table 2.3. Variations of statistical data of particles for different CO_2 laser powers at high carrier gas flow rate of 150 cc/min; $h_L =$ 15 mm, $h_p = 20$ mm.

	P = 0 W	P = 259 W	P = 741 W	P = 1485 W
d _{avg} [nm]	82.7*	59.4	50.8	48.6
STD[nm]		20.1	14.8	10.8
STD/d _{avg}		0.34	0.29	0.22

* corresponds to average projected-area-equivalent diameter for non-spherical particles.

	α-quartz	β-quartz	β-cristobalite	vitreous
Melting pt.[K]	1823		1976	(1773)
Boiling pt. [K]	3223	3223	3223	3223
Density [g/cm ³]	2.65	2.53	2.26	2.20
Index of	1.54		1.48	1.46
refraction at 514.5nm				

Table 2.4. Physical properties of SiO₂.^a

^aBailar et al.(1973)



Fig. 2.1. Schematic of the present control method.



Fig. 2.2. Schematic of experimental setup.



Fig. 2.3. Top view of the burner.



Fig. 2.4. Schematic of the localized thermophoretic sampling device.



Fig. 2.5. Radial distributions of flame temperature at various heights for different distances from the burner exit.



(b) medium carrier gas flow rate, 100 cc/min

to be continued



(c) high carrier gas flow rate, 150 cc/min

Fig. 2.6. Axial variations of scattered intensity with increasing CO₂ laser power along the centerline of the flame.



Fig. 2.7. TEM photographs of particles captured at various heights and r = 0 mm for low carrier gas flow rate of 50 cc/min without CO_2 laser irradiation.



Fig. 2.8. TEM photographs of particles captured at 11 mm for low carrier gas flow rate of 50 cc/min; $h_p = 11 \text{ mm} (h_L = 6 \text{ mm}), r = 0 \text{ mm}.$



Fig. 2.9. TEM photographs of particles captured at 17 mm for low carrier gas flow rate of 50 cc/min; $h_p = 17$ mm ($h_L = 12$ mm), r = 0 mm.



Fig. 2.10. TEM photographs of particles captured at 23 mm for low carrier gas flow rate of 50 cc/min; $h_p = 23$ mm ($h_L = 18$ mm), r = 0 mm.



Fig. 2.11. TEM photographs of particles captured at 20 mm for high carrier gas flow rate of 150 cc/min; $h_p = 20$ mm ($h_L = 15$ mm), r = 0 mm.



Fig. 2.12. Radial distributions of scattered intensity for different CO₂ laser powers at low carrier gas flow rate of 50 cc/min.



Fig. 2.13. TEM photographs of particles captured at $r = 0, -2.5 \text{ mm}, h_p = 11 \text{ mm} (h_L = 6 \text{ mm})$ for low carrier gas flow rate of 50 cc/min, (a) captured at r = 0 mm, (b) captured at r = -2.5 mm.



Fig. 2.14. TEM photographs of particles captured at $r = 0, -2.5 \text{ mm}, h_p = 17 \text{ mm}(h_L = 12 \text{ mm})$ for low carrier gas flow rate of 50 cc/min, (a) captured at r = 0 mm, (b) captured at r = -2.5 mm.



to be continued



Fig. 2.15. TEM photographs of SiO₂ particles for low carrier gas flow rate of 75 cc/min (a) captured at various heights without CO₂ laser irradiation (b) captured at 19 mm with CO₂ laser irradiation; $h_p = 19$ mm ($h_L = 14$ mm), r = 0 mm.



(a) variations of Q_{vv} and mean diameter of particles with increasing CO_2 laser powers



(b) variations of volume distribution of particles with increasing CO₂ laser powers Fig. 2.16. Variations of Q_{vv} and size of particles with increasing CO₂ laser powers for intermediate carrier gas flow rate of 75 cc/min; $h_L = 14$ mm, $h_p = 19$ mm.



Fig. 2.17. Variations of number density and volume fraction of SiO₂ particles with CO₂ laser powers for intermediate carrier gas flow rate of 75 cc/min; $h_L = 14 \text{ mm}$, $h_p = 19 \text{ mm}$.

Chapter 3

Coalescence Enhanced Synthesis of Titania Nanoparticles

3.1 Introduction

Nano crystalline or non-crystalline particles have been widely used in various industrial areas, such as ceramics, catalysis, electronics, metallurgy and optic device. In the last decade, TiO_2 powders and films have been extensively investigated due to remarkable optical, electronic and chemical properties. For example, the high refractive index and high dielectric constant of TiO_2 film provides an excellent optical coating and protective layer on lenses and optical fibers. Other applications include humidity and gas sensors, gate electrodes in semiconductors, and testing for good blood compatibility (Zhang et al., 1997). Therefore, titania particles have also great potentials in the above applications.

TiO₂ polymorph is known to have three phases (anatase, brookite and rutile) which have their own applications. For example, anatase has been proved to be most active photocatalyst in environmental remediation (Fox and Dulay, 1993), while rutile has been used as a white pigment because of its thermochemical stability (Mezey, 1966). In all applications, synthesizing the crystalline particles as small as possible and controlling the crystalline phase according to its purpose are requisite for the enhancement of processing performance. In addition, producing dense nanostructured bulk ceramics has recently attracted much interest by virtue of their unsual properties, specially enhanced ductility at high temperature relative to the coarse-grained ceramics. But, in manufacturing the nanostructured bulk materials with high density close to theoretical value, there have been some obstacles. The major one is due to the great difficulty in synthesizing nanosized *unagglomerated* powders. Among the recently-used many manufacturing methods, sol-gel technique have produced relatively readily nanocrystalline powders (< 10nm in diameter), but have great problems such as aggregation, contamination during the processing and

residual small pores (Kumar et al., 1992). Among the problems, the aggregation may be the worst one because the rapid grain growth along necks can result in an elongated grain structure, so called "a vermicular structure" which is known to be detrimental to subsequent densification (Park et al., 1999) and the aggregation also has packing problems. These needs motivate the present attempt to control size, morphology, phase of nano TiO_2 particles.

The morphology and size of particles are determined by the competition between collision and coalescence of particles (Windeler et al., 1997). The formation of aggregates is due to faster collision of particles than coalescence. Even though the method of salt addition to coat on particles generated in a flame had been shown to produce unagglomerated nanoparticles (DuFaux et al., 1995), high purity of particles could not be obtained and the subsequent process of washing may pose an additional problem of agglomeration. The electrical field had been applied in a particle generating flame to successfully control the size of primary particles and aggregates, however, the formation of aggregates could not be avoided (Vemury and Pratsinis, 1995, 1996; Vemury et al., 1997). The present method relies on controlling the characteristic time for coalescence of nanoparticles by irradiation of CO₂ laser beam on the early stage aggregates formed during flame synthesis that has been considered as the most effective way to produce high concentration nanoparticles (Pratsinis, 1998). The coalescence characteristic time depends strongly on particle temperature following the exponential decay ($\propto \exp(E/RT_p)$, R: gas constant, E: activation energy for coalescence) (Kingery, 1976) while the collision characteristic time of nanoparticles decays according to $T_p^{-1/2}$ (Windeler et al., 1997; Matsoukas and Friedlander, 1991). Therefore, the coalescence characteristic time can be controlled nearly independently of Brownian collision by heating aggregates rapidly. As shown in Fig. 2.1, early stage aggregates formed in a flame are irradiated by a high power CW CO₂ laser beam to rapidly coalesce and become spherical particles. Since spherical particles have much smaller collision cross-sections than volume equivalent aggregates (Windeler et al., 1997; Matsoukas and Friedlander, 1991), much slower growth of nanoparticles can be achieved. Therefore, smaller, at the same time, spherical nanoparticles can be successfully produced at high concentrations (Lee and Choi, 2000). To verify this principle, the variations of number density and volume fraction of nano particles as well as the variations of their sizes and shapes are quantitatively measured for titania generated in a coflow oxy-hydrogen diffusion flame under the irradiation of CO₂ laser beam. TEM image analysis with localized thermophoretic sampling (Cho and Choi, 2000), Mie scattering technique (Bohren and Huffman, 1983) and Rayleigh-Debye-Gans/Fractal Aggregate theory (Koylu and Faeth, 1994) are utilized to estimate variation of number density and volume fraction of titania particles having circular or irregular shapes. The number density and volume fraction prove that our control strategy, i.e. the coalescence enhanced synthesis as proved for silica particles in Chapter 2 is also applied successfully for production of much smaller spherical titania particles (~20nm).

The controllability of crystalline phase of titania nanoparticles are also investigated using X-ray diffraction (XRD). Surprisingly, stable rutile titania particles are transformed into metastable anatase nanoparticles and the weight percent of each phase is controllable.

Raman scattering is used to examine the effect of the laser irradiation on the phase stability (Parker and Siegel, 1990a and 1990b). Using the Raman peak shift and broadening, we find two phenomena such as increasing or reducing the oxygen-deficient defects (or the residual strains) in our samples depending on the applied laser powers. Also, Fourier analysis of the XRD line broadening is applied to determine microstrains in the samples which may affect the phase stability. Variations of the microstrains with the laser powers are correlated with the measured degree of the oxygen-deficient defects. Details are explained later.

To check the efficiency of our controlled anatase particles by the laser irradiation, we attempted to produce bulk TiO_2 by compacting and subsequent sintering. As a result, we obtained dense nanostructured titania, with density > 98% of the theoretical maximum and an average grain size of ~70nm.

3.2 Experiments

3.2.1 Experimental apparatus and instrumentation

 TiO_2 particles are generated in an oxy-hydrogen diffusion flame by hydrolysis of $TiCl_4$. A laminar diffusion flame burner is also used as in Chapter 2 because the diffusion flame burner provides some advantages over a premixed flame burner, i.e., flame stability over a wide range of operating conditions.

Local thermophoretic sampling device (see Fig. 2.4) is also used for observation of the particle morphology and measurement of the size. The procedure to obtain images involves selecting aggregates or spheres randomly at relatively low magnifications near the center of the TEM grids. Almost all TEM photographs are shown in figures at a magnification of 5 x 10^4 while additional photographs are taken at a magnification of 2 x 10^4 for estimating size information. The TEM measurements include primary particle diameters (d_p), projected areas (A_a) and maximum lengths (L) of aggregates. Experimental uncertainties of these morphological measurements on any one aggregate / particle are expected to be less than 5%.

Laser light scattering experiments are also conducted and experimental details were
already explained in Chapter 1. Experimental setup and alignment used in this work is nearly the same as those in Chapter 2, but scattering angle is modified to be 65 degree. The experimental uncertainties (95% confidence range) of the light scattering measurements are estimated to be less than 10%, generally dominated by small difference of CO₂ laser beam alignment relative to the measuring volume, although the optic alignment are very carefully made during all experiments. It should be noted that light extinction (transmission) measurement is not possible in this work because titania particles do not appreciably absorb green light, i.e., their refractive index is approximately real. This fact does not allow the scattering to extinction ratio technique (Koylu and Faeth, 1994) to be applied to obtain number density and volume fraction of non-absorbing particles. It is also emphasized that particles existed in our flame are not generally spheres and particles heated by CO_2 laser have morphological change from aggregates to spheres. The traditional angular dissymmetry scattering technique (Chang and Biswas, 1992) is applicable only to spheres using equivalent-Mie theory. In this work, therefore, a new method proposed by our group, i.e., combining TEM image analysis with fixed angle light scattering technique is used for estimation of number density and volume fraction of aggregates or spherical particles (details will be explained later and see Cho and Choi (2000)).

Titania particles flowing through the flame are thermophoretically deposited onto a quartz tube (6 mm in outer diameter and 300 mm in length) which is cooled by flowing water and moved back and forth by air cylinder. The tube height from the burner end (h_d) is also adjusted precisely with 2-D traversing system (see Fig. 3.1). TiO₂ particles are deposited for only 1 - 2 min to prevent undesirable heating the outer deposited layer up to phase transition temperature of titania and the deposited layer is then collected for further measurement of the titania crystallinity. This procedure is iterated 10 - 20 times until the

collected powder weighs at 80 mg.

In contrast to the case of $SiCl_4$, the bubbler containing $TiCl_4$ is maintained at relatively high temperature above 40 °C because the vapor pressure of TiCl₄ (Aldrich, 99.9 %) is much lower than that of SiCl₄. Four experimental conditions (see Table 3.1) are used for each objective as follows: relatively low-temperature flame is at first chosen (Condition A in Table 3.2) because low-temperature flame facilitates collecting powders without undesirable overheating the deposited layer. Secondly, since the present coalescence enhanced control method seems to be more effective at high precursor concentration, high carrier gas flow rate is necessary for our purpose and more, high-temperature flame are requisite for complete chemical reaction of TiCl₄ (Condition B in Table 3.1). Additional two conditions such as higher precursor jet exit velocity (Condition C) and lower $TiCl_4$ concentration (Condition D) are planed for an optimization of process conditions. The reason for choosing the above two conditions is as follows: increase of precursor jet exit velocity through the center nozzle (compare Condition C with B) decreases primary particle size of aggregates within the laser beam, which may decrease the size of the transformed spherical particles. Decrease of precursor concentration (Condition D and B) decreases the primary particle size and then, smaller nano-spherical particles may be synthesized.

3.2.2 Characterization of aggregates

Titania and silica aggregates synthesized in this work exhibit tenuous structures. The complex morphology of aggregates with wide size and shape variations can be characterized as mass fractals. This implies the following statistical relationship between

the number of primary particles in an aggregate, N_p , and its radius of gyration, R_g (Jullien and Botet, 1987):

$$N_p = k_g \left(\frac{2R_g}{d_{pm}}\right)^{D_f}$$
(3.1)

where k_g , d_{pm} and D_f are the fractal prefactor, mean primary particle diameter, and fractal dimension, respectively. In Eq. 3.1, the aggregates are assumed to consist of monodisperse non-overlapping spherical primary particles, i.e., the mean value of d_p is used in Eq. 3.1. In this work, the primary particles had highly narrow distributions of the size d_p . Measurement of the projected area equivalent diameter d_a from TEM image is used to estimate N_p , following the method of Koylu et al. (1995a), i.e.,

$$N_p = 1.15 \left(\frac{d_a}{d_{pm}}\right)^{2.18} (3.2)$$

Since the actual three-dimensional radii of gyration of aggregates are not readily available from the projected TEM images, an alternative form of Eq. 3.1 can be expressed as follows:

$$N_p = k_L \left(\frac{L^a}{d_{pm}}\right)^{D_f}$$
(3.3)

where L^a is maximum length of aggregate and the fractal prefactor based on L^a , k_L , is related to k_g in Eq. 3.1 (Koylu et al., 1995a and 1995b) by

$$k_g/k_L = \left[(D_f + 2)/D_f \right]^{D_f/2} \tag{3.4}$$

The fractal dimension, D_f , can be estimated from the slope of a log-log plot of N_p vs L^a/d_{pm} for a set of aggregates and k_L is also obtained from the y-intercept of the plot. Eq. 3.4 gives k_g from the known D_f and k_L . Although there is a wide variation in the k_g values reported by Koylu et al. (1995a) and Cai et al. (1993), Koylu et al. (1995b) found that the differences in the mean values of $L^a/2R_g$ from one study to another was always smaller than 19%, i.e., a consistent observation similar to D_f . From this fact, they derived a relation between the $L^a/2R_g$ and D_f as follows:

$$L^{a}/2R_{g} = \left[(D_{f}+2)/D_{f} \right]^{1/2}$$
(3.5)

One can easily calculate R_g from Eq. 3.5.

3.2.3 Number density and volume fraction of aggregates

For spherical particles, the procedure for estimating the number density and volume fraction was already explained in detail in the section of 2.2.2. But, for the readers, we would like to summarize simply again here. The mean volumetric differential scattering coefficient of polydisperse spheres, Q_{vv} (measured by calibrating SR using nitrogen gas) is expressed in terms of number density (N_s), the differential scattering cross section (C_{vv}) and the probability density function of the spheres (f(d_p)) (see Eqs. 2.1 and 2.2). f(d_p) is also determined from TEM image analysis and is approximately log-normal. The known Q_{vv} , f(d_p) and C_{vv} give the number density N_s and volume fraction f_v of spherical particles (see Eqs. 2.1 – 2.4).

For fractal-like aggregates, Rayleigh-Debye-Gans/Fractal-Aggregate (RDG/FA)

theory (Sorensen et al., 1992; Koylu and Faeth, 1994; Farias et al., 1995 and 1996) had been applied to obtain the number density and volume fraction of soot particles using extinction-scattering ratio. But unfortunately this method cannot be utilized for titania aggregates for the same reason as the silica case. In this work, therefore, a new method, combining RDG/FA theory with TEM image analysis (proposed by Cho and Choi (2000)), is used to obtain the number density and volume fraction of aggregates. Details for the procedure are explained here. The mean volumetric differential scattering coefficient of randomly oriented polydisperse aggregates, Q_{vv} , are found by integrating over all aggregate sizes, as follows:

$$Q_{vv}(\vartheta) = N_a \int C_{vv}^a(\vartheta) f(N_p) dN_p$$
(3.6)

where N_a is the number density of aggregates in a flame, N_p is the number of primary particles per aggregate, and C^a_{vv} is the differential scattering cross section of a fractal-like aggregate. From RDG/FA theory, C^a_{vv} can be expressed by adopting the proposal of Dobbins and Megaridis (1991) as follows (Jullien and Botet, 1987; Martin and Hurd, 1987):

$$C_{\nu\nu}^{a}(\mathcal{G}) = N_{p}^{2} C_{\nu\nu}^{p}(X_{p},\mathcal{G}) exp(-\frac{(qR_{g})^{2}}{3}) \quad \text{for } qR_{g} < 1.5D_{f} \text{ (Guinier regime)} \quad (3.7a)$$
$$= N_{p}^{2} C_{\nu\nu}^{p}(X_{p},\mathcal{G})(qR_{g})^{-D_{f}} \quad \text{for } qR_{g} > 1.5D_{f} \text{ (Power-law regime)} \quad (3.7b)$$

where C_{vv}^{p} is the differential scattering cross section of a primary particle (assuming the primary particles have the same size) and q is the modulus of scattering vector, q = $4\pi/\lambda_i \sin(\theta/2)$. The probability density function of aggregate size, f(N_p), is also expressed as following relation similar to Eq. 2.3:

$$f(N_p) = \frac{1}{\sqrt{2\pi}N_p Ln(\sigma_g)} exp[-\frac{(Ln(N_p) - Ln(N_g))^2}{2Ln(\sigma_g)^2}]$$
(3.8)

where N_g is the geometric mean number of primary particle per aggregate σ_g is the geometric standard deviation of aggregate size N_p .

Finally, the aggregate number density N_a can be obtained from Eq. 3.6 and volume fraction f_v is also calculated from following expression:

$$f_{v} = N_{a} \frac{\pi}{6} d_{pm}^{3} \int N_{p} f(N_{p}) dN_{p} = N_{a} \frac{\pi}{6} D_{30}^{3}$$
(3.9)

The RDG approximation generally ignores effects of multiple- and self-scattering so that the electric field of each primary particle is the same as the incident electric field, and differences of the phase shift of scattered light from various points within a particular primary particle are ignored. Therefore, RDG scattering requires that both $|m-1| \ll 1$ and $2X_p|m-1| \ll 1$ (Bohren and Huffman, 1983; van de Hulst, 1957) where m is the complex refractive index. Although SiO₂ aggregates synthesized in this work fulfill the above criteria, the first criteria is questionable for TiO₂ due to its high refractive index (m = ~2.5). But, Farias et al. (1996) evaluated the range of validity of the RDG approximation for the optical cross sections of fractal aggregates in comparison with the integral equation formulation for scattering (IEFS) accounting for the effects of multiple scattering and selfinteraction. For example, the error for the differential scattering cross section of a representative anatase aggregate synthesized in this work (d_p = 10 nm, $\lambda_i = 514.5$ nm, D_f = 1.6, N_p ≤ 256 , m = 2.55) is shown to be less than 10 % from their result. In addition, the error for the another approximation that absorption cross section is not affected by the aggregation process (C^a_{abs}= N_pC^p_{abs}) is also within 20 %. Consequently, RDA/FA theory can be adopted for estimation of number density and volume fraction of TiO₂ aggregates.

3.2.4 Crystallinity of titania particles

The cystalline phase of the collected TiO₂ particles is determined by X-ray diffraction (MAC/Science, MXP18XHF-22), using CuK α radiation (λ_I = 1.54056 Å). Both the nano crystalline samples and the reference materials were measured at a step width of 0.01° for typical count times of 12 s. The K α_2 component of the scattering of the CuK α radiation (1.5444 Å) was removed using the Rachinger algorithm (Klug and alexander, 1974).

Two different coarse-grained samples were used as standard samples for the correction of the instrumental broadening function of the diffractometer: first, well annealed rutile powder (99 %, Aldrich, particle size of ~400 nm, originally anatase powder which fully transforms to rutile by heating for 12 hr at 1300 °C in air); secondly, bulk standard Si (polycrystalline, supplied by Mac/Science). Standard rutile powder gave highly sharp diffraction peaks because heating for longer time resulted in removal of any pre-existed strain and further growth of crystallite size.

The weight fractions of the rutile phases in the samples are calculated from the relative intensities of the strongest peaks corresponding to anatase ($2\theta = 25.3^{\circ}$ for the (101) reflection) and rutile ($2\theta = 27.5^{\circ}$ for the (110) reflection) peaks, as described by Spurr and Myers (1957):

$$\alpha_r = [1 + 1.26 \frac{I_a}{I_r}]^{-1}$$
(3.10)

Crystallite sizes of each phase are estimated from the Sherrer equation after fitting

each peaks to Gaussian profile and the correction for the instrumental broadening (Klug and Alexander, 1974) as:

$$D = \frac{K\lambda_i}{\beta\cos\theta} \tag{3.11}$$

where D is effective crystallite size, θ is the reflection angle in radians, β is the breadth of the peak profile and the Sherrer constant, K, varies with crystallite shape such as cube, tetrahedron, octahedron or sphere from 0.89 to 1.21. In this work, the Sherrer constant is chosen to be 1.0 as an average value. It should be reminded that β corresponds to the value of the pure diffraction profile corrected for instrumental broadening.

The Sherrer equation was originally derived for small cubic crystals assumed to be free from strains and stacking faults. But, the broadening of the peak profile can be produced by small crystallite size, faulting on certain (hkl) planes and microstrains within the crystallite. Also, the changes in peak position may be due to the faulting, lattice parameter changes produced by dislocations and segregation of solute atoms, which is very complex phenomena, therefore, these effects are not considered in this work. Since many polycrystalline materials generally possess considerable strains, the Sherrer's method could yield significant errors. From this reason, alternative method for estimating crystallite size in the strained samples should be necessary and thus Fourier analysis proposed at first by Warren and Averbach (1950) was adopted for estimating both the size and microstrain (Klug and Alexander, 1974; Wagner, 1966). The detailed procedure of this method is explained in Appendix B.

3.2.5 Distortion of crystal structure of titania particles

Raman spectroscopy has been widely employed for studying the characterization of nano crystalline TiO_2 polymorphs and investigation of degree of intragrain defects due to oxygen deficiency (Melendres et al., 1989; Parker and Siegel, 1990). Strain, the intragrain defects and size can affect the line shapes of the Raman peaks of nanophase TiO_2 , i.e. broadening of line shape and shift of peak position. In this work, using this fact, Raman spectra of the present TiO_2 samples are used for determining degree of oxygen stoichiometry, i.e., oxygen / titanium ratio as a criterion of phase stability of anatase. Details for factors affecting the phase stability of anatase are explained and simply reviewed later.

Laser Raman spectroscopy of the present TiO_2 samples is performed using a RFS-100/s (Bruker) Fourier Transformed (FT) Raman spectrometer consisted of a Nd:YAG laser operating at 1064 nm, a filter avoiding Rayleigh scattering, a broad-range quartz beamsplitter, frictionless interferometer and precise InGaAs detector. The spectral response ranges from 70 to 3600 cm⁻¹ (Stokes shift) and spectral resolution is better than 1 cm⁻¹.

3.2.6 Thermal stability of titania particles

Thermal stability of the synthesized nanophase TiO₂ samples are investigated by High-Temperature X-Ray Diffraction (HT-XRD) using CuK α radiation ($\lambda_I = 1.54056$ Å). A Philips X'PERT MPD attached with a furnace (heating up to 1600 °C) is used for determining rutile contents variation with temperature. Each sample is heated from room temperature to 1400 °C in vacuum (0.2 Pa) with the rate of 10 °C/min and XRD patterns are recorded from 400 to 1400 °C at 100 °C intervals. When sample temperature reaches each recording temperature, the samples are measured from 23° to 29° at a step width of 0.01° for typical count times of 12 s. The well-annealed rutile powder in Section 3.2.4 is also used as a standard sample. In this case, the Sherrer equation can estimate the crystallite size with a good accuracy because any possible strain is released during the heat treatment. Therefore, the rutile contents and effective crystallite size of each phase in the sample are also estimated by Eq. 3.10 and 3.11, respectively.

3.2.7 Production of bulk TiO₂

To check the efficiency of our controlled anatase particles by the laser irradiation, we attempted to produce bulk TiO₂ by compacting and subsequent sintering. The smallest sized and spherical titania particles (20nm in diameter) are used as a best sample. The procedure is as follows. Each 80mg unit of TiO₂ powder is uniaxially pressed into cylindrical pellets of 5.0mm in diameter at 5 Mpa and the pellets are then isostatically pressed at 10 Mpa for 3 min. To sinter the pressed pellets, the pellets are heated in air with the rate of 10 °C/min to various sintering tempature such as 700 °C, 750 °C and 800 °C and is then constantly heated for 30min at the assigned sintering temperature. After this heat treatment, properties of the pellets such as density, crystallinity, grain size and the grain morphology are measured by Archimedes principle, XRD and Field-emission scanning electron microscopy (FE-SEM, Philips XL30), respectively.

3.3 Results and Discussion

3.3.1 Control of size and morphology

We applied the present method to control the growth of crystalline titania particle. Four experimental conditions with different gas and precursor flow rates (see Table 3.1) are designed to optimize process condition for synthesizing titania particles as small as possible, as explained in section of 3.2.1. The results of measurements of particle size and light scattering without CO_2 laser irradiation under Condition A are at first presented for basic understanding of titania particle formation, growth and morphological change.

Figure 3.2 shows the evolution of TiO₂ nanoparticles along the flame height under the condition A in Table 3.1 without CO₂ laser beam irradiation. At the lowest height (z = 11 mm), large monomers (24 nm) rather than aggregates mostly exist in contrast to the previous silica case. This is not a surprising discovery due to much faster sintering of TiO₂ than that of SiO₂, especially at low temperature and the existence of the monomers at the TiO₂ particle forming stage was also reported by Yang and Biswas (1997). At z = 13 mm, aggregates with fine partimary particles start appearing and at the same time, the fraction of the monomers becomes decreased (see Fig. 3.2(b)). At z = 16 mm, only aggregates with many and slightly smaller primary particles are observed in Fig. 3.2(c), which implies the monomers are not TiO₂ but intermediate materials to TiO₂. Since the monomer is likely to have less dense structure than TiO₂, the monomer size is slightly larger than the primary particle size of the aggregates. As the aggregates go further upward, the aggregates are coalesced into more spherical particles (Fig. 3.2(d) and (e)) and finally transforms to isolated spheres (Fig. 3.2(e)).

Mean particle sizes such as d_a and d_p, and number of primary particle per an aggregate N_p are measured from TEM image analysis with averaging 1500 or more spheres and 150 - 200 aggregates. Fig. 3.3(a) shows the change of average d_a , d_p and N_p along the flame. The mean projected area equivalent diameter d_a is related to the free molecule regime mobility diameter of aggregates (Rogak and Flagan, 1993; Koylu et al., 1995b). The d_a for titania produced in the present flame was observed to lie mostly in the range of 20 and 200nm. Therefore, The titania aggregates can be treated as being in the near freemolecular regime in our present atmospheric pressure flame. Additionally, the ratio of d_a and d_p or N_p can be utilized as a indicator of degree of aggregation. In Fig. 3.3(a), one can easily notice that the aggregation reaches maximum due to dominant particle collision at 16 mm. Above 16 mm, both d_a and N_p are rapidly decreased due to fast coalescence, which results in releasing additional heat due to decrease of surface energy. Consequently, the coalescence might be accelerated. Fig. 3.3(b) illustrates the number of primary particles in an aggregate as a function of its maximum length L (outer diameter) for aggregates captured at different heights. The aggregates shown in Fig. 3.3(b) included only those $N_p > 10$. The least-square fit in the form of Eq. 3.3 yielded $D_f = 1.62$ and $k_L =$ 1.1, which corresponds to $k_g = 2.11$. Although appreciable coalescence took place, the fractal characteristics were almost insensitive to sampling position in this condition. This result also indicates that these titania aggregates are similar to other flame-generated materials, including carbonaceous soot (Koylu et al, 1995b).

Fig. 3.4 shows the radial variations of d_a and d_p of TiO₂ particles captured at 16 mm and 20 mm without CO₂ laser irradiation. At low height (16 mm), as the sampling position goes toward off-center region, d_p increases from 24 nm to 39 nm while d_a decreases rapidly from 173 nm to 83 nm. The change implies obvious morphological change from aggregates to isolated-spheres, due to faster coalescence at higher temperature off center, and was also confirmed from the corresponding TEM images (not shown). The same trend is maintained at higher position (r = 20 mm), but the degree of aggregation, i.e., the ratio of d_a and d_p is much smaller than at 16 mm due to longer residence time in the flame. Radial variation of Q_{vv} is presented in Fig. 3.5 to know qualitatively the radial distribution of particles. Nearly symmetrical profiles are obtained at all heights and large particles exist off center (at r = 1.5 mm) in great numbers. Note that the peak position of Q_{vv} moves toward the centerline of the flame from off-center region as the measuring height increases. This observation implies that the particles existing off center are driven to the center line by thermophoretic force due to higher temperature off center at low height and radial pushing to the centerline at high position by the dry air jet, respectively. A radial diffusion of particles is likely to be not significant.

Fig. 3.6 shows the axial variation of Q_{vv} of TiO₂ particles under Condition A measured by altering the irradiation heights of CO₂ laser with different powers. One can readily notice the significant difference between the Q_{vv} profiles for SiO₂ and TiO₂, especially at low height (compare Fig. 3.6 with Fig. 2.6). At low irradiation height, Q_{vv} of SiO₂ increased sharply with increasing the laser powers due to the particle generation, while the laser-induced particle generation could not be occurred for TiO₂. Hydrolysis of TiCl₄ produces Ti(OH)₄ as a intermediate product which is converted to TiO₂ at high temperature (Jang, 1997; Akhtar et al., 1994). The intermediate material cannot directly absorb CO₂ laser beam, while SiO as a intermediate product of silica is a strong absorber of CO₂ laser beam (Emel'yanov et al., 1989; Palik, 1985). From this reason, the particle generation effect could not take place for TiO₂ case. Further, small aggregates start appearing at about 11 – 13 mm from the burner surface (Fig. 3.2(a) and (b)), therefore, the decrease of Q_{vv} at $h_p = 15 - 20$ mm with the laser powers in Fig. 3.6 is due to the coalescence effect (note $h_L = h_p - 5$ mm). For further confirmation of the effect, TEM images of TiO₂ particles captured at $h_p = 16$ mm ($h_L = 11$ mm) and two radial positions (r = 0 mm and -1.5 mm) are shown in Fig. 3.7 for different laser powers. As the laser powers increase, original aggregates are coalesced into more spherical particles and finally isolated-spheres at all radial positions. Note that the efficiency of the laser irradiation with the same power is better off center than at centerline (compare Fig. 3.7(a) and (b)). The reason can be explained by regarding Eq. 2.7: since larger particles can be heated to higher temperature, aggregates with larger primary particles off center (see Fig. 3.7) are more readily coalesced. It is also noted that the finally transformed spheres (Fig. 3.7(a4) and (b4)) are large as much as spheres that can be produced without CO_2 laser irradiation (see also Fig. 3.2(f)). We ascribed at first the production of large spheres (even by shining CO₂ laser beam) to low number concentration of particles. That is, if particle collision is negligible compared to the coalescence due to very low concentration of particles, the reduced collision rate by irradiating the laser beam is still much smaller than the sintering rate. Thus, in this case, the effect of the laser irradiation on the size could not be apparently observed. Consequently, higher concentration of titania particles might be necessary for verifying usefulness of the present control method more clearly as same as the case of silica.

Thus, we chose Condition B (higher carrier gas flow rate and higher temperature of TiCl₄ liquid) for producing much smaller spheres (see Table 3.1). Figure 3.8 shows the changes of size and morphology of titania particles captured at 16 mm from the burner surface without or with CO_2 laser irradiation done at 13 mm. As CO_2 laser power increases, the original aggregates with fine and polyhedral primary particles are changed into more-sintered aggregates (Fig. 3.8(b) and 3.8(c)) and finally into isolated spherical particles (Fig. 3.8(d)). The trend of morphological change is exactly the same as the previous case (in Fig. 3.7). The magnified TEM image indicates that seemingly

agglomerate particles in Fig. 3.8(d) turn out to be just multiple deposition of isolated sphere particles on TEM grid.

Formenti et al (1972) suggested that when (1) flame temperature is higher than the melting point of the oxide, (2) and the residence time in the flame is sufficiently long, the particles form droplets that give spherical particles. But, if these conditions are not fulfilled, the particles conserve polyhedral forms. According to their suggestion, existence of spherical particles at the highest laser power tells us that titania particles are heated up to significantly high temperature above their melting point.

As laser power increases, projected area equivalent diameters significantly decrease (projected area equivalent diameters: 166 nm for P = 0 W and 29 nm for P = 1665 W). Furthermore, it is estimated that average volume of particles also decreases substantially by about 30 times. This significant volume reduction of titania particles would be mainly due to the reduction of collision cross-sections of transformed more-spherical particles from aggregates. Evaporation might be also possible. However, the possibility may be low since boiling temperature of titania is as high as 3273K (see Table 3.4) and titania could not be dissociated thermally below boiling point. In contrast, silica can be easily dissociated into SiO and O at substantially lower temperatures than its boiling point (Emel'yanov et al., 1989; Bailar et al., 1973). Indeed, for silica, aggregates composed of very fine primary particles appeared again at high laser powers due to evaporation and subsequent recondensation. Whereas, for titania, even at extremely high laser power of 2400W, recondenced aggregates could not be observed. Further confirmation of the hypothesis that the volume reduction of TiO_2 particles is solely due to the coalescence effect of our control method will be made later by estimating number density and volume fraction of titania.

Higher precursor concentration condition yielded much smaller spheres (29 nm in

size) than in low concentration as our expectation. Here, we felt that a careful comparison between Condition A and B was necessary for producing further smaller spheres. The two conditions are differed in flame temperature, precursor concentration and precursor jet exit velocity. Among them, we paid attention to the third one rather than the second one because the primary particle size of original aggregates without CO_2 laser irradiation in Condition B is smaller than that in Condition A by about two times (compare Fig. 3.8(a) with Fig. 3.2(c)). But, higher precursor concentration generally increase both primary particle size of aggregates and the aggregate size when the coalescence rate or solid state diffusion coefficient for TiO₂ is not significantly small. Windeler et al. (1997) reported that the primary particle size of aggregates significantly decreased with increasing the exit velocity when the other experimental parameters (volume loading of precursor, fuel and oxidizer flow rates) were the same. In this case, therefore, producing the smaller primary particles of aggregates in Condition B is mainly due to the faster precursor jet exit velocity, i.e., the shorter residence time in the flame.

If one can lay smaller aggregates with smaller primary particles within the laser beam, smaller spheres can be produced. From this viewpoint, finding an experimental condition to produce the smallest primary particles without the laser irradiation may be necessary for obtaining the smallest spheres. Thus, we designed two additional experimental conditions for our objective: first, increasing the precursor jet exit velocity by injecting the excessive nitrogen (compare Condition A with C in Table 3.1), and secondly, decreasing the precursor concentration (volume loading of TiCl₄) at the same jet exit velocity (compare Condition B with D).

Fig. 3.9(a) and (b) show TEM images of TiO₂ particles captured at 21 mm ($h_L = 17$ mm) under Condition C with and without CO₂ laser irradiation, respectively. We could obtain obviously smaller spheres ($d_{avg} = 22.6$ nm and $\sigma_g = 1.41$) than those in Condition B

 $(d_{avg} = 29.4 \text{ nm and } \sigma_g = 1.43)$, as expected. The smallest spheres that could be obtained without CO₂ laser irradiation were shown in Fig. 3.9(c). Although the capturing positions are different each other, one can readily notice that only irradiating the laser beam can significantly affect the finally obtained sphere size. Also, we would like to emphasize that the size distribution of the spheres becomes narrower with the laser irradiation (σ_g decreases from 1.50 to 1.41).

Fig. 3.10(a) and (b) show TEM images of TiO₂ particles captured at 18 mm ($h_L = 15$ mm) under Condition D with and without CO₂ laser irradiation, respectively. We could obtain the smallest spheres ($d_{avg} = 20.3$ nm, $\sigma_g = 1.44$) in all used experimental conditions. For verifying the effect of the laser irradiation, the smallest spheres that could be obtained without CO₂ laser irradiation ($d_{avg} = 38.9$ nm, $\sigma_g = 1.47$) were also presented in Fig. 3.10(c). The magnified TEM image proves obviously the particles in Fig. 3.10(b) to be isolated spheres.

Fig. 3.11(a) shows the size distribution of the transformed spheres in Fig. 3.10(b) and that of the original spheres at $h_p = 25$ mm in Fig. 3.10(c). One can readily notice that the laser irradiation yields much smaller spheres with narrower size distribution. Fig. 3.11(b) shows the size distribution of aggregates which originally existed at the same height ($h_p = 18$ mm) as a function of N_p. The size distributions of both aggregates and the transformed spheres are well fitted to lognormal profiles (shown as solid lines in Fig. 3.11(a) and (b)). Fig. 3.12 shows the number of primary particles (N_p) in an aggregate as a function of its normalized outer diameter (L^a/d_{pm}) for aggregates captured at 18 mm without CO₂ laser irradiation. Fractal characteristics of the original aggregates are shown as follows: $k_L = 1.34$ and D_f = 1.60, yielding $k_g = 2.56$ (see Eq. 3.4). This result is nearly the same as in Fig. 3.3(b), which represents the fractal characteristics are relatively insensitive to the material composition of aggregates and process condition.

The fractal characteristics and size distributions of the original aggregates were used for estimating number density and volume fraction of the aggregates in Fig. 3.10(a), with corresponding Q_{vv} (see Eqs. 3.6 – 3.9). Moreover, number density and volume fraction of the transformed spheres in Fig. 3.10(b) were also estimated using Eqs. 2.2 – 2.4. All measured parameters for calculating the number density and volume fraction are shown in Table 3.3. As a result, the number density N_a and volume fraction f_v of the aggregates and spheres are 1.77×10^9 [#/cm³] and 2.71×10^{-7} [cm³/cm³], while N_s and f_v of the spheres are 3.77×10^{10} and 2.49×10^{-7} , respectively. Surprisingly, each volume fraction is nearly the same, considering gas expansion due to indirect heating the surrounding gas by CO₂ laser irradiation. This implies that particles within the laser beam were not evaporated even at the highest laser power and also proves obviously that irradiating the laser on early-stage aggregates can produce significantly small spheres due to the coalescence effect of our laser-enhanced coalescence control method.

Experimental errors for estimating number density and volume fraction are estimated to take place mostly by the accuracy of the fitted size distribution. Because scattered intensity is strongly affected by larger particles rather than smaller ones, slight difference of the large-side tail in lognormal size distribution can lead to considerable uncertainty. In this case, maximum uncertainty is calculated to be 19% (95% confidence).

In summary, from the above results for SiO_2 and TiO_2 , we can affirm without hesitation that our control method can be applied to synthesizing smaller spherical particles (made by any materials), only if the wavelength of the laser beam is close to the absorption band of the material, i.e., the laser beam can heat small aggregates enough to enhance the coalescence rate.

3.3.2 Control of crystalline phase

Many previous researchers found that the transformation behavior of anatase to rutile can be affected by many factor, such as impurities (Shannon and Pask, 1965; Akhtar and Pratsinis, 1992; MacKenzie, 1975) and process condition. Atomic structures of the two phases are represented in Fig. 3.13 from which one can notice the rutile has more dense structure than anatase. In fact, rutile has higher density (see Table 3.2) and thus, the anatase to rutile phase transformation takes place accompanied by volume contraction about 10 % (Gribb and Banfield, 1997). An energy commonly as a heat, therefore, should be supplied to become more dense structure (rutile) via atomic rearrangement. Jang and Jeong (1995) found that rutile content was significantly increased with reactor temperature. Indeed, the activation energy reported for the phase transform ranges from 335 to 619 kJ/mol (Shannon and Pask, 1965; Hishita et al., 1983). Therefore, when a laser beam irradiates on anatase particles, one can easily expect that rutile content should be increased due to supplying the additional energy through laser irradiation. But, our result is directly opposite to the expectation.

Figure 3.14 shows X-ray diffraction profiles of titania particles collected at 65 mm for different laser powers when the laser beam is irradiated at 25 mm. In the figure, A and R denote Brag peaks of anatase and rutile, respectively. It is interesting that rutile contents decrease monotonically with the increase of laser power. Even for different CO_2 laser irradiation positions, the trend of decreasing rutile weight percent is the same, although the decrements of the rutile contents are different depending on the irradiation heights (Fig. 3.15). For sufficiently high laser powers, rutile peaks completely disappear. From this result, one may imagine that a laser irradiation on anatase phase results in the rutile-to-anatase reverse transformation, which is actually impossible (Shannon and Pask, 1965).

Zhang and Banfield (1998) proved from the thermodynamic analysis that rutile is the only thermodynamically stable phase when particle size exceeds 14 nm. Moreover, most of previous researchers (Gribb and Banfield, 1997; Ding and Liu, 1996; Shannon and Pask, 1964) reported the transformation of anatase to rutile was enhanced as the calcination temperature increased. To the extents of our knowledge, we could not find any studies on the transformation from rutile to anatase phase.

In the absence of CO₂ laser irradiation, rutile weight percent increases monotonically with flame height; 2.6 % at 15 mm, 6.9 % at 20 mm, 10.3 % at 25 mm, 13.3 % at 40 mm and 16.6 % at 65 mm. This is consistent with previous studies. But, the present study with CO₂ laser irradiation reveals that the laser irradiation can alter the phase from rutile to anatase. For example, 17 % rutile weight percent in particles at 65 mm without CO₂ laser irradiation is now changed to almost zero percent when CO₂ laser beam is irradiated at 25 mm with P = 326 W (see Fig. 3.15). It should be reminded that original rutile content at 25 mm is 10.3 %. This represents the rutile within the laser beam (at 25 mm) transforms to anatase.

This result can be explained by melting and subsequent re-crystallization within the crystalline particle. If the particles are melted or partially melted at least within the laser beam, anatase phase should be preferred during re-crystallization process from the liquid phase in our experimental conditions by the following reasons. Although rutile is only thermochemically stable phase, rutile has more compact lattice structure than anatase (Gribb and Banfield, 1997). In order to directly form rutile from liquid phase, residence time in the flame should be sufficiently long for atomic rearrangement into the compact rutile structure. But, the residence time in our system is highly short in the order of 1 ms, which may lead to forming anatase phase predominantly from liquid phase. Alternative explanation can be made by concept of critical radius of nucleus. Gribb and Banfield

(1997) calculated the critical radius of anatase nucleus in solution was 10 % smaller than that of rutile and thus, supposed that the metastable anatase is formed predominantly from solution during recrystallization.

However, since rutile contents are originally very low at low height (\leq 15mm), the above explanation by means of melting may not be correct, especially, at very low laser power. In addition, one may ask why anatase particles formed after melting at low height are not transformed to rutile along the flame even if original anatase particles are melted. Some reviews about governing mechanism for the transformation are necessary for answering the question. Shannon and Pask (1964) proposed a mechanism involving the formation of rutile nuclei on the surface of anatase particles and the nuclei growth. Gribb and Banfield (1997) expanded the surface nucleation and growth mechanism to nanocrystalline materials and suggested that the fundamental factors determining the rate of the transformation are composed of: (1) number of potential nucleation sites (2) the driving force for the transformation (strain energy associated with nucleus formation). From their kinetic experiments, they concluded that the nucleation rate on the anatase surface rather than the growth rate of rutile nucleus is the rate-determining factor. Namely, the transformation rate is directly proportional to number of nucleation site for rutile nucleus.

Next problem is where are potential nucleation sites. From further analysis of their kinetic results, Zhang and Banfield (1999) concluded that the nucleation site should be interface between the contacting anatase particles, since activation barrier for rutile nucleation is lowered due to the interface structure. Indeed, Park et al. (1999) found that the higher compact density of anatase powders yielded the lower onset temperature of the anatase to rutile transformation. This result was also attributed to the lowered activation energy for the transformation due to increase of the number of contact. The above reviews

are likely to say that the phase transformation is strongly dependent on the particle size and also, especially, particle morphology (spheres or aggregates). In our experimental result, when the laser irradiation changes original aggregates into volume-equivalent spheres, both disappearance of necks (largely existed in the original aggregates) and significantly decreasing surface area (decrease of surface free energy, i.e., a driving force) can stabilize anatase particles. Here, we could not affirm the role of the neck in the phase transformation as a nucleation site. But, we can say at least obviously that the anatase aggregates should be transformed than the anatase spheres, regarding that the contacting points in a flame are generated by collision between the particles. The reason is that the aggregates should supply more contracting points due to larger collision rate than the spheres. Consequently, spherical anatase particles could be not transformed to rutile along the flame due to the above reasons even if anatase particles grow and are heated by the flame.

Another possibility of stabilizing anatase particles with the laser irradiation may be a change of microstrain or defects in anatase particles. Depero et al. (1999) found that anatase particles had a larger microstrain than that in rutile with the same size, using Fourier analysis of X-ray diffraction line broadening. They also proposed that the larger amount of the microstrain might be a cause of the phase instability of anatase and that of the phase transformation. In addition, recent X-ray absorption study revealed that the disorder of the lattice was attributed to a decrease in the coordination number for the third shell of O atoms, i.e., oxygen deficiency or vacancy (Chen et al., 1997). The microstrain may be connected with oxygen vacancy or intrinsic defects in nanocrystalline anatase. Also, the larger oxygen vacancy or defects in anatase enhances generally the phase transformation (Mackenzie 1975). Therefore, if one can reduce the microstrain in anatase through thermal annealing, one may expect that the transformation can be retarded. In our

case, the laser irradiation is likely to cure the defect due to oxygen deficiency or the strains within anatase particles, especially at low laser power (not enough to melt the particles). Measuring variations of the microstrains or degree of oxygen deficiency in titania particles during the laser irradiation may be very important to understanding the effect of laser irradiation on phase stability of anatase particles. Moreover, the thermal stability of our samples produced by the laser irradiation should be compared with other samples (sample without the laser irradiation or commercial samples or sample by other manufacturing method). The oxygen deficiency and thermal stability of our samples will be discussed in following section.

3.3.3 Effects of CO₂ laser irradiation on the crystal structure

3.3.3.1 Oxygen deficiency in TiO₂ samples

Raman scattering has recently been used to determine defect structures within materials by measuring the shifting and broadening of some of the spectral peaks (Parker and Siegel, 1990a and 1990b). Campbell and Fauchet (1986) showed that grain size effects could produce large shifting and broadening of the Raman spectrum of silicon. In contrast to silicon, the grain size of nanophase TiO_2 powders (larger than 10 nm) had no effect on the observed Raman spectra (Melendres et al., 1989; Parker and Siegel, 1990a). However, defect structures within the TiO_2 powders strongly affect the Raman spectrum by producing large shifting and broadening of the Raman lines. Parker and Siegel (1990a) proved that the above changes observed in the Raman spectra (specially, at 144 cm⁻¹ peak) were related to the oxygen stoichiometry of the TiO₂ samples and were not due to any

internal stress or grain size effect. But, they neglected the possibility that the size effect occurred in smaller sized TiO_2 samples (< 10 nm). In deed, Ivanda et al. (1999) observed the blue shifting and broadening of 144 cm⁻¹ E_g peak of anatase with decreasing the size from 9.2nm to 6.4nm. From these result, we can conclude that the size effect is negligible for TiO_2 particles larger than 10 nm. Also, we could use Parker and Siegel's result to determine the degree of oxygen deficiency in our samples because the present crystallite size is above 10 nm.

To confirm the effect of the laser irradiation on the phase stability of anatase suggested in the previous section, Raman spectra of TiO₂ powders collected at 20 mm ($h_L = 15$ mm) by altering the laser powers (0, 212 and 550 W) under Condition A were measured and are shown in Fig. 3.16. All three lines in the figure shows that anatase phases mostly exist in the three samples. Based on the factor group analysis, the 144 cm⁻¹, 399 cm⁻¹, 519 cm⁻¹ and 639 cm⁻¹ peaks are assigned to $E_g (v_1)$, $B_{1g} (v_4)$, $A_{1g} + B_{1g} (v_3 + v_2)$ and $E_g (v_1)$ modes of anatase phase, respectively (refer to Table 3.4). Although original rutile content is determined to about 7 % by XRD at zero laser power, the zero-power line (P = 0 W in the figure) does not show traces of the existence of the rutile phase: the strongest peaks of the rutile appear at 447 and 612 cm⁻¹. The disappearance of the rutile peaks even in the P = 0 W case can be regarded as screening the rutile peaks by relatively strong anatase peak tails due to low weight fraction of the rutile (7 %).

According to Parker and Siegel's assertion, we focused on the variation of peak position and its full width at half-maximum intensity (FWHM) with increasing the laser powers. Although we could not find large peak shifting and broadening as in Parker and Siegel (1990b), we observed small changes in the anatase E_g peak position and FWHM for different laser powers. As the power increases to 212 W, the peak position moves from 144.52 to 143.98 cm⁻¹ and FWHM decreases from 11.66 to 11.25 cm⁻¹. But, as the power

increases further, on the contrary, the peak position shifts to slightly higher wavenumber (144.19 cm⁻¹) and FWHM increases from 11.25 to 12.53 cm⁻¹. Considering the experimental error (± 0.5 cm⁻¹ for peak position and ± 0.3 cm⁻¹ for FWHM), the variations of the peak positions are likely to lie within the error range, while the FWHM is obviously changed with the laser powers. The change of the FWHM not accompanied by the peak shifting may be related to the possible strains in the samples.

We'd like to emphasize two points from the changes of Raman spectra. First, even though the peak positions are slightly varied with the laser powers, all peak positions are close to theoretical value (143.5 cm⁻¹). Thus, the degree of oxygen deficiency of the TiO₂ samples is quite low at all laser powers, that is, the samples are nearly fully oxidized (stoichiometric) TiO₂. Whereas, Parker and Siegel's as-compacted TiO₂ showed much larger peak shifting (E_g peak of 154 cm⁻¹) and broadening (FWHM = ~35 cm⁻¹) in their Raman spectra. Considering each synthesis route (hydrolysis or oxidation in oxygen-excess atmosphere in our case vs. evaporation and highly rapid oxidation in their case), one can easily solve why our system even without the laser beam produces a nearly stoichiometric TiO₂. Namely, the oxygen-excess and high-temperature atmosphere suppresses the possible formation of the oxygen-deficient defects. From this point, we can expect that our synthesized anatase samples will show excellent thermal stability due to Oxygen/Titanium ratio very close to 2 (refer to Mackenzie (1975) and Parker and Siegel (1990b)).

Secondly, two phenomena seem to take place according to the applied laser power. At low laser power (P = 212 W), the peak narrowing by the laser irradiation implies that the laser irradiation cures the distorted structures due to oxygen deficiency or strains within the original samples. This possibility is reasonable because thermal annealing in air had been used to further oxidize the oxygen-deficient samples (Melendres et al., 1989; Parker and Siegel, 1990a) and the laser-induced annealing at oxygen-excess atmosphere can play the same role or reduce at least the strains in the sample. Accordingly, the laser irradiation with low power can stabilize anatase phase.

On the other hand, if the particles are once melted within the high-power laser beam, the phase change and the defect structure are strongly affected by the cooling time of the particles from liquid phase. In the present case, the cooling time corresponds to the residence time for which the particles flow from the laser beam to the deposition tube (see Fig. 3.1) and is estimated to be about 1 ms. This significantly short cooling time may result in considerable structural distortion, thus, the once-melted TiO₂ particles by the laser beam can be locally oxygen-deficient or have relatively large strains. The peak broadening by the high power laser irradiation (P = 550 W) supports this hypothesis.

To support more firmly the above inferences, measurements of Raman spectra for different cases were scheduled. First, in the absence of the laser beam, the Raman spectra of samples collected at different height revealed that the peak position starting at 145.1 cm⁻¹ moves progressively to theoretical value (143.5 cm⁻¹) and spontaneously, FWHM also decreases from 14.60 to 11.29 cm⁻¹, as the collecting height increases. This means that the possible oxygen-deficient defects or strains or both are cured or released along the flame due to thermal annealing in high temperature oxygen-excess atmosphere.

The next Raman spectra of samples collected at 65 mm ($h_L = 25$ mm) for five different laser powers revealed that the peak positions were not changed within the experimental error range and were about 144 cm⁻¹. While, FHWM increased monotonically from 10.91 to 12.07 cm⁻¹ as the laser power increased. Now, the changes of the Raman characteristics should be examined connected with the corresponding phase change because the observation of the phase change allows us to determine where melting is occurred. Note that the laser irradiation height is 25 mm and rutile content is originally ~7 % at that height. Even for low laser power of 115 W, the resultant rutile content is lower than the original value, which implies that the melting is occurred at least in part. From this point, the above inference related to the melting predicts that the once melted particles may have larger strain or more distorted structure. Surprisingly, the experimental observation agreed well with the prediction.

Finally, this Raman analysis was applied also to the smallest-sized anatase samples in this work (see Fig. 3.13(a) and (b)). The Raman peak position and FWHM in the absence of the laser beam are observed to be 145.46 and 13.92 cm⁻¹, respectively. While, at the maximum laser power, the position and FWHM are 145.98 and 14.87 cm⁻¹, respectively. The particles must be melted at the maximum-power laser irradiation; otherwise, their shape should be polyhedron (see Fig. 3.13(b)). According to our inferences, melting and subsequent quenching processes produce more oxygen-deficient or strained particles. The broadened peak profile due to the laser irradiation supports again our inferences. But, here, we can not assert that the high-power laser irradiation un-stabilizes the anatase phase due to increased strains or detects and thus enhances the phase transformation during heat treatment. The reason is that there is another factor strongly affecting the phase stability of anatase; for examples, particle morphology (refer to the section of 3.3.2). The melting and subsequent quenching the particles can not only increase defects or strains but also change the particle morphology from aggregates to spheres. Regarding the phase and thermal stability of the anatase, the latter effect may be more important in our conditions from the following reasons. First, the morphology change may result in the reduction of both the possible nucleation sites and surface free energy (as a driving force for the phase transformation). Another reason is that the oxygen-deficient defects even at the highest laser power are considerably small compared to those in titania particles produced by gas condensation although the peak profile is slightly broadened at the high power laser

irradiation.

Table 3.7 summarizes all Raman analysis results connected with the corresponding X-ray diffraction results and the crystallite size.

3.3.3.2 Microstrains in TiO₂ samples

The laser irradiation may reduce or increase oxygen-deficient defects according to the applied laser powers, as explained in the previous section of 3.3.3.1. That is, the occurrence of the melting is highly likely to be a critical boundary between the above two effects, i.e. increasing or reducing oxygen-deficient defects (or the residual strains). We felt that the degree of defects may be correlated with the strains. To check this possibility, changes of the strains in the titania samples (collected at 20 mm ($h_L = 15$ mm) under Condition A for three different laser powers) are estimated by Fourier analysis of the XRD line broadening (refer to Appendix A).

The XRD profiles obtained for the different laser powers are corrected for instrumental broadening with the well annealed rutile samples by the Stokes correction method (Klug and Alexander, 1974; see Appendix B). Since there are no pairs of multi-order reflections (for example, 101 and 202, or 200 and 300 reflections, etc) for the anatase phase, we should choose unavoidably two strong peaks such as 101 and 200 peaks to examine at least qualitatively the trend of microstrains change (see Appendix A). In deed, the trend of the strain change estimated by this method was exactly the same as that by alternative method (Katayama's single line analysis in Crist and Cohen (1979)).

From the plots of Ln A(L) against s_0^2 , we obtained the y-intercepts of the lines at fixed L and the slopes. The intercepts and the slopes as a function of L yield the size

coefficients A^S(L) and the rms microstrains, respectively (see Eq. A6). Fig. 3.17(a) and (b) show the A^S(L) and the rms microstrains against column length L, respectively. In Fig. 3.17(a), the open circles represent the Fourier size coefficients that are re-normalized such that y-intercept of the tangent becomes unity (see Appendix A). The effective crystallite size D is given by the intercept of the tangent with the L axis (see Eq. A7). Note that this figure corresponds to the zero-power laser irradiation case. D is determined to be 49.3 \pm 0.9 nm, while the mean primary particle diameter d_{pm} was obtained to be 42.1 \pm 1 nm from TEM image at the same height. The discrepancy between the two sizes from XRD and TEM is not due to experimental error but due to the difference of particle sampling methods. That is, d_{pm} corresponds to the mean diameter of titania particles nearly at r = 0mm, while D corresponds to that in the range from r = -1.5 to 1.5 mm because particles were deposited on the deposition tube (6 mm in diameter). In addition, we can expect from light scattering measurement (Fig. 3.5) that the larger particles exist off center (especially at $r = \pm 1$ mm) with larger number density, compared to those at r = 0 mm. Considering Fig. 3.4 where d_{pm} was ~50 nm at r = 1 mm, we can say that the measured effective crystallite size is quite consistent with the mean primary particle diameter obtained from TEM.

Fig. 3.17(b) shows the rms strains as a function of L for three different laser powers. As the laser power increases to 212 W, the microstrains decrease obviously from 1.7 % to 1.4 %. But, further increasing the power, the microstrains become increased rapidly. One can notice that the change of the microstrains according to the laser powers is well correlated with that of the oxygen-deficient defects (compare Table 3.6 with Table 3.5). Therefore, we can conclude that the laser irradiation reduces or increases oxygen-deficient defects or microstrains according to the laser powers.

3.3.4 Effects of CO₂ laser irradiation on thermal stability

Thermal stability of the smallest and spherical particles (see Fig. 3.10(b)) is investigated by High-Temperature X-Ray Diffraction (HT-XRD). Fig. 3.18 shows the XRD profiles of the TiO₂ particles (20 nm in diameter) collected at 18 mm for the maximum laser power. As the heating temperature increases, rutile contents are progressively increased; starting at ~850 °C, the phase transformation is ended at 1200 °C. In addition, very-broadened XRD profiles of the original anatase phases represents that the samples are highly fine. The effective anatase size, in this case, is calculated to be ~18 nm by the Sherrer equation.

Remind that our inference suggested from the Raman scattering analysis predicts that our samples may have excellent thermal stability compared to the samples made by other production methods. We based this inference upon the highly low degree of oxygen deficiency (O/Ti ratio close to 2) or very low strains. Because the degree of structural distortion is strongly affected by manufacturing method, it is very important to compare the thermal stability of the various samples made by different methods. For more correct comparisons, we found some previously published thermal-stability data for the anatase samples undergoing the same heat treatment (the same heating rates and heating time) as that for our sample.

The anatase sample of Park et al. (1999) is a commercial product (Nanophase Tech. Co., 30 - 38 nm, nearly spherical) which was made by gas condensation. The heating time is zero, which means that a specimen is taken out of the furnace just after reaching the designated temperature. Ding and Liu (1996)'s sample is made by sol-gel route, and its size is 11.3nm, and the heating time is 4min shorter than in our case.

Fig. 3.22 shows clearly that our non-agglomerated sample synthesized with the highest laser power reveals the most excellent thermal stability of the anstase phase. Also, it should be emphasized that the gentle slope of the curve for our sample means higher activation energy for the phase transformation than that of other samples. Although sol-gel route can produces highly fine particles, their anatase phase is significantly unstable due to high degree of aggregation or a certain contamination by foreign ions during manufacturing process.

3.3.5 Effects of CO₂ laser irradiation on grain growth of bulk TiO₂

Nanophase bulk materials have stimulated much interest recently by virtue of their excellent properties. But, preparing materials to be denser and finer grained has proved difficult because higher sintering temperature necessary for increasing the density could result in significant grain growth. Hahn et al. (1990) sintered TiO₂ samples produced by gas condensation method at 1000 °C and 900 °C, thus obtained much finer grain size (~51 nm) at the lower temperature (900 °C) but only 91 % of the theoretical density. In addition, they could produce dense TiO₂ bulk with a grain size of ~40 nm by pressure-assisted sintering and sinter-forging with near theoretical density. Barringer and Bowen (1982) prepared fine powders (3 to 10 nm in size) by sol-gel technique and sintered the samples to almost 100 % density at 800°C with a grain size of ~150 nm. Two years later, Barringer et al. (1984) proposed the liquid phase sintering and hot pressing to achieve near theoretical density. Kumar et al. (1992) reported that much finer grained (< 60 nm) bulk titania with density > 99% could be produced by sintering near the phase transformation temperature (~600 °C), liquid phase sintering and hot pressing.

As shown in the previous section, we attributed the excellent thermal stability of our anatase sample (~20 nm in crystallite size) to the lack of necks (exist only in agglomerates) and the lower degree of structural distortion. The better thermal stability may require the high sintering temperature for producing bulk titania with higher density. But, one should not underestimate the morphological change by the laser irradiation. Producing fine spherical particles is important as much as its difficulty because disappearance of necks yields much better packing than for agglomerates at the same pressure. Therefore our un-agglomerated samples could be sintered to bulk titania near the theoretical density not accompanied by significant grain growth due to the fact that the grain growth during sintering could be occurred very rapidly through necks.

We tested our samples at three different sintering temperature (700 °C, 750 °C and 800 °C) for 30 min. As a result, density of the pellet heated at 800 °C was above 98 % and the grain size was only 70 nm. This result is quite promising in practice, because we didn't use the additional or special sintering method such as liquid phase sintering and hot pressing. Also we would like to emphasize that our samples were only pressed at 10 Mpa. Fig. 3.20 proves obviously that our bulk materials possess fine grains and also there are no apparent pores.

3.4 Conclusions

We applied the new control method to producing nanosized and un-agglomerated TiO_2 particles and spontaneously controlling the crystalline phase. The transformation from large aggregates to nanosized spheres was obviously observed and was solely due to the coalescence effect. This assertion was justified also by estimating number density and

volume fraction. Among these, volume fraction of titania particles was nearly maintained constantly in the presence or absence of the laser irradiation.

As for controllability of crystalline phase, the laser irradiation yielded very interesting results: as the laser power increases, the rutile contents decreases, i.e. the laser irradiation stabilized the anatase phase. This was understood by 1) the concept of melting and subsequent quenching at high power 2) cure of the oxygen-deficient defect structure or the residual strains in the anatase particles at low power not enough to melt the particles. Raman scattering analysis and Fourier analysis of XRD peak broadening verify these two inferences.

Also, the phase stability was determined by HT-XRD measurement, the presently controlled anatase samples revealed much excellent thermal stability and had higher activation energy for the phase transformation than other previous published anatase material. In addition, we tried to produce ultrafine grained bulk titania with high density near the theoretical value via pressureless heat treatment. As a result, density of our pellet heated at 800 °C was above 98 % and the grain size was only 70 nm. The disappearance of necks in our samples yields much better packing than for agglomerates at the same pressure. Therefore our un-agglomerated samples could be sintered to bulk titania near the theoretical density not accompanied by significant grain growth due to the fact that the grain growth during sintering could be occurred very rapidly through necks. We can conclude that the present control method could be successfully applied to controlling the size, morphology and the crystalline phase.

experimental conditions	А	В	С	D
carrier gas N ₂ [cc/min]	200	300	200	100
dilution gas N ₂ [cc/min]	0	0	222.8	222.8
TiCl ₄ vapor [cc/min]	6.9	26.3	6.9	3.5
Q _{total} [cc/min]	206.9	326.3	429.7	326.3
Shield gas N ₂ [cc/min]	700	700	700	700
H ₂ [l/min]	1.5	2.5	2.5	2.5
O ₂ [l/min]	4.0	5.0	5.0	5.0
Dry air [l/min]	50	70	70	70
Mole rate of TiCl ₄ vapor [mol/min]	2.7×10^{-4}	9.6x10 ⁻⁴	2.7×10^{-4}	1.4x10 ⁻⁴
Precursor jet exit velocity [m/s] ^a	1.355	2.137	2.814	2.137

Table 3.1. Gas flow rates used for generating TiO_2 particles in this study at the standard condition.

^a The velocity injected through the center nozzle of this burner (1.8mm in diameter) is calculated at room temperature.

The bubbler containing TiCl₄ liquid is maintained at 40°C for A, C and D conditions, while maintained at 60 °C for B condition. Condition A corresponds to a low-temperature low-concentration condition and was originally designed to facilitate collecting powders without undesirable overheating the deposited layer. Conditions B, C and D are planed to synthesize particles as small as possible via an optimization of systematic parameters: increase of precursor jet exit velocity through the center nozzle (compare Condition C with D) decreases primary particle size of aggregates within the laser beam. Decrease of precursor concentration (Condition B and D) decreases the primary particle.

crystalline phase	anatase	brookite	rutile	
Melting pt. [K]	change to rutile	change to rutile	2128	
Boiling pt. [K]			3273	
Density [g/cm ³]	3.9	4.1	4.3	
Index of refraction	2.55	2.6	2.71	
at 514.5 nm				
crystallography	tetragonal	orthorhombic	tetragonal	
cell parameter [Å] (a,c)	(3.783, 9.51)	(9.184, 5.145)	(4.594, 2.958)	
(b) for brookite		(5.447)		
space group	$D^{19}_{4h}(I4_1/amd)$	D ¹⁵ _{2h} (Pbca)	$D^{14}_{4h}(P4_2/mnm)$	

Table 3.2. Physical properties of TiO2.

^bShannon and Pask (1964)

^cBalachandran and Eror (1982)

Table 3.3. Size information used for estimating number density and volume fraction of TiO₂ particles produced under Condition D.

For aggregates in Fig. 3.10(a); $h_L = 15 \text{ mm}$, $h_p = 18 \text{ mm}$, P = 0 W

d _{pm} [nm]	10.23	
N_{g}	155.48	
σ_{g}	2.89	
k _L	1.34	
D_{f}	1.60	
$Q_{vv} [cm^{-1}]$	1.36x10 ⁻⁴	

For spheres in Fig. 3.10(b); $h_L = 15 \text{ mm}$, $h_p = 18 \text{ mm}$, P = 2408 W

19.05
1.44
3.14x10 ⁻⁵
Anatase
--
Raman shift ^a [cm ⁻¹]
144
197
399
519
639
796

Table 3.4. Assignment of the Raman bands for anatase and rutilephases of TiO2 particles.

^aBalachandran and Eror (1982)

Experimental condition A						
P [W] (h _L =25mm, h _p =65mm)	peak position [cm ⁻¹]	FWHM [cm ⁻¹]	α _r [%]	d _{avg} [nm]		
0 115 235 329 416	143.76 144.03 143.99 144.08 144.16	10.91 11.74 11.86 12.03 12.07	16.6 9.9 3.2 0 0	> 50 not changed not changed not changed not changed		
z [mm] (P = 0W)	peak position [cm ⁻¹]	FWHM [cm ⁻¹]	α _r [%]	d _{pm} or d _{avg} [nm]		
11 13 15 17.5 20 25	145.11 145.04 144.74 144.31 144.52 144.03	14.60 13.61 12.68 11.67 11.66 11.29	0 0 2.6 4.0 6.9 10.3	25.7 23.2 ~ 25 ~ 32 42.1 48.1		
$\begin{array}{c} P [W] \\ (h_L=15mm, h_p=20mm) \end{array}$	peak position [cm ⁻¹]	FWHM [cm ⁻¹]	α _r [%]	d _{pm} or d _{avg} [nm]		
0 212 550	144.52 143.98 144.19	11.66 11.25 12.53	6.9 not changed 0	42.1 		
Experimental condition D						
$\begin{array}{c} P[W]\\ (h_L=15mm, h_p=18mm) \end{array}$	peak position [cm ⁻¹]	FWHM [cm ⁻¹]	α _r [%]	d _{pm} or d _{avg} [nm]		
0 2300	145.46 145.98	13.92 14.87	< 5 0	10.2 20.3		

Table 3.5. The shift and broadening of Raman peak of 144 cm⁻¹ of TiO₂ particles synthesized under various conditions.

note : α_r , d_{pm} and d_{avg} denote rutile contents in TiO₂ crystallites, mean primary particle diameter and mean spherical particle diameter, respectively.

Table 3.6. Estimation of crystallite size and rms strain by Fourier analysis for X-ray line broadening of TiO₂ crystallites synthesized under Condition A for different CO₂ laser powers.

P [W] (h_L =15 mm, h_p =20 mm)	D [nm]	maximum ε _{rms}	d _{pm} [nm]
0	42.3	0.00172	42.1
212	45.5	0.00138	
550	40.9	0.00241	

note : D, ε_{rms} and d_{pm} denote effective crystallite size, rms strain in TiO₂ crystallites and mean primary particle diameter from TEM image analysis, respectively. The rms strains decreases generally with increasing column length L. To facilitate comparison of strain values, maximum ε_{rms} was determined by extrapolating $\varepsilon_{rms}(L)$ to L = 0 mm.

Change	zero power	low power not enough to melt particles	high power enough to melt particles
morphology	aggregates	still aggregates but more sintered	spheres
Raman peak shift peak width	Both are close to standard values	small red shift sharpening	small blue shift broadening
oxygen-deficient defects or residual strains	small	slight decrease	slight increase
effective rms strain by X-ray line broadening	medium	decrease	increase
Thermal stability			Excellent compared to previous results

Table 3.7. Summary of the role of CO2 laser irradiation on anataseaggregates in the corresponding morphology and phase.

^a The Raman peak position is very close to theoretical values compared to the previous results and also the peak shifts are nearly the same within the experimental error for different laser powers, while FWHM is slightly increased at high power.



Fig. 3.1. Schematic of the burner head and the used coordinate system.



Fig. 3.2. TEM photographs of TiO_2 particles captured at several heights without CO_2 laser irradiation under Condition A; r = 0 mm.



(a) variations of average diameter and number of primary particles per aggregate



(b) Determination of fractal dimension and fractal prefactor

Fig. 3.3. Size information from TEM image analysis of TiO_2 particles captured at several heights along centerline without CO_2 laser irradiation under Condition A; r = 0 mm.



Fig. 3.4. Radial variations of mean primary diameter and projectedarea-equivalent diameter of TiO₂ particles in the absence of CO₂ laser irradiation under Condition A.



Fig. 3.5. Radial variations of Q_{vv} of TiO₂ particles existed at different heights in the absence of CO₂ laser irradiation under Condition A.



Fig. 3.6. Axial variations of Q_{vv} of TiO₂ particles for different irradiation heights of CO₂ laser with different powers under Condition A; $h_p - h_L = 5$ mm, r = 0 mm.





to be continued



Fig. 3.7. TEM photographs of TiO₂ particles captured at two radial positions under Condition A (a) r = 0 mm, (b) r = -1.5 mm; $h_p = 16$ mm ($h_L = 11$ mm).



Fig. 3.8. Morphological variation of TiO_2 particles with increasing CO_2 laser powers under Condition B; $h_p = 16 \text{ mm} (h_L = 13 \text{ mm})$, r = 0 mm.



Fig. 3.9. Morphological variation of TiO_2 particles with CO_2 laser irradiation under Condition C; (a) and (b) $h_p = 21$ mm ($h_L =$ 17 mm, zero and maximum powers), (c) $h_p = 40$ mm (zero power), r = 0 mm.



Fig. 3.10. Morphological variation of TiO_2 particles with CO_2 laser irradiation under Condition D; (a) and (b) $h_p = 18$ mm ($h_L =$ 15 mm, zero and maximum powers), (c) $h_p = 25$ mm (zero power), r = 0 mm.



Fig. 3.11. Size distributions of TiO_2 particles with and without CO_2 laser irradiation under Condition D; (a) $h_p = 18 \text{ mm} (h_L = 15 \text{ mm}, P = 2408 \text{ W})$ for spheres (b) $h_p = 18 \text{ mm}(P = 0 \text{ W})$ for aggregates.



Fig. 3.12. Determination of Fractal dimension of TiO_2 aggregates without CO_2 laser irradiation under Condition D; $h_p = 18$ mm (P = 0 W).



Fig. 3.13. Schematic for structural change during anatase-to-rutile phase transformation.



Fig. 3.14. Variations of XRD profile of TiO_2 particles with increasing CO_2 laser powers under Condition A; $h_d = 65 \text{ mm}(h_L = 25 \text{ mm})$.

note : A and R in the figure denote peaks of anatase and rutile, respectively.



Fig. 3.15. Variations of rutile contents in TiO_2 particles with increasing CO_2 laser powers for various the laser irradiation position under Condition A; $h_d = 65$ mm.



Fig. 3.16. Raman spectra of TiO_2 particles collected at 20 mm for different CO_2 laser powers under condition A; $h_L = 15$ mm.



Fig. 3.17. Estimation of (a) effective crystallite size and (b) rms strains of TiO₂ particles collected at 20 mm for different CO₂ laser powers under condition A; $h_L = 15$ mm.



Fig. 3.18. Variations of XRD profiles of TiO_2 particles collected at 18 mm for maximum CO_2 laser power under condition D with heating temperature; $h_L = 15$ mm.



Fig. 3.19. Comparisons of thermal stability of our controlled sample with previous results and commercial powder as a function of temperature; our sample is collected at 18 mm for maximum CO_2 laser power under condition D; $h_L = 15$ mm.



Fig. 3.20. Field-emission scanning electron micrograph image of the controlled TiO_2 sample by CO_2 laser irradiation; the sample collected at 18 mm ($h_L = 15$ mm) with maximum CO_2 laser power under condition D was heated at 750 °C for 30 min in air after isostatically pressing at 10 MPa.

Chapter 4

Conclusions

A new approach for control of size, morphology and the crystalline phase of flamegenerated particles using laser irradiation was proposed. Our method relies on controlling the characteristic time for coalescence of nanoparticles by irradiation of CO_2 laser beam on the early stage aggregates formed in a flame. Since the coalescence characteristic time depends strongly on particle temperature as an Arrhenius form, the high-power CO_2 laser irradiation can transforms early-stage aggregates formed in a flame into more spherical particles. Since spherical particles have much smaller collision cross-sections than volume equivalent aggregates, much slower growth of nanoparticles can be achieved. Therefore, smaller, at the same time, spherical nanoparticles can be successfully produced at high concentrations.

We applied the new control method to producing nanosized and un-agglomerated SiO₂ and TiO₂ particles and spontaneously controlling the crystalline phase. As for SiO₂, depending on the irradiation height of CO₂ laser beam in a flame, significantly different mechanisms were found. At the low irradiation height in a flame, the particle generation effect becomes dominant due to the gas absorption of laser power, which was called as "*Generation Effect*". At the intermediate height of laser irradiation, the effect of sintering of aggregates was observed and resulted in smaller spherical particles as laser power increased, which was called as "*Coalescence Effect*". At the high irradiation position, particles could be ablated by the high-power laser beam, which was called as "*Ablation* or *Evaporation Effect*". The *Coalescence Effect* of the CO₂ laser irradiation played a dominant role in reducing the sphere size at the optimum irradiation height, which was verified by measuring the number density and volume fraction of the particles with light scattering and localized sampling. At sufficiently high laser powers, both the *Coalescence Effect* and *Ablation* or *Evaporation Effect* occurred.

As for TiO₂, the transformation from large aggregates to nanosized spheres was

obviously observed and was solely due to the *Coalescence Effect*. This assertion was verified also by estimating number density and volume fraction. Among these, volume fraction of titania particles was nearly maintained constantly in the presence or absence of the laser irradiation.

As for controllability of crystalline phase, the laser irradiation yielded very interesting results: as the laser power increases, the rutile contents decreases, i.e. the laser irradiation stabilized the anatase phase. This was understood by 1) the concept of melting and subsequent quenching at high power 2) cure of the oxygen-deficient defect structure or the residual strains in the anatase particles at low power not enough to melt the particles. These two inferences are verified by Raman scattering analysis and Fourier analysis of XRD peak broadening.

Also, the phase stability was determined by HT-XRD measurement, the presently controlled anatase samples revealed much excellent thermal stability and had higher activation energy for the phase transformation than other previous published anatase material. In addition, we tried to produce ultrafine grained bulk titania with high density near the theoretical value via common heat treatment. As a result, density of our pellet heated at 800 °C was above 98 % and the grain size was only 70 nm. The disappearance of necks in our samples yields much better packing than for agglomerates at the same pressure. Therefore our un-agglomerated samples could be sintered to bulk titania near the theoretical density not accompanied by significant grain growth due to that the grain growth during sintering could be occurred very rapidly through necks. We can conclude that the present control method could be successfully applied to controlling the size, morphology and the crystalline phase.

Research needs

The present coalescence-enhanced control method was successfully used to produce more smaller and non-agglomerated inorganic particles such as silica and titania particles. Also, we verified that this method could control the crystalline phase of materials to their application purpose. But, we feel some further researches are necessary for putting to practical use, especially in a view of efficient use of the energy. The particles within a laser beam absorb only very small amounts of the applied laser beam energy. Therefore, most of the laser beam energy are thrown away after only once passing the particle stream. This waste of energy can be prevented with some modifications of arrangement of optics or burner; for examples, putting several burners in series along the laser beam path or reciprocating the laser beam around the particle stream by mirrors.

Control parameters in the present method are laser irradiation position, the laser power and the precursor jet speed. To apply this method to other materials, one should find the optimized condition that may be different depending on the materials. Fortunately, the laser irradiation position is intrinsically not varied, according to our results. That is, the laser beam should irradiate early-stage small aggregates to reduce the resultant spherical particle size. But, the laser power should be optimized depending on the desirable crystalline phase. Also, increasing the jet speed is more desirable to reduce the particle size but the corresponding residence time within the laser beam should be long enough to coalesce aggregate particles at a designated laser power. Consequently, if we find universal relations between the above control parameters, this method should yield breakthrough in nano technology. To do that, much more studies should be performed further.

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Appendix A. Fourier analysis of X-ray line broadening

After correction for instrumental broadening, a Bragg-peak profile is expressed in terms of a Fourier series by Warren and Averbach (1950):

$$P'(s) = K_1 \sum_{n = -\infty}^{\infty} C_n \exp[-2\pi i n a_3(s - s_0)]$$
(A1)

where λ is the X-ray wavelength (1.54056Å), K_1 is a slowly varying function of $s = 2 \sin \theta / \lambda$ or the diffraction angle θ (for filtered radiation $K_1 \propto f_1 (1 + \cos^2 2\theta) / \sin^2 \theta$, in which f_1 is the average scattering factor for the sample corrected for temperature), $na_3 = L$ is the distance normal to the reflecting planes of interplanar spacing $a_3 = d_{hkl}$, and n is the harmonic number.

Defining the quantity $I(s) = P'(s)/K_1$ as the scattered intensity, one can write:

$$I(s) = \sum_{n=-\infty}^{\infty} C(L) exp[-2\pi i L(s-s_0)]$$
(A2)

The Fourier coefficients C(L) are usually complex quantities:

$$C(L) = A(L) + iB(L) \tag{A3}$$

Therefore Eqs A2 can be written as:

$$I(s) = \sum_{n=-\infty}^{\infty} A(L) \cos[2\pi L(s-s_0)] + B(L) \sin[2\pi L(s-s_0)]$$
(A4)

If I(s) is a real symmetric function to the line of $s = s_0$, B(L) becomes mathematically zero.

Since one exclude the possibility of stacking faults, positive and negative strains will occur with approximately equal probability and thus the sine coefficient can be assumed negligible. Accordingly, the Fourier cosine coefficient A(L) will be only analyzed. Warren and Averbach (1950) showed that the coefficients A(L) can be written as the product of a purely size-broadening term and a purely strain or distortion broadening term: $A(L) = A^{S}(L)A^{D}(L)$. Furthermore, they developed a procedure for separation of the size and strain broadening terms from measurements of two or more orders of the same Bragg reflection:

$$Ln A(L) = Ln AS(L) + Ln AD(L)$$
(A5)

For small values of L and root-mean-square strain $< \epsilon_L^2 >$, one can write:

$$Ln A(L) = Ln A^{S}(L) - 2\pi^{2} < \varepsilon_{L}^{2} > L^{2} s_{0}^{2}$$
(A6)

For a Gaussian strain distribution assumption, Eq. A6 is exact for all values of L and s_0 , and the plots of Ln A(L) against s_0^2 will be linear out to indefinitely large values of s_0^2 . Thus, the slope of the plots yields the rms strain $\langle \epsilon_L^2 \rangle$ and the $s_0 = 0$ intercepts via extrapolation of the lines at fixed L determine the size coefficient A^S(L). The negative initial slope of the A^S(L) curve plotted vs. L yields the effective particle size D(hkl):

$$1/D(hkl) = -[dA^{S}(L)/dL]_{L=0}$$
(A7)

Eq. A7 shows that the size coefficient decreases exponentially within the small values of L. Additionally, It should be emphasized that the separation of A^{S} and A^{D} is possible only in the case that there are two or more orders of reflection, i.e., 101, 202 and 303, etc. The

reason is as follows. If the sample has a elastically isotropic cubic structure, the rms strains are independent of the crystallographic orientation. In addition, if there are no stacking faults, all values of A(L=constant) vs. s_0^2 (see Eq. A6) fall on a straight line. But, when these two limit conditions are not fulfilled, the values do not fall on a single curve. TiO₂ samples synthesized in this work correspond to the latter case, and any pairs of multi-order reflections do not exist unfortunately. Although the slopes $\langle \epsilon_L^2 \rangle$ are sensitive to which pair of the reflections is used, the resulting size coefficients A^S(L) from different pairs are not varied significantly (Wagner, 1966). Therefore, we firmly say that the accuracy for the measured crystallite size is not doubtful and the rms strains in the samples synthesized with different CO₂ laser powers can be compared at least each other.

In addition, the second derivative of $A^{S}(L)$ vs. L yields directly the particle size distribution function f(L):

$$\frac{d^2 A^S(L)}{dL^2} = \frac{f(L)}{D}$$
(A8)

The $A^{S}(L)$ curve usually exhibit the well-known "hook effect" at small L, i.e., negative curvature. Since the negative value of the particle size distribution function is not possible, the well known hook must be an experimental effect. It arises from an underestimation of the value A(0) (proportional to the area under the peak profiles) relative to the other Fourier cosine coefficients A(L). The area under the peak is difficult to measure because of the long tails of the broad reflections. In practice, one should neglect the initial part of the A^S(L) at small L ($\leq 0.1D$) and recalculate A^S(0) by fitting a straight line to the A^S(L) at L values just above the hook and extrapolating to L=0. After then, A^S(L) curve should be normalized by the A^S(0) value. Now, one can obtain the effective crystallite size D from the initial slope of A^S(L) curve (see Eq. A7).

Appendix B. Stokes correction for instrumental broadening

The diffraction profile of the samples h(s) is a convolution of the functions representing pure broadening (due to small crystallite size and strains) and instrumental broadening. In addition, the profile of the standard samples g(s') is regarded as being free from the size and strain broadening (that is, representing solely instrumental broadening), since the particle size of the standard sample is large enough to eliminate the size broadening and also the sample are well annealed to release the possible strains. Thus, the pure diffraction profile of the samples due to only the size and strain, f(s') can represented by the following convolution theorem.

$$h(s) = \int g(s - s') f(s') ds'$$
(B1)

This equation can be solved either by describing the functions in terms of Fourier series or Fourier integrals, i.e.,

$$h(s - s_0) = \sum_{L} H'(L) exp[-2\pi i n(s - s_0) / \Delta s]$$
(B2)

where H'(L) is Fourier coefficient of the function of $h(s-s_0)$, and n, s and s_0 are exactly the same as in Appendix A. Similar equations can be written for f(s') and g(s'), and F'(L') and G'(L').

The normalized Fourier coefficients H(L) are given by the relation:

$$H(L) = (1/\Delta sA) \int_{-\Delta s/2}^{\Delta s/2} h(s-s_0) exp[2\pi i n(s-s_0)/\Delta s] ds$$
(B3)

where A is the area of the f(s') curve and Δs is chosen large enough to include the entire peak. In terms of the Fourier coefficients, Eq. B1 can be written :

$$H'(L) = \Delta s F'(L) G'(L)$$
(B4)

Since we are interested only in the peak profile, we again normalize the quantities involved such that

$$F(L) = H(L)/G(L)$$
(B5)

where H(L) = H'(L)/H'(0) and G(L) = G'(L)/G'(0). Using the obtained F(L), the pure diffraction profile $f(s-s_0)$ is written as:

$$f(s - s_0) = \sum_{L} F(L) exp[-2\pi i L(s - s_0)]$$
(B6)

where $L = na_3 = n/\Delta s$ and is the distance normal to the reflecting planes (hkl) of interplanar spacing a_3 . Note that all Fourier coefficients may be complex involving real and imaginary parts. Comparing Eq. B6 with Eq. A2, one can notice that the Fourier coefficients F(L) obtained by Stokes correction is exactly the same as C(L) in Eq. A2. Therefore, real part of F(L) corresponds to the required Fourier cosine coefficients A(L).

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30	grain	가	70 nm	가	bulk
titania	•				

: , , , , , , anatase, rutile, silica, titania

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