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Formation and Growth of Silicon Nitride Particles in a Laser-Driven Aerosol Reactor Investigated with Photon Correlation Spectroscopy and Electron Microscopy

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ABSTRACT. This paper investigates the formation and growth of silicon nitride particles in a laser-driven aerosol reactor. This investigation is done on-line with photon correlation spectroscopy (PCS) and off-line with electron microscopy. The results of the measurements are compared with each other and with a monodisperse growth model that incorporates the influence of particle shape. PCS proved to be a good and fast monitoring technique, but it provides limited information: the intensity-weighted average particle size and approximate velocity. Electron microscope studies of samples showed good agreement with both the spectroscopy and the modeling results. The incorporation in the model and in the determination of the PCS diameter of the extra information about particle size and phase from the electron microscope photographs increases their accuracy. This is necessary if PCS combined with growth model are to be used for process control. Although the analysis techniques and the model are applied to a specific case, they are applicable in all types of flame reactors. © 1997 American Association for Aerosol Research. AEROSOL SCIENCE AND TECHNOLOGY 26:55-73 (1997).

INTRODUCTION

The manufacturing of ceramic materials such as titania, zirconia, borides, carbides, and nitrides in flame aerosol reactors is a subject of investigation all over the world. These materials all exhibit special features such as high temperature strength, hardness, wear, and corrosion resistance, and a selection of conducting or insulating properties as desired, which makes them ideal for specific applications. However, their good high temperature properties make

them inherently difficult to process. If ceramic powders can be produced in the nanometer size range their reactivity increases as a result of the extremely large specific surface area, which facilitates their processing into reliable parts.

The use of flame aerosol reactors for the production of these extremely fine powders has some considerable advantages, but it is usually very difficult to control particle properties in these reactors. For example, the formation of large aggregates and phase control can pose a problem. There is a need to be able to monitor the reaction in real time in order to improve both the

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understanding and the control of these reactions. Light scattering techniques are the obvious method of achieving this, but in practice the high temperatures and the small particle size make it difficult.

In an earlier paper (van Drunen et al., 1994), we showed that photon correlation spectroscopy (PCS) using an optical fiber detector can be applied to monitor average particle size with high spatial resolution in an aerosol reaction flame, even at high temperatures. The agglomerate sizes of the particles predicted by an agglomeration model derived by Kruis et al. (1993) were in good agreement with the measurements provided that the characteristic sintering time was properly fitted. In this study PCS measurements performed with the setup described above and model predictions are compared with each other and with samples, which were collected at different heights in the flame with a thermophoretic sampling device and studied under a transmission electron microscope (TEM). Our objectives were (i) to find the right conditions for the production of pure, crystalline, stoichiometric Si_3N_4 , (ii) to evaluate the usefulness of PCS as an on-line monitoring technique in flame reactors by comparing the PCS measurements to the particle size in the samples, and finally (iii) to establish if the model predicts not only the agglomerate size accurately but the size of the constituting primary particles as well.

Before the experiments can be discussed, the operation of the reactor and the measurement equipment are first described. A brief theoretical discussion of the measurement techniques is included, the model is described, and the choice of starting parameters is explained.

In order to investigate whether different particle properties can be detected by the PCS measurements it is necessary to vary the process conditions in such a way that particles with different histories are generated. The influence of changes in the process conditions on particle size and morphology should be predicted correctly by the model if sufficient information on the relevant input parameters is available. Pre-

liminary experiments were performed showing the influence of the experimental settings on the conditions in the reactor and the resulting powder characteristics. A brief summary of this earlier work by Kruis (1993) and its consequences is given in the section on powder synthesis. A standard reactor configuration, including gas flow settings, based on these previous results was defined and variables were changed so that a positive influence on the final powder properties could be expected. A full justification for the choice of experimental settings in this work is also given in this section.

The last section contains the results of the PCS measurements and of the simulations, and compares them with the samples. This work is an extension of the work done on PCS reported by van Drunen et al. (1994).

REACTOR SETUP

The reactor setup is shown in Figure 1. Details of the aerosol reactor can be found in the thesis by Kruis (1993). Silane (SiH_4) and ammonia (NH_3) are used as precursors for the synthesis of Si_3N_4 . The gases are introduced through four concentric nozzles below the laser beam. The mixing of the reactants is controlled with a small flow of inert N_2 sheath gas between the silane and ammonia flow. A large nitrogen flow through the outer nozzle serves as a confining flow, as a carrier gas for the particles formed, and as a cooling agent. This laminar gas flow is heated very quickly by a 160 W infrared (IR) carbon dioxide (CO_2) laser beam and a bright reaction flame results. The laser was operated at wavelengths around $10.6 \mu\text{m}$ (10P20 line). The height between the nozzle exit and the infrared laser can be varied by moving the reactor up and down.

TEMPERATURE MEASUREMENT

A precise knowledge of the temperature profile in the reactor is of importance for

FIGURE 1. Schematic side view of the laser reactor.

three reasons:

- interpretation of the PCS measurements
- prediction of particle size and morphology through modeling
- explanation of the particle phase and composition

Temperature profiles were measured with a two-color pyrometer similar to the one used by Bauer et al. (1991). The temperature measurements are reproducible and tests with multicolor pyrometry showed that the light emitted by the flame deviates by only 1% from an ideal black body so that the temperatures determined are accurate. The particle size distribution and concentration are such that the flame is optically thin except possibly in the hottest part of the flame, which could account for the dip in the temperature profiles in the center area of the flame (Figure 2). Here radiation from the hot center of the flame is largely absorbed and scattered by the surrounding particles; hence only radiation from the colder edges reaches the detectors. This explanation is corroborated by the fact that experiments with a lower SiH₄ flow and, consequently, lower particle concentration do not show this dip in the temperature curve.

The high temperatures measured with two-color pyrometry were corroborated by multicolor pyrometry tests. The limitation of the multicolor pyrometer used is that only the average temperature over a relatively large part of the flame could be measured. The two-color pyrometer can render the detailed information necessary for system interpretation, but systematic errors may occur due to inaccurate calibration. This error is estimated to be less than 3%.

The temperature measured is, of course, that of the particles. It is conceivable that the temperature of the surrounding gas is somewhat lower, because the Si-N bond in the particles has a broad and strong absorption band around the wavelength of the CO₂-laser radiation.

THERMOPHORETIC SAMPLING

In order to obtain information about particle development regarding size, morphology, and phase composition, samples were taken at different heights in the flame. A copper TEM grid with a carbon coating was fastened in a small holder and pneumatically propelled through the reaction flame. The sampling apparatus used was based on a device developed by Dobbins and

FIGURE 2. Temperature measurements at the centerline of the reactor as a function of h , the height relative to the center of the CO_2 -laser beam, for four sets of experimental conditions. The lines through the measurements are polynomial fits used for the modeling.

Megaridis (1987) for the sampling of soot aggregates. This technique has three important advantages:

- Thermophoretic velocity is independent of particle size in the free molecular regime. Thus, unlike diffusion and impaction, thermophoretic sampling does not give rise to bias errors in the size distribution.
- Because the sample is collected on a relatively cold surface, the reaction is frozen and the sample is representative of the situation in the flame.
- Since the sample holder is very small and moves through the reaction flame very quickly (approximately 1.25 m/s) the device causes relatively little disturbance.

There are three possible collection mechanisms: diffusion, impaction, and thermophoresis. That thermophoresis is the main collection mechanism was verified as follows for particles between 50 and 200 nm diameter at 2000–3000 K, with particle velocity 5 m/s and grid velocity 1.0–1.5 m/s, which are typical sampling conditions.

The impaction mechanism is described by the Stokes number (Stk), which is defined as

$$\text{Stk} = \frac{\text{stopping distance particle}}{\text{characteristic length obstacle}} = \frac{\rho_p d_p^2 v_0}{18\eta L} \quad (1)$$

Here ρ_p is the particle density, d_p particle diameter, v_0 initial particle velocity, L the characteristic length (here the diameter of the TEM grid, 2.5 mm), and η the fluid viscosity. The viscosity of mixtures of gases is a complex function of their volume fraction. For mixtures of the nonpolar diatomic molecules hydrogen and nitrogen the method of Lucas (Reid et al., 1987) can be used to determine the viscosity. It is calculated from a set of reduced variables and the volume fraction of the gases and was typically 5.5×10^{-5} . The Stokes number for a particle in the reactor is typically 7.5×10^{-5} , meaning that the particles follow the gas stream lines almost exactly, and hence impaction is absolutely negligible.

The second alternative mechanism for thermophoresis is diffusion. D , the diffusion coefficient of the particle, determines the displacement due to diffusion:

$$D = \frac{kTC_C}{3\pi\eta d_d} \quad (2)$$

Here k is the Boltzmann constant, T the temperature in Kelvin, C_C the Cunningham slip correction factor (Fuchs, 1964), and d_d the diffusion diameter of the particle, which is by definition the PCS diameter. Then, the thermophoretic velocity (v_{th}) was compared to the mean square displacement for 1 ms due to diffusion Δx_d :

$$v_{th} = \frac{-0.55\eta \nabla T}{\rho_{gas} T_g}, \quad \Delta x_d = \sqrt{2Dt} \quad (3)$$

T_g is the average temperature of the surrounding gas, t is time, and ∇T is the temperature gradient. The formula for v_{th} , which is only valid in the free molecular regime, is due to Waldmann and Schmitt (1966). As was mentioned above the thermophoretic velocity of small particles is independent of particle size. For the conditions mentioned above the displacement in 1 ms due to diffusion is on the order of 10^{-7} m. Assuming that the sampling grid is not heated to more than 500 K, $v_{th} = 0.5$ – 1.0 mm/ms. It can be concluded that diffusion is negligible compared to thermophoresis.

The validity of the above is supported by other results. Measurements by Dobbins and Megaridis and some heat transfer calculations done here indicate that the average temperature of the grid during sampling does not even exceed 350 K average, although it must be mentioned that the temperature of the copper is lower than that of the carbon layer where the particles are collected. Also, the vast majority of the particles collected on the grid lay close to the copper rims, the coolest part of the grid.

For interpretation of the samples it is assumed that the aggregates do not grow during sampling and that the reaction is

frozen as soon as a particle has been intercepted by the cold surface. Dobbins and Megaridis found that the reaction is indeed quenched and that if less than 10% of the sampler surface is covered, no additional aggregation takes place due to longer residence in the flame. However, since the 10% criterion is not always met and growth takes place much faster, this may not be the case for the system investigated here. In fact some samples strongly suggested that additional aggregation on the sampling grid had taken place. Specifically, the existence of aggregates consisting of two different types of primary particles which were found on some TEM photographs can only be readily explained if particles collected at the outer boundary of the flame have formed one aggregate with particles collected from the flame center. The residence time of the sample in the flame at one height, about 2 ms, also makes this type of aggregate formation during sampling likely.

PCS MEASUREMENTS

As the on-line measurement technique for the particle size distribution photon correlation spectroscopy, PCS was chosen. van Drunen et al. (1994) give a comprehensive explanation of the mechanism behind PCS and the deconvolution techniques applied here. For more extensive information about deconvolution problems, the reader is referred to Berne and Pecora (1976) and Finsey (1993).

Briefly, in PCS an ensemble of particles is irradiated and the interference pattern created is recorded with time. The Brownian motion exhibited by the particles causes fluctuations in the interference pattern and the faster the particles move, the faster are the fluctuations caused by this movement. Hence, the fluctuations of the scattered light depend on the diffusion coefficient of the particles, and this is quantified by autocorrelation. From the diffusion coefficient an average diameter of the particles can be calculated from Eq. (3) provided the Stokes–Einstein equation pertains.

The PCS technique is well suited for measurements in this type of reactor since the particles are very small and their concentration is extremely high as a consequence of homogeneous nucleation. This is important since fluctuations due to changes in particle concentration are slower than those due to Brownian motion and thus cause an overestimation of the particle size. Also it is usually necessary that the flame is laminar since fluctuations due to turbulence are often of the same time order as the Brownian fluctuations and therefore cannot be distinguished from them.

From the autocorrelation function the average diffusion coefficient was determined by the normal method of cumulant analysis with standard commercial software. In flowing media with a translational component perpendicular to the scattering plane, as is the case with the aerosol reactor investigated here, in addition to the average diffusion coefficient, the mean velocity can be found. Chowdhury et al. (1984) defined a function to compare autocorrelation data in a convenient way:

$$Y(\tau) = Dq^2 + \frac{v^2}{2w^2} \tau. \quad (4)$$

Here D is the diffusion coefficient, q the scattering vector, v the flow velocity of the particles, and w the diameter of the laser beam waist. Plotting $Y(\tau)$ versus τ gives a straight line with intercept Dq^2 , the first cumulant, and slope $v^2/2w^2$, determined by the second cumulant. For a polydisperse flowing sample the slope contains a velocity component and a polydispersity index. However, if $-v^2/2w^2$ is much larger than the relative variance as is the case here, the polydispersity component is negligible and a value for the flow velocity can be obtained from the slope (i.e., the second cumulant in the cumulant analysis). However, this is not very accurate because the second cumulant is strongly influenced by noise.

ERRORS

Three types of error occur when PCS is used for the determination of the particle

size distribution. The first type of error is of a statistical nature: noise on the autocorrelation function. This statistical error was usually small (van Drunen et al., 1994).

The second type is introduced by the choice of model, in this case the cumulant fit method, which provides only an intensity-weighted average of the particle size but no information about the width of the distribution because of the large velocity component in the second cumulant. Second, velocity components in the scattering plane are ignored, but they may influence the measurements if they are large, for instance in the reaction zone where a vast gas expansion due to the reaction occurs. A third assumption of the model is that the particles are spherical, which the aggregates in the reactor are not. We will elaborate on this in the discussion of the results. The last assumption of the model is that the Stokes-Einstein equation for diffusion in the free molecular regime pertains. This assumption is valid as was shown in van Drunen et al. (1994).

The third type of error is caused by the measuring conditions. It has already been mentioned that any error in the temperature measurement will cause an error in the calculated particle size because the diffusion coefficient strongly depends upon it. An almost linear relationship exists between the relative error in temperature and the relative error in particle size it causes, and they are about equal. This was determined by calculating the particle size from the measured diffusion coefficient for the measured temperature and for $T_{\text{meas}} \pm 200$ K. Other sources of errors of this type are (i) multiple scattering, which probably did not occur as could be seen from the relatively low scattering count rate, (ii) afterpulsing and dead time of the photomultiplier, which was minimized by not including the first data channel, (iii) the measuring angle is not known exactly, which causes an error in the value of the scattering vector, and finally (iv) refraction by the quartz window can disturb the incoming signal. To minimize this the detector was mounted at

a small angle of 12° relative to the He-Ne laser beam, which also helps to obtain a high count rate.

PCS SETUP

The configuration used for the PCS measurements (Figure 3) was identical to that used in earlier experiments and is described in detail by van Drunen et al. (1994). In brief, a 5 mW helium–neon laser, vertically polarized, was mounted perpendicular to both the gas flow and to the infrared laser beam in a laser holder that enabled it to move both horizontally and vertically. Thus the height of this laser was varied relative to the infrared laser. A lens with a focal length of 100 mm was mounted on its end. The He-Ne laser probed the center-line of the flame, above the center nozzle. The detector was a single mode optical fiber with a gradient index lens mounted at its end. In front of the detector were placed an interference filter (633 nm, the wave-

length of the He-Ne laser) and a polarizing filter which passed only vertically polarized light. These filters prevented most of the light from the flame from entering the detector. The fiber led to a photomultiplier tube connected to a pulse amplifier discriminator. The signals were correlated by a Brookhaven Instruments BI 8000 correlator.

MODELING

The monodisperse model used here to describe particle growth of Si_3N_4 was developed by Kruis et al. (1993). They found that the results of the monodisperse model were in good agreement with both the results of a very detailed sectional model (Xiong et al., 1992) and with the experimental results of tests investigating the growth of silicon particles in the same reactor. Silicon was chosen as the model material because this simple system has been extensively investi-

FIGURE 3. Schematic top view of the PCS setup (van Drunen et al., 1994).

gated and reliable literature data about its sintering kinetics exist.

The model assumes homogeneous nucleation which is followed by particle growth through cluster-cluster aggregation with simultaneous sintering of the primary particles. The input parameters for the simulation are:

- The initial number concentration of primary particles. The development of the particle number concentration N is determined by the collision frequency and sticking probability (assumed in the following to be 100%).
- The initial particle volume. This was chosen to be the volume of one unit cell β - Si_3N_4 . The aggregate volume V is determined by the number of aggregate collisions.
- The initial particle area. This is the calculated area of a spherical particle with the initial volume. The aggregate area A is controlled by the aggregate volume and aggregate shape. This shape is in turn determined by the primary particle size and the fractal dimension.
- The characteristic sintering time τ_s . This is defined as the time needed for complete coalescence of two spherical particles of equal size. Thus it controls the primary particle size.
- The fractal dimension of the aggregate D_f . Although it changes in the very early stages from an initial value of 3 to about 1.9 for very small aggregates and to 1.8 for larger aggregates (Meakin, 1990), it was assumed here to be constant at 1.8 or at 1.9.
- The temperature profile. This was measured as stated above and fitted to a second order polynomial.

The growth model makes use of a collision radius, which is defined as

$$R_c = \frac{3V}{A} \left(\frac{A^3}{36\pi V^2} \right)^{1/D_f} \quad (5)$$

Thus, since they are all functions of R_c , the evolution of N , V , and A is described by

three interdependent differential equations, which were solved with the Runge-Kutta method using a commercially available solver from the Reactor Research Institute in Delft.

The reactant gases were heated up at a rate of $\pm 10^6$ K/s to about 2000 K. The high supersaturation thus attained causes homogeneous nucleation which makes the model applicable to this system. Various other assumptions were made in order to be able to calculate the number concentration of nuclei formed. First of all it was assumed that the NH_3 , the sheath gas, and the SiH_4 are completely mixed at the level where the flow crosses the CO_2 -laser beam but that no mixing takes place with the N_2 flowing through the outer nozzle. Thus the local partial pressure of silane is established and since excess ammonia is available, this silane concentration determines the maximum amount of Si_3N_4 formed. Second all the SiH_4 is supposedly converted during nucleation to β - Si_3N_4 : the reaction is instantaneous and complete. Finally the reaction zone is assumed to be infinitely small. As a consequence of the last two assumptions, growth through condensation cannot take place and the particles grow solely by agglomeration.

Simulations with the monodisperse model are simple and fast because it is presumed that all the aggregates contain the same number of equally sized primary particles which reduces the number of calculations needed for a size distribution by several orders of magnitude.

Since, to the best of our knowledge, no fundamental data exist for the sintering of silicon nitride in the absence of additives, an expression for the characteristic sintering time of similar components was adapted to get reasonable agreement of the simulations with our experimental findings (van Drunen et al., 1994):

$$\tau_s = c_1 T d_p^3 \exp\left(\frac{c_2}{T}\right) \quad (6)$$

Here τ_s is the characteristic sintering time in seconds, c_1 and c_2 are constants, T is

the temperature in Kelvins, and d_p is the primary particle diameter in nanometers.

POWDER SYNTHESIS

Three series of experiments were conducted. The base case, denoted *H4.5*, is characterized by the following settings:

- diameter CO_2 -laser beam $d_b = 3.5$ mm
- incident laser power $P = 160$ W
- distance between nozzle exit and center of the CO_2 -laser beam $H = 4.5$ mm
- gas flows in standard cubic centimeters (scm^3) per minute (from inner to outer nozzle):

1. SiH_4 , 80 scm^3/min
2. N_2 sheath gas, 50 scm^3/min
3. NH_3 , 320 scm^3/min
4. N_2 carrier gas, 2 sl/min .

The influence of changes in the laser beam diameter and sheath gas velocity have been investigated and discussed by Kruis (1993). He found that when the laser beam is focused to less than 2 mm diameter, the Si_3N_4 content decreases and the powder is amorphous. This is unfavorable for subsequent treatment since the amorphous phase reduces considerably in volume when it becomes crystalline during sintering. The better nitrification achieved with a broad laser beam is probably caused by absorption of the CO_2 radiation by NH_3 which causes the formation of NH and NH_2 radicals that form a strong bond with Si. This is consistent with the findings of Bauer et al. (1991) that use of a different wavelength, which is mainly absorbed by the NH_3 flow instead of by the SiH_4 flow, greatly improved the quality of the product powder in terms of its Si_3N_4 content. Similar tests in this reactor however resulted in amorphous silicon-rich powders containing fibrous material. The reason that these very low quality powders are produced in this reactor under otherwise similar conditions is probably the lack of mixing of the reactants in our reactor with its laminar reaction flame, whereas Bauer worked with a turbulent flame reac-

tor. A beam diameter of 3.5 mm was chosen in the basic settings because it gave the best resulting powder.

To investigate the influence of the temperature, the incident laser power P was decreased. In Figure 2 it is seen that in the base case (*H4.5*) the temperature in the reaction zone rises to almost 3000 K, although Si_3N_4 is only thermodynamically stable up to ca. 2200 K (the exact dissociation temperature depends heavily on the partial pressure of N_2 and less so on the absolute pressure). Therefore the high temperatures encountered in the reaction zone may cause Si_3N_4 that has already been formed to dissociate into silicon and nitrogen. When P decreased, the radiation absorption decreased simultaneously and as a result the temperature in the reactor remained much lower which is shown by the $P120$ line (incident laser power 120 W; all other settings as in the base case) in Figure 2. X-ray pdiffraction (XRD) analysis (Figure 4) showed that the effect of this lower temperature is, as expected, a very low content of free silicon in the product powder, but also a decrease in crystallinity. Furthermore, the conversion of SiH_4 to Si_3N_4 is incomplete. If the incident laser power is less than 110 W, amorphous Si_3N_4 with a very high content of free silicon is produced.

Next the variable H —the measured distance between the nozzle exit and the center of the laser beam, which is effectively the time available for premixing of the reactants—was varied. Increasing this distance resulted in increasingly high reaction temperatures and increased nitrogen deficiency of the resulting powders. These results indicate that mixing of the gases is not complete after 2 mm as predicted by Kruis on the basis of diffusion calculations.

The sheath gas flow rate is based upon experiments by Kruis (1993). When the sheath gas flow is high, SiH_4 first dissociates to form liquid silicon particles that are only partly converted to Si_3N_4 when they come into contact with the NH_3 . In principle a very low sheath gas flow is most favorable for the formation of Si_3N_4 , but

when this flow is too low, the particles formed tend to clog the nozzles instead of being transported upward. This is especially dangerous since the Si-N bond also absorbs the CO₂-laser radiation as was mentioned earlier and a blast may occur. A sheath gas flow of 30–40 scm³/min was found to give the best powders, but to make it easier to detect small changes due to other variables, a slightly higher flow of 50 scm³/min was chosen.

Finally the NH₃/SiH₄ ratio was varied. Janiga et al. (1991) found that to attain stoichiometric Si₃N₄ powder in a tube furnace the NH₃/SiH₄ ratio had to be as high as 10 or 12. Other authors needed an even larger excess of NH₃. Increasing the NH₃/SiH₄ ratio in this reactor from 4 to 6 or 8 increased the N content of the powder almost to its stoichiometric value, which could not be improved by increasing this ratio further. This indicates that either the intensive contact between the reactants due to better mixing or the role of radicals formed by the laser radiation reduces the NH₃ requirement and makes the reaction more efficient.

COMPARISON OF THE RESULTS

Because the particles formed are not spherical, their shape has to be taken into account when comparing the particle sizes determined with the different techniques. As was mentioned earlier, particle shape has a large effect on the results of PCS, which measures the mobility radius R_m . In the literature it has become customary to describe aggregates and similar particles with a radius of gyration R_g and a so-called Hausdorf or fractal (or rather fractallike) dimension D_f . Accordingly R_g and D_f have been used to describe the particles in the model and in the TEM photographs. The relationship between the two radii R_m and R_g is not well documented although recently some relevant research has been conducted in this area (Wiltzius, 1987; Schmidt-Ott, 1990; Kütz, 1994; Cai and Sorensen, 1994). The consequences will be discussed below.

In the growth model the fractal dimension of the clusters is an important parameter. Values for D_f of 1.8 and 1.9 were chosen based on values found in the literature for cluster-cluster agglomeration

FIGURE 4. X-ray diffraction patterns of powders produced at different incident laser powers (denoted P) taken with Cu + K α radiation: $\bullet$ denotes α -Si₃N₄; $\times$ denotes β -Si₃N₄; $\blacktriangle$ denotes Si.

(Meakin, 1990), which is in reasonably good agreement with the values for the fractal dimension that were determined from TEM photographs (Figure 5). Aggregate size and fractal dimension were determined using the particle counting method described by Samson et al. (1993). They defined the cluster size as the geometric mean of L , the cluster length, and W , the projected length perpendicular to the axis through L . When instead R_g , the radius of gyration, was taken as the cluster size, the resulting D_f was 1.95. This value lies about 0.1 higher than the value determined with $\sqrt{LW}$. However this discrepancy was expected since only small clusters were used for the comparison. The value of R_g was on average about 20% lower than $\sqrt{LW}$.

Note that the fractal dimension determined from a two-dimensional image can

never exceed the value of 2. Mandelbrot (1987) and Weitz and Huang (1984) demonstrated that if D_f of the three-dimensional particle is less than 2, the fractal dimension in two dimensions is equal to that in three dimensions. Therefore the D_f determined from TEM photographs is equal to the real three-dimensional fractal dimension if the latter is smaller than 2.

For particles in the continuum regime. Wiltzius (1987) found that a linear relationship exists between R_m and R_g . However for particles in or close to the free molecular regime, that is $Kn \geq 1$, this does not hold. Recently Cai and Sorensen (1994) found that if $qR_g < 1$ and $D_f \approx 1.8$, then

$$R_m = k_1 a N^x \quad \text{with } x = 0.43 \pm 0.03,$$
$$R_g = k_2 N^{1/D_f} \quad \text{with } 1/D_f = 0.56. \quad (7)$$

FIGURE 5. Determination of the fractal dimension D_f of aggregates from TEM photographs. The slope of the fitted line equals $1/D_f$.

Here k_1 and k_2 are constants, a is the monomer size, and N is the number of monomers per aggregate.

They explained the value of x quantitatively as follows. The drag depends on the projected area of the cluster which would mean x has a value of 0.5. However, screening of monomers by other monomers occurs, resulting in a projectional area for fractallike particles of $A \propto R^{0.82-0.92}$. In the limiting case where $N = 1$, R_m/R_g is 1.29. For $N > 5$, R_m will become smaller than R_g . As a consequence the radius of gyration and the mobility radius are comparable for small aggregates or aggregates consisting of a few large crystals, but larger aggregates comprised of many small primary particles show an increasing discrepancy between the two radii.

The collision radius used in the model was defined in such a way that for $N = 1$ this collision radius is equal to the monomer size and for $N > 1$ it approaches the radius of gyration. This facilitates the comparison of PCS, TEM, and model results.

The particle size obtained by PCS is inherently skewed toward larger diameters since the particle diameter is obtained as $\sum_i (n_i d_i^6 / n_i d_i^5)$ in the Rayleigh limit so larger particles scatter light much more efficiently than small particles. Therefore the PCS diameters should be comparable to the larger particles found in the samples, even though the effect is abated by the effect of particle structure as discussed above. In addition to particle size, the samples also render information about the crystallinity of the particles and about particle morphology, for example, the degree of agglomeration and the monomer size.

Figure 6a and b shows the growth of the aggregates as a function of h , the height in the reactor relative to the center of the CO_2 -laser beam, as determined by TEM, PCS, and modeling for the base case, $H = 4.5$. In Figure 6a the aggregate and primary particle size obtained from photographs are compared with those predicted by the model for τ_{s1} . Figure 6b compares the aggregate sizes obtained from the TEM photographs

(R_g) with the aggregate size determined with PCS (R_m) and with model predictions for aggregate size (R_g) for two different values for τ_s :

$$\tau_{s1} = 1 \times 10^{-11} T d_p^3 \exp\left(-\frac{53.65}{T}\right),$$

$$\tau_{s2} = 1 \times 10^{-12} T d_p^3 \exp\left(-\frac{53.65}{T}\right)$$

with d_p in nanometers. (8)

Figure 6a shows that the model predictions for τ_{s1} are in good agreement with both the average aggregate size (d_{ag} photo) and the primary particle size (d_p photo) obtained from the photographs. The aggregate sizes determined by PCS (d_{PCS}) are much smaller in the lower part of the flame ($h < 0$) than the largest aggregates found in the samples. This is contrary to expectations and partly due to the fact that, at the beginning of the aggregation process, particles have a more closed structure than assumed by the model with $D_f = 1.8$. Also the fact that R_m is smaller than R_g for these small particles plays a role. In addition microscale turbulence caused by the fast reaction may also have had some influence. Finally the statistical error of the PCS measurements is so large for these small particles that they could well belong on the upper model line. However since this tendency of small particles to lie below the line is present in all experiments performed (see Figures 8 and 9), the influence of significant statistical errors is unlikely.

The photographs also show another phenomenon that takes place during particle growth shown in Figure 7a-c. Just after nucleation the particles are amorphous as determined by electron diffraction, but they rapidly become crystalline at the high temperatures in the flame. The diffraction patterns show that the dominant species are probably a mixture of α - and β - Si_3N_4 , but usually the results are unsatisfactory since some dominant lines are missing and others that are present are not sufficiently separated to distinguish the two phases. The presence of crystalline Si in some otherwise

FIGURE 6. Particle growth as obtained from modeling, from PCS, and from TEM photographs for H4.5 (a) comparing aggregate and primary size and (b) comparing two types of particles: normal and recrystallized d_{ag} denotes aggregate diameter and d_p diameter of the primary particles, and d_{PCS} the (aggregate) diameter measured with PCS.

FIGURE 7. TEM photographs and electron diffraction patterns showing the development of particles in the reactor. (a) Low in the flame, $h = -1.0$, the particles are very small and amorphous. (b) Between $h = -0.5$ and $h = +0.5$ crystallinity is developing. (c) High in the flame, $h = 0.8$ mm, large crystals are formed. Magnification is $36000 \times$.

(c)

FIGURE 7. continued

amorphous samples was determined. At about $h = 0.8$ mm a recrystallization process begins where relatively large oblong crystals of β - Si_3N_4 are formed from the original small spherules, substituting them as primary particles. Figure 7c clearly shows this process and the difference between the two types of particles. We assume that the recrystallized particles are only formed in the center of the flame due to the absorption of laser radiation. Samples from the outer parts did not contain these big crystals. The formation of these crystals has a large influence on the aggregate and primary particle size determined by the model, but a relatively small impact on the PCS diameter. Both the aggregates consisting of one or a few large crystals and the primary particles comprising them are accurately described by the model with τ_{s2} (Figure 6b).

Figure 8 shows the results for the case of $H = 10$. It can be seen from TEM analysis that contrary to the circumstances discussed above, at a value of $H = 10$ no sili-

con is formed during the initial reaction. This may be explained by a more complete premixing of the reactants as the path between the nozzle exit and the laser beam is longer. It may simultaneously at least partly clarify why the temperature curve is higher than those for all the other experiments: the formation of silicon from silane is an endothermic reaction, whereas the formation of silicon nitride is strongly exothermic.

Because the temperature rises so quickly the recrystallization begins lower in the flame and is more complete than at $H = 4.5$. There are many aggregates consisting of a few "primary particles" and large single crystals present in the center of the flame where the PCS measurements were made, so $R_m \approx R_g$. As expected d_{PCS} is comparable to the average particle size low in the flame and to the larger particles higher in the reactor.

When the SiH_4 flow was diluted with H_2 ($\text{NH}_3/8$) while keeping all the other flows equal to those in the base case, the initial

FIGURE 8. Particle growth as obtained from modeling, from PCS, and from TEM photographs for (a) H10, (b) NH₃8, and (c) P120 where d_{avg} is the average aggregate diameter and d_{high} is the diameter of the largest aggregates, from from the TEM photographs.

particle number concentration theoretically was expected to reduce proportionally with the SiH_4 concentration. The predicted particle size for the experiments with a reduced SiH_4 flow was much smaller than that actually found on the TEM grids or with PCS (Figure 8b). Two possible causes contribute to this result. A somewhat lower velocity of the particles moving through the monitored zone (indicated by the second cumulant of the autocorrelation functions) results in an increase of the time for growth to take place relative to the position in the reactor. Also the difference in diffusion coefficients between hydrogen and silane probably has a large influence on the concentration profiles of the reactants in the reaction zone.

The x-ray diffraction of the end product shows that no free silicon is present in the powder produced under these conditions although spherical silicon particles are found in samples taken at about $h = 1.5$. These silicon droplets are converted later into large $\beta\text{-Si}_3\text{N}_4$ crystals, which is possible as a consequence of the large excess of ammonia.

Since the temperature in the reaction flame exceeds the stable temperature of Si_3N_4 over a short trajectory, it was assumed that decreasing the incident laser power would improve the characteristics of the resulting powder. As stated, this was indeed the case to a certain extent. Figure 8c shows a rather different picture than the other experimental results. Even after correction for the reduced efficiency (the conversion of silane drops from nearly 100% at $P = 160$ W to less than 80% when $P = 120$ W), we have to look at the particle shape to explain why the measured PCS diameters are so much lower compared to the diameters determined by TEM. The particles are cauliflower shaped and are grouped together in large aggregates and agglomerates and thus $R_m < R_g$. Also the aggregate structure seems to be more closed. This could be due to the formation of primary particles in a larger reaction zone causing

monomer-cluster aggregation, which generally yields denser structures than cluster-cluster aggregation. Large rectangular crystals are never formed.

It is remarkable that, although temperatures in the reactor exceed the stable temperature of silicon nitride by as much as 500–1000 K, the silicon nitride, once formed, does not seem to disintegrate. When studying the kinetics of the decomposition of Si_3N_4 , Dean Batha and Dow Whitney (1973) found that the initial stage of this decomposition in vacuum follows first order kinetics with the rate constant expressed as

$$k_1 = 3.9 \times 10^7 \times \exp\left(\frac{-389 \times 10^3 \pm 27.6 \times 10^3}{RT}\right) \text{ s}^{-1}. \quad (9)$$

In the later stages the experimental data followed the Jander solid state kinetic law, with the Jander rate constant given by

$$k_2 = 2.6 \times 10^{16} \times \exp\left(\frac{-778 \times 10^3 \pm 41.8 \times 10^3}{RT}\right) \text{ s}^{-1}. \quad (10)$$

Based on the first order kinetics, which was assumed to be applicable in this reactor, decomposition of Si_3N_4 that is already formed will only be significant for the experiments where $H = 10$. After 2 ms at 3000 K the fractional decomposition α was 0.012 while at 3500 K, α was 0.12 after the same period of time. If the Jander law is applicable even after this short time, α becomes 0.1 after 2 ms at approximately 2500 K. However, the rate constant k_2 is dependent on the particle size, which was 8 μm on average in their study. The particles in this reactor were, of course, much smaller which would increase the decomposition rate still further. On the other hand, the inhibiting effect of an N_2 environment on

the decomposition may reduce its rate so much that it is not significant even at the highest temperatures encountered in the reactor because the residence time of the particles at these high temperatures is very short. Based on the experimental results it seems most likely that usually little decomposition of Si_3N_4 occurs. However, in the experiments where $H = 10$, silicon was encountered only high in the flame and was not formed in the initial stages of the reaction, suggesting that decomposition had taken place. The fact that the end product contained the most free silicon when H was high supports this hypothesis.

SUMMARY AND CONCLUSIONS

Si_3N_4 powder was produced in a laser-driven aerosol reactor from silane and ammonia. A silane flow of 40–60 scm^3/min with an ammonia flow of 320 scm^3/min proved to give the best Si_3N_4 powder with respect to free silicon content, crystallinity and phase composition of the powder, and the lowest agglomeration. Although an incident laser power of about 120 W with the standard silane flow also results in more or less stoichiometric Si_3N_4 , the low conversion rate and the amount of amorphous particles make this a less preferable procedure.

The growth model seems to describe the situation in the reactor accurately if appropriate values for τ_s and D_f are used. Uncertainties in the values of the variables included in the model, such as initial particle number and the mixing of the reactants, make the model less reliable. Modeling and measurement of the gas concentration profiles are necessary to improve this.

The PCS measurements are in good agreement with the particle sizes obtained from TEM analysis of samples, but sampling gives important additional information on particle morphology. This is especially important since two particles with equal PCS diameters may have totally different characteristics in other areas. If this condition is met, PCS is a good monitoring

technique for particle sizes in all types of flame reactors.

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References

- Bauer, R. A., Becht, J. G. M., Kruis, F. E., Scarlett, B., and Schoonman, J. (1991). Laser synthesis of low agglomerated submicrometer silicon nitride powders from chlorinated silanes, *J. Am. Ceram. Soc.* 74:2759–2768.
- Berne, B., and Pecora, R. (1976). *Dynamic Light Scattering*. Wiley, New York.
- Cai, J., and Sorensen, C. M. (1994). Diffusion of fractal aggregates in the free molecular regime, *Phys. Rev. E* 50:3397–3400.
- Chowdhury, D. P., Sorensen, C. M., Taylor, T. W., Merklin, J. F., and Lester, T. W. (1984). Application of photon correlation spectroscopy to flowing Brownian motion systems, *Appl. Optics* 23:4149–4154.
- Dean Batha, H., and Dow Whitney, E. (1973). Kinetics and mechanism of the thermal decomposition of Si_3N_4 , *J. Am. Ceram. Soc.* 56:365–369.
- Dobbins, M. A., and Megaridis, C. M. (1987). Morphology of flame-generated soot as determined by thermophoretic sampling, *Langmuir* 3:254–259.
- Finsey, R. (1993). Particle sizing in the submicrometer size range by dynamic light scattering, *Kona* 11:17–32.
- Fuchs, N. A. (1964). *The Mechanics of Aerosols*. Dover, New York, Chap. 2.
- Janiga, J., Sin, K. P., and Figusch, V. (1991). Synthesis of silicon nitride powder by gas-phase reaction, *J. Eur. Ceram. Soc.* 3:153–160.
- Kruis, F. E. (1993). *Particle formation in a laser heated aerosol reactor*. Thesis, Delft University of Technology.
- Kruis, F. E., Kusters, K. A. Pratsinis, S. E., and Scarlett, B. (1993). *Aerosol Sci. Technol.* 19:514.
- Kütz, S. (1994). In-situ Methoden zur Bestimmung von Struktureigenschaften gasgetragener Agglomerate. Ph.D. Thesis, University of Duisburg.
- Mandelbrot, B. B. (1987). *The Fractal Geometry of Nature*. W. H. Freeman & Co., New York.

- Meakin, P. (1990). Fractal structures, *Prog. Solid State Chem.* 20:135–233.
- Reid, R. C., Prausnitz, J. M., and Poling, B. E. (1987). *The Properties of Gases and Liquids*. McGraw-Hill, Inc., New York, Chaps. 9 and 10.
- Samson, R. J., Mulholland, G. W., and Gentry, J. W. (1987). Structural analysis of soot agglomerates. *Langmuir* 3:272–281.
- Schmidt-Ott, A. (1988). New approaches to in-situ characterization of ultrafine agglomerates. *J. Aerosol Sci.* 19:553–563.
- van Drunen, M. A., Tuinman, I. L., Marijnissen, J. C. M., and Scarlett, B. (1994). Measurement of aerosols in a silicon nitride flame by optical fiber photon correlation spectroscopy, *J. Aerosol Sci.* 25:895–908.
- Waldmann, L., and Schmitt, K. H. (1966). In *Aerosol Science* (C. N. Davies, ed.). Academic Press, London.
- Weitz, D. A., and Huang, J. S. (1984). In *Kinetics of Aggregation and Gelatin* (F. Family, and D. P. Landau, eds.). Elsevier Science, Amsterdam, p. 19.
- Wiltzius, P. (1987). Hydrodynamic behaviour of fractal aggregates. *Phys. Rev. Lett.* 58: 710–713.
- Xiong, Y., Pratsinis, S., and Weimer, A. W. (1992). Modeling the formation of boron carbide in an aerosol flow reactor. *AIChE J.* 38:1685.

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