DETERMINATION OF PARTICLE AGGREGATION IN ULTRAFINE SILICON NITRIDE POWDERS

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Clusters of primary silicon nitride particles made by Laser-Chemical Vapor Precipitation were studied by Sedimentation Field Flow Fractionation and Quasi Elastic Light Scattering techniques. The average degree of agglomeration and a first approximation to the fractal dimension of these clusters were determined.

INTRODUCTION

Particle size and degree of agglomeration are vital characteristics of ceramic powders and determine the sinter activity and the packing density of the green product. Fast routine methods to determine these parameters in submicron powders are scarce and in this paper we report the first results of our work which is aimed at combining two recently developed particle sizing techniques suitable for submicron particles. These techniques, Sedimentation Field Flow Fractionation (SFFF) and Quasi Elastic Light Scattering (QUELS) are used to determine degree and type (compact or ramified) of particle agglomeration. We have applied these techniques to relate the characteristics of ultrafine silicon nitride powder made by Laser-Chemical Vapor Precipitation (CVP) to the formation process parameters [1,2] in order to control the characteristics of the powder produced by the process.

In Sedimentation Field Flow Fractionation [3] an aqueous suspension of the powder is flown through a gravitational field in a centrifuge. The particles are exponentially distributed in the field as a result of a counteracting combination of diffusion and gravitation. The parabolic flow rate gradient in the laminar flow fractionates the particles according to their weight, the heavier particles being the last to emerge from the field. The method yields average values of particle weights or particle diameters if particle and eluent densities are known [3].

Quasi Elastic Light Scattering or Photon Correlation Spectroscopy measures intensity autocorrelation of laser light scattered by particles in a liquid suspension [4]. The scattered intensity fluctuates as the result of time modulated interference due to Brownian motion of the dispersed particles which scatter the light. The autocorrelation function or power spectrum of the scattered light allows determination of the average hydrodynamic size of the dispersed particles.

Alternative methods to determine the size of particles in submicron powders are Transmission Electron Microscopy (TEM) and gas adsorption measurements (BET). Both techniques have been used here to establish the size and porosity of the primary powder particles while SFFF and QUELS yield average mass and size of the aggregates.

Once masses and sizes of particle aggregates are known, their dimension can be calculated. This is a parameter which is expected to be strongly dependent on the characteristics of the agglomeration process [5] and hence could be useful for optimization of the reaction process parameters.

EXPERIMENTAL METHODS

Submicron particles of silicon nitride were synthesized by CO_2-laser excited CVP using dichlorosilane and ammonia as reactants as reported in detail in the companion paper [2]. The particles were made under different process conditions. Laser excitation of mixed reactants as well as selective excitation of dichlorosilane or ammonia prior to mixing was done by matching the frequency of the tunable laser to the absorption bands of the reactants, in order to invoke different reactions. The silicon nitride powders were collected in an electrostatic precipitator, ultrasonically dispersed in an aqueous NH_3 solution (0.002 M) and characterized by a Dupont SF^3 sedimentation field flow analyzer and a Coulter N4 light scattering analyzer. These instruments have been recently compared and calibrated using standard silica and latex particles [6].

From SFFF (the particles were assumed to be spherical and to have a density of 3.4) and TEM determined particle diameters L, the average number of primary particles per cluster n (degree of agglomeration) was calculated as:

$$n = \left(\frac{L(SFFF)}{L(TEM)}\right)^3 \qquad (1)$$

The average dimension of the agglomerates was derived from the assumption that the density of chaotically formed clusters is size dependent:

$$\rho = \rho_0 \, L^{D-3} \qquad (2)$$

in which ρ is the effective cluster density, ρ_0 is the bulk material density, L the cluster diameter (here the QUELS value should be taken) and D the fractal dimension [5] of the cluster. It follows from (2) that:

$$D = 3 \, \frac{\log L(SFFF)}{\log L(QUELS)} \qquad (3)$$

in which L represents the average particle diameter which is measured with the instrument indicated. Implicit in equation (2) is also the assumption that compact agglomerates (having dimension D = 3) have the same density as the bulk material of the primary particles.

RESULTS

The results of experiments to determine the size, degree of agglomeration and dimension of powder particles synthesized under different process conditions are summarized in table 1.

The upper half of the table shows a pronounced difference between particle size as determined from transmission micrographs and from gas adsorption measurements. This indicates that reacting cold ammonia with excited dichlorosilane produces large porous particles, while heating premixed reactants

Table 1. Particle Characteristics of silicon nitride powders

Sample number	Si/N	diameter nm TEM	BET	SF^3	QELS	D	n
1	4.8	100	7.2	172	335	2.66	5
2	4.1	115	5.2	168	194	2.92	3
3	3.7	75	6.7	159	134	3.11	10
4	5.1	50	6.9	147	314	2.60	25
5	2.4	120	17.6	122	233	2.64	1
6	2.2	50	13.8	102	332	2.39	8
7	2.9	70	10.0	136	198	2.79	7
8	2.2	17	14.9	73	155	2.55	79
9	2.7	100	-	128	245	2.65	2
10	3.1	50	10.5	140	107	3.17	22
11	1.9	20	17.3	96	214	2.55	111
12	2.0	25	30.4	94	177	2.63	53
13	1.8	30	15.2	112	182	2.72	52
14	2.3	16	12.3	106	207	2.62	291
15	1.7	25	16.6	111	171	2.75	88

Meaning of symbols used: the number in column 2 indicates weight ratio of silicon to nitrogen in the powders (theoretically 1.5 for Silicon nitride); in columns 3 to 6 particle diameters in nm are given as determined with transmission electron microscopy, gas adsorption, sedimentation field flow fractionation, and quasi elastic light scattering respectively; column 7 gives the cluster dimension D and column 8 the average number n of primary particles in the clusters.

produces small dense powders (lower third of table). In this regime the average degree of agglomeration is considerably higher. Between these two regimes there is a transition regime (samples 6 to 10) in which powders with irregularly shaped particles having widely different sizes are produced. Figures 1 and 2 show micrographs of clusters typical for the two deposition regimes.

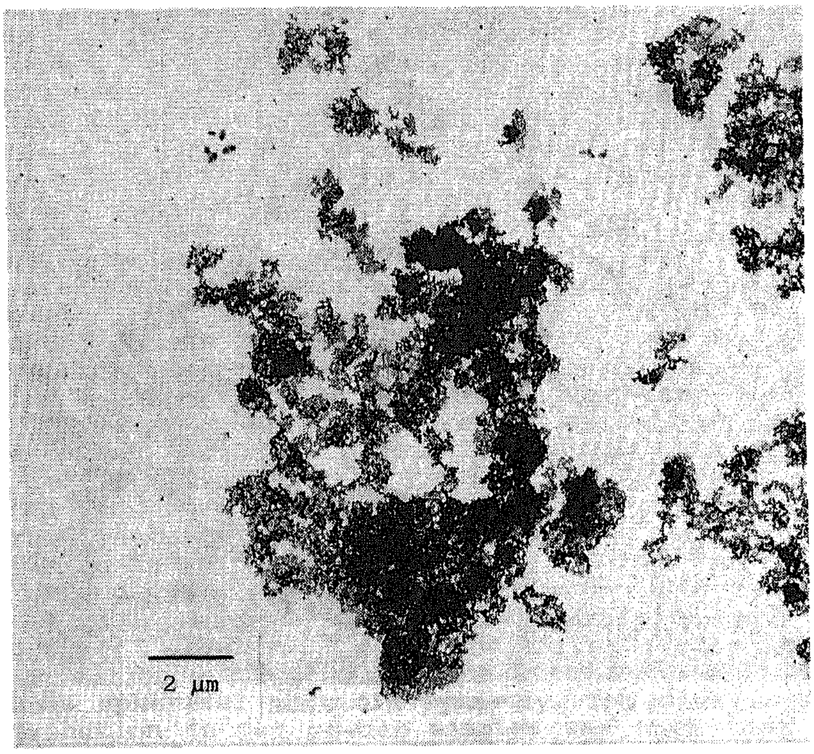

Figure 1. Transmission electron micrograph of highly agglomerated silicon nitride powder made by NH_3 excitation in premixed gas (sample 14)

DISCUSSION

Table 1 shows that particles made by preexcitation (samples 1-5) are larger and considerably less agglomerated than those produced by excitation of one precursor in a mixture of reactants. This result is consistent with nitridation of molten silicon drops [2].
The dimension D which should be indicative of the agglomeration process in the reactor or during electrostatic filtration however, does not vary systematically from one regime to the other (premixing

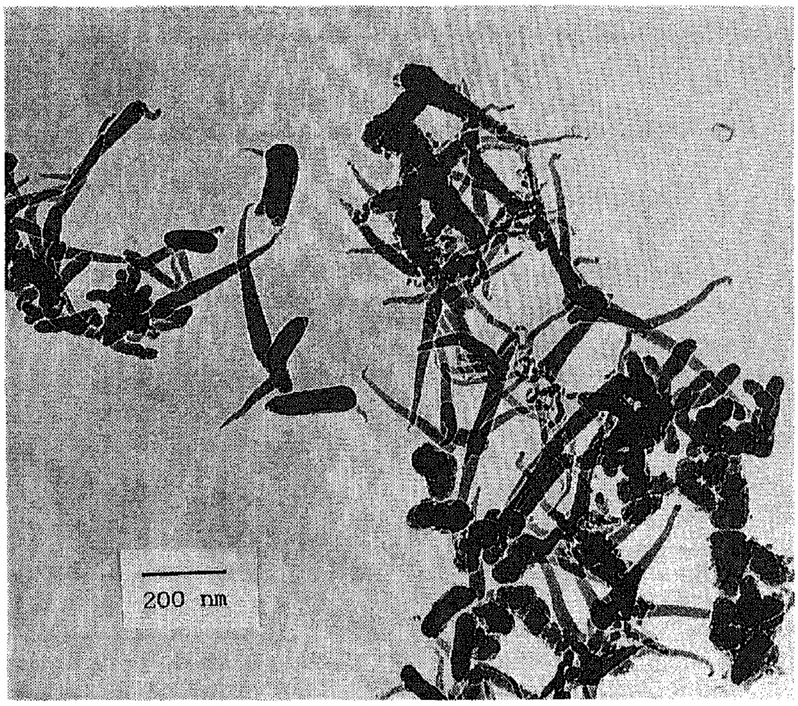

Figure 2. Transmission electron micrograph of silicon nitride powder obtained by postmixed nitridation of silicon (sample 5).

versus postmixing). In the premixed regime (samples 11 to 15) where the gas adsorption (BET) size and the TEM-determined size match, dimensions are consistently in the range 2.5-2.7 which is to be expected for clusters formed mainly by diffusion limited monomer-cluster aggregation [5]. Values of D lower than 2.5 could indicate contributions from cluster-cluster aggregation, either in the gas phase during deposition or in the liquid suspension. D-values approaching 3 indicate dense, compact agglomerates, formed by reaction limited growth
Dimensions of clusters are usually determined by measuring masses of agglomerates having widely different sizes. The slope of the doubly logarithmic

plot of mass (determined by SFFF) versus linear size (QUELS-determined) gives the dimension D. This determination of D does not need evaluation of the prefactor in (2). The cluster dimension could thus be evaluated by collecting samples during the SFFF fractionation of a powder sample, measuring the average QUELS diameter of the fractions separately and determining the slope of the logarithmic plot. Lacking such data at this stage however, we have tried to determine D from (2) which holds if a few reasonable assumptions concerning the prefactor are valid in the range considered here.
There are corrections to D which increase the apparent dimension and others which decrease D. The QUELS determined size may be D-dependent or it may contain contributions from rotational cluster diffusion which could lower the apparent L(QUELS). Non-stoichiometry in the bulk material or partial oxidation of the silicon nitride particles would lower the bulk density and this would affect L(SFFF) and decrease the calculated dimension. Since the size of the necessary corrections is unknown at present, we have chosen to omit them in this paper.
The method proposed here to determine n and D could be expected to fail if the powder particles are not spherical, (samples 3, 5, 9, and 10) since the method to calculate cluster diameters with SFFF and QUELS assumes spherical particle symmetry. The cluster size distribution in our powder samples was such that the average QUELS-determined diameter was insensitive to the assumed type of size distribution (which the Coulter N4 software needs to determine L(QUELS)).

CONCLUSION

A combination of sedimentation field flow fractionation and quasi elastic light scattering data allows a first approximation of the dimension of clusters in a powder to be determined. The degree of agglomeration is established by a combination of average SFFF-determined cluster size and the diameter of the primary particles as measured from transmission electron micrographs.

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