MICROSTRUCTURE OF LASER-DEPOSITED SILICON NITRIDE POWDERS

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ABSTRACT

The microstructure and agglomeration of fine silicon nitride powders made by laser-excited chemical vapour deposition are studied using sedimentation field flow fractionation and quasi elastic light scattering. The fractal dimension of the powder agglomerates is estimated.

1. INTRODUCTION

It is a truism to state that the properties of ceramic products are determined by the microstructure, which is imposed during sintering of the green form by suitable processing conditions. The ceramic processing stages are usually considered to be more important than the precursor powder properties. In many cases however, the characteristics of the ceramic powders are vital for property control because they can be the major factor determining the product microstructure. For example, high green densities may result from judiciously chosen particle size distributions in the ceramic powders. Small particle size enhances sinter activity, which is an important factor allowing a lower processing temperature in covalent ceramics. On the other hand, Wakai et al. (1990) have recently shown that very small spherical particles with inhibited sinteractivity are required in the production of dense, strong and tough ceramic composites having sufficient plasticity to be formed at elevated temperature. High access materials, i.e., those that are well exposed to the ambient, are catalysts, gas membranes, and gas storage solids. The microstructure of such materials often shows fractal characteristics as reported by Avnir et al. (1985). To some extent, fractal behaviour can be generated in materials during heat treatment. Spinodal decomposition in alloys and glasses (Schaefer, 1988; Schaefer et al., 1988) and porosity which developes during ceramic sintering (Veringa, 1990) are well known examples. High access or high porosity ceramics are not made by thermal processing of standard powders however, but are most expediently obtained by using specially taylored ramified powders, prepared either from colloidal solutions or from gaseous reactants. Oxide ceramic powders are conveniently produced from aqueous solutions, e.g., by sol-gel methods, as reviewed by Johnson (1987), which allow control of powder microstructure and composition within wide ranges. Fine non-oxide powders are best made by vapour phase methods (Kato, 1987). Laser-CVP (Cannon et al., 1982; Bauer et al., 1989) is particularly suitable for

synthesis of ultrafine ceramic powders because of its unsurpassed ease of control of powder microstructure and composition by the process parameters.

In this paper we report the synthesis of silicon nitride powders by vapour phase reaction between partially chlorinated silanes and ammonia as reactants. A tunable CO_2 laser was used to excite either of the reactants. We have also applied a combination of sizing techniques in order to determine the microstructure of the powder particles produced by laser-CVP, and to estimate their fractal dimension. In contrast with "porosity" and "specific surface area", fractal dimensions are well defined concepts with which chaotic solids such as agglomerates may be characterized. The applied sizing techniques are Sedimentation Field Flow Fractionation, or SFFF (Scarlett et al., 1988), and Quasi Elastic Light Scattering or QUELS (Dahneke, 1983). In Sedimentation Field Flow Fractionation 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. Quasi Elastic Light Scattering or Photon Correlation Spectroscopy measures intensity autocorrelation of laser light scattered by particles in a liquid suspension. 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. In addition to SFFF and QUELS, both Transmission Electron Microscopy (TEM) and gas adsorption measurements (BET) have been used here in order to estimate the size and porosity of the primary powder particles. Once the average masses and sizes of particle aggregates are known, their average dimension can be calculated. This is a parameter which is not only useful for characterization of the powders obtained but is also expected to be strongly dependent on the characteristics of the agglomeration process as shown by Meakin (1989). Thus, the dimension could be used for optimization of the reaction.

2. EXPERIMENTAL PROCEDURES

The silicon nitride powder is made in a cold wall reactor at atmospheric pressure. The central SiH_2Cl_2-nozzle has an internal diameter of 1 mm and the four adjustable side nozzles for ammonia, 0.4 mm. These nozzles inject the reactants in the laser beam spot where the silicon nitride particles form. The laser beam was focused by zinc selenide optics to a spot having a diameter of 1.5 mm. The reaction process conditions that were varied were precursor gas mixing and laser excitation sequence. By varying the point of NH_3 introduction into the laser excited dichlorosilane jet, the powder characteristics could be changed. The submicron particles were electrostatically removed from the aerosol at elevated temperatures in order to separate them from volatile ammonium chloride which is a waste product of the reaction. The 150 W CO_2 laser from Edinburgh Instruments (type PL 6) was tuned to output the 10P20 line ($\lambda = 10.6\ \mu m$) for selective excitation of dichlorosilane. The 9R30 line ($\lambda = 9.2\ \mu m$) was used to excite ammonia. The ammonia flow rate was 110 sccm and the dichlorosilane flow 53 sccm. The residence time of the gas in the visible laser flame (above the ammonia introduction point) was estimated to be 20 ms. The silicon nitride production rate under these conditions was approximately 1 g/h. Primary particle sizes were determined from transmission electron micrographs while

the average degree of agglomeration, n was derived from the cluster size, determined by SFFF as follows. The powder was suspended in a dilute aqueous ammonia solution (0.002 M); these suspensions were ultrasonically dispersed over a 10 minute period before introduction into the Dupont SF^3 analyzer and a Coulter N4 light scattering analyzer. These instruments have been recently compared and calibrated using standard silica and latex particles by Mori et al. (1989). The composition of the powders was determined by chemical analysis for silicon by Inductively Coupled Plasma, and nitrogen by ammonia titration using conductivity as described by Puxbaum and Vendl (1977). The flame temperature was monitored by a two-colour pyrometer which permitted measurement of the temperature distribution in the laser flame.

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:

$$n = \{\frac{L(SFFF)}{L(TEM)}\}^3 \tag{1}$$

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

$$\rho = \rho_0 L^{D-3} \tag{2}$$

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 [11] of the cluster. It follows from (2) that:

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

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.

3. 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. There are three regimes of reaction process parameters producing different powder characteristics. The samples in the lower third of Table 1 (number 11 to 15) were obtained by laser excitation of either reactant in a gas mixture. The highly agglomerated powders obtained in this premixed regime had a high nitrogen content and a composition close to the stoichiometric value. The particles were dense as shown by the similar values of their TEM and BET determined diameters. If ammonia was excited in this regime, the powders were invariably white, whereas those powders obtained with selective dichlorosilane excitation had a tan colour. This however, was their only difference, the other characteristics were quite similar. This color change was not accompanied by a significant difference in the Si/N ratio. The samples prepared in the postmixed regime (numbered 1 to 5 in Table 1) were produced by excitation of dichlorosilane with injection of cold ammonia gas into the laser generated flame. These powders were brown to tan colored, had an excess of elementary silicon as shown by chemical analysis, a low degree of agglomeration and large primary particles. There is a considerable difference in the particle size as determined from transmission electron micrographs and from gas adsorption measurements which indicates porous primary particles. The samples numbered 6 to 10 were produced in a transition regime and consisted

of an mixture of whiskers and large distorted porous particles also with an excess of silicon. The peak temperature in the laser flame which was invariably observed at the ammonia introduction point was 2400°C in the premixed and intermediate regimes. In the postmixed regime the maximum flame temperature was 1500°C.

Table 1. Particle Characteristics of silicon nitride powders

#	h	fib	$\frac{Si}{N}$	diameter nm				D	n
				TEM	BET	SF^3	QUELS		
1	2.9		4.8	100	7.2	172	335	2.66	5
2	1.6		4.1	115	5.2	168	194	2.92	3
3	1.5		3.7	75	6.7	159	134	3.11	10
4	1.2		5.1	50	6.9	147	314	2.60	25
5	1.1	3	2.4	120	17.6	122	233	2.64	1
6	1.0	2	2.2	50	13.8	102	332	2.39	8
7	1.0	1	2.9	70	10.0	136	198	2.79	7
8	0.9	1*	2.2	17	14.9	73	155	2.55	79
9	0.8	2	2.7	100	–	128	245	2.65	2
10	0.5		3.1	50	10.5	140	107	3.17	22
11	0.3		1.9	20	17.3	96	214	2.55	111
12	-0.5	2	2.0	25	30.4	94	177	2.63	53
13	-0.8	*	1.8	30	15.2	112	182	2.72	52
14	-1.5	*	2.3	16	12.3	106	207	2.62	291
15	-1.5	1	1.7	25	16.6	111	171	2.75	88

Meaning of symbols used: h (column 2) indicates relative height of NH3 injection nozzles; the number in column 3 gives the relative amount (in arbitrary units) of fibrous particles in the powder deposit if present; the asterisk indicates powders made using selective NH3 excitation; the number in column 4 is the weight ratio of silicon to nitrogen in the powders (theoretically 1.5 for Silicon nitride); in columns 5 to 8 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 9 gives the cluster dimension D and column 10 the number n of primary particles in the clusters.

4. DISCUSSION

The mechanism of silicon nitride formation has been studied by Morosanu et al. (1982). The characteristics of the powders made in the premixed regime are consistent with their reactions. Because of rapid energy equilibration at atmospheric pressure, the results are not expected to be heavily dependent on the choice of reactant excited by the laser. The overall reaction as proposed by Morusanu et al. (1982) is in the premixed case:

$$SiH_2Cl_2^* \implies SiCl_2 \xrightarrow{NH_3} SiNH \xrightarrow{NH_3} Si_3N_4$$
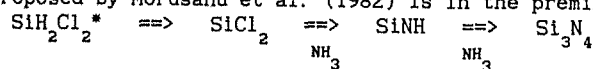
The analytically undetected but visually surmised excess of silicon in the dichlorosilane excitation experiments is probably the result of the presence of a sufficiently high concentration of the intermediate product SiCl₂, producing traces of silicon by reduction.

The reactions of silicon nitride formation in the postmixed regime is expected to be quite different because dichlorosilane is excited and decomposed to silicon before it is allowed to react with ammonia. Silicon droplets form which increase in size upon colliding. Hence the large size of the primary particles as seen in the electron micrographs. Exposure of the hot silicon mist to ammonia results in growth of a solid surface crust of silicon nitride on the surface of the silicon droplets and irregularly shaped large porous particles obtain, usually incompletely converted to the nitride. In several cases in the transition regime, carrot-like particles form, which is usually an indication of a Vapor-Liquid-Solid (VLS) mechanism. A simultaneous growth of solid silicon nitride and liquid silicon drops probably occurs which explains the observed morphology. The formation reaction consistent with the observed morphology in the transition and the postmixed regimes is:

$$SiH_2Cl_2{}^* \quad ==> \quad Si(l) \quad \underset{NH_3}{==>} \quad Si_3N_4(s)$$
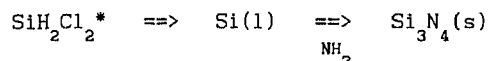
The observed excess of silicon is the result of a residence time of theparticles in the laser flame which is too short for complete reaction of silicon to silicon nitride.

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 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 (Meakin, 1989). 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 be applied when establishing the apparent dimension which increase D 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)).

ACKNOWLEDGEMENTS

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