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MODELLING AND DESIGN OF A NEW LAMINAR MIXING-TYPE AEROSOL REACTOR USING LASER-HEATING

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ABSTRACT

In thermodynamic calculations on ceramic powder formation from the gas-phase, we found that there are several mechanisms in which submicron Si and Si_3N_4 powder can be formed. As some mechanisms lead to porous particles or low-temperature imide contamination, a new reactor is designed and built in which the mixing of the reactant gases, the (chlorinated) silane and the ammoniak, can be precisely controlled.

KEYWORDS

CVD phase diagrams; ceramics; Si_3N_4; image analysis of agglomerated particles; laminar mixing-type aerosol reactor; laser-heating.

INTRODUCTION

Technical ceramics have important advantages for structural applications (e.g. in engines), like good high-temperature and oxidation resistance, lightness and extreme hardness. Structural ceramic parts have to be made by sintering a ceramic powder, which has to be very small (preferably submicron) and narrow size-distributed. Strongly agglomerated powder may give problems in sintering.

Submicron Si_3N_4 powder can be made by heating a precursor gas with a high-powered IR laser. The overall reaction is e.g.:

$$3\ SiH_2Cl_2 \;+\; 4\ NH_3 \;\text{----->}\; Si_3N_4 \;+\; 6\ HCl \;+\; 6\ H_2$$

Our research is aimed at the use of chlorinated silanes, which are much cheaper and less dangerous than the ordinarily used SiH_4. The particle synthesis is carried out in an aerosol reactor, in which several mechanisms play a role: nucleation, coagulation, growth and agglomeration.

EXPERIMENTAL SET-UP

The system consists of a tunable 200 W CO_2 laser, a set of mass-flow controllers, a reactor and an electrostatic precipitator. A two-color pyrometer is used for temperature measurements, a Mach-Zehnder interferometer for stability analysis of the flame. Aerosol apparatus like DMA/CNC can be used.

To prevent low-temperature imide ($Si(NH)_2$) formation, the chlorinated silane gas and the NH_3 have to be seperately injected in the laser beam (Fig.1). A new nozzle system has been developed (Fig.2), consisting of four concentric nozzles. The two reactant gases are seperated by an intermediate gas like H_2 or N_2. Advantages are the laminar mixing, a better defined geometry and so better reproducibility, and a very good control of the mixing by varying the relative gas velocities or the nozzle diameters.

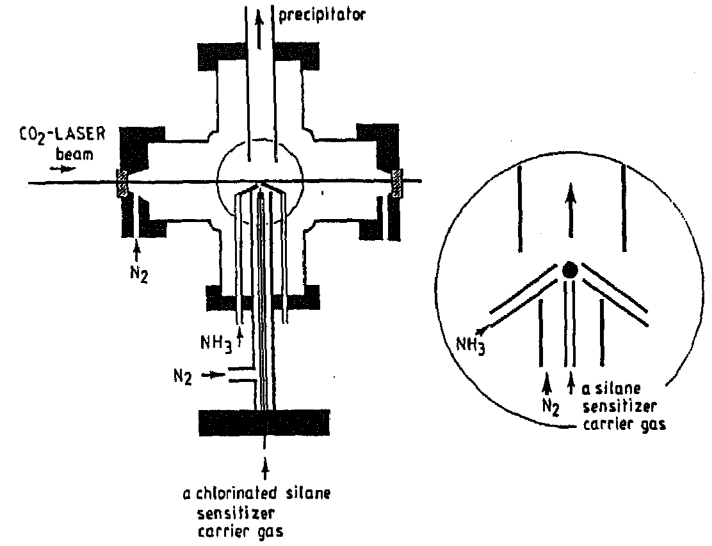


Fig.1. Nozzle system to prevent imide formation.

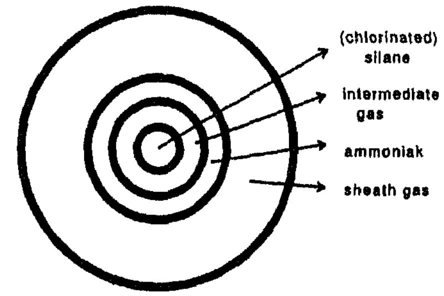


Fig.2. New laminar mixing-type nozzle system.

IMAGE ANALYSIS OF AGGLOMERATED PARTICLES

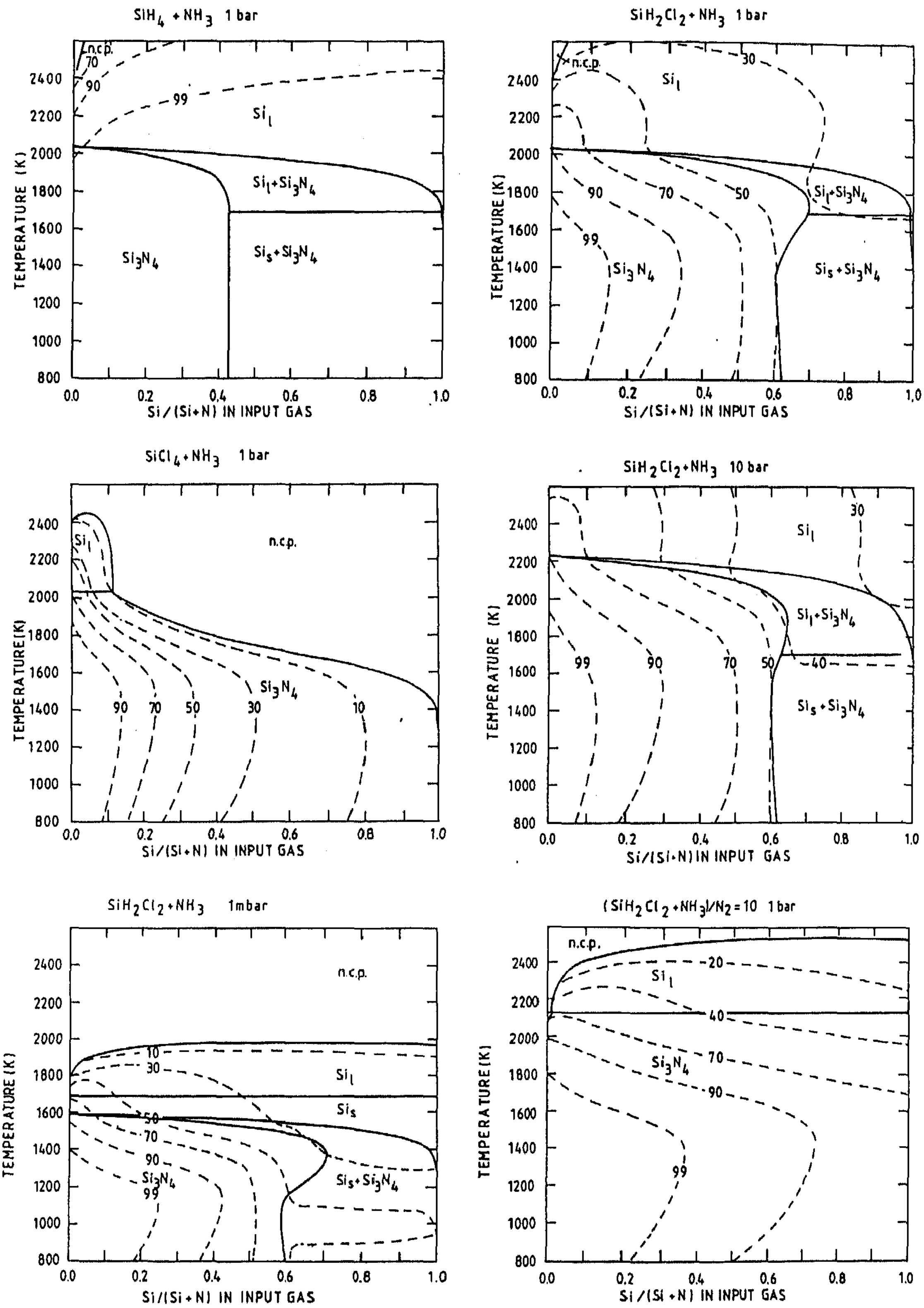
Using an image analysis package (TIM), software was developed to recognize primary particles in a TEM photograph of an agglomerate. The inner contours are also used for recognition. With this method, an estimation of the number of primary particles and the primary particle size distribution can be given. When Brownian movement of submicron particles is important, e.g. in case of high aerosol number densities, agglomerates are often fractals. Three methods for the determination of the fractal dimension by image analysis were investigated on a set of 24 agglomerates.

Table 1. The fractal dimension of Si_4N_4 powder

fractal	method	fractal dimension
perimeter	structured walk, corrected for discrete step sizes	1.33 +/- 0.06
mass	density-density correlation	1.38 +/- 0.14
mass	mass within circle	1.42 +/- 0.22

CVD PHASE DIAGRAMS

CVD-phase diagrams predict deposition efficiencies and phase boundaries of Si and Si_3N_4. Software has been developed to control the SOLGASMIX-PV software and search for phase boundaries. In a CVD-phase diagram the effect of temperature and source gas/reactant ratio is shown. The effect of pressure variation, changing the source gas and adding a carrier gas was investigated (Fig.3).


SiH4 + NH3 1 bar
n.c.p.
70
90
99
Si_l
Si_l+Si3N4
Si3N4
Sis+Si3N4
TEMPERATURE (K)
Si/(Si+N) IN INPUT GAS
SiH2Cl2+NH3 1 bar
n.c.p.
30
Si_l
90
70
50
99
Si_l+Si3N4
Si3N4
Sis+Si3N4
SiCl4+NH3 1 bar
n.c.p.
Si_l
90
70
50
30
10
Si3N4
SiH2Cl2+NH3 10 bar
30
Si_l
Si_l+Si3N4
99
90
70
50
40
Sis+Si3N4
SiH2Cl2+NH3 1mbar
n.c.p.
10
30
Si_l
Sis
50
70
90
Si3N4
99
Sis+Si3N4
(SiH2Cl2+NH3)/N2=10 1 bar
n.c.p.
20
Si_l
40
70
Si3N4
90
99
2400
2200
2000
1800
1600
1400
1200
1000
800
0.0
0.2
0.4
0.6
0.8
1.0

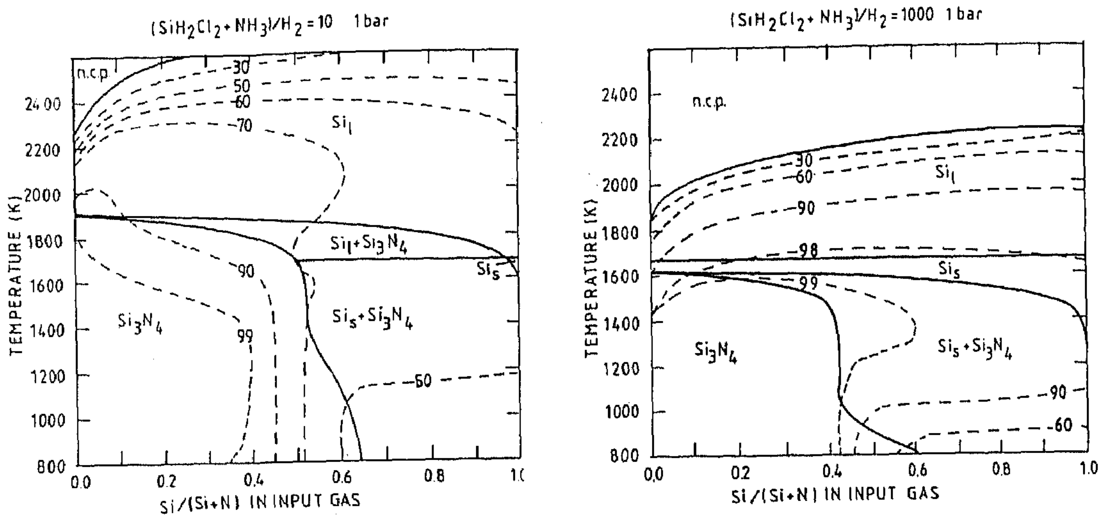


Fig. 3. CVD phase diagrams for the Si-H-Cl-N system. Regions of different phases are shown, and also contours of constant deposition efficiency (%).

The most important conclusion is that the way a phase diagram is wandered through, is vital for the mechanism of particle formation. There are essential three reaction paths for producing Si_3N_4:

1. Premixed reactants, going from low to high temperatures: formation of Si_3N_4 via $Si(NH)_2$;
2. Seperate heating of the reactants and going through a no-condensed-phase region: homogeneous nucleation of Si_3N_4;
3. Seperate heating of the reactants and going through a Si region: nitrification of Si, resulting in porous particles.

Thermodynamics is also needed to examine the driving force for particle formation, the supersaturation. It was found that not only the supersaturation but also the actual number of silicon molecules determines the nucleation rate, as the supersaturation decreases with increasing temperature, contrary to experimental observation.

MODELLING OF THE AEROSOL REACTOR

Two methods for calculating the particle size distribution as a function of the proces parameters are presently being developed: the method of moments, assuming a log-normal distribution, and a discrete-sectional model. This model simulates particle coagulation including discrete-sized molecular scale clusters, up to 20 molecules, and a sectional representation of larger particles, and is probably the only model capable of simulating the initial stage of the proces. The model will be capable of handling non-isothermal systems, as an essential feature of the laser reactor is a steep temperature gradient.

CONCLUSIONS

Essential in understanding ceramic particle formation, is a thorough examination of the CVD phase diagrams, from which different mechanisms of particle formation can be understood. Based on these considerations, we developed a new laminar mixing system. Particle characterization is based on image analysis of agglomerates and is capable of recognition of primary particles, resulting in a primary particle size distribution. Several methods of determining the fractal dimension are developed.

REFERENCES

Kruis, F.E., Scarlett, B., Bauer, R.A. and Schoonman, J. (1991) Thermodynamic calculations on the chemical vapour deposition of Si_3N_4 and Si from chlorinated silanes. Submitted to J.Am.Ceram.Soc.

Bauer, R.A., Kruis, F.E., Put, P. van der, Scarlett, B. and Schoonman, J. (1990) Chemical vapour precipitation of silicon nitride powder in a laser reactor. KONA, **8**, 145-154.