DEVELOPMENT OF WATER BASED PROCESSING OF SILICON NITRIDE MATERIALS

Kent Rundgren
Permascand AB
P O Box 42
SE-840 10 Ljungaverk, Sweden

Ola Lyckfeldt
Swedish Ceramic Institute
P O Box 5403
SE-402 29 Göteborg, Sweden

ABSTRACT

To strengthen the position of Si_3N_4 as a competitive material in structural applications, cheap raw materials as well as efficient and environmentally friendly processing routes are required. In this work, water-based processing of a medium-cost commercial Si_3N_4 powder (SICONIDE P95, Permascand AB, Sweden) was developed. This was done by planetary milling to improve the sintering performance and by freeze granulation to ensure high granule quality. Re-dispersing of a milled and freeze granulated/freeze-dried powder resulted in significantly improved rheological properties, enabling high solids-loaded suspensions (< 57 vol%). Adding sintering aids (6 wt% Y_2O_3 and 2 wt% Al_2O_3) prior to milling and pressing aids (PVA/PEG or latex/PEG) prior to freeze granulation gave excellent pressing performance and CIPed components, which sintered to nearly full density using GPS (Gas Pressure Sintering). The microstructures were characterized by a bimodal grain size distribution and negligible porosity. Mechanical data, flexure strength of 600-900 MPa, indicated possibilities of approaching material properties obtained with more expensive powders and processing routes. PVA/PEG was shown to be the more favorable pressing aid system compared to latex/PEG that gave lower strength.

INTRODUCTION

High-purity, expensive raw powders are normally used to meet the high demands on high-performance silicon nitride materials for structural applications. However, there is also a significant market pressure to minimize the total cost to make these ceramics competitive with alternative materials, although the gain in performance might be large. It is therefore desirable to use low-cost raw materials and less expensive processing routes. One way to achieve this with Si_3N_4

materials can be to use direct-nitrided powder and low-pressure sintering instead of powders produced by the imide method and hot isostatic pressing [1, 2].

To succeed in reaching the high material requirements, it is also necessary to optimize each processing operation. Pre-treatment of the raw powder by milling to narrow the particle size distribution might be the first step. This will favor the sintering properties of the shaped materials. For materials produced by pressing, the pre-dispersing and granulation steps are crucial for the granule homogeneity and pressing performance. Freeze granulation is a novel granulation process in which a suspension is sprayed into liquid nitrogen [3]. The frozen droplets (granules) are then freeze-dried to remove the frozen liquid. The dispersed homogeneous state of the suspension is kept during drying with no migration of binder or sintering additives. Consequently, this technique has the potential of giving granules that are easy to break during pressing, which, in turn, results in a homogeneous microstructure in compacts and superior sintering performance [4].

The aim of this work has been to study the densification and mechanical properties of a medium-cost (direct-nitrided) Si_3N_4 powder using freeze granulation and sintering by GPS.

MATERIALS AND EXPERIMENTAL

Materials

The materials used in this work are listed in Table I.

Table I. Ceramic powders and pressing aids used in this study

Material	Trade name	Producer
Si_3N_4	SICONIDE P95L	Permascand AB, Sweden
Y_2O_3	Grade C	HC Starck, Germany
Al_2O_3	AKP-30	Sumitomo Corp., Japan
PVA	Mowiol 4-88	Hoechst, Germany
Latex	Duramax B-1014	Rohm & Haas, USA
PEG	400 DAB 8	Hoechst, Germany

Slip Preparation

Water-based slips were prepared at 45 vol% solids loading using a planetary mill (PM 400, Retsch, Germany) with Si_3N_4 linings and balls. No dispersant was used as the Si_3N_4 powder by itself adjusts the pH to around 10 and adequate electrostatic stabilization can be achieved. The milling was carried out from 1 up to 48 h at 100 rpm, with or without the addition of sintering aids (6 wt% Y_2O_3 and 2 wt% Al_2O_3). For further processing (granulation, pressing and sintering) slips milled for 24 h were used. In this case the slips were sieved (20 μm) and

pressing aids were added. Based on solids the amount of binder (PVA or latex) was 6 vol% and the amount of plasticizer (PEG 400) was 1.5 vol%.

Freeze Granulation

Freeze granulation (LS-2, PowderPro, Sweden) was conducted by spraying the slips into liquid nitrogen resulting in frozen droplets that were freeze dried to obtain a free-flowing granulate.

Powder Properties

As-received and milled Si_3N_4 powders were characterized by the particle size distribution using X-ray sedimentation (Sedigraph 5100, Micromeritics, USA) and by measuring the BET specific surface area (FlowSorb II 2300, Micromeritics, USA). The dispersing properties of freeze-granulated/freeze-dried powders were demonstrated by preparing slips without any additives at 45 vol% solids loading using 1 h planetary milling at 200 rpm. Furthermore, a slip was prepared based on a powder composition consisting of 96 wt% milled (48 h) and freeze granulated P95L and 4 wt% Y_2O_3. In this case a total solids loading of 57 vol% was reached using a polyacrylate type of dispersant (Dolapix PC75, Zschimmer & Schwarz, Germany). All slips were characterized by measuring the equilibrium viscosity at various shear rates with a CS rheometer (StressTech, ReoLogica Instrument, Sweden).

Material Processing

Small cylinders (∅ = 10 mm, h = 7 mm) and large discs (∅ = 65 mm, h = 7 mm) were shaped using uniaxial pressing at 80 MPa and subsequent cold isostatic pressing at 350 MPa.

Removal of organic material was conducted in a nitrogen atmosphere with 1°C/min up to 500°C with a dwell time of 60 min.

Using a GPS furnace (FPW 250/300, FCT, Germany) specimens, placed inside a Si_3N_4 powder bed in either a Si_3N_4 or a BN crucible, were sintered at 1800-1900°C for 3 h with a nitrogen pressure of 1-2 MPa.

Material Evaluations

Densities of sintered materials were measured by the water intrusion method. Plasma-etched microstructures were studied by SEM. Bars were machined from the large sintered discs and the flexural strength tests, 4PB, were made at Saint-Gobain, Northboro, MA. The fracture toughness and hardness were measured by Vickers indentation method with 10 and 1 kg load, respectively. Finally, fracture surfaces of tested bars were analyzed by SEM to detect the strength-limiting defects or factors.

RESULTS AND DISCUSSIONS

Powder Properties

Figure 1 shows the effect of the planetary milling on the particle size distribution and the BET area. Most pronounced is the reduction of large particles but also the increased amount of fines is evident.

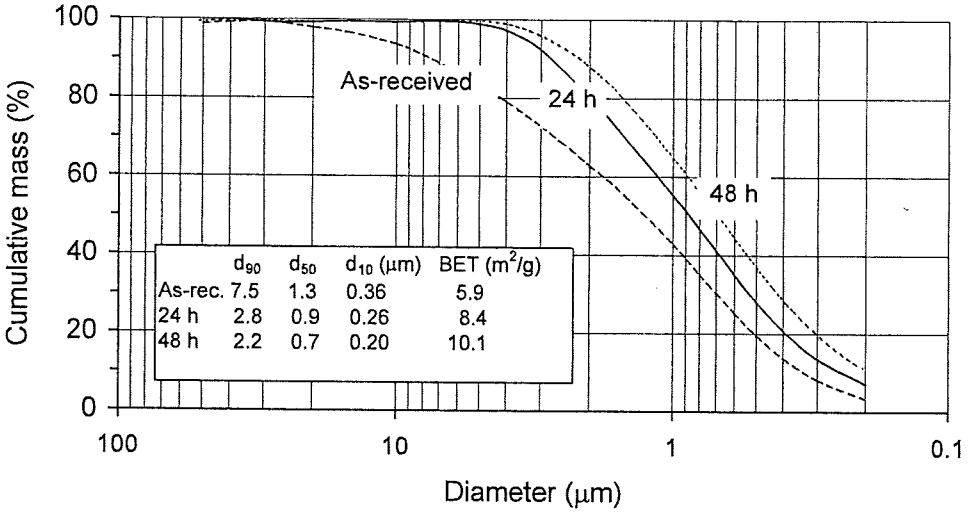


Figure 1. Particle size distributions and BET surface area of as-received and milled P95L.

After freeze granulation/freeze drying, the milled powders showed improved dispersability illustrated by the lower viscosity curves in Figure 2. For the powder milled for 48 h, there was a remarkable decrease in viscosity. This can be a result of the change in particle size distribution but the main reason is believed to be the breakdown of agglomerates in the pre-milling step. By freeze granulation the re-agglomeration is avoided, which results in a powder that is very easy to disperse and low-viscosity slip properties.

The upper viscosity curve in Figure 2 shows the slip characteristics when forcing the solids loading up towards the limit of what can be considered as a processable state. The approach to this limit is indicated by the dilatancy at high shear rates. In this case a dispersant was used to obtain more time-stable properties of the slip for further processing, for example by shaping using a direct casting technique (gel casting etc). Merely the natural pH adjustment by the powder is not sufficient as destabilizing effects occur in time owing to certain solubility both of SiO_2 from the Si_3N_4 particle surfaces and of sintering additives such as Y_2O_3.

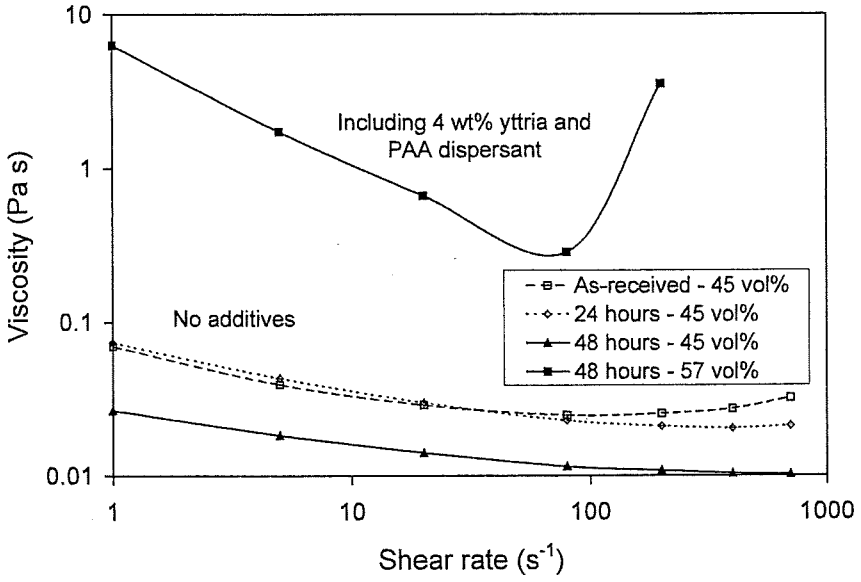


Figure 2. Apparent equilibrium viscosity vs shear rate of suspensions based on as-received and pre-milled/freeze granulated P95L.

Evaluation of Sintered Materials

The sintering and density data together with the results from the mechanical testing are presented in Table II.

Table II. Results from sintering (3 h dwell) of Si_3N_4 materials obtained by pressing using two different pressing aids.

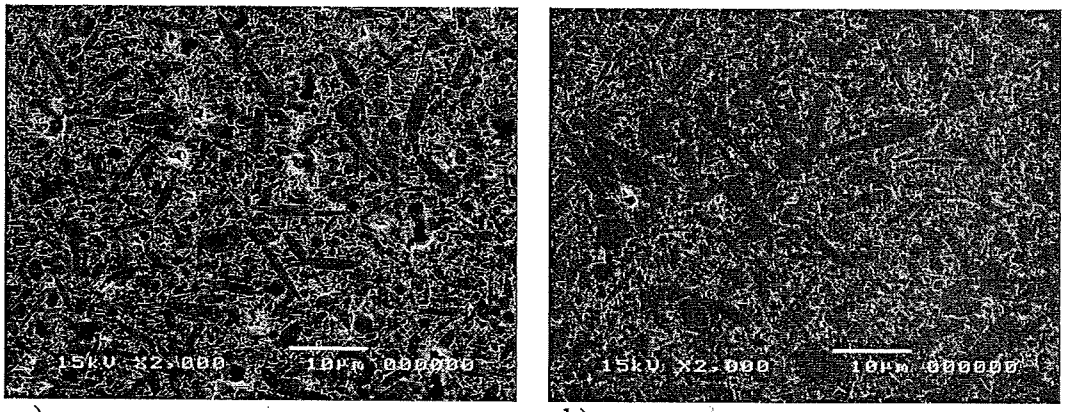
Specimen	Sintering			Properties			
	Temperature (°C)	Pressure (MPa)	Crucible	ρ_{rel} (%)	4PB* (MPa)	K_{Ic}** (MPa$\sqrt{m}$)	H_v (GPa)
PVA/PEG	1800	1	Si_3N_4	88.5			
	1850	1	Si_3N_4	95.5			
	1850	1	BN	99.2			
	1900	2	Si_3N_4	99.7			
	1900	2	BN	100	764/891	6.7	14.5
Latex/PEG	1800	1	Si_3N_4	91.1			
	1850	1	Si_3N_4	96.8			
	1850	1	BN	98.9			
	1900	2	Si_3N_4	100			
	1900	2	BN	100	592/624	6.0	14.0

*Average strength of six bars from two different discs each.

** K_{Ic}: Vickers indentation 10 kg, Laugier.

With the sintering aids composition used, at least 1850°C was required to approach full densification. It was obvious that the use of a BN crucible favored the sintering by restricting the decomposition of Si_3N_4. The bending strength indicated that latex/PEG as pressing aids was less favorable. The level of bending strength, close to 900 MPa for the specimens obtained with PVA/PEG is considered to be sufficient for most structural applications, in which Si_3N_4 components, produced with more expensive powders, are used today.

The SEM images in Figure 3 show plasma-etched microstructures of materials sintered by GPS under different conditions.



a) b)

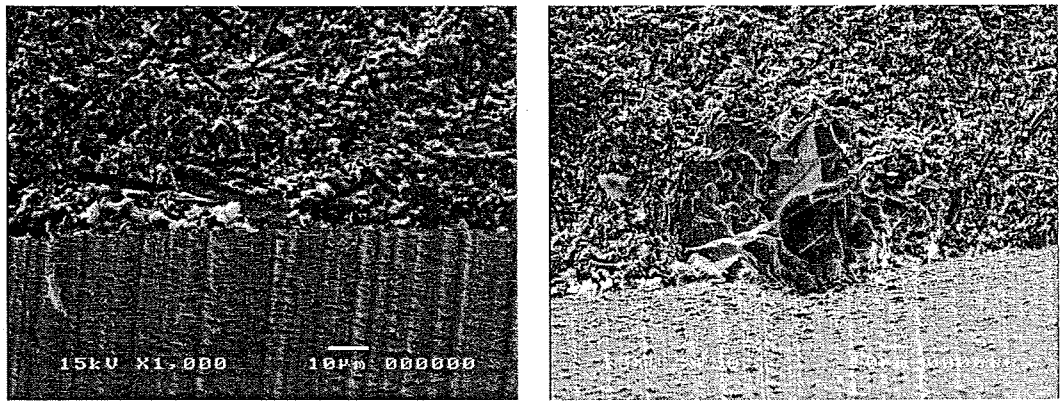
Figure 3. SEM images of sintered materials obtained with PVA/PEG as pressing aids, a) 1800°C (3 h), 1 MPa and b) 1900°C (3 h), 2 MPa.

With the lower sintering temperature and pressure, larger amounts of small pores, in the range of 1-10 μm, could be seen. In the case of the material sintered at 1900°C/2 MPa, only a few, very small pores (< 3 μm) remained, which are considered to be non-critical for the mechanical strength. The specimens obtained with latex/PEG as pressing aids showed similar microstructure. Consequently, it was not possible to detect the origins that limited the strength in this case. Otherwise, the microstructure in all materials was characterized by a bimodal grain size distribution, a mix of small equi-axed and large, 10-20 μm, elongated grains, which indicate a good balance between strength and toughness in these GPS materials.

Fractographic Study

The SEM images in Figure 4 show typical fracture surfaces of tested 4PB samples. Figure 4a shows large grains in PVA/PEG samples to be the strength-limiting defect, due to the *in-situ* reinforced microstructure formed by GPS at 1900°C, 3 h. The strength-limiting defect in the latex/PEG samples, shown in

Figure 4b, was large pores and agglomerates, which probably originate from the latex/PEG binder system. These results show that the latex/PEG system needs to be improved before it can be used for high-strength advanced silicon nitride ceramics.



a) b)

Figure 4. SEM images of fracture surfaces in PVA/latex samples, a) large grains in a PVA sample (4PB = 900 MPa) and b) surface pore and agglomerate in a latex sample (4PB = 600 MPa).

CONCLUSIONS

It has been shown that, by optimizing the processing, a low-cost powder and sintering can be utilized for the manufacture of high-performance Si_3N_4 materials. Wet milling favors the particle size distribution and the dispersing properties if the powder is freeze granulated after the milling. This treatment enabled the preparation of slips with a solids loading as high as 57 vol% which is crucial if the powder is to be used for direct casting or injection molding. Pressed specimens based on powders milled for 24 h together with sintering aids reached full density at GPS sintering with negligible micro porosity. With PVA/PEG as pressing aids and optimized sintering conditions, a flexural strength of nearly 900 MPa was achieved.

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REFERENCES

[1]K Rundgren, Y Iwamoto and H Matsubara, "*In-situ* Reinforced Si_3N_4". In "Ceramics: Getting into the 2000's" Part B Advances in Science and Technology 12, Proceedings of 9th Cimtec '98, ed. by P. Vincenzini, Elsevier, 1999.

[2]P Brännvall and K Rundgren, "Grain Growth Mechanisms in *In-Situ* Reinforced Si_3N_4", pp. 7-8 in Sixth ECerS Conference & Exhibition of the European Ceramic Society, Extended Abstracts Volume 2, British Ceramic Proceedings No. 60, IOM Communications Ltd, 1999.

[3]L Carlinger and E Carlström, "The Influence of the Granule Structure on the Strength of Pressed and Sintered Si_3N_4", pp. 43-44 in Sixth ECerS Conference & Exhibition of the European Ceramic Society, Extended Abstracts Volume 2, British Ceramic Proceedings No. 60, IOM Communications Ltd, 1999.

[4]B Nyberg, E Carlström and R Carlsson, "Freeze Granulation of Liquid Phase Sintered Silicon Carbide". pp. 107-113 in Ceramic Transactions, Vol. 42 "Silicon-Based Structural Ceramics", ed. by B.W. Sheldon and S.C. Danforth, American Ceramic Society, 1994.