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PRESSING AND SINTERING DEVELOPMENTS OF FREEZE GRANULATED Si_3N_4 MATERIALS

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ABSTRACT

The effects of binder type, pressing cycle, and sintering schedule on the mechanical and microstructural properties of freeze-granulated Si_3N_4 materials have been studied. Produced materials were based on a medium-cost, direct-nitrided, powder (SicoNide P95H, Permascand AB) and a sintering-aid composition consisting of Y_2O_3, Al_2O_3, and Fe_2O_3. The pre-processing included wet milling and freeze granulation to obtain favourable pressing and sintering performance. It was shown that a pressing-aid composition of PVA/PEG favoured the compaction at pressing whereas PEG/PEG gave better sintering performance. Further, a higher initial uniaxial pressure at pressing (higher green density) tended to support grain growth that resulted in improved fracture toughness.

INTRODUCTION

Manufacture of silicon nitride (Si_3N_4) components utilizing pressing concerns many aspects that need to be considered in order to reach desired relations between material properties and manufacturing cost[1-3]. This includes the raw-powder quality, dispersing and granulation, pressing and sintering aids, pressing procedure, debinding and sintering procedure. High performance and expensive Si_3N_4 powders and sintering by hot isostatic pressing have so far dominated the manufacture of advanced Si_3N_4 components. However, recent demands for lower manufacturing cost have turned the focus to cheaper powders and low-cost sintering. This has resulted in an increased use of direct-nitrided rather than chemically derived Si_3N_4 powders, adapted type and amount of sintering aids, and pressureless or gas pressure sintering (GPS)[4].

In pressing of advanced ceramics utilising very fine (submicron) powders, addition of pressing aids, and granulation is required. The most common types of

pressing aids are based on polyvinyl alcohol (PVA) and/or polyethylene glycol (PEG) whereas granulation takes place by spray-drying (large-scale) or sieve granulation (small-scale). The amount and distribution of the pressing aids will influence the compaction behaviour at pressing and the strength of pressed specimens. The granulation will influence the flowability and tap density at filling of the pressing tool. In general, spray drying gives spherical free-flowing granules with high density but supports segregation of pressing aids and fines to the periphery of the granules. This may cause incomplete crushing of the granules at pressing and micro-scale inhomogeneities. An alternative and very promising granulation technique is freeze-granulation. Instantaneous freezing of a sprayed powder suspension followed by freeze drying without risks of migration phenomena, produces spherical, free-flowing, and homogeneous granules that are easy to crush at pressing[5-7].

This study was based on the processing of a medium-cost direct-nitrided Si_3N_4 powder (SicoNide P95H, Permascand AB, Sweden). The processing included dispersing, milling, granulation and pressing with different pressing aids, debinding and gas pressure sintering according to various schedules. Sintered materials were investigated with respect to density, microstructure and mechanical properties.

MATERIALS AND EXPERIMENTAL

All powders and organic additives used are listed in Table 1.

Table 1. Materials used in this study.

Material	Label	Manufacturer
Si_3N_4	SicoNide P95H	Permascand AB, Sweden
Y_2O_3	Grade C	HC Starck GmbH, Germany
Al_2O_3	AKP-50	Sumitomo Corp., Japan
Fe_2O_3	Chemical grade	Panreac Quimica SA, Spain
PVA (M_w 31000)	Mowiol 4-88	Clariant GmbH, Germany
PEG 400		Merck-Schuchardt, Germany
PEG 20000	Carbowax 20M	Union Carbide, Belgium

40 vol% slips with the powder proportions of 93.63 wt% Si_3N_4, 4% Y_2O_3, 2% Al_2O_3 and 0.37% Fe_2O_3 were prepared by planetary milling for 24 h (Retsch PM400) using linings and balls of Si_3N_4. No dispersing agent was used due to the strong capacity of the SicoNide powder to adjust the pH to a high level (ca 10), which provides efficient electrostatic slip stabilization.

After milling the slips were 50 micron sieved before the addition of pressing aids by mild mixing. Two different pressing aid compositions were used based on either 6 vol% PVA and 1.5 vol% PEG 400 or 6 vol% PEG 20000 and 1.5 vol% PEG 400, all based on powder + polymers. Another wet sieving at 100 μm was carried out before freeze granulation was conducted using a lab-scale granulator (LS-2, PowderPro HB, Sweden). The frozen granulates were freeze dried on

plates in a Lyovac GT2 (Leybold AB, Sweden). The dried granulates were stored under dry conditions to avoid moisture uptake until pressing was carried out.

Uniaxial pressing of small quadratic (14.5 × 14.5 × 10 mm) specimens was conducted at 10 or 60 MPa and subsequently isostatically pressed at 300 MPa.

Removal of the organic material was conducted in nitrogen with 1°C/min up to 500° and a dwell time of 30 minutes. For this a debinding rate-controlled equipment (RCE, SCI, Sweden) was used that continuously monitors the weight loss related to time and temperature.

Sintering was conducted with a gas-pressure (N_2) sintering furnace (FPW 250/300, FCT, Germany) with the specimens placed in a Si_3N_4 powder bed in a Si_3N_4 crucible. A double-dwell sintering was utilized; 1st dwell at 1800°C - 1 MPa for 1 to 2 h and 2nd dwell at 1900°C - 2 MPa for 0.5 to 2 h.

Material evaluations took place by density measurements using the water intrusion method according to Archimedes' principle. Some specimens were polished and etched for SEM studies (JEOX-8600, JEOL, Japan). Hardness and fracture toughness were measured by Vickers indentation.

RESULTS AND DISCUSSION

The measurements of moisture content of the two granulates showed that the PVA/PEG batch contained 3.5 wt% whereas the PEG/PEG batch contained 1.5 wt% moisture. The reason for this difference is probably explained by the higher degree of hygroscopic character of PVA. The densities, manually measured after debinding, showed that PEG/PEG gave 58.9% with low and 59.7% with high uniaxial pressure, whereas PVA/PEG gave 60.3% and 60.7% of the theoretical density, respectively. Obviously, PVA/PEG (including higher moisture content) and the higher initial uniaxial pressing supported the degree of compaction, although the same pressure was used in the subsequent isostatic pressing.

Debinding of the pressed specimens showed that the main removal of PEG appeared between 200 and 300°C, whereas the major part of PVA was removed just above 300°C. Table 2 summarizes the results from the sintering and shows that all specimens sintered to full or near full density (theoretically 3.245 g/cm^3). Obviously, the powder composition with milled P95H and the sintering aids together with the applied processing yielded good sintering performance in general. However, there are minor differences that can be observed. For example, it appeared crucial to use sufficiently long time (2 h) at the first dwell. This was to achieve closed porosity that allowed complete densification in the second dwell at a higher temperature and pressure. The second dwell could then be short (0.5-1 h) to minimize exaggerated grain growth. Another trend was that a higher pressure at the initial uniaxial pressing promoted the densification, and can basically be referred to as an effect of the higher pressed density.

In spite of lower pressed density, PEG/PEG tended to give higher sintered density than PVA/PEG. According to other findings PVA is expected to leave carbon residues when debinding is conducted in nitrogen atmosphere[8]. The carbon residues are expected to take away oxygen and, therefore, retard densification.

Table 2. Results from sintering of small Si_3N_4 specimens by GPS.

Pressing aids	Isostatic pressing (MPa)	Sintering (h at 1st/2nd dwell)	Weight loss (wt%)	Density (g/cm^3)
PEG/PEG	10	1/2	2.7	3.23
		2/1	2.9	3.24
		1/0.5	2.5	3.21
		2/0.5	2.1	3.23
		2/2	3.1	3.24
PEG/PEG	60	1/2	2.8	3.23
		2/1	2.8	3.24
		1/0.5	2.4	3.22
		2/0.5	2.3	3.24
		2/2	3.2	3.24
PVA/PEG	10	1/2	2.9	3.21
		2/1	3.0	3.23
		1/0.5	2.5	3.20
		2/0.5	2.4	3.23
		2/2	3.2	3.23
PVA/PEG	60	1/2	2.9	3.22
		2/1	2.8	3.24
		1/0.5	2.5	3.23
		2/0.5	2.3	3.24
		2/2	3.2	3.24

The SEM studies of specimens sintered with 2 h 1st dwell and 0.5 or 2 h 2nd dwell showed essentially dense and bimodal microstructures (Fig. 1). Only traces of micropores in the size range of 1-3 μm were detected at this magnification.

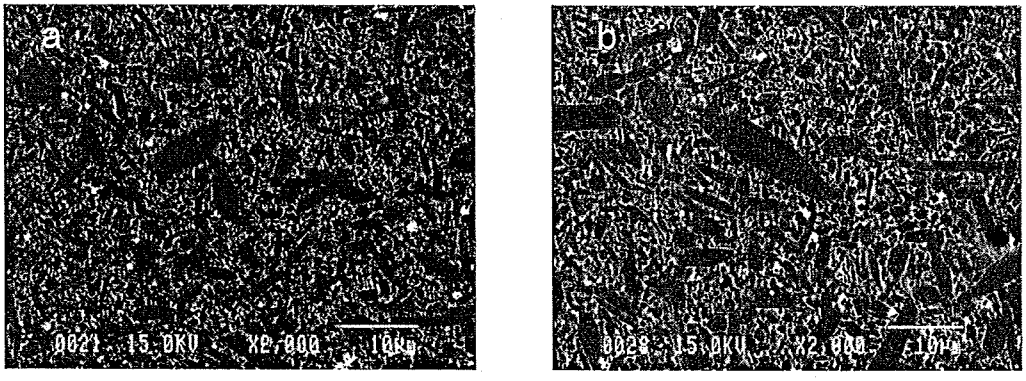

Figure 1: SEM images of Si_3N_4 specimens pressed with PVA/PEG at high uniaxial pressure, sintered with 2 h 1st dwell and 0.5 h (a) or 2 h (b) 2nd dwell.

The images in Fig. 1 indicate that the longer time at the second dwell (image b) causes a grain coarsening. Additionally, lower magnifications showed more

frequent larger pores indicating that the grain growth (Oswald ripening) was accompanied by coalescence of small pores.

Figure 2 shows SEM images of specimens pressed with PEG/PEG and sintered with long (2 h) 1st and short (0.5 h) 2nd dwell. The images show a slightly coarser grain structure when high initial uniaxial pressing was used (b), which also was indicated by the pore coalescence shown at a lower magnification. One reason for this could be that the higher pressed density gave a complete densification earlier and, hence, resulted in longer time available for Oswald ripening.

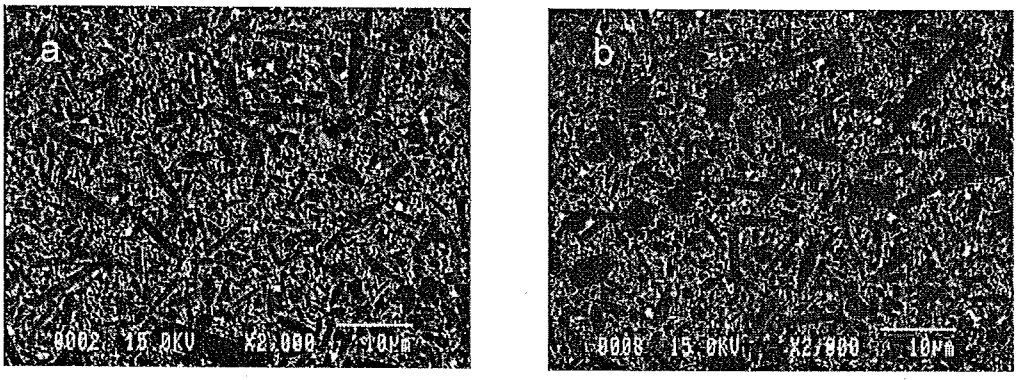

Figure 2: SEM images of Si_3N_4 specimens pressed with PEG/PEG and low (a) or high (b) initial uniaxial pressure and sintered for 2 h 1st dwell and 0.5 h 2nd dwell.

The results from the mechanical testing are summarized in Table 3 and show similar hardness values for all specimens, but with some differences in fracture toughness. The highest value, 7.2 MPa$\sqrt{m}$, was achieved with the PEG/PEG, pressed with high uniaxial pressing and sintered with a long 2nd dwell.

Table 3. Results from the mechanical testing of produced Si_3N_4 specimens.

Pressing aid	Isostatic pressing (MPa)	Sintering (h at 1st/2nd dwell)	Density (g/cm^3)	Mechanical properties	
				H_v (GPa)	K_{Ic} (MPa$\sqrt{m}$)*
PEG/PEG	10	2/0.5	3.23	12.8	5.7
PEG/PEG	60	2/0.5	3.24	12.9	6.3
PEG/PEG	60	2/2	3.24	12.3	7.2
PVA/PEG	10	2/0.5	3.23	12.8	5.5
PVA/PEG	60	2/0.5	3.24	12.2	6.3
PVA/PEG	60	2/2	3.24	12.2	6.4

*According to Laugier

Longer dwell and higher pressed density supported the grain growth and increased the toughness. The same effect was not achieved with the corresponding PVA/PEG specimens. In this case a higher carbon residue caused a lower amount of glassy phase by oxygen removal and/or formation of SiC. Both these effects

could be responsible for the reduced toughness, in spite of the grain growth observed in the SEM studies. Lowest fracture toughness was achieved for both binder systems when low uniaxial pressure (low pressed density) and short 2nd dwell at sintering was used, factors that limited grain growth.

SUMMARY - CONCLUSIONS

By applying freeze granulation and adequate processing additives (pressing and sintering aids) as well as adapted processing (pressing and sintering), dense Si_3N_4 materials based on a medium-cost, direct-nitrided Si_3N_4 powder have been produced. Factors, found to promote densification were PEG/PEG as pressing aid (lower carbon residues), higher uniaxial pressure (higher green density), sufficiently long (2 h) initial dwell at 1800°C and 1 MPa nitrogen pressure. Results in terms of density data, SEM studies and mechanical data suggested that PEG/PEG as pressing aid resulted in the formation of a tough microstructure by lower carbon residues versus the PVA/PEG system.

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