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Processing, microstructure, mechanical properties of Si_3N_4 obtained by slip casting and pressureless sintering

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Abstract

The slip casting and subsequent pressureless sintering route has been revealed as a powerful method to obtain a high-density silicon nitride. The optimisation of the slip casting preparation and of the sintering conditions has been investigated. The relation between microstructure, mechanical properties and thermal shock behaviour of Si_3N_4 is also outlined. Finally, this process is successfully employed to produce a Si_3N_4 material with interesting properties in regard to those obtained by a hot pressing process.

Keywords: A. Sintering; A. Slip casting; B. Microstructure; C. Mechanical properties; D. Si_3N_4

1. Introduction

Silicon Nitride (Si_3N_4) is one of the best ceramic materials for high temperature structural components. Si_3N_4 has high strength at high temperature, good thermal resistance due to the low thermal coefficient of expansion, and good resistance to oxidation [1].

High dense silicon nitride may only be obtained by the addition of densification aids, which allow liquid phase sintering. In addition many forming methods were developed to facilitate densification and improve Si_3N_4 properties [2,3]. Hot pressing (HP), gas pressure sintering (GPS) and hot isostatic pressing (HIP) are all successfully employed to produce high strength Si_3N_4 based ceramics [3–5], but all these techniques are limited by their cost [6]. Slip casting and pressureless sintering process is an ideal forming method because of its low cost, its simplicity, its flexibility and its suitability to form complex shapes. But, nowadays this process is not very developed because it leads to moderate thermomechanical properties [7].

As the properties of a material are closely related to the nature and structure of its constitutive elements, the realisation of a material with good properties can be achieved through the control of many factors: phase composition of the starting powders, type and amount of sintering additives, processing parameters (time, temperature, pressure) and microstructure (grain size and morphology) [8–12].

The aim of this work is to propose slip casting and a pressureless sintering route for developing a high-density Si_3N_4 with good mechanical properties similar to those obtained by the common processes. The effect of attrition on microstructure has been particularly evidenced. Finally, the mechanical properties were compared with those obtained by hot pressing a silicon nitride powder under the same sintering conditions [13].

2. Experimental procedure

A commercial α-Si_3N_4 powder (SNE-05, UBE Industries, Japan) containing 95% α-Si_3N_4 and 5% β-Si_3N_4, was used in this study. The mean diameter and the specific surface area were 0.8 μm and 4–6 m^2/g respectively. A mixture of 8 wt.% Y_2O_3 (RHODIA, France) and 1.5 wt.% Al_2O_3 (HR8, CRICERAM) was used as the sintering aids.

The rheological behaviour of the slips was characterised by a rotation viscometer (Haake viscometer VT501) with a measuring cell for low viscosity (type NV). The stability of the slips was evaluated by the sedimentation test. The test was conducted in two 100 ml graduated test tubes by observing the height of the interface between the settled suspension and the supernatant solution, during 4 days. Granulometry of the

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slips was measured by centrifugation (Horiba, particle size distribution analyse CAPA 700) with an acceleration rate of 960 rpm. The green compacts density was measured by geometrical method. The bulk density of the sintered bars was determined by water immersion (Archimed method). The calculated theoretical density of sintered specimen is about 3.27 g/cm^3.

The evolution of the amount of β phase was determined using X-ray diffractometry (XRD). Microstructure of the sintered specimens was observed by scanning electron microscopic examination of polished and plasma-etched surfaces. The dimensions of the sintered specimens were approximately 30×4×3 mm^3. The strength was measured by 4-points bending (inner and outer spans: 10–21 mm) at room temperature. The tension face of the beams was subsequently polished down to 1 μm diamond paste. The fracture toughness was evaluated by the single edge notched beam (SENB) at room temperature. An initial notch of 2 mm depth and 0.3 mm wide was conducted. Cumulated thermal shock test was conducted by heating polished bars in an electric furnace followed by water quenching at 25°C.

After determination of the optimum conditions of dispersion (deflocculant amount, pH) and stability, slips with a solid content of 64.5 wt.% were prepared by addition of 0.07 wt.% Darvan C deflocculant (Ammonium polymethacrylate) and sintering aids at natural pH ≈ 9. In order to investigate the effects of attrition on the liquid phase sintering, two alternative ways have been used. The flow chart of the process is shown in Fig. 1:

(A) Powder blends (α-Si_3N_4, 8 wt.% Y_2O_3 and 1.5 wt.% Al_2O_3) were mixed and homogenised in a two step process. First, the powders were premixed by attritor milling in ethanol for 4.5 h with alumina balls. After evaporation of the solvent, the dried blend was again dispersed in water with 64.5 wt.% of dry blend and 0.07 wt.% of deflocculant (Darvan C) in a horizontal rolling mill for 24 h with alumina balls (2–2.5 mm).

(B) Powder blends were directly dispersed in water with 64.5 wt.% of dry blend and 0.07 wt.% of deflocculant in a horizontal rolling mill for 24 h with alumina balls.

Then, these two aqueous slips coming from batches A (as reference to Attrition) and B respectively, were cast on a plaster of Paris mould in a disc shape. After drying, the green compacts were embedded in a Si_3N_4 powder bed in a graphite crucible. Then they were pressureless sintered in nitrogen atmosphere (1 atm) at 1800°C for three different sintering times (1, 1.5 and 2 h).

3. Results and discussion

3.1. Rheological study

Slip casting of Si_3N_4 requires well-dispersed low viscosity suspensions. In order to determine the optimum of deflocculation (lower viscosity of the slip), 10 different aqueous slips without sintering aids and with an

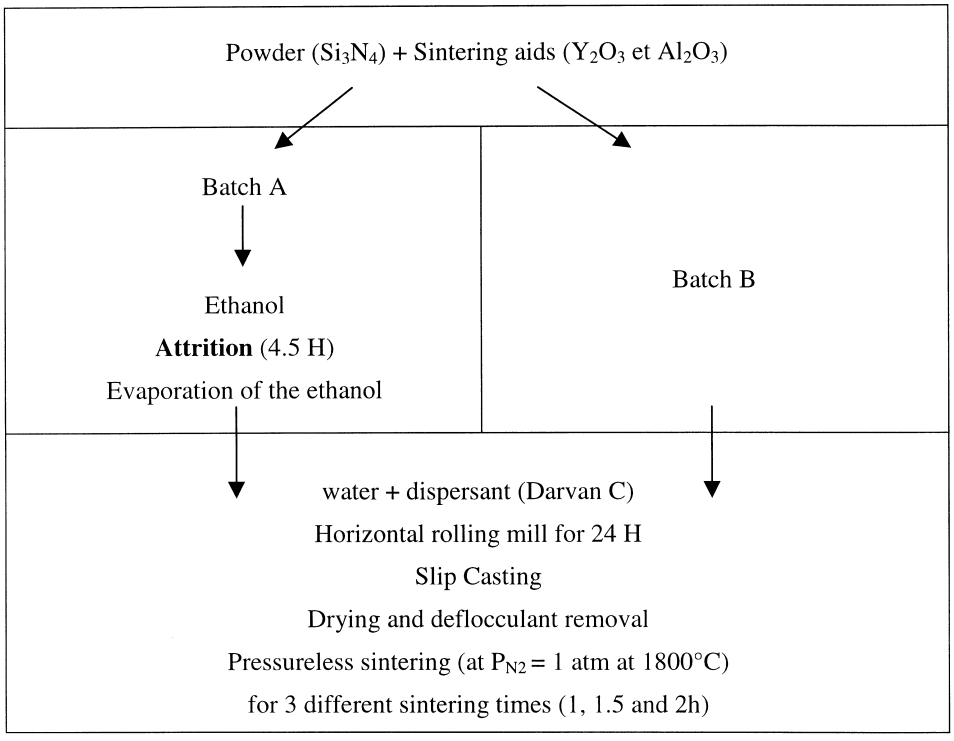


Fig. 1. Elaboration flow chart.

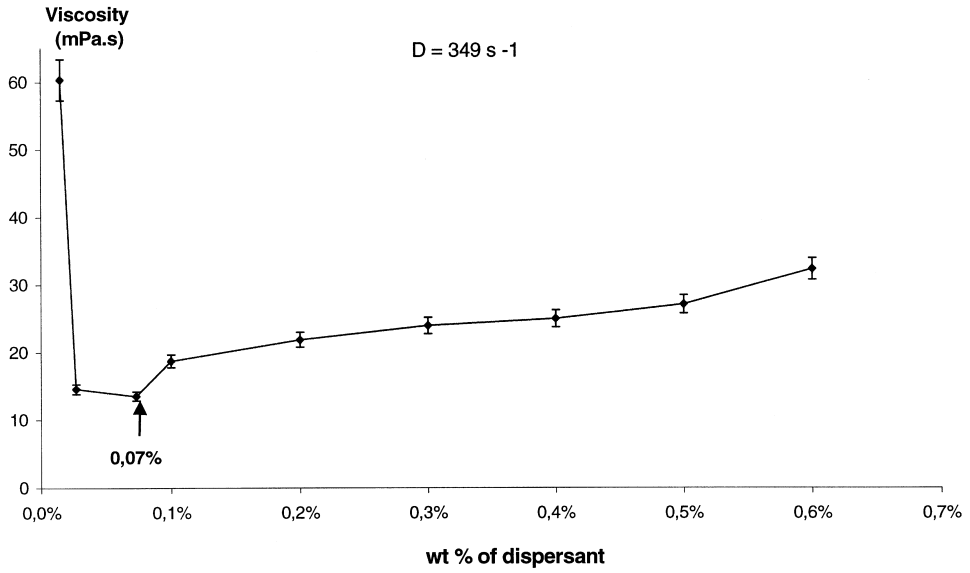


Fig. 2. Viscosity of 64.5 wt.% slips versus amount of ammonium polymethacrylate at a shear rate of 349 s^{-1}.

increasing amount of deflocculant were prepared. This optimum is obtained around 0.07 wt.% of dispersant (Fig. 2) and remains constant with increasing dry silicon nitride rate. Apparent viscosity was given at a shear rate of 349 s^{-1} and measurements were carried out at a temperature of 25°C. Flow curve for the slips was generally non-Newtonian, characterised by a pseudo-plastic behaviour in the low shear region and near Newtonian at higher shear rates. The sedimentation rate of the single particle, calculated by Stocks' law is higher than that obtained with our well-dispersed suspension. Thus the stability of the slips is well confirmed. The Si_3N_4 can be stabilised either in the range of the acid pH or in the range of the basic pH. But, in this study, the evolution of the viscosity with pH shows that the lowest viscosities are obtained in the range of the basic pH (7–9.5) which includes the natural pH of these slips (about 9). Moreover, the isoelectric point is around pH = 3.3.

The results of granulometry show that the attrition favours the diminution of the particle size distribution. The median grain diameter measured under the best conditions of dispersion of powder from the batch A is about 1 and 1.3 μm for the powder from the batch B.

3.2. Physicochemical characterisation of the compacts

The green density values show that all the samples (A and B) have a density above 56% of the theoretical density. The samples A and B sintered at 1800°C under N_2 atmosphere for 1, 1.5 and 2 h are called A1, B1, A1.5, B1.5, A2 and B2, respectively.

Table 1 shows the evolution of density for the sintered specimens A and B. In all cases, a high density has been achieved. The samples from batch A exhibit the higher densities in comparison with samples from batch B.

The transformation of α-Si_3N_4 to β-Si_3N_4 evolves with the sintering time. The results of the ratio $\beta/(\alpha+\beta)$ evaluation are shown in Table 2. For all previous sintering conditions, the transformation $\alpha \rightarrow \beta$ is clearly depending on the processing procedure. Indeed the granulometry results show that the attrition favours the diminution of the particle size and so increases the transformation $\alpha \rightarrow \beta$. Fig. 3a–c shows SEM micrographs of the samples from the batch A as a function of the sintering time and Fig. 3d shows SEM micrograph of the sample B2. All the samples have a microstructure with elongated β-grains. However, the sample A2 developed,

Table 1
Physical, mechanical and thermomechanical properties of the sintered silicon nitride

Samples	A1	A1.5	A2	B1	B1.5	B2
Flexural strength σf (MPa)	753±33	730±37	778±96	709±42	708±116	630±46
K_{IC} (MPa.$\sqrt{m}$)	8.4±0.3	8.7±0.7	9.5±0.1	6.8±0.5	7.9±0.6	9.3±0.3
Density (g/cm^3)	3.26	3.24	3.20	3.15	3.17	3.16
Relative density (%)	99.7±0.2	98.8±0.2	97.7±0.1	96.5	96.8±0.1	96.7±0.8
Grain average diameter (μm)	0.8	1.1	1.6	–	0.9	1
ΔT_{max} (°C)	950	950	950	950	773	950
σ_f After cumulated thermal shock (MPa)	768	179	742	249	–	713

Table 2
Evolution of the β phase as a function of the sintering time

	Ratio $\beta/(\alpha+\beta)$	
Sintering time (h)	Samples from batch A	Samples from batch B
1	0.78	0.35
1.5	0.88	0.53
2	0.92	0.71

at the end of 2 h of sintering time, more homogeneous microstructure with elongated and intermingled β-grains, while the samples B presented a heterogeneous microstructure with large elongated β-grains in fine-grained matrix. In addition, the sintering time has a great influence on the development of the β-grains. The A2 and B2 samples exhibit an average grain diameter of about 1.6 and 1 μm, respectively. It may be noted that the average grain diameter grows by a factor of 2 when the sintering time increases from 1 to 2 h (Table 1).

3.3. Mechanical characterisation

Normally, strengthening requires a fine grained, homogeneous microstructure whereas toughening requires rather a coarse grained anisotropic microstructure. Current microstructure control methods, developed to achieve either high strength or high toughness in silicon nitride, made these properties seldom compatible. However, it seems that our process succeeds in combining these two properties, by controlling the microstructure with the processing procedure and the sintering time, as shown by the results obtained.

The mechanical properties of these six series of samples are presented in Table 1. We note that samples from the batch A present the higher strength. The strength remains nearly constant with sintering time. Indeed the lengthened grains get into a tangle and create a greater strength network, which is probably at variance with the Hall and Petch law. On the other hand the strength of the samples from the batch B decreases when the sintering time is about 2 h. It is probably due to the localized grain enlargement as described by the Hall and Petch law.

The fracture toughness of self-reinforced Si_3N_4 as a function of sintering time is shown in Table 1. The fracture toughness increases with the sintering time. This increase comes from the development of the microstructure: the longer the sintering time, the more the β-grains grow, and so increase the reinforcement of the material. Less important is the lengthened β-grains population of samples from batch B, so lower values of fracture toughness, in comparison with samples from batch A.

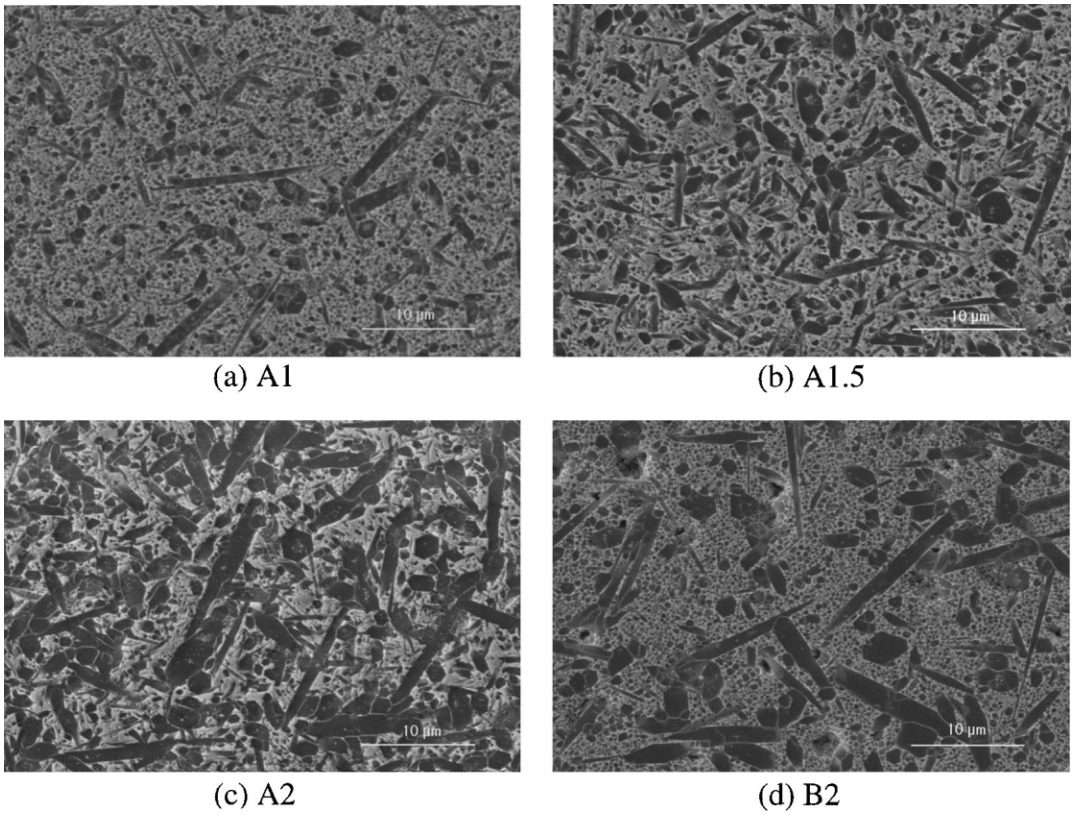
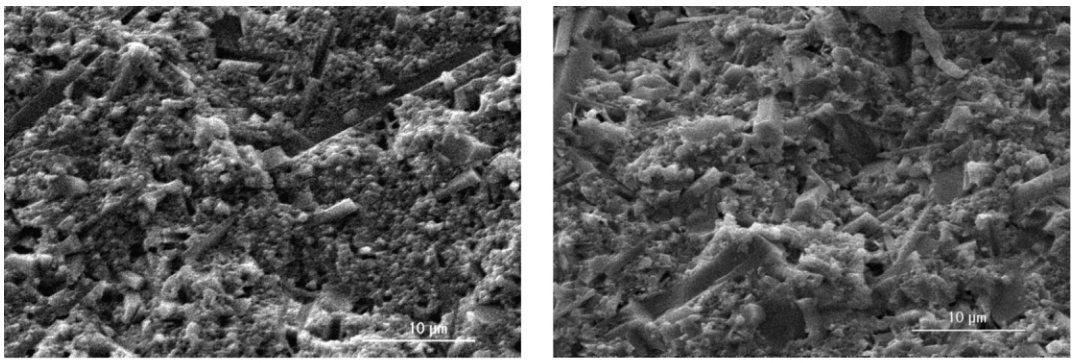


Fig. 3. SEM micrographs of polished and plasma etched specimens A1, A1.5, A2, and B2 sintered at 1800°C for: (a) 1 h, (b) 1.5 h, (c) 2h and (d) 2 h, respectively.



(a) B1 (b) B2

Fig. 4. SEM micrographs of fracture surface: (a) B1, (b) B2. Large grains of Si_3N_4 were pulled out during fracture at room temperature.

The observation of the fracture micrographs (Fig. 4) shows that the rupture is intergranular. The extraction phenomenon is also observed (large grains of Si_3N_4 were pulled out during fracture at room temperature). And so, the improved resistance to crack propagation of the resulting microstructure has been attributed to crack bridging, crack deflection and grain pull out.

The thermal shock resistance has been evaluated by recording the evolution of dynamic Young's modulus after each increasing temperature difference. The Young's modulus drop corresponds to the critical temperature difference (ΔT_C). The majority of samples from batch A have a $\Delta T_C > 950°C$. Moreover, we have tested in a destructive way, the samples not broken after the thermal shock ($\Delta T = 950°C$), by a flexural 4-points bending test. The results are presented in Table 1 and show that the strength of the majority of samples remains constant (no damage) after cumulated thermal shock at a temperature difference of 950°C.

These results show that materials with the high strength values are not accompanied by a significant damage after thermal shock. Finally, in this part, the properties of the Si_3N_4 investigated in this study are compared with those obtained by hot-pressing in our laboratory [13] under the same sintering conditions (Table 3). The hot-pressed Si_3N_4 is sintered under N_2 atmosphere for 1 h at 1800°C at constant applied pressure of 45 MPa. The materials elaborated by slip casting followed by pressureless sintering show a density comparable with the hot-pressed Si_3N_4. In fact, a high green density up to 56% for the slip cast samples means a great reactivity due to more homogeneity in the particle rearrangement and to a small quantity of agglomerates. This makes it possible to better control the microstructure development during sintering. The slip cast and pressureless sintering materials give better results (and/or at least comparable) for the mechanical properties in comparison to hot-pressed Si_3N_4. Moreover, the slip-cast samples show matrix with a finer microstructure, homogeneous and more reinforced by elongated grains compared to the hot-pressed samples.

Table 3
Comparison of physical and mechanical characteristics of materials from SNE-05 powder, sintered during 1 h at 1800°C

Properties	Slip casting and pressureless sintering		Hot pressing
	Sample A1	Sample B1	Hot pressed Si_3N_4
Density (g/cm^3)	3.27	3.16	3.25
σ (MPa)	753 ± 33	709 ± 42	700 ± 37
K_{IC} (MPa.m$^{1/2}$)	8.4 ± 0.3	6.8 ± 0.5	7
Hardness (GPa)	15	15.4	14.3
ΔT_C (°C)	>950	773–950	690

4. Conclusion

The analysis of the results of mechanical characterisation and of the microstructure show that the structures of grains obtained from acicular type were more or less developed. An increase in toughness was observed with a larger grain diameter. However, a correlation between toughness, strength and apparent aspect ratio could not be clearly established. The best mechanical and thermomechanical properties are obtained for the reference sample A2 ($K_{IC} = 9.5$ MPa.m$^{1/2}$, $\sigma_f = 778$ MPa and $\Delta T_C > 950°C$).

These results show that the evolution of silicon nitride microstructure is strongly dependent on the powder dispersion, processing procedure and sintering time. The influence of attrition is particularly important for the formation and the growth of β-grains. The sintering time is a very significant parameter in the evolution of the self-reinforced microstructure by the development of acicular β-grains. This type of self-reinforcement contributes significantly to combine high fracture toughness and high flexural strength of Si_3N_4 materials elaborated by slip casting and pressureless sintering.

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