

Grain coarsening in gas pressure sintered silicon nitride

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Abstract

The grain growth of silicon nitride sintered by GPS has been studied in the case of an α -rich initial powder. As time increases, the microstructure becomes bimodal. A few large grains grow abnormally at the expense of the smallest ones. The growth rate of the major portion of grains is slow and can be assimilated to a normal growth with interface-reaction control. This rate limiting mechanism has been determined by three different methods: a method based on the Kingery's rate laws, a more direct method based on the variation of the grain size vs. the amount of the liquid phase and considerations on grain morphology according to Lee. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: D. Silicon nitride; Grain coarsening; Diffusion control; Interface-reaction control

1. Introduction

Microstructural designing of GPS silicon nitride is a great challenge in order to improve its mechanical properties. It is, in particular, well-known that the toughness can be improved by the in situ growth of large elongated grains which can activate toughening mechanisms such as crack deflection and crack bridging [1–3]. Toughness is also strongly dependent on the chemistry and crystallisation of the secondary glassy phase [3,4].

In order to control the microstructure, grain coarsening has to be well understood. In liquid-phase sintering of α silicon nitride, the main process is dissolution of α - Si_3N_4 grains and reprecipitation as β - Si_3N_4 grains, either by precipitation on the larger β -grains and/or by spontaneous nucleation. Traditionally, the rate-controlling mechanism is determined from the coarsening-rate-law exponent, with reference to the Lifshitz and Slyozov [5] and Wagner [6] theory (LSW). A coarsening-rate-law exponent of $n=3$ implies diffusion control, whereas $n=2$ implies interface-reaction control. This work shows that this method is not adequate for α - Si_3N_4 sintered with Y_2O_3 and Al_2O_3 , probably because the kinetics of grain growth is relatively slow. An alternative

approach has been used to determine the rate-controlling mechanism. It consists in measuring the grain size as a function of the amount of liquid in the system (V_f) at fixed treatment duration. If coarsening is diffusion controlled, the grain size, i.e. the coarsening grain constant, is expected to decrease significantly with increasing V_f . This effect is ascribed to the increase of the average diffusion path. On the contrary, if coarsening is interface-reaction controlled, the grain size is expected to remain independent of V_f .

The morphologies of grains in the final microstructure also provide clues to the rate-controlling mechanism for coarsening [7]. Faced grains (atomically smooth interfaces) are relevant of a control by interface-reaction, whereas rounded grains (atomically rough interfaces) are generally observed in systems where the coarsening rate is diffusion controlled.

As the relation between densification, α -to- β phase transformation and grain growth is complex in the sintering of α - Si_3N_4 powders, the grain growth behaviour was studied after complete α -to- β phase transformation in sintering conditions which lead to high densification.

2. Experimental procedure

Si_3N_4 powder (UBE-SNE10, α content = 98%) was mixed with the sintering aids (Y_2O_3 , 5 wt.%, Meldform Metals, Al_2O_3 , 2 wt.%, Pechiney and SiO_2 gel). The

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Table 1
Densification rate and weight loss after sintering

t_2 (min)	%TD	$\Delta m/m$ (%)
10	97.0 \pm 0.1	0.0 \pm 0.0
45	98.1 \pm 0.2	0.4 \pm 0.5
90	97.8 \pm 0.5	0.9 \pm 0.8
180	98.2 \pm 0.2	3.2 \pm 0.6
540	97.3 \pm 0.4	5.0 \pm 0.6

powder mixture was sintered by nitrogen gas pressure sintering following a two-stage process optimised in a recent work (1800 °C, 0.1 MPa, 1 h 30/1950 °C, 4 MPa, t_2) [8]. Different sintering times and different amounts of sintering aids were tested: $t_2 = 10, 45, 90, 180, 540$ min and aids amounts = 7, 14, 21, 28 wt.% (with a constant ratio $Y_2O_3/Al_2O_3 = 5/2$ in weight).

Bulk density was measured by the Archimedes method. Microstructural characterisation was carried

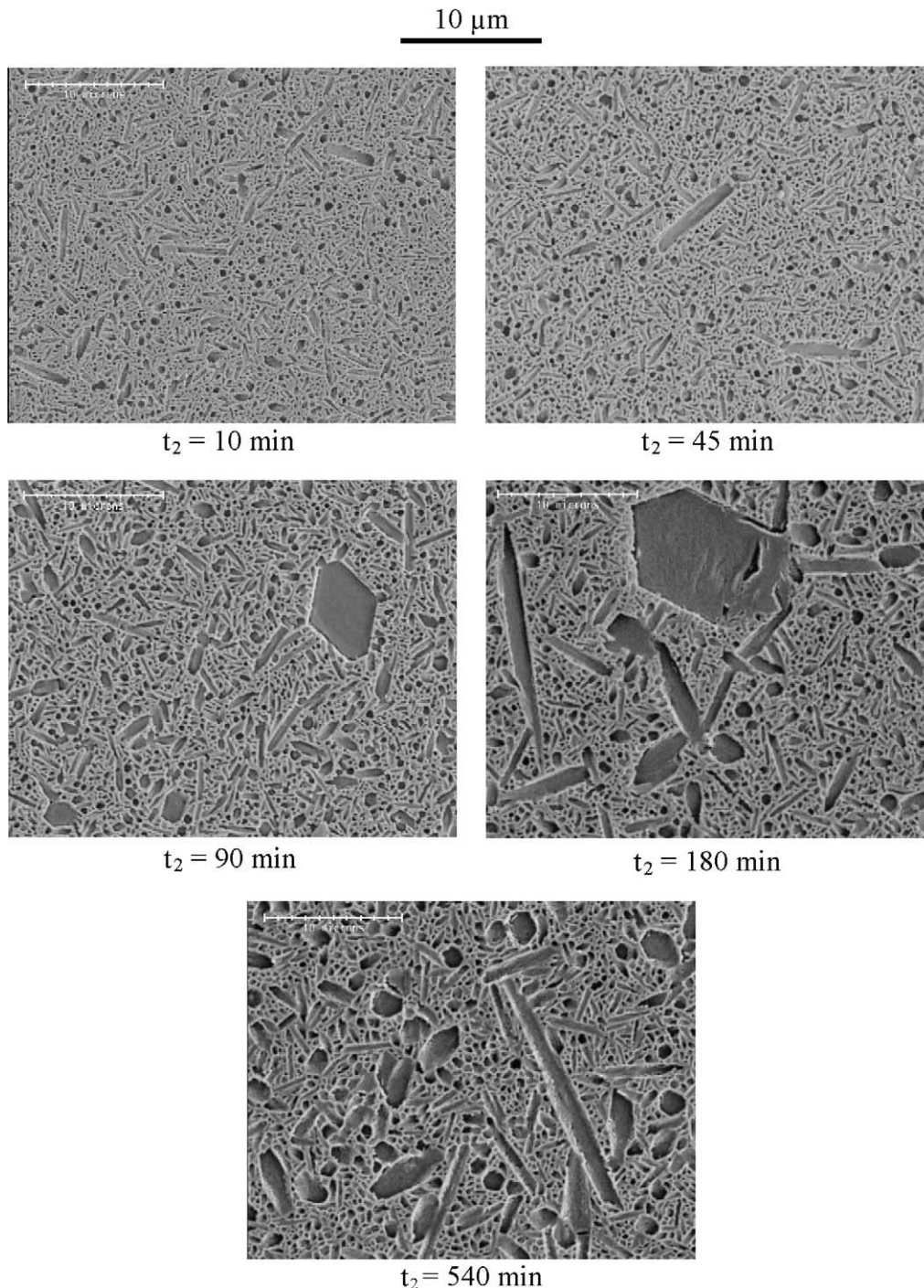


Fig. 1. Microstructural evolution as the second-sintering-stage duration increases (SEM micrograph on polished and plasma etched surface).

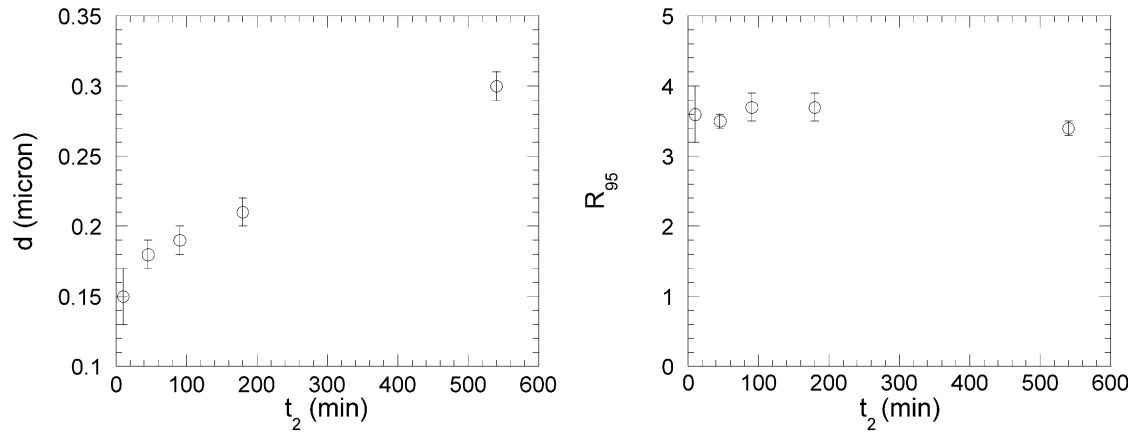


Fig. 2. Variation of the mean grain diameter and the aspect ratio vs. the sintering time.

out by SEM on polished and plasma etched sections. An image analyser (CUE SERIES, Olympus) was used to characterise the microstructure (1000 grains were investigated). The grain diameter d was defined as the minimum Feret diameter and the aspect ratio R_{95} as the mean aspect ratio of the 10% largest grains [9]. The grain size distribution was evaluated by plotting fractional area against grain diameter as suggested by Hirotsaki et al. [10]. This representation is a better means to reflect the presence of large grains than the distribution curve of the grain number.

3. Results and discussion

The effect of the sintering time on densification is reported in Table 1. As expected, a high final density of 97–98%TD is reached in all cases. The weight loss slightly increases as the time increases. X-ray diffraction study reveals the presence of crystallised phases after $t_2 = 9$ h (YSiO₂N, Si [4]) suggesting that a slow partial crystallisation of the intergranular phase occurs during the sintering.

The kinetic growth rate is illustrated on Fig. 1 and quantified in Fig. 2. As the sintering time increases, the mean grain size increases (grain diameter is doubled and mean surface is multiplied by 5.6 after 9 h of second-sintering stage). The aspect ratio R_{95} remains almost constant, suggesting that the growth is isotropic. At short sintering times ($t_2 = 10$ –45 min), the grain size distribution is monomodal (Fig. 3). As time increases, the distribution becomes multimodal ($t_2 = 1$ h 30, 3 h, 9 h), indicating that the larger grains grow at the expense of the smaller ones. This is in good agreement with a dissolution reprecipitation mechanism. The grain size distribution shows that the growth of the matrix grains is slower than the growth of the larger grains. This indicates that the growth of the few large grains is abnormal. A normal grain growth would have led to a higher

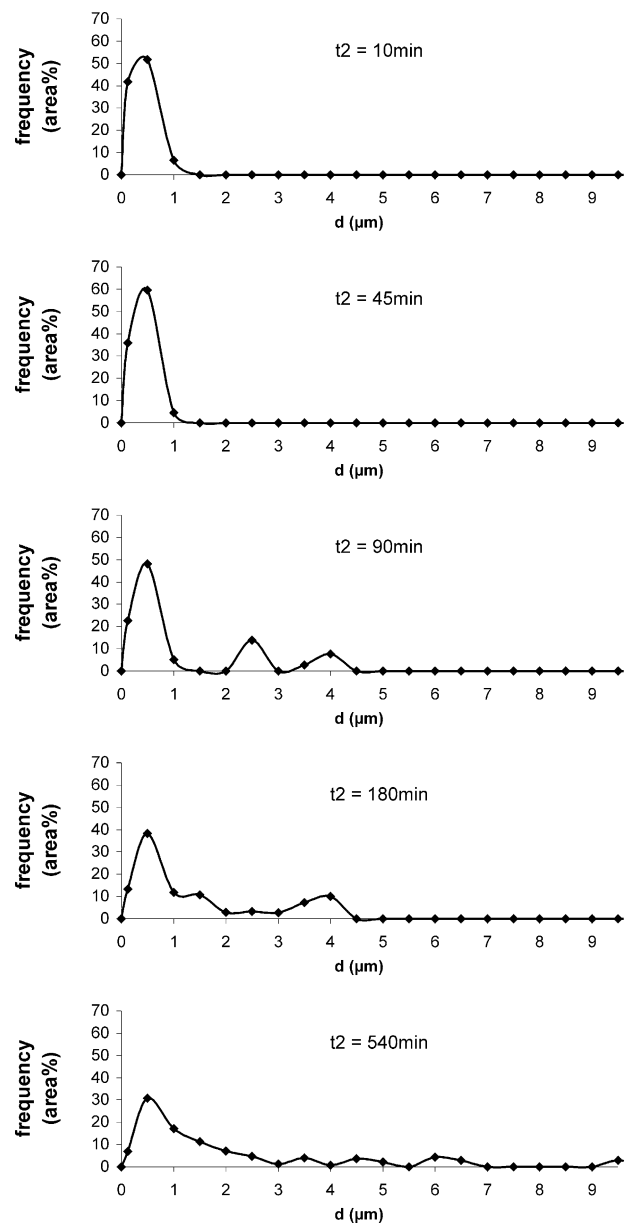


Fig. 3. Distribution of mean grain diameter as area fraction for different sintering times.

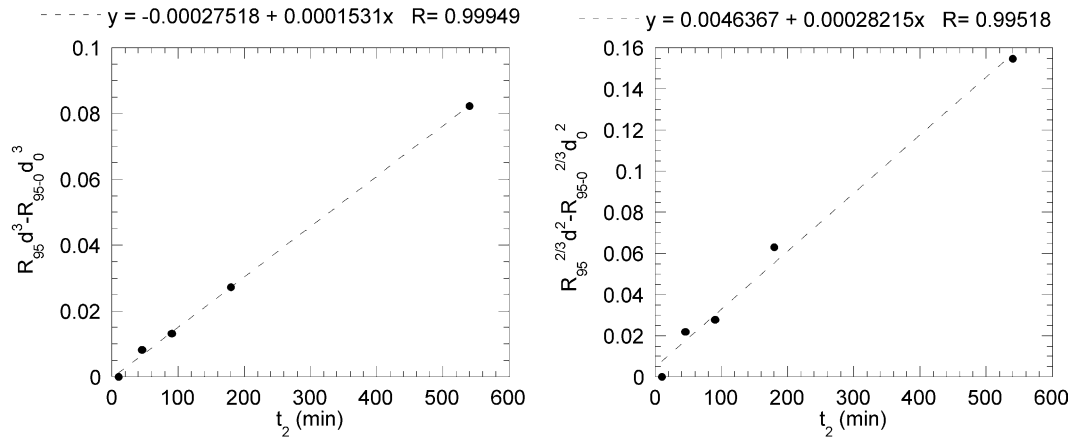


Fig. 4. Cubic and square laws for grain coarsening during the second-sintering stage.

growth rate of the matrix grains compared with the one of the larger grains.

The coarsening-rate laws $r^n - r_0^n = kt$ with $n=2$ and 3 have been plotted in order to determine the rate-controlling mechanism. As most of the grains are elongated ($R_{95} = 3.6$), the average radius r in the coarsening law has been replaced by the radius of the equivalent sphere [11]

$$r_e^3 = \frac{3}{4} \left(\frac{d}{2} \right)^2 d R_{95}.$$

The growth laws become

$$R_{95} d^3 - R_{95-0} d^3 = K_D t$$

$$R_{95}^{2/3} d^2 - R_{95-0}^{2/3} d^2 = K_R t$$

with the zero point of time taken at $t_2 = 10$ min. K_D is the rate constant connected with the diffusion mechanism, K_R with the interface-reaction mechanism. It can be noted that R_{95} remains constant in this study so that the results would be the same with the classic laws for

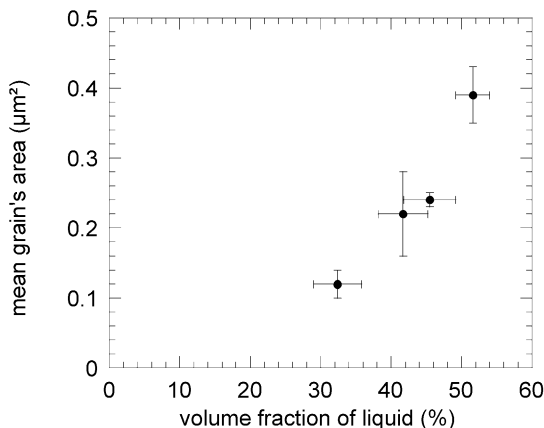


Fig. 5. Mean area of grains vs. vol.% liquid (without SiO₂% adjustment).

spherical grains. Fig. 4 shows that in both cases (cubic and square law), the linear curve fit is obtained with a high correlation parameter ($R=0.99$). This method is thus not adapted to distinguish between the limiting mechanisms. This might be due to the low grain growth kinetics [12]: the mean grain diameter is doubled after a long second sintering stage duration of 9 h.

The comparison between the theoretical rate constant ($K_{D \text{ theo}}$) and the experimental one (K_{exp}) questions the diffusion control. Calculation of $K_{D \text{ theo}}$ taking $D = 9.0 \times 10^{-10}$ m²/s, $\gamma = 0.94$ J/m² and $C_o = 7.0 \times 10^3$ mol/cm³ in $K_D = \frac{8\gamma_{SL}\Omega^2}{9RT} D C_o$ (c.f. [13]) leads to $K_{D \text{ theo}} = 5.3 \times 10^{-19}$ m³/s. This value is much higher than the experimental one calculated from the cubic-law slope, $K_{\text{exp}} = 4.9 \times 10^{-25}$ m³/s. Such a gap can not be explained even when considering the new coarsening theories which accommodate finite solid volume fraction and non-spherical particle morphologies. On the contrary, a simple calculation shows that taking into account the contiguity G (i.e. the average fraction of the surface area of a grain of the solid phase shared with all neighbouring grains [14]) and the volume fraction of the liquid phase V_l would enhance the gap. According to Warren [12], the following equation for diffusion-controlled growth is obtained:

Table 2

X ray diffraction analysis of the intergranular phase composition after sintering for the different sintering phase amounts tested

Aids amount (wt.%)	Position on the ternary diagram (Fig. 6)	X-rays
7	a	$\beta\text{Si}_3\text{N}_4$ (amorphous intergranular phase)
14	b	$\beta\text{Si}_3\text{N}_4 + \text{YSiO}_2\text{N}$
21	c	$\beta\text{Si}_3\text{N}_4 + \text{YSiO}_2\text{N}$
28	d	$\beta\text{Si}_3\text{N}_4 +$ non identified crystallised phase

$$r^3 - r_0^3 = \frac{9}{8}(1 - G) \left(\frac{1 - V_V}{V_V} \right) K_D t$$

Taking $G=0.8$ and $V_V=0.1$, the growth rate law can be expressed as $r^3 - r_0^3 = 2 K_D t$ so that $K_{\text{exp}} = 2.45 \times 10^{-25} \text{ m}^3/\text{s}$. It would be interesting to follow the same line of argument in the case of interface-reaction control. The lack of information about the interfacial-reaction rate constant keeps us from studying it thoroughly.

Recently Kleebe et al. [3] have proposed a growth mechanism controlled by diffusion with a growth rate exponent equal to 5. They used different additives (Y_2O_3 , ZrO_2 , Al_2O_3 , Sc_2O_3 , $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{Y}_2\text{O}_3\text{-ZrO}_2$) which led to composite materials with ZrO_2 . They utilized D , the diffusion coefficient of Si_3N_4 in the residual glass, inversely proportional to the viscosity η , according to the Stokes–Einstein relation:

$$D = \frac{kT}{3\pi\lambda\eta}, \text{ with } \lambda \text{ being the molecular distance.}$$

The viscosity depends on the nature of the additives (different from ours in the Kleebe's work) and is generally unknown, thus this expression of D could not be used by us.

A more direct method in order to determine the coarsening rate-controlling mechanism consists in measuring the grain size as a function of the vol.% liquid in the system. The volume fraction of the liquid has been increased by increasing the wt.% of the sintering aids in the initial powder. Note that its quantification by image analysis may be overestimated because plasma etching attacks the Si_3N_4 grains, leaving the intergranular phase intact. At first, the amounts of the sintering aids, Al_2O_3 and Y_2O_3 , were increased with a constant $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ ratio (2/5 in weight). Fig. 5 is a plot of the mean grain area vs. vol.% liquid after a sintering with $t_2 = 3 \text{ h}$. This plot shows that the mean grain size increases as the amount of the liquid phase increases. This is not typical neither of a diffusion-controlled growth nor of an interface-reaction-controlled growth. X-ray diffraction

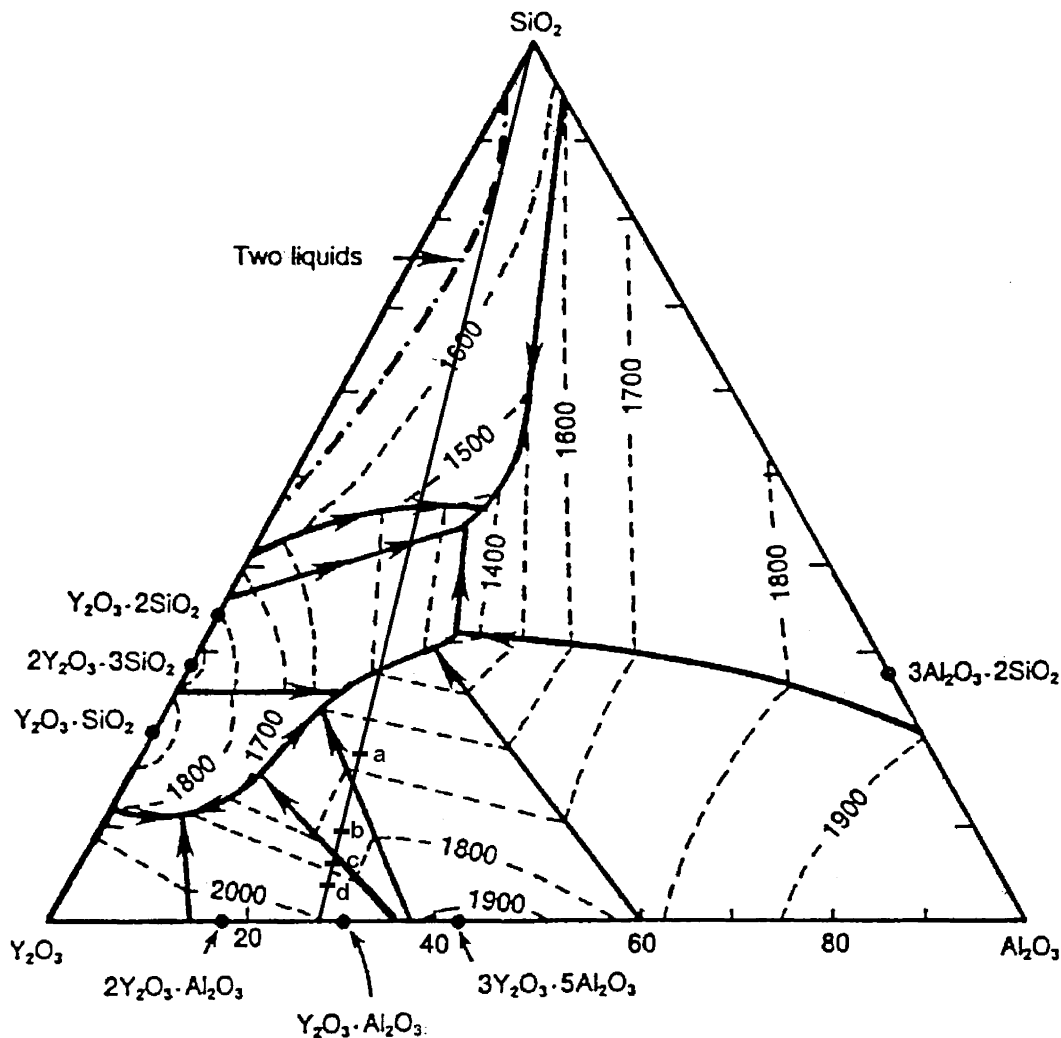


Fig. 6. Position of the tested compositions in the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ ternary phase diagram [15] [(a) 7 wt.% of sintering aids; (b) 14 wt.%; (c) 21 wt.%; (d) 28 wt.%].

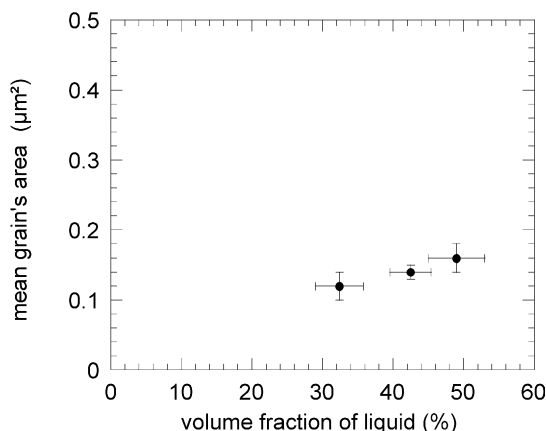


Fig. 7. Mean area of grains vs. vol.% liquid (after SiO₂% adjustment).

analysis reported in Table 2 shows that the intergranular phase composition after sintering changes depending on the sintering aids amount. This change can be ascribed to the variation of the vol.% SiO₂ present at the grains surface. Fig. 6 shows that the initial compositions studied are indeed significantly different considering the SiO₂–Y₂O₃–Al₂O₃ ternary phase diagram [15]. It is thus not surprising that these different initial compositions lead to different final compositions. According to Kitayama [16], the solubility of the solid phase increases as the ratio Y₂O₃/SiO₂ increases in the YSiON system, due to the modifier role of the yttrium ion in the amorphous phase. This can explain the observed growth rate increase as the wt.% SiO₂ decreases, i.e. as the wt.% Y₂O₃ and Al₂O₃ increase. In order to rightly use the method, the amount of SiO₂ has been fitted by adding silica gel so that the composition of the intergranular phase remains constant in the SiO₂–Y₂O₃–Al₂O₃ diagram (a composition). Results, reported in Fig. 7, show that the mean grain size remains unchanged as the volume fraction of the liquid phase increases, in agreement with a reaction-controlled mechanism. It is worthy of note that keeping the composition of the initial powder constant in the system SiO₂–Y₂O₃–Al₂O₃ does not signify that the composition of the liquid remains constant in the Si₃N₄/Al₄N₄/Y₄N₄–Si₃O₆/Y₄O₆/Al₄O₆ system. In particular, the substitutions in Si₃N₄-grains (N↔O and Si↔Al) modify the phase chemistry during sintering [17]. In this study, it is assumed that the resulting variations of liquid composition have negligible effects on growth rate for all different samples.

This control by interface-reaction mechanism is in good agreement with the general law proposed by Lee et al. [7]. This one correlates the grain growth limiting mechanism with the shape of the grains after sintering. The faced grains observed in the present study, as shown in Fig. 8, are relevant to atomically smooth surfaces. This implies a very slow interface-reaction during the reprecipitation.

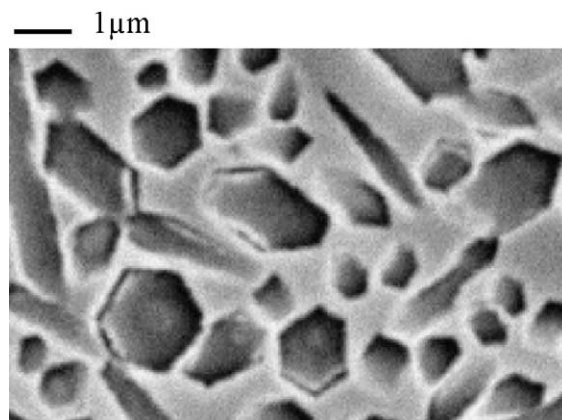


Fig. 8. SEM micrograph of a polished and plasma etched surface showing faced grains (28 wt.% of sintering aids).

4. Conclusion

The growth of silicon nitride grains sintered by GPS has been studied in the case of an α -rich initial powder. As time increases, the microstructure becomes bimodal. The matrix-grains growth rate is slow whereas the growth of the few large grains is exaggerated. The growth of the major portion of grains can be assimilated to a normal growth with interface-reaction control. This rate-limiting mechanism has been determined by three different methods. The method based on the Kingery's rate laws is not helpful probably because the growth is too slow to distinguish between controlling mechanisms. A more direct method based on the variation of the grain size vs. the amount of the liquid phase indicates an interface-reaction control, in agreement with considerations on grain morphology.

It is inferred from these results that increasing the sintering time should be an interesting way of microstructural control. It has been shown in particular that increasing the mean Si₃N₄-grain diameter improves the toughness according to a square root law [1–3].

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