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Sintering of silicon nitride in a powder bed

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Silicon nitride with the addition of MgO as a sintering aid can be sintered at atmospheric pressure by embedding the powder compacts in a loose powder mixture. By choosing a suitable composition of the powder in the bed it is possible to control both the decomposition of the Si_3N_4 and the loss by volatilization of the MgO. In this way one can obtain homogeneously sintered articles of complex shapes of density $> 3.0\ Mg\,m^{-3}$.

1. Introduction

At present there are two methods practised commercially for the production of silicon nitride components:

(a) reaction sintering: in this the component is formed from silicon powder (approx. 98% Si) and then heat-treated in a nitrogen atmosphere below the melting point of silicon. The conversion to silicon nitride is accompanied by a weight gain (theoretically 66%) but no dimensional changes take place;

(b) hot-pressing: certain sintering aids are added to silicon nitride which is then densified under pressure at high temperatures in a graphite die.

Both methods have disadvantages. Because reaction-sintered material is of necessity porous (~20%) its strength is limited. Whilst the strength of hot-pressed silicon nitride is very high, only very simple shapes can be produced directly and more complex components require very expensive grinding with diamond-impregnated wheels. There exists, therefore, a need for the pressureless-sintering of silicon nitride powder.

Silicon nitride, like many "special ceramics" (e.g. SiC, BN) is difficult to sinter due to its covalent bonding. This has become evident from several experimental investigations. Terwilliger and Lange [1] hot-pressed a commercial Si_3N_4 powder at 1650° C for 4 h but obtained only 68% of the theoretical density. Similar results were obtained by Yeh *et al.* [2] working at 1700° C with a pressure of 28 MPa.

Prochazka and Rocco [3], experimenting at extremely high pressures, concluded that sintering obtained under these conditions depended critically and inversely on the purity of the powder. Pure stoichiometric Si_3N_4-powder pressed at 5 GPa and 1600° C attained only moderate values of microhardness.

At the present state of knowledge one has to conclude that it is necessary to employ sintering aids which act by forming suitable liquid phases. Many compounds, oxides and non-oxides, have been investigated as sintering aids and Deeley *et al.* [4] found in 1961, that MgO was one of the most effective additives for hot-pressing Si_3N_4. Since then the sintering mechanism involving MgO has been studied [1, 5, 6], pointing out its shortcomings and proposing alternative sintering aids. However, MgO has maintained its importance as a sintering aid and the properties obtained have been improved.

An important factor in sintering is the thermal decomposition $Si_3N_4 \rightarrow 3Si + 2N_2 \uparrow$. Its kinetics and mechanisms has been studied by Batha and Whitney [7] who show that its magnitude is such that it will interfere with sintering even at the temperature necessary for sintering when employing additives. Terwilliger and Lange [8] have demonstrated that Si_3N_4 can be sintered in nitrogen at atmospheric pressure to a density of 90% theoretical using commercially available Si_3N_4 powder with an addition of 5% MgO. However, under the experimental conditions employed,

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considerable weight losses were noted which resulted from the dissociation of Si_3N_4.

In order to improve sintering it is obviously necessary to slow down this dissociation. Various attempts have been made:

(i) Mitomo [6] has increased the degree of densification of Si_3N_4 + MgO by sintering in an autoclave at 10 atm nitrogen. In this way he attained 95% theoretical density.

(ii) Another approach to sintering has been to increase the sintering activity by reducing the particle size of the Si_3N_4 powder. Very fine powders can be obtained by the reaction of Si halides and NH_3 in the gas phase. Two types of powder are now commercially available: GTE Sylvania SN402 and SN502. Such fine powders usually present compaction problems and give low green densities. Using SN502 and 4% Y_2O_3 as sintering aids, Rowcliffe and Jorgensen [9] achieved high densities by sintering in 2 atm N_2. However, sintering was accompanied by a weight loss of 14% contributing further to shrinkage.

(iii) The solid gas reaction due to thermal decomposition, can be slowed down by embedding the solid in a powder bed of appropriate composition.

It was the purpose of this investigation to apply the last mentioned method for the sintering of Si_3N_4 + MgO.

2. Experimental details

The Si_3N_4 powder employed in this investigation was AME CP85 (Advanced Materials Engineering Gateshead UK); its chemical and physical characteristics are reported in Table I. The α and β contents were determined quantitatively by comparing the intensities of the two strongest X-ray diffraction lines (α: 1 0 2, 2 1 0; β: 1 0 1, 2 1 0) with a calibration curve derived from known mixtures of pure α and β Si_3N_4. This powder was dry milled for 60 h with steel balls (ball:powder weight ratio – 3:2). After comminution 5% MgO (reagent grade, surface area 38 $m^2 g^{-1}$) was added; mixing was carried out in the same jar in isopropyl alcohol for 50 h.

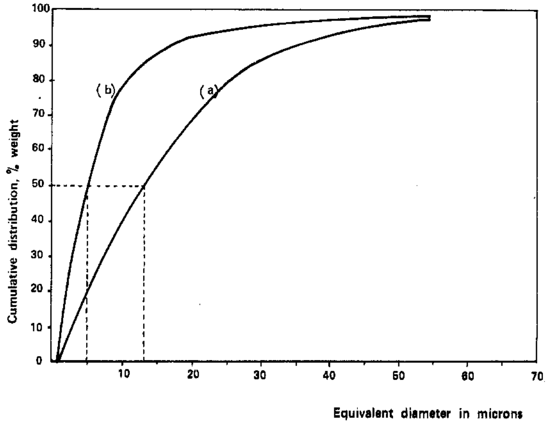

Figure 1 Cumulative particle size distribution of silicon nitride powder: (a) as-received; (b) milled.

After this treatment the iron content was 1.9% and the mean particle diameter 5 μm. Fig. 1 shows the particle size distribution before and after milling and Fig. 2a and b are photomicrographs which indicate the morphology of the powder. The powder was compacted isostatically at 350 MPa to form cylinders ($d = 30$ mm, $h = 40$ mm) of green density 2.0 Mg m^{-3}.

The compacts were sintered in an induction-heated furnace using a graphite susceptor. After obtaining a vacuum better than 10^{-4} Torr high-purity nitrogen was admitted and maintained during the heat-treatment at a pressure slightly below atmospheric.

The samples were sintered in the range 1600 to 1850° C. The temperature was measured on the susceptor with a pyrometer which controlled the power of the furnace in order to keep the temperature constant.

During sintering, the compacts were placed in graphite containers, not directly in contact with graphite but immersed in a 1:1 (by weight)

TABLE I Chemical and physical characteristics of Si_3N_4 powder AME CP 85

Chemical composition (%)												Si_3N_4 phases		Mean particle diameter†
O*	C	Al	Ca	Fe	Mg	Ti	Ni	Cr	Cu	N*	Si	α	β	
0.9	0.11	0.42	0.24	0.8	0.05	0.01	0.01	0.005	0.01	37.5	bal	85	15	13 μm

*Determined by fusion in He.

†Determined by sedimentation balance (see Fig. 1).

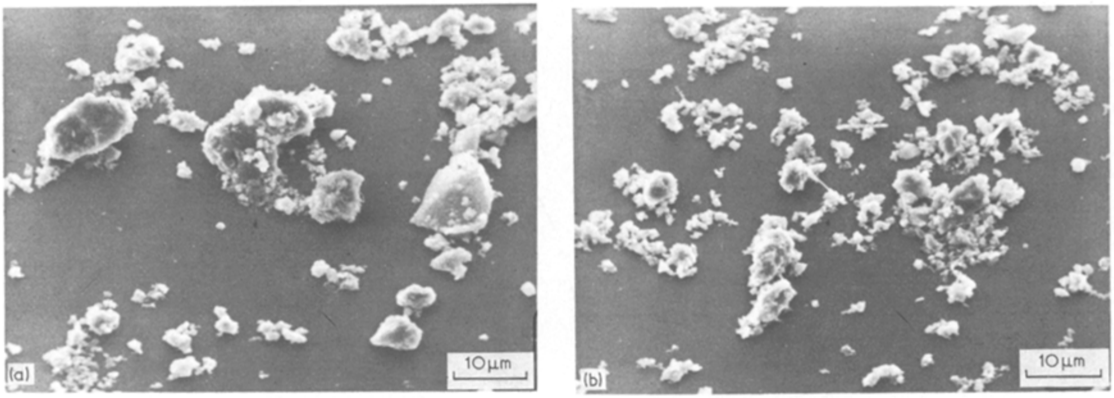

Figure 2 SEMs of AME CP 85 Si_3N_4 (a) before milling, (b) after milling.

powder mixture silicon nitride*: boron nitride† in some cases 5% MgO was added.

3. Results and discussion

The results of the sintering experiments time $(\frac{1}{2}$ h) are shown in Fig. 3.

The weight losses obtained as a function of sintering temperature are shown and compared with those obtained under different experimental conditions, i.e. in N_2 at atmospheric pressure [8] and in N_2 at 10 atm [6]. The closeness of the results of weight losses at 10 atm N_2 and when samples were embedded in a powder bed at atmospheric pressure becomes immediately apparent. The weight losses at atmospheric pressure with the samples not-embedded are considerably higher.

The results on densification (Fig. 4) are in agreement with the weight losses observed. The maximum density obtained by sintering in a powder bed was 2.85 Mg m^{-3} or 89% theoretical density.

However, microstructural investigations of the samples sintered in a powder bed of Si_3N_4/BN has shown a considerable inhomogeneity. This is readily seen in Fig. 5 which demonstrates the existence of surface layers. By measuring the densities of the whole sample and samples with the skin removed by grinding, the density at the surface was deduced to be of lower density than the bulk material at the centre. A larger degree of porosity was also observed under the microscope. The observed density variations correspond to differences in chemical composition as can be seen

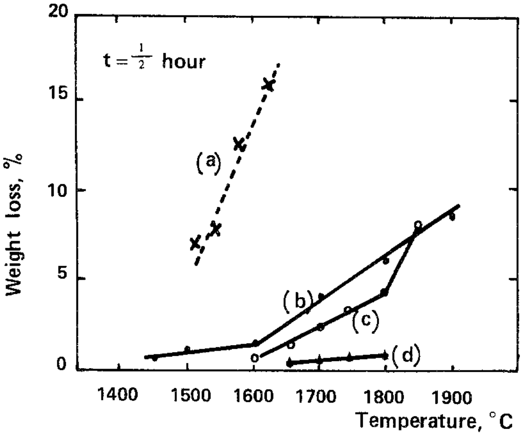

Figure 3 Weight loss during sintering versus sintering temperature (a) obtained in nitrogen at atmospheric pressure [8], (b) obtained at 10 atm N_2 [6], (c) obtained in the present work at atmospheric pressure in a powder bed, (d) as (c) but with the addition of MgO to the powder bed (see Fig. 8).

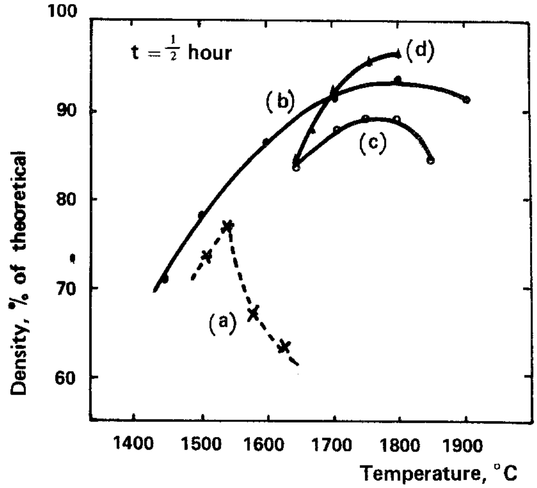

Figure 4 Density of sintered Si_3N_4 + 5% MgO versus sintering temperature. (a) to (d) as in Fig. 3.

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*AME, CP85 as-received.

†Pure grade code 120, 106 Europrind.

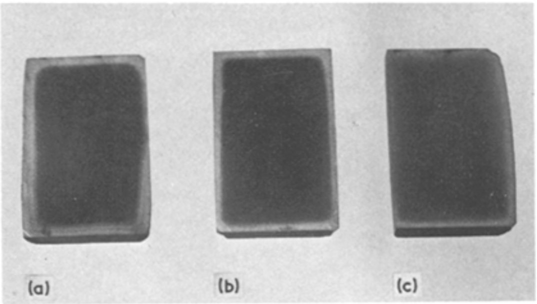

Figure 5 Sections through cylinders sintered in a powder bed of Si_3N_4/BN for (a) 2, (b) 2, and (c) $\frac{1}{2}$ h at 1800° C.

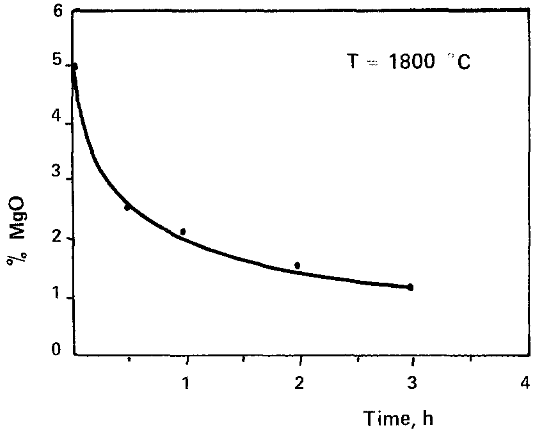

Figure 7 Content of MgO versus sintering time.

in Fig. 6 which shows the results of a laser microspectral analysis of different zones of a sintered sample. The results indicate an almost complete absence of Mg in an external zone 1.4 mm thick and a concentration of impurities at the surface. It is thus evident that the weight losses shown in Fig. 3 are not entirely the result of the thermal decomposition of silicon nitride but also partially due to a loss of MgO by volatilization; the latter is easily explained by the high vapour pressure of MgO at high temperatures, i.e. 10^{-4} Torr at 1600° C.

Wet chemical analysis of the total MgO content has been carried out on samples treated for different times (Fig. 7). The initial rapid decrease from the 5% added value confirms the previous

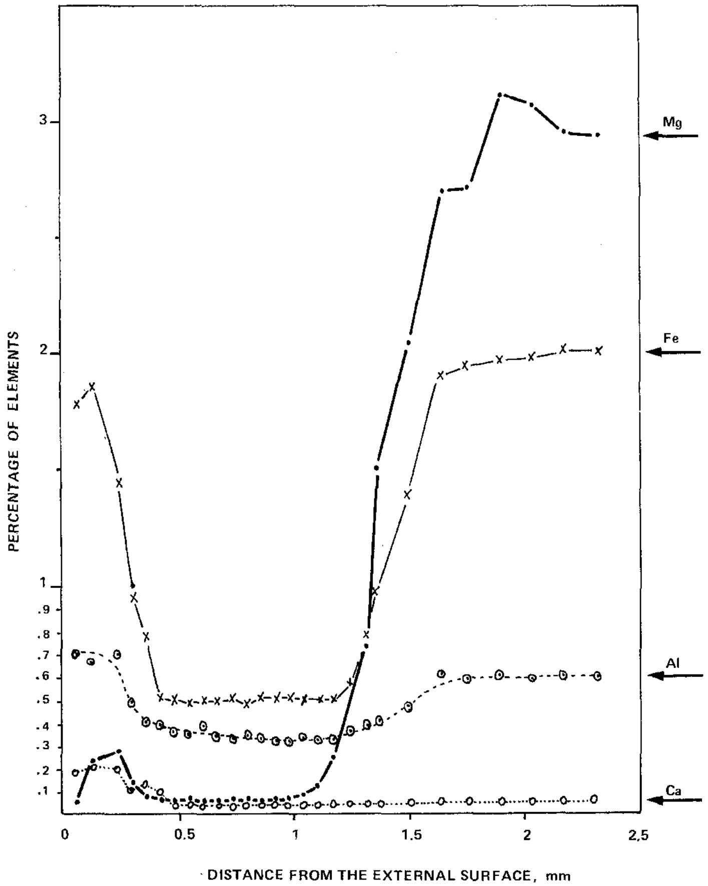

Figure 6 Concentration profile of different elements versus distance from external surface.

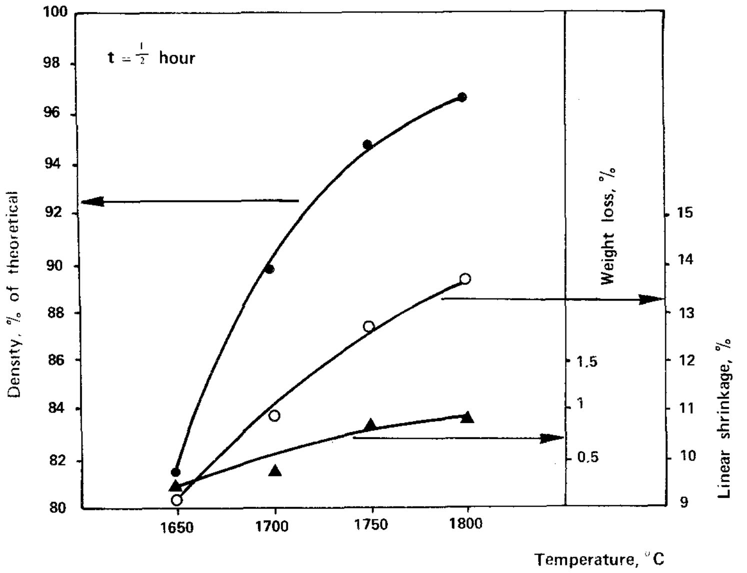

Figure 8 Density, weight loss and shrinkage versus temperature for Si_3N_4 + 5% MgO sintered in a powder bed containing MgO.

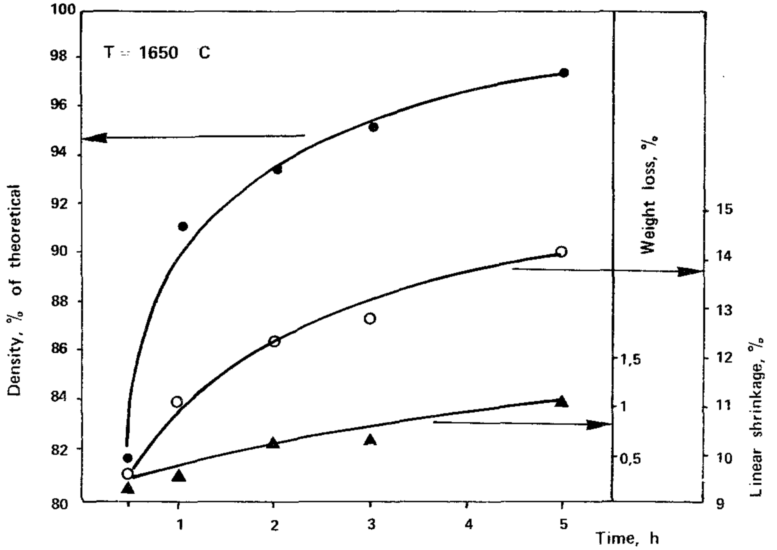

Figure 9 Density, weight loss and shrinkage versus time for Si_3N_4 + 5% MgO sintered in a powder bed containing MgO.

results. It is worth noting that after several hours the value appears to approach asymptotically 1% MgO. Several reasons suggest themselves:

(i) the vapour pressure of MgO in the sample and the powder bed may reach equilibrium;

(ii) as the sample reaches a high density where all porosity is in the form of closed pores, loss of MgO is greately impeded.

Based on these results, it was decided to include an equivalent amount of MgO in the powder bed, the composition of which was therefore Si_3N_4/BN/MgO 50/45/5% by weight, in order to decrease the loss of MgO by volatilization. The cylindrical samples ($d \simeq 30$ mm) sintered in this way appeared visually completely homogeneous. Chemical analysis showed negligible differences in MgO content in samples before and after sintering. As a result of this procedure the overall density of the sintered samples was substantially increased.

Figs. 8 and 9 shows the dependence of densification, shrinkage and weight loss on temperature and time. The improvement obtained can be seen clearly in Figs. 3 and 4. The maximum density reached was 3.12 $Mg\,m^{-3}$ corresponding to 97.5% assumed theoretical density of 3.20 $Mg\,m^{-3}$

An interesting consequence of these results is the suggestion that compacts of silicon nitride which do not contain a sintering aid in powder form can be sintered by applying the sintering aid in vapour form from the powder bed.

TABLE II Sintering of a powder compact of Si_3N_4 with the sintering aid contained in the powder bed

Green* density (g cm^{-3})	Heat-treatment	Linear shrinkage (%)	Gain in weight (%)	Mg initial (%)	Mg final (%)	Sintered density* (g cm^{-3})
1.90	3 h 1800° C	15	0.8	0	1.02	3.02

*Measured by mercury displacement.

Thus the powder bed will have to contain the sintering aid which during sintering will achieve a high enough vapour pressure to penetrate in sufficient quantity the porous powder compact. It is essential that pores do not close, since this would impede access of the sintering aid. A preliminary result (Table II) shows that considerable densification has taken place with a total MgO content of only 1% MgO. Such a material should exhibit much less deterioration at high temperatures (loss of strength, creep resistance, non-linearity of stress and strain) because of the diminution in quantity of the secondary phases.

Probably the presence of about 2% iron in the starting powder is responsible for some of the crystalline phases observed qualitatively by X-ray diffraction in the sintered material, besides the main phase β-Si_3N_4. These are a solid solution of fayalite and forsterite approximately $(Fe_{0.4}Mg_{0.6})_2SiO_4$ [10] and traces of FeSi and $FeSi_2$. Apart from a small amount of SiC, there is no detectible evidence of another phase, not even free Si. At the lowest sintering temperatures used, a small amount of α-Si_3N_4 remained untransformed. The sintering mechanism is thought to be the same as with hot-pressing, i.e. solution and reprecipitation via a liquid phase.

4. Conclusions

The conclusions which can be drawn from this work, which forms the basis of a process for sintering silicon nitride at atmospheric pressure, may be summarized as follows:

(1) it is possible to sinter suitably doped silicon nitride at atmospheric pressure by embedding it in a suitable mixture of nitride powders. The results thus obtained are comparable to those achieved at 10 atm nitrogen;

(2) the weight losses occurring during sintering of Si_3N_4 + MgO are not only due to the dissociation of Si_3N_4 but also due to volatilization of MgO which migrates from the compact to the powder bed leading to inhomogeneity of the density;

(3) suitable doping of the powder bed can suppress the loss of sintering aids from the compact. In this way one can obtain greater homogeneity and higher densities;

(4) the addition of MgO to the powder is a means of sintering compacts of pure Si_3N_4. The minimum amount necessary for densification is furnished by transfer of the sintering aid in vapour form from powder bed to compact.

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