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Pressure sintering of Si_3N_4

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The sintering of Si_3N_4 with 5% MgO was investigated at 1450 to 1900° C under a pressure of nitrogen. A maximum density of 95% of the theoretical value was obtained, which is greater than that obtained by pressureless sintering. The sintering process was inferred to be liquid-phase sintering and divided into two processes; rearrangement and solution-precipitation. The contribution of rearrangement to densification was about 10% in the present system, and the rest, up to 17% was due to solution-precipitation. Application of the present method of sintering Si_3N_4 with a high strength grain-boundary phase at high temperature is surveyed.

1. Introduction

Pressureless sintering of Si_3N_4 with MgO as a sintering aid had already been investigated [1–3]. However, Si_3N_4 of greater than 90% theoretical density was not obtained. In pressureless sintering, maximum density was attained at ~1650° C because although the densification process should be more rapid at higher temperatures, the density was lowered by the weight loss due to thermal decomposition of Si_3N_4 [3, 4].

It has been shown [4] that it is possible to obtain Si_3N_4 of greater than 90% theoretical density by heating compacted Si_3N_4 and MgO under pressure of nitrogen or/and an inert gas at temperatures higher than 1650° C.

In the hot-pressing of Si_3N_4 with MgO, an $MgO-SiO_2$ liquid phase was obtained [5–9]. In the present method, the same system (in the thermodynamic sense) was used, liquid-phase sintering was assumed and the densification process was analysed on the basis of Kingery's theory [10]. The results were compared with those of pressureless sintering [2,3].

The present work reports an analysis of the effect of MgO on the densification process. Application of the present method for sintering Si_3N_4 was also investigated using other additives.

2. Experimental procedures

TABLE I The compositions of starting Si_3N_4 (wt%)

Si	N	Fe	Ca	Al	C	O
58.3	38.5	1.3	0.2	0.2	0.1	1.5

The result of chemical analysis of $Si_3N_4^*$ is shown in Table I and the crystalline composition determined by X-ray diffraction was mostly β-Si_3N_4 (> 95%). The amount of oxygen was determined by neutron activation analysis. Laser-microspectrochemical analysis (LMA) showed the existence of small amounts of Mn, Ni, B, Cr, Ti and Cu.

The size and shape of Si_3N_4 powder after mixing MgO is shown in Fig. 1. The Si_3N_4 powder was mixed in ethanol with 5 wt% MgO in an agate mortar for 24h. The mixture was dried and about 1 g was pressed in a steel die, 12 mm diameter, under a pressure of 300 kg cm^{-2} (~4.3 x 10^3 psi) and then isostatically pressed under 1.5 ton cm^{-2} (~2.1 x 10^4 psi). The density of the compact was about 2.18 g cm^{-3} (68.3% of theoretical density

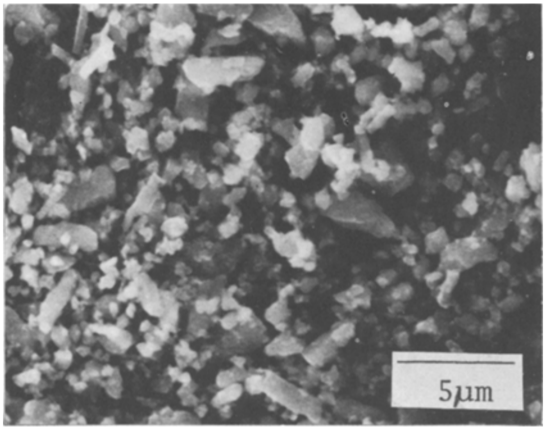

Figure 1 Scanning electron micrographs of Si_3N_4 powder.

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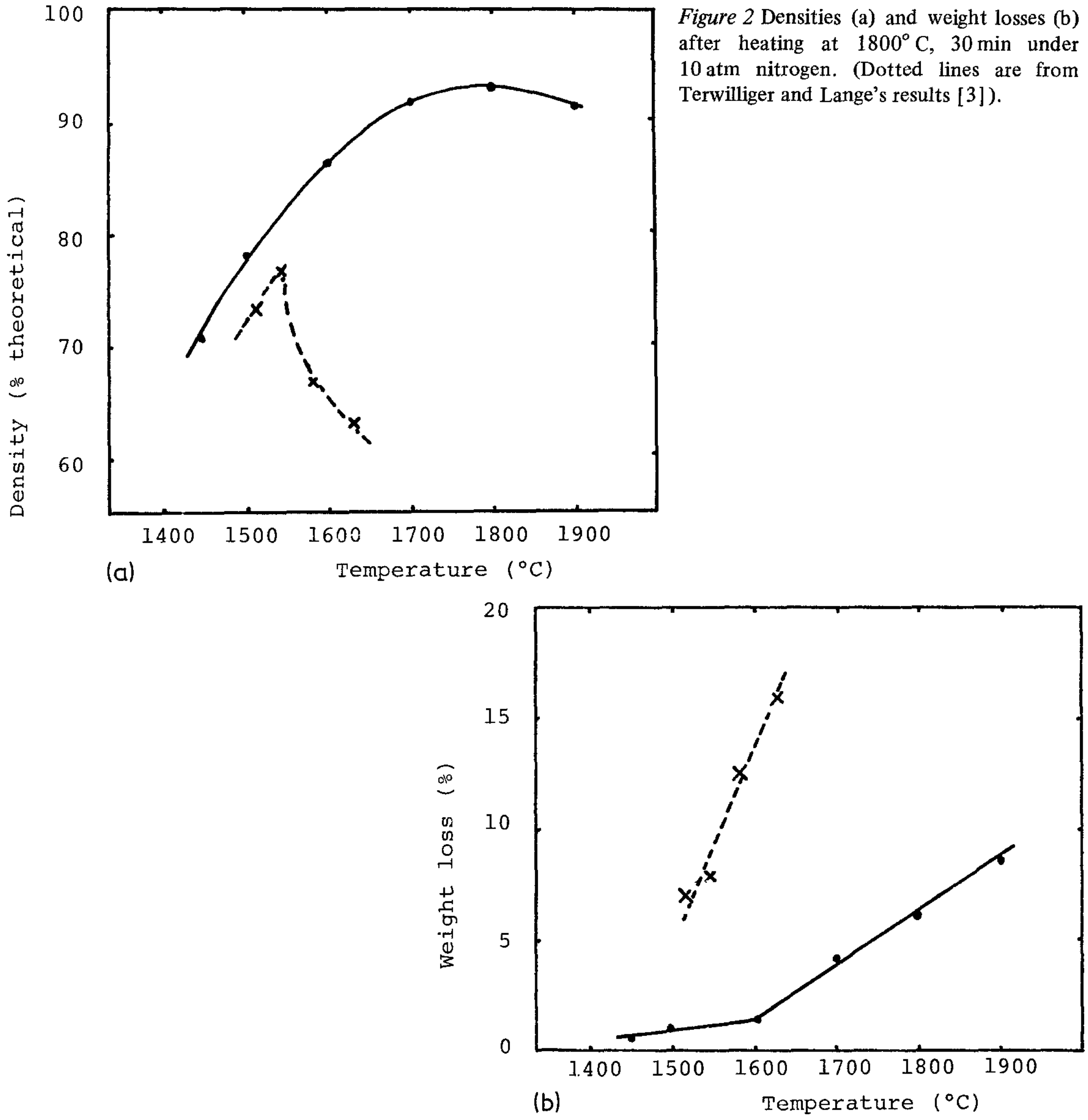

Figure 2 Densities (a) and weight losses (b) after heating at 1800° C, 30 min under 10 atm nitrogen. (Dotted lines are from Terwilliger and Lange's results [3]).

3.19 g cm^{-3}). The compact was heated by high frequency induction under a pressure of 10 atm nitrogen for 30 min at 1450 to 1900° C in a high pressure furnace.† The carbon crucible, which was also a susceptor, was lined with BN powder to prevent a reaction between Si_3N_4 and carbon. The temperature was measured by an optical pyrometer calibrated at the melting point of Si (1414° C).

After cooling, the compact was weighed and the density obtained by measuring its dimensions with a micrometer.

The effect of other additives on the sintering of Si_3N_4 was also investigated at 1800° C for 30 min under 10 atm nitrogen. The additives were Al_2O_3, Y_2O_3, Y_2O_3–Al_2O_3, La_2O_3, Ga_2O_3–Al_2O_3 and AlN–Al_2O_3. These additives have been shown to be effective in making dense Si_3N_4 or "sialons" under hot-pressing conditions [11–16].

3. Results and discussion

3.1. The effect of MgO

The values of density and weight loss after heating at 1450 to 1900° C for 30 min under 10 atm nitrogen are shown in Fig. 2a and b. The results for pressureless sintering of Si_3N_4 and 5% MgO for 20 min [3] are also plotted in the figure.

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† Arthur D. Little Inc, Massachusetts, USA.

Si_3N_4 of up to 93% theoretical density was obtained by the present method. Fig. 2 shows the superiority of this method over pressureless sintering.

In the present method and pressureless sintering, the density and weight loss were initially increased at higher temperatures. The density was then decreased above a certain temperature because it was determined by two countervailing processes, shrinkage and thermal decomposition of Si_3N_4. They predict an optimum temperature at which the most dense material is obtained. In pressureless sintering, this was ~ 1550° C [3] or ~ 1650° C [4, 17]. At lower temperatures shrinkage was dominant, and at higher temperatures thermal decomposition was dominant. On the other hand, the optimum temperature was ~ 1800° C in the present method and the shrinkage was enhanced at temperatures higher than 1650° C.

The shrinkage was due to liquid-phase sintering as for hot-pressing [3]. The densification may be divided into two processes, rearrangement and solution-precipitation [10]. Evidence for two processes is shown below by analysing the results of pressureless sintering [17].

Kingery obtained theoretically the relation between the fractional shrinkage ($\Delta L/L_0$) and the time (t) under isothermal conditions for liquid-phase sintering [10, 18].

For the rearrangement process, the relation was expressed by,

$$\frac{\Delta L}{L_0} = k_1 t^{1+y}, \qquad (1)$$

where k_1 is a constant and y some small fraction.

For the solution-precipitation process,

$$\frac{\Delta L}{L_0} = k_2 r^{-4/3} t^{1/3} = k_3 t^{1/3}, \qquad (2)$$

where k_2 is a constant and r the pore size which was assumed to be constant during sintering [3, 10].

The results of isothermal pressureless sintering of Si_3N_4 with 5% MgO at 1512, 1540, 1600 and 1673° C [17] are plotted in Fig. 3. The figure shows two stages of densification represented by two straight lines. The slopes for the first stage are 0.63, 0.90 and 0.91 at 1512, 1540 and 1600° C respectively. For the second stage, they are 0.19, 0.31 and 0.34 respectively. The first stage is thought to be the rearrangement process even though the slopes differed from the expected values of 1.3 to 1.4 [18]. The reason for this may be attributed to the difficulty in achieving isothermal conditions in such a short length of time (30 to 50 sec). The second stage is identified as the solution-precipitation process because the slopes are nearly equal to the theoretically predicted value of $\frac{1}{3}$.

The amount of liquid phase ($MgO-SiO_2$) in present method was assumed to be 7 to 8% because Fe and Al compounds were not included in the grain-boundary phase [7]. The rearrangement process contributed about 10% in densification by Kingery's prediction [10]. This suggests that the melting point of the grain-boundary phase in the present system was 1450 to 1500° C from the results in Fig. 1 and the densification up

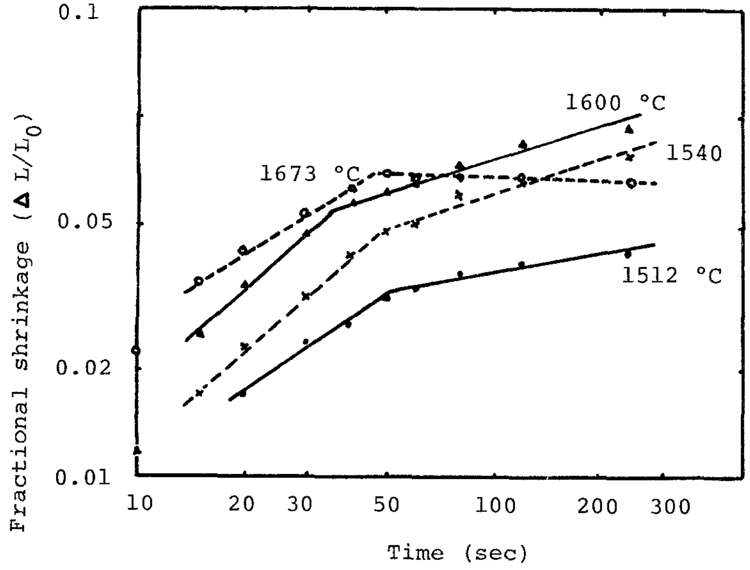
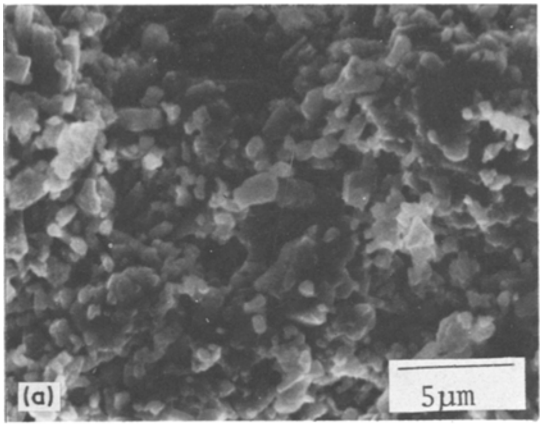
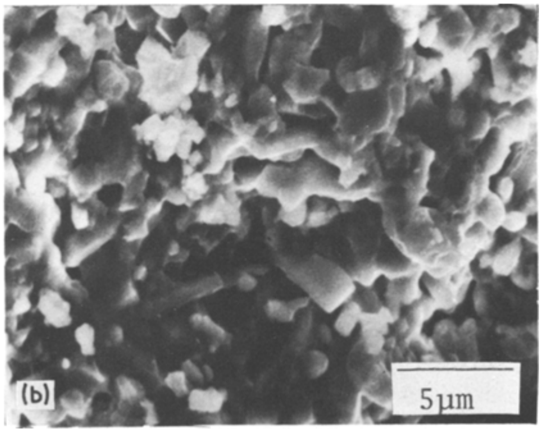


Figure 3 Log fractional shrinkage versus log sintering time for isothermal experiments [17].





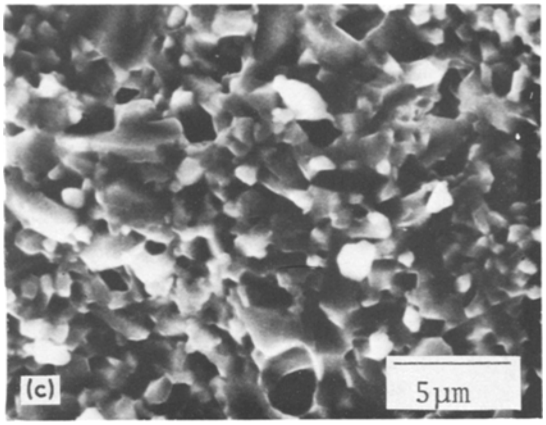


Figure 4 Scanning electron micrographs of fractured surfaces of sintered Si_3N_4 at (a) 1500° C, (b) 1600° C, and (c) 1700° C.

to 1500° C was attributed to the rearrangement process in which Si_3N_4 particles moved close together in the presence of an $MgO-SiO_2$ grain-boundary liquid phase.

At higher temperature than 1500° C, the solution-precipitation process began in which the centre-to-centre distance between particles was decreased by the transfer of materials away from contact points which resulted in further densification.

Further work on this system at 1800° C resulted in a density of 2.91 to 3.04 $g\,cm^{-3}$ and a maximum density of 95% of the theoretical value was obtained.

The scanning electron micrographs of fractured surfaces of Si_3N_4 sintered at 1500, 1600 and 1700° C are shown in Fig. 4a to c. At 1500° C, the same size and shape of grains as in the starting powder were observed. This suggests that the shrinkage at this temperature was based on a rearrangement process. At 1600° C, the dissolution of smaller grains and precipitation on larger grains was observed. At 1700° C, however, the size and shape of the grains were different from those of the starting powder. The results are consistent with the process discussed above.

The characteristic of this method with respect to pressureless sintering was to inhibit thermal decomposition of Si_3N_4 and enabled the use of high temperatures.

3.2. The effect of other additives

The effect of other additives on the sintering of Si_3N_4 was surveyed with 5 wt% additives. The results are shown in Table II (in which a combination of two materials signifies a mixture of equal weights). The addition of La_2O_3, $Ga_2O_3-Al_2O_3$ or $AlN-Al_2O_3$ was least effective; however, Al_2O_3, Y_2O_3 or $Y_2O_3-Al_2O_3$ were most effective and it was possible to densify to greater than 80% of the theoretical value. $Y_2O_3-Al_2O_3$ was the most interesting because formation of a grain-boundary phase with a high melting point, resulting in high strength at high temperatures, was expected [13]. Also, high temperature properties are not sensitive to the presence of impurities

TABLE II The results after sintering at 1800° C for 30 min under 10 atm nitrogen

Additives	Density		Weight loss (%)
	$g\,cm^{-3}$	% theoretical	
Y_2O_3	2.58	80.9	4.9
Al_2O_3	2.62	82.1	5.2
$Y_2O_3-Al_2O_3$	2.66	83.4	1.3
La_2O_3	2.40	75.2	1.5
$Ga_2O_3-Al_2O_3$	2.35	73.7	3.5
$AlN-Al_2O_3$	2.35	73.7	2.0

which seriously impair the high temperature strength of Si_3N_4 sintered with MgO [13]. The lower density of the Y_2O_3–Al_2O_3 system compared to that of MgO was attributed to the high melting point of Y_2O_3–Al_2O_3–SiO_2 grain-boundary phases. The high density was expected to be obtained by prolonged heating at 1800° C or at higher temperatures.

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