Pressureless sintering of Si_3N_4 ceramics with oxide additives in different packing powder

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Attempts to pressureless sinter Si_3N_4 powders with an MgO densification aid have resulted in only limited success [1–8] e.g., a maximum density of 80% (based on a theoretical density of 3.14 gcm^{-3}) was achieved by Kazakov [7], and materials sintered to 90% of theoretical density [4, 8, 9] were only achieved when a large quantity (5–10 wt%) of MgO was added. Early attempts by the present workers were also unsuccessful and in several cases, resulted in lower sintered densities than the bulk density of the precompacted powder specimens. During these early attempts, it was recognized that the decomposition of Si_3N_4 was one of the factors limiting its sinterability and this occurs readily in on open pressureless sintering furnace at temperatures above ~1500 °C. The more restricted gas-access environment of a conventional hot-press more successfully avoids weight loss, and fully dense discs of Si_3N_4 (densified with 5 wt% MgO) can be produced by hot pressing at 1650 °C for 30 min.

The disadvantage of hot-pressing is that it is an expensive process limited to the formation of fairly simple shapes and small (if not single) batches. The present work focuses on MgO densified samples of silicon nitride prepared by the much cheaper pressureless sintering technique. The initial aim of the work was to explore whether MgO plus extra silica (in addition to the 4% naturally present in the silicon nitride powder) could help promote a larger volume of liquid phase and thus aid densification.

The following compositions (Tables I and II) were wet ball-milled in isopropanol for three days. Sample compositions were prepared as follows:

These compositions were compacted and fired at temperatures in the range 1400–1800 °C. The resulting samples were tested for density using the mercury immersion technique and the amount of $\alpha \rightarrow \beta$ transformation measured using X-ray powder diffraction.

Apart from using MgO/SiO_2 additions, powdered Mg-Si-O-N glass was also used to densify Si_3N_4. In order to prepare this glass, mixed 39% MgO + 51% SiO_2 + 10% Si_3N_4 powders were ball-milled for three days in isopropanol using high density sialon balls. The mix was dried and sieved, and then cold-pressed into pellets. To synthesize the glass, the pellets were melted in carbon element sintering furnace at 1650 °C under a nitrogen atmosphere for 30 min. X-ray diffraction analysis showed that 100% Mg-Si-O-N glass was obtained. The glass was crushed in a percussion pestle and mortar and sieved through a 53 μm sieve. The glass powder was then mixed in with Si_3N_4 powder as a densification aid in place of the binary oxides. In order to find the optimum amount of glass for densification, different glass additions were explored.

Because the as-sintered ceramics contained glassy intergranular phase, it is difficult to make reliable calculations of the theoretical density of the final ceramic. To experimentally establish the maximum obtainable density, some samples were densified by hot-pressing. After hot-pressing there is very low porosity (typically <0.5%) and the samples can be considered to be fully dense. To achieve theoretical densities for the above compositions, the samples were hot-pressed at 1650 °C for 30 min. After establishing theoretical densities by hot-pressing, all samples were pressureless sintered for venous times over a wide range of temperature.

When MgO-containing silicon nitride mixes are pressureless sintered, weight losses inevitably occur due to the volatility of MgO. It is therefore necessary to surround the sample with a powder bed which at sintering temperatures emits the same volatile species and opposes loss of volatiles from the sample.

The main volatile species are Mg and SiO when MgO-densified Si_3N_4samples are sintered. Reactions with carbon which result in gas evolution are:

$$MgO + C \rightarrow Mg + CO \quad (1)$$

$$SiO_2 + C \rightarrow SiO + CO \quad (2)$$

To determine an optimum packing powder and to show the effect of packing powder, Si_3N_4-5% MgO mixtures were densified in different packing powders [10] in the carbon furnace for 30 min under a nitrogen atmosphere. It was found that the mix 5% MgO + 45% BN + 50% Si_3N_4 gave the maximum final sintered density. In order to assess the effect of packing powder on densification, selected samples were fired at 1750 °C for 2 hr in a nitrogen atmosphere in a carbon element sintering furnace in both BN and the optimised powder bed. Table III shows the results obtained.

Significant differences in densification were observed. The addition of as little as 5% MgO to the packing powder provided a source of Mg vapour, and the increased partial pressure of Mg in the surrounding

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TABLE I Starting compositions of Si_3N_4 samples containing MgO/ SiO_2 additions

	Compositions (wt.%)		
Sample no.	MgO	SiO_2	Si_3N_4
M1	1	–	99
M2	2	–	98
M5	5	–	95
M10	10	–	90
S55	5	5	90
S31	3	10	87
S64	4	6	90

TABLE II Mg-Si-O-N glass containing samples

	Compositions	
	39% MgO + 51% SiO_2 + 10% Si_3N_4	
Sample no. Glass	Mg-Si-O-N glass (%)	Si_3N_4 (%)
G3	3	97
G5	5	95
G8	8	92
G10	10	90
G13	13	87

TABLE III Effect of packing powder on the densification of Si_3N_4 at 1650 °C for 30 min

	Density (gcm^{-3})		
Samples	Bed 1	Bed 2	Bed 3
M5	2.91	3.05	2.99
G5	2.85	2.91	2.88
G10	2.82	2.88	2.85
S64	2.51	2.87	2.81

Bed 1: 100% BN. Bed 2: 5% MgO, 50% Si_3N_4 and 45% BN. Bed 3: 10% MgO, 50% Si_3N_4 and 40% BN.

gaseous environment prevented volatilisation of Mg from the sample. In a similar way, surface silica generated from the Si_3N_4 in the powder bed, provided an SiO gaseous environment which retained a higher SiO_2content in the samples. This is particularly important because the more silica lost as SiO, the less is available in the sample to react with MgO and Si_3N_4 to form a liquid phase to aid densification.

It would appear from the results that the powder bed was successful but in fact all the Mg and SiO in the bed had been lost before the chemical reactions in the sample were complete. This problem can be avoided either by using less active silica or by adding more silica to the powder bed so that loss of SiO from the sample takes a longer time.

All compositions listed in Tables I and II were pressureless sintered by firing compacted pellets prepared as described above in the carbon sintering furnace in a nitrogen atmosphere for various lengths of time between 1400 and 1800 °C using the previously optimised powder bed (5w/o MgO, 50 w/o Si_3N_4 and 45 w/o BN). Table IV shows the sintering behavior of all the compositions sintered in this way. Up to 1750 °C, the weight loss during pressureless sintering is fairly small, typically 2–2.5% but as the temperature rises to 1800 °C the weight loss rises dramatically (accompanied by a large reduction in density) showing that at this temperature a substantial amount of Mg and SiO_2 is being lost. The reasons for these high weight losses are almost certainly the inadequacy of the powder bed at these temperatures and the highly reactive nature of the silica used.

Table IV and Fig. 1 show pressureless sintered densities for different compositions. Best results for all samples were obtained by sintering in the range 1600–1650 °C. The maximum densities were obtained for sample M5 which contained MgO as the only additive, and gave final densities of up to 97% of theoretical [11]. However, it has reported the coated powder reached >99% of theoretical density [12]. Because of the problem of Mg volatilisation in this system, the presence of large amounts of MgO ensured that the liquid was not short of magnesium, and this was retained in the from of a liquid phase for longer times to aid densification. Even though high levels of Mg and SiO were present in gaseous form during sintering, this appeared not to seriously hinder the particle rearrangement and solution re-precipitation processes.

The samples densified with 10% crushed Mg-Si-O-N glass addition also gave best results at 1600–1650 °C for 30 min. However these samples gave densities of only 90–92% of theoretical; it is believed that better results could have been obtained by further particle size reduction of the starting glass powders.

From the samples that were pressureless sintered with additional silica, the maximum density was obtained at sintering temperatures of 1650 °C. The addition of extra silica did nothing to improve the final density, showing that compared with the silica round the surface of the silicon nitride particles, the additional particulate silica is more vulnerable to carbothermal reduction into CO + SiO. This is supported by the

TABLE IV Pressureless sintering of various silicon nitride samples sintered in the carbon furnace for 30 min at temperatures in the range of 1400–1750 °C

Sample no.	T.D.	1400 °C	1450 °C	1500 °C	1550 °C	1600 °C	1650 °C	1700 °C	1750 °C
G5	3.12	2.11	2.3	2.35	2.58	2.84	2.91	2.74	2.73
G8	3.11	2.06	2.24	2.39	2.61	2.91	2.89	2.81	2.73
G10	3.10	2.15	2.4	2.48	2.65	2.88	2.87	2.85	2.81
G13	3.09	2.23	2.45	2.52	2.71	2.81	2.86	2.76	2.71
M5	3.14	2.01	2.3	2.33	2.58	2.98	3.05	2.92	2.74
M10	3.06	–	–	–	–	2.93	3.01	2.73	2.82
S55	3.11	2.10	2.21	2.34	2.43	2.84	2.86	2.82	2.79

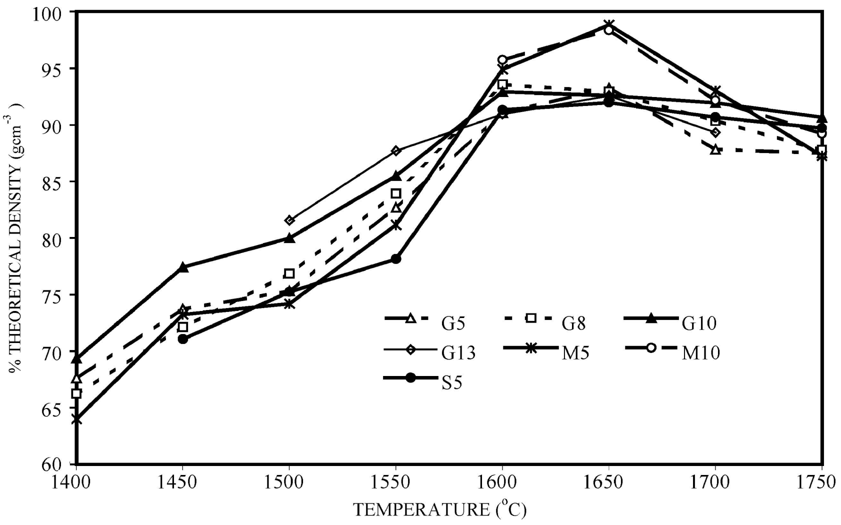

Figure 1 % T.D. after 30 min pressureless sintering at different temperatures.

fact that sample S55 (which contained additional silica formed by pre-oxidation of the silicon nitride powder), did show marginally improved densities. Fig. 1 shows pressureless sintered densities for all the different compositions. Surprisingly, the absolute maximum density values (3.05 gcm^{-3}) were obtained in samples M5 and M10 containing respectively 5 and 10% MgO as the only additive. This is believed to be because the eutectic temperature for these composition is higher than for mixed MgO/SiO-containing compositions, and loss of volatiles from these more refractory liquids takes place less readily.

Successful pressureless sintering of pure silicon nitride with either MgO or MgO plus SiO_2 additions was found to be extremely difficult. Best results were obtained using 5 and 10 w/o of MgO which gave sintered densities of 97 and 98.3% respectively. Additions of silica resulted in lower densities, believed to be due to the reactive nature of the silica used, and also to the strongly reducing nature of the sintering environment. The improved densities obtained by other researchers working in this field are almost certainly due to trace amounts of aluminum impurities present in the starting mix.

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