

MICROSTRUCTURE AND DENSIFICATION BEHAVIOUR OF SURFACE-COATED SILICON NITRIDE POWDER

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Abstract - For better control of the mechanical properties of Si_3N_4 ceramics, it is necessary to generate homogeneous microstructures, and for this purpose, chemical heterogeneities must be minimised, by careful control of powder processing and the subsequent consolidation steps. Coating of the starting silicon nitride powder is a convenient way of incorporating a liquid forming sintering aid more homogeneously than can be achieved by current commercial methods such as ball-milling.

Thin layers of oxides, corresponding to additions of 5 w/o MgO have been deposited on the surface of grains of a commercial silicon nitride powder using alcoholic solutions containing appropriate amounts of the metal alkoxide. The resulting powders have been densified by pressureless sintering techniques, and their sintering characteristics identified in comparison with equivalent materials produced by adding the oxide in particulate form. In every case, a better sintering performance was observed at lower temperatures for the oxide-coated materials, with fully dense pressureless-sintered materials being obtained at temperatures as low as 1525 °C. Microstructures were observed using a S-2400 Hitachi Scanning Electron Microscope (SEM), and final microstructure was more uniform than that obtained by conventional method.

Index Terms - Silicon nitride, MgO, Sintering, Microstructure

I. INTRODUCTION

The mechanical properties of ceramic materials are generally controlled by microstructure, and factors such as grain size distribution and morphology, type and amount of grain boundary phase(s) and pore size/distribution all play a significant role in influencing properties. Improvements in material performance must therefore be sought by optimising these factors.

Ceramic fabrication procedures involve the three main steps of powder mixing, powder compaction/green body formation and finally sintering. Each step has the potential for introducing detrimental heterogeneities into the final microstructure [1]. Silicon nitride in pure form is a covalently-bonded material in which bulk diffusion is too slow to allow densification under normal sintering conditions. To overcome this problem, small amounts of metal oxides are added to the starting powder to form a liquid phase by reaction with the Si_3N_4 and the surface silica on the Si_3N_4 powder at high temperatures, and this promotes densification by a liquid phase sintering mechanism. Most metal oxide sintering additives do not dissolve in the Si_3N_4 lattice and instead remain at the grain boundaries after sintering in the form of an M-Si-O-N glass; certain additives (e.g. Be, Al) can dissolve in the Si_3N_4 grains in the final stages of sintering, to produce an essentially single phase ceramic [2].

To achieve dense, microstructurally and chemically homogeneous Si_3N_4 -based materials, heterogeneities must be minimised in the powder blending stage and must not be reintroduced during the subsequent processing. A recent development to achieve improved microstructural homogeneity involves the use of silicon nitride powders, each individual grain of which has been coated with a thin layer of the sintering additive(s) [3]. In this way, a more uniform dispersion of the sintering additive is achieved, and this is also useful for mixing in small amounts of the additive.

Previous work [4], has focused on the use of alumina as a sintering additive, and it has been established that materials prepared by coating offer significant advantages compared with mechanically mixed powders. Current work focuses on the use of magnesium oxide as the sintering additive.

II. EXPERIMENTAL

A high purity α - Si_3N_4 powder (H.C. Starck-Berlin, Grade LC12N), containing 96% α -phase with a specific surface area (BET) of $17.4 \text{ m}^2/\text{g}$ and a mean grain size of 500 nm as determined by standard sedimentation methods was used. Magnesium methoxide was dissolved in methanol at a concentration of 10 g per 100 ml . Silicon nitride powder, in amounts corresponding to an overall $\text{MgO}/(\text{Si}_3\text{N}_4 + \text{MgO})$ concentration of up to 5 w/o , was added to the solution and dispersed by magnetic stirring for 24 hours, in a pyrex bottle under a nitrogen atmosphere. After mixing, the slurry was transferred to a beaker and heated up to 60°C and stirred with a magnetic stirrer under a nitrogen atmosphere. Coating of the Si_3N_4 powder was achieved by the controlled addition of water in methanol to this solution in just sufficient amounts to ensure complete hydrolysis of the magnesium methoxide. A water/methoxide molar ratio of $20:1$ was used based on the work of Wang & Riley [5] with the addition of dilute HNO_3 (a 10% solution of HNO_3 in water). After hydrolysis, the slurry was slowly stirred at 22°C for a further 24 hours, and the solvent removed by evaporation using an infra-red heater. The powder was then sieved through a $100 \mu\text{m}$ sieve and calcined at 800°C . For comparison, the same amount of magnesium oxide powder (5 w/o) was added to Si_3N_4 by ball milling for 24 hours in isopropanol in a polythene bottle using cylindrical silicon nitride grinding media of total mass six times that of the powder. The resulting powder was then dried, sieved and calcined as before.

To compare the densification behaviour of coated and ball-milled powders, samples were initially hot-pressed at 1700°C for 30 minutes in graphite dies coated with boron nitride powder. The samples were then pressureless-sintered over a range of temperatures for various lengths of time, to compare the densification behaviour. After cooling to room temperature, samples were weighed, and densities determined by Archimedes principle, using flotation in mercury. Product phase composition was determined by X-ray diffraction using a Hagg-Guinier camera and $\text{CuK}\alpha_1$ radiation, and microstructures were observed using a S-2400 Hitachi Scanning Electron Microscope.

III. RESULTS AND DISCUSSION

Figure 1 shows the densification behaviour of coated and particulate oxide containing Si_3N_4 powders pressureless-sintered for increasing lengths of time at 1650°C , with the sintering carried out in BN-lined alumina crucibles in a nitrogen atmosphere. Most of the

sintering took place in the first 30 minutes for both coated and particulate oxide samples, and in both cases, a maximum followed by a subsequent decrease in density was observed with increasing time. The latter arises because MgO present either as the oxide or as an Mg-Si-O-N liquid is appreciably volatile at temperatures in excess of 1500°C , especially in the reducing atmosphere of the sintering furnace [4]. Figure 1 clearly shows that coated powders reproducibly exhibit $7\text{-}10\%$ higher densities than particulate oxide powders at all temperatures when sintered under comparable conditions, the effect increasing slightly with increasing time. Clearly, if a higher density can be achieved in the early stages of densification, there is less internal surface area within the microstructure from which weight loss by volatilisation can subsequently occur.

$\alpha:\beta$ transformation at 1650°C is also plotted on Figure 1. As before, more rapid transformation occurs for coated powders, and in the early stages of densification, transformation proceeds twice as quickly for the coated compared with the particulate oxide powders, consistent with the larger contact area between Mg-Si-O-N liquid and Si_3N_4 grains. Whereas 150 minutes was necessary to achieve complete $\alpha:\beta$ transformation for 5% MgO coated powder, the mixed oxide powder was only 90% dense after the same time.

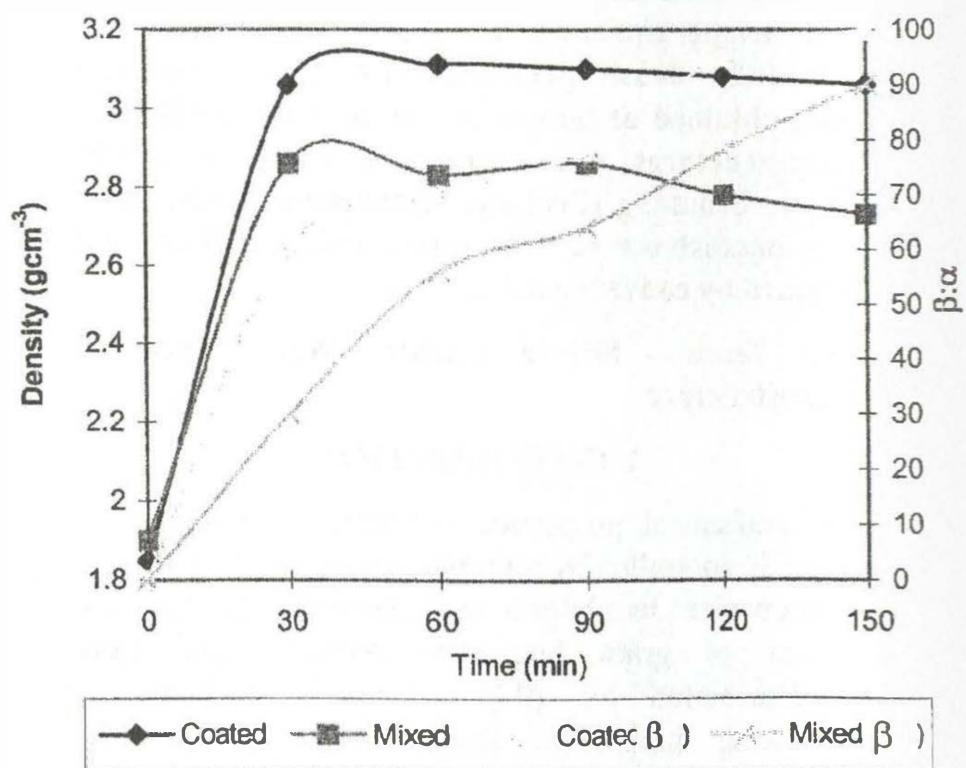


Figure 1. Density and $\beta:\alpha$ ratio as function of time for Si_3N_4 pressureless sintered with 5% MgO additions at 1650°C .

The weight losses observed show that 1650 °C is too high a sintering temperature for a sinterable silicon nitride powder with such a high level of additive as 5% MgO. Figure 2 shows sintering data as a function of temperature for the same powders sintered at various temperatures in the range 1500 - 1650 °C. At the lower temperatures, the difference in behaviour between the two types of powder becomes more marked, so that at 1500 °C, whereas a negligible level of densification occurs for the particulate oxide powder, the coated powder densifies to $\approx 2.5 \text{ gcm}^{-3}$. The greatest density difference between coated and particulate oxide powders is seen at the lower sintering temperatures (1500 and 1525 °C), and densities of $\approx 98\%$ of theoretical (3.08 gcm^{-3}) were achieved after 90 minutes at 1525 °C, whereas similar conditions for the mixed oxide powder resulted in densities of only 2.83 gcm^{-3} . 1525 °C is just above the eutectic in this system (1515 °C [6]), and this temperature provides a good test of the uniformity of distribution of the additive in the mix. Because of the almost complete densification achieved at this relatively low temperature, negligible weight loss occurs with increasing time. The only reason for incomplete densification under these conditions is believed to be the non-uniform distribution of the MgO additive by the current coating process

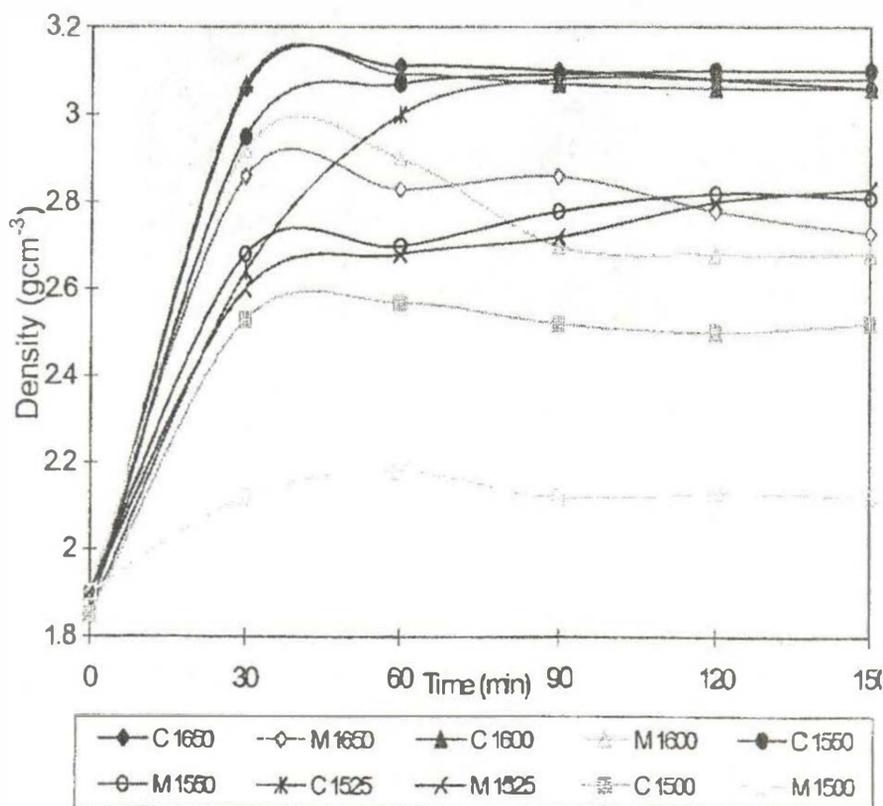


Figure 2. Density as a function of sintering time for Si_3N_4 pressureless sintered with 5% MgO additions at various temperatures

Figure 4 compares the microstructures of powders sintered for 60 minutes at 1500 and 1525°C. Clearly the more uniform local composition of the coated powder has allowed more rapid sintering as soon as the eutectic temperature has been reached. The more inhomogeneous dispersion of additive in the case of the

mixed oxide powder results in "patchy" localised melting, with large pores remaining in the microstructure in regions where, because of inadequate mixing, a low level of sintering additive is present.

$\alpha:\beta$ ratios for different times of sintering at the various temperatures are shown in Figure 3. The extent of transformation increases almost linearly with time at each temperature, and also increases with temperature. The coated samples always exhibited more β at a given time and temperature, as already noted for the 1650 °C samples (Figure 1).

IV. CONCLUSIONS

Silicon nitride powders were sintered to full density by coating with 5% MgO using the alkoxide route. Equivalent samples in which the additive was incorporated in powder form could not be sintered to comparable densities at the same temperatures and times.

Densities greater than 98% of theoretical could be achieved at temperatures as low as 1525 °C using the coated powder route. These results are in good agreement with the measured eutectic temperature in

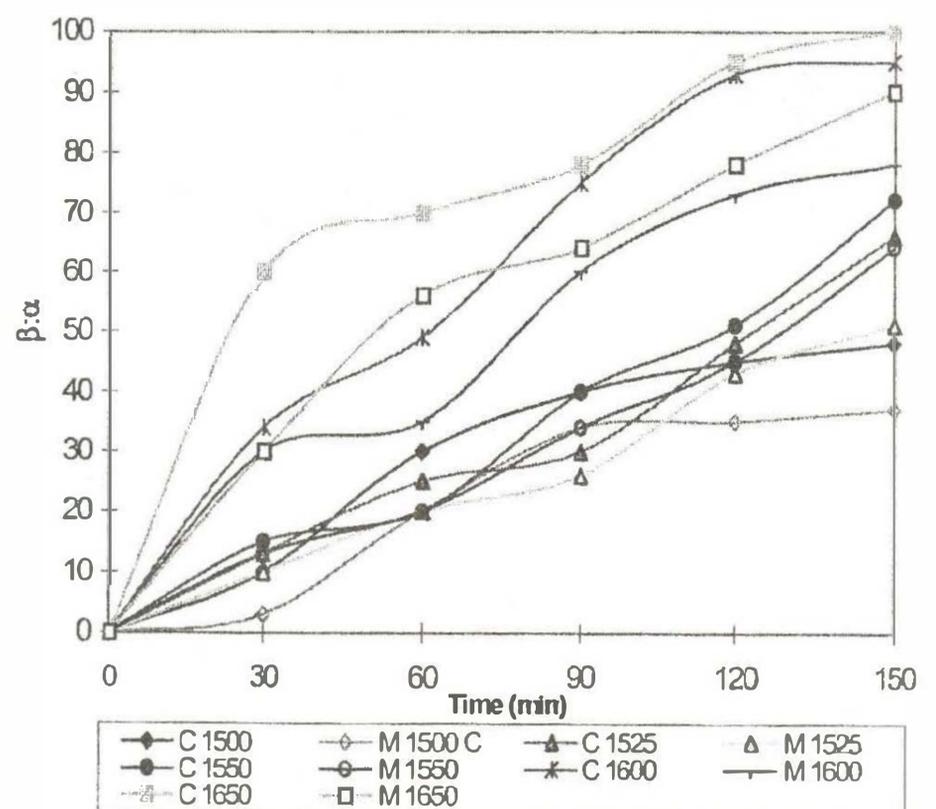
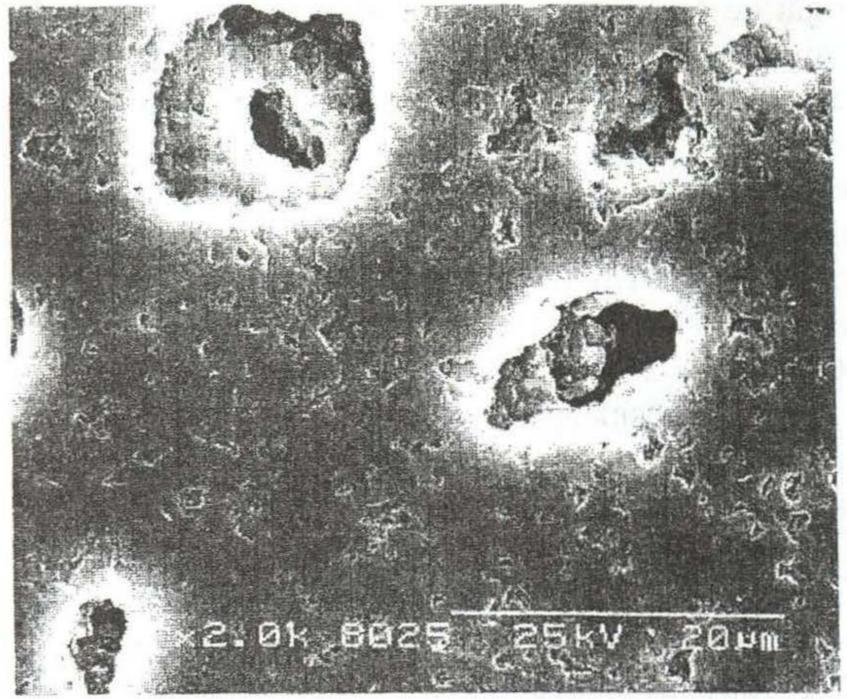


Figure 3 $\beta:\alpha$ ratio as function of time for Si_3N_4 pressureless sintered with 5% MgO additions various temperature.

the Mg-Si-O-N system (1515 °C), and show that the viscosity of the liquid phase formed just above the eutectic is sufficiently low to permit rapid rearrangement and solution/precipitation.[9].



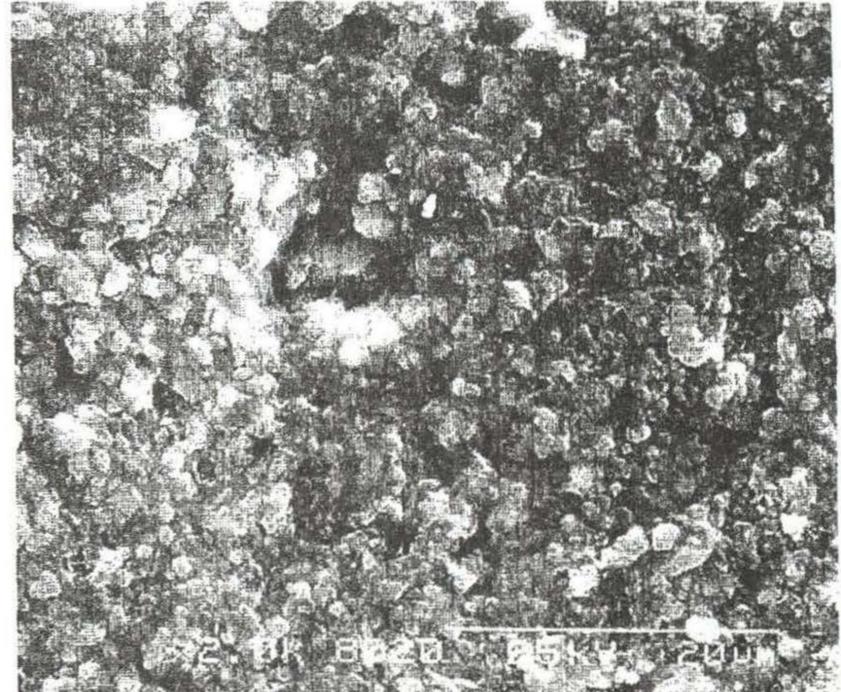
(a)



(b)



(c)



(d)

Figure 4 SEM images of polished surfaces of materials pressureless sintered (a) coated and (b) mixed at 1525°C, (c) coated and (d) mixed at 1500°C.

Microstructures for samples produced from coated powders were very uniform and showed an absence of large pores which characterise similar samples prepared by particulate oxide containing materials.

The absence of such large pores is expected to have a significant effect on increasing the strength of the resulting ceramic, and further work is in progress to eliminate pores entirely from samples sintered at these low temperatures.

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