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Low temperature densification of silicon nitride materials

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Abstract

Thin layers of oxides, corresponding to additions of up to 5 w/o Na_2O 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 hot pressing and 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 all temperatures for the oxide-coated materials, with ~97% dense sintered materials being obtained at temperatures as low as 1400–1500 °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. It is concluded that the powder coating technique is an excellent method of homogeneously incorporating minor amounts of sintering additive into a powder.

Keywords: Sintering; Si_3N_4; Na_2O

1. Introduction

Silicon nitride based ceramics are widely used in high temperature applications due to their excellent mechanical, physical, and chemical properties.[1] Because of the covalent bonding character, the poor sinterability of Si_3N_4 ceramics is generally encountered during fabrication. However, the application of this materials is still limited, mainly because of its low reliability and high machining costs.[2] The densification of Si_3N_4 can be by using oxide additives, such as yttria, alumina, and magnesia, which allow sintering to proceed via a transient liquid phase.[3,4] Silicon nitride ceramics are conventionally prepared by mechanical mixing of silicon nitride powder and sintering additive.[5] However, this processing does not guarantee a homogeneous distribution of the additives. An alternative method involves the coating of the silicon nitride particles with precursors of the sintering additives.[6,7] Further more conventional method is not well suited for the doping of Si_3N_4 with small amounts of sintering additive. Particle coating techniques are receiving increasing attention as they offer several advantages. They provide a convenient means of incorporating sintering aids and dopants more uniformly than can be obtained by conventional powder mixing.[8,9]

The work described in work chapter explores the densification behaviour of silicon nitride powders, again with the oxide sintering additives present as thin layers on the surface of the powder grains, but with the oxides selected to generate low melting eutectic liquids when heated with silicon nitride. In this way, it should be possible to use lower sintering temperatures to densify the silicon nitride. Previous work[10] on coating has discussed the use of alumina (Al_2O_3,) magnesia (MgO) and lithia (Li_2O) as individual and mixed oxide additives, and this work now focuses on the use of sodium oxide (Na_2O) as lower temperature sintering additives.

Previous attempts to densify silicon nitride with sodium oxide have not been successful because the extreme volatility of sodium resulted in it being lost from the mix below densification temperatures. However, the deposition of volatile additives such as sodium as coatings on the silicon nitride powder offers a number of advantages. When Na is deposited by the alkoxide route, the sodium is linked to the surface via Si–O–Na or Si–OH–Na bonds which may offer increased thermal stability rather then when present as particulate sodium oxide or sodium carbonate.

Sodium oxide is a relatively unstable compound, and for example in the presence of silicon will readily react to form

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SiO_2 + Na, the sodium being in vapour form above 883 °C. Similarly, sodium oxide reacts with silicon nitride, and for the reaction:

$$6Na_2O(s) + Si_3N_4(s) \rightarrow 12Na(g) + 3SiO_2(s) + 2N_2(g) \quad (1)$$

for simplicity a typical reaction temperature of 1200 °C has been assumed, and the states of the reactants and products refer to this temperature; the quartz form of silica has been assumed, but cristobalite gives very similar results; the free energy change is given by 1108.7 − 0.8101 T kJ/mol, indicating feasibility above 686 K (413 °C). Almost certainly, any sodium oxide introduced into the mix at room temperature would convert to sodium hydroxide very quickly during processing in air, and for the similar reaction:

$$12NaOH(l) + Si_3N_4(s) \rightarrow 12Na(g) + 3SiO_2(s) + 6H_2O(g) + 2N_2(g) \quad (2)$$

the free energy is given as 2549.3 − 1.7387 T kJ/mol, which becomes favourable above 1466 K (1193 °C). However, there are a multiplicity of possible reactions in this system, and for example, the release of silica indicated by Eqs. (1) and (2) would facilitate further reaction with Na_2O or NaOH to give the more stable sodium silicate, Na_2SiO_3 (melting point 1088 °C), by the equation:

$$18NaOH(l) + Si_3N_4(s) \rightarrow 3Na_2SiO_3(l) + 12Na(g) + 9H_2O(g) + 2N_2(g) \quad (3)$$

for which the free energy is given by the expression 2892.5 − 2.4989 T kJ/mol, giving a feasibility temperature of 1157 K (884 °C), considerably lower than that for Eq. (2). The formation of sodium metasilicate as a reaction product would therefore be favoured over silica alone. This is significant because in a reducing atmosphere, Na_2SiO_3 is fairly resistant to reaction with carbon, and for the reactions:

$$Na_2SiO_3(l) + 2C(s) \rightarrow 2Na(g) + SiO(g) + 2CO(g) \quad (4)$$

or

$$Na_2SiO_3(l) + C(s) \rightarrow 2Na(g) + SiO_2(s) + CO(g) \quad (5)$$

the free energy expressions are 1233.4 − 0.5247 T and 531.3 − 0.1626 T kJ/mol, giving feasibility temperatures of 2351 K (2078 °C) and 3268 K (2995 °C), respectively. From these arguments, it would appear that the use of sodium oxide/hydroxide as a sintering additive would result in loss of sodium, but with some sodium retained in the sample as sodium silicate (liquid at reaction temperatures), which would therefore be available to promote densification. The use of a sodium-containing powder bed should further favour the retention of sodium in the sample.

2. 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 m^2/g and a mean grain size of 500 nm as determined by standard sedimentation methods was used. Sodium methoxide in methanol at a concentration of 25 g/100 ml was used. 5 w/o Sodium methoxide in methanol solution was added to the silicon nitride powder and dispersed by magnetic stirring for 24 h, in a Pyrex bottle under a nitrogen atmosphere. After mixing, the slurry was heated up to 60 °C and stirred with a magnetic stirrer under a nitrogen atmosphere. Si_3N_4 powder was coated by the controlled addition of water in methanol to the slurry in just sufficient amounts to ensure complete hydrolysis of the sodium methoxide. A water/methoxide molar ratio of 20:1 was used based on the work described elsewhere.[11,12] After hydrolysis, the slurry was stirred at room temperature for a further 24 h and dried using an infra-red heater. The powder was then sieved through a 100 μm sieve and calcined at 600 °C. For comparison with coated powders, the same amount of sodium oxide powder (5 w/o) was added to Si_3N_4 by ball milling for 24 h in isopropanol in a polythene bottle using cylindrical silicon nitride grinding media. 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 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 Hägg–Guinier camera and Cu Kα$_1$ radiation, and microstructures were observed using a S-2400 Hitachi Scanning Electron Microscope (SEM).

Table 1
Densities of Si_3N_4 hot-pressed with 5%Na_2O at 20 MPa pressure

Sintering condition		Density (g cm^{-3})	
T (°C)	Time (min)	Coated powder	Mixed powder
1350	20	2.55	2.55
1450	20	2.83	2.54
1500	20	2.98	2.52

Table 2
Densities of Si_3N_4 pressureless sintered with 5%Na_2O addition

Sintering conditions		Density (g cm^{-3})	
T (°C)	Time (min)	Coated	Mixed
1000	60	2.18	2.05
1100	60	2.00	1.83
1200	60	2.00	1.82
	180	2.24	1.97
1300	60	2.29	2.05
	180	1.96	1.78
1400	30	2.00	1.87
	60	2.36	2.00

3. Results and discussion

A value for the theoretical density of Si_3N_4 silicon nitride sintered with Na_2O can be calculated based on the composition $5\%SiO_2$, $5\%Na_2O$ and $90\%Si_3N_4$. Assuming that no impurities are present or picked up during sintering, the metal oxides and silica will be converted into a Na–Si–O–N glassy phase. Sodium oxide (Na_2O) in the presence of silica converts to a liquid at 789 °C (eutectic Na_2O–SiO_2 phase diagram after Levin et al.).[12]

The remaining Si_3N_4 is then completely transformed to β-Si_3N_4. An approximate idea of the expected maximum density can be obtained by assuming that all the Na_2O additive (5 w/o) has reacted with all the silica present on the silicon nitride (3.5 w/o) plus some silicon nitride (e.g. 1 w/o) to give 10 w/o of Na–Si–O–N glass in the final product. Assuming a density of $2.3\ \mathrm{g\,cm^{-3}}$ for this glass and $3.2\ \mathrm{g\,cm^{-3}}$ for silicon nitride, then using the relationship:

$$\frac{100}{\rho} = \frac{\mathrm{w/o\ Si_3N_4}}{3.2} + \frac{\mathrm{w/o\ glass}}{2.3},$$

an overall density can be calculated as $3.07\ \mathrm{g\,cm^{-3}}$. This value has been used throughout the results as a guideline for density comparisons.

3.1. Hot-pressing of Si_3N_4 with Na_2O

Silicon nitride powders containing $5\%Na_2O$ were hot-pressed at temperatures of 1350–1500 °C at 20 MPa for 20 min. The densification behaviour is summarised in Table 1 and it is immediately apparent is that relatively poor densities are being achieved at temperatures significantly above the autectic temperature, and therefore merely the presence of a low melting liquid is not enough to ensure densification. The improved performance at the higher temperatures confirms that a liquid is present, and that α-Si_3N_4 is dissolving more effectively in that liquid at 1500 °C than at 1350 °C. Since it is well established that silica on its own gives almost no densification, it is believed that at least some levels of sodium are being retained in the liquid, and

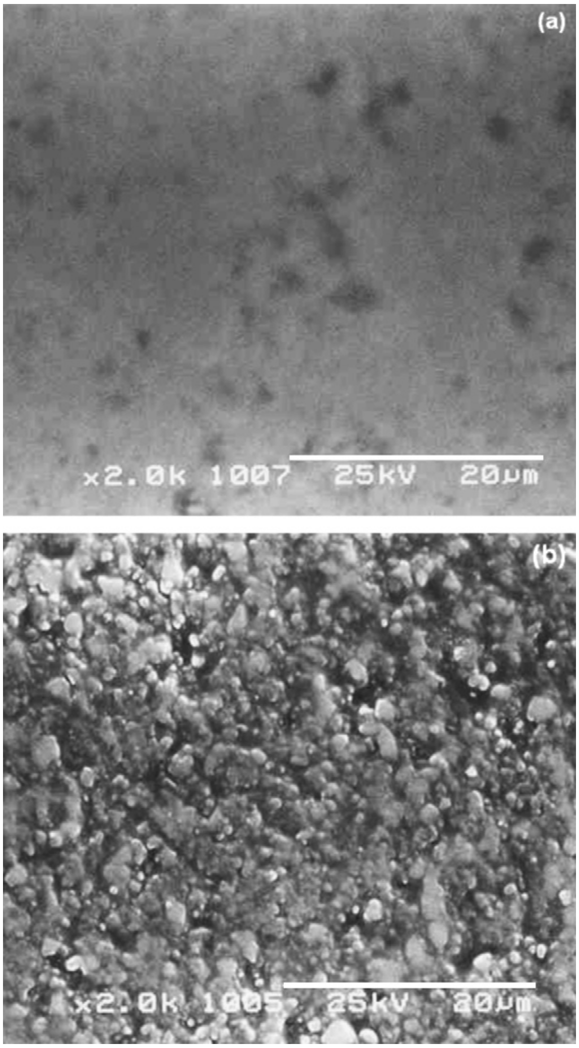

Fig. 1. SEM images of polished surfaces of Si_3N_4 hot pressed with $5\%Na_2O$: (a) coated and (b) mixed, at 1500 °C for 20 min.

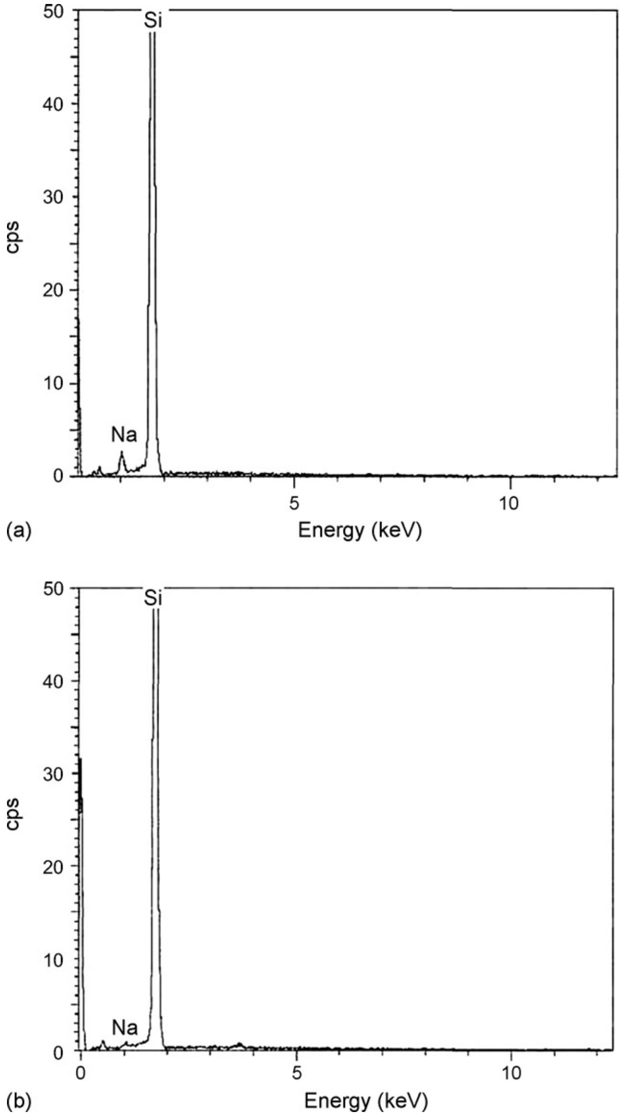

Fig. 2. EDX results: (a) coated, (b) mixed Si_3N_4 hot-pressed with $5\%Na_2O$ at 1500 for 20 min.

this is achieving the value of 2.5 g cm^{-3} observed at 1350 °C. This is substantially due to rearrangement, and proceeds to a similar extent with both coated and mixed oxide powders. However, once the $\alpha \rightarrow \beta$ transformation temperature has been exceeded (typically ~1400 °C), the better distribution of liquid phase in the coated sample allows solution–reprecipitation to proceed with consequent density increase. If is perhaps surprising that no density increase with increasing temperature is observed in the case of the mixed powder samples. Possibly the improved densification arising from some $\alpha \rightarrow \beta$ transformation is being cancelled out by increased porosity arising from liquid loss by volatilisation. In Fig. 1 SEM micrographs show that the mixed powder samples give more porosity compared with coated powder samples. Nevertheless, the final density of 2.98 g cm^{-3} obtained for the coated sample hot-pressed at 1500 °C (~97% of theoretical density) is an excellent result. EDX results for hot pressed samples at 1500 °C show that there is still some Na present after 20 min in coated samples (see Fig. 2a), as expected from the thermodynamic calculations given in Section 1.

3.2. Pressureless sintering of Si_3N_4 with Na_2O

Silicon nitride powders containing 5%Na_2O were pressureless sintered at temperatures of 1000–1400 °C for various times using a powder bed (5%Na_2O + 45%Si_3N_4 + 50%BN) as shown in Table 2. Both the coated and mixed silicon nitride powders containing 5%Na_2O experienced limited densification because of volatility of sodium at high temperatures. Nevertheless, the coated powders do show better densities than equivalent mixed powders, presumably due to the better distribution of the liquid phase giving rise to improved rearrangement. The highest densities observed (approximately 77% of theoretical for the 1400 °C coated sample after 60 min) show that same densification is taking place.

In Fig. 3 SEM micrographs show that the coated powder samples give better microstructures compared with mixed powder samples at 1400 °C. EDX analysis for coated and mixed samples shown in Fig. 4 and EDX results prove that there is more Na

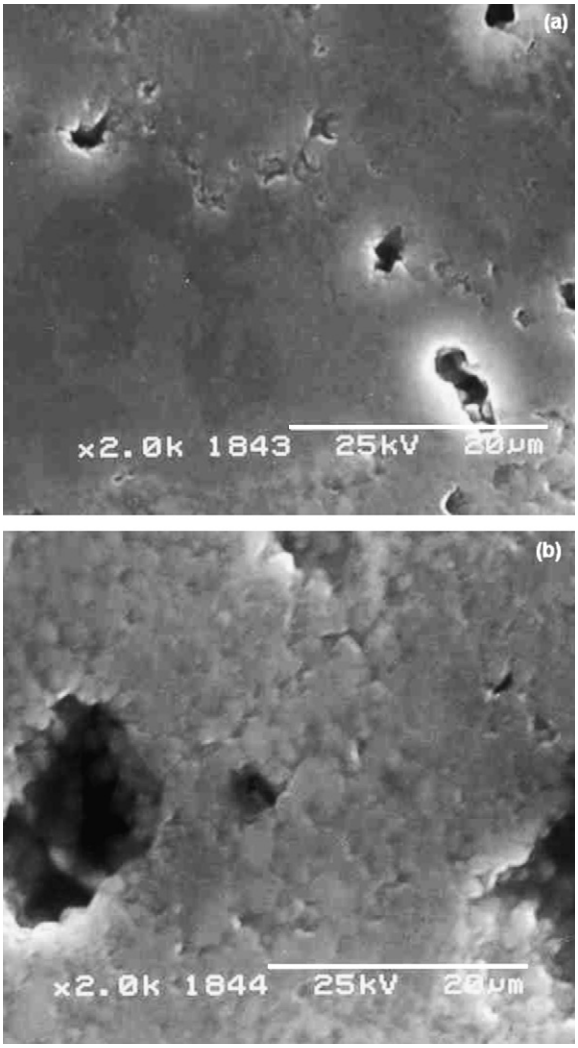

Fig. 3. SEM images of polished surfaces of Si_3N_4 pressureless sintered with 5%Na_2O: (a) coated and (b) mixed, at 1400 °C for 60 min.

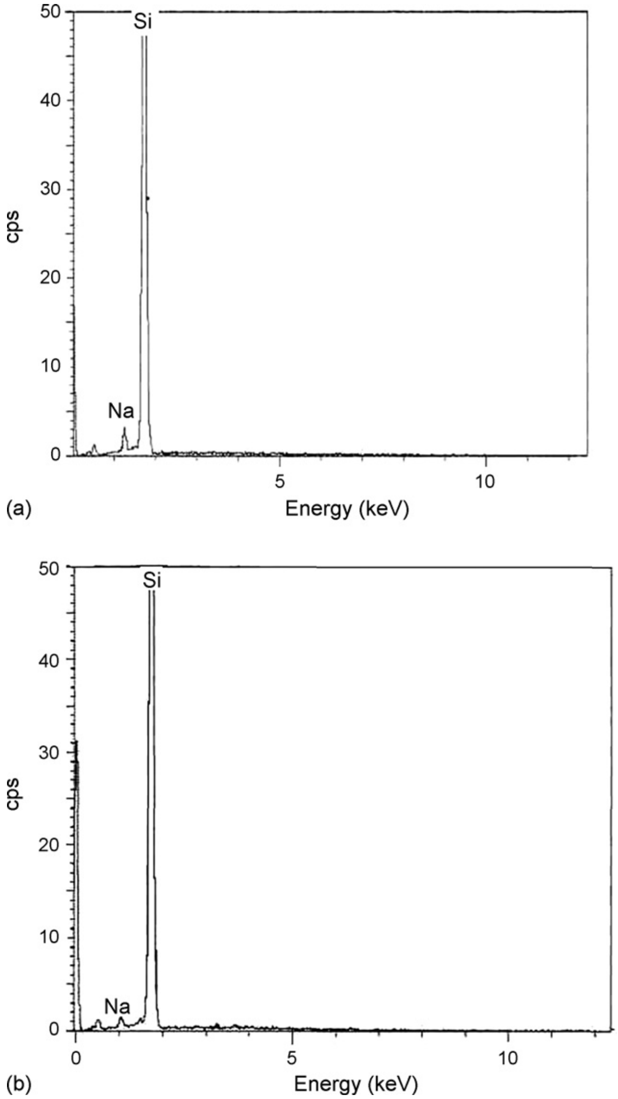

Fig. 4. EDX analyses for: (a) coated and (b) mixed samples after pressureless sintered at 1400 °C for 60 min.

present in the coated sample (see Fig. 4a) than mixed samples after sintered at 1400 °C.

4. Conclusions

The results have demonstrated that sodium shows some promise as an additive for the densification of silicon nitride, and that this is better when the additive is present in the form of a coating rather than when present as a mixed powder. Below 1400 °C very little densification was observed is probably because α-Si_3N_4 has a low solubility in Na–Si–O–N liquids at these temperatures, and perhaps it is necessary to exceed the α → β transformation temperatures before this solubility increases and densification can start. The achievement of a density of 2.98 $g\,cm^{-3}$ at 1500 °C (∼97% of theoretical density) is impressive, and shows that sodium can be used to densify silicon nitride. With further processing modifications no doubt this figure could be increased to give theoretical density. Maximum density achieved by pressureless sintering with sodium was about 2.36 $g\,cm^{-3}$ at 1400 °C (∼70% of theoretical density) presumably because as stated above, densification below 1400 °C does not seem to be possible with sodium, and above this temperature, volatilisation of sodium becomes high. There is scope for further work using alternative powder beds, and starting mixes containing increased levels of sodium.

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