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Review paper

Low temperature densification of silicon nitride using Li_2O-based surface coatings

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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 up to 5 w/o Li_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 pressurelesss 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 1250 °C. An added observation was that for the coated samples, the final microstructure was more uniform, and showed an absence of large pores.

Keywords: Sintering; Si_3N_4; Oxide-coating; Li_2O

Contents

1. Introduction

Silicon nitride based ceramics are widely used in high temperature applications due to their excellent mechanical, physical, and chemical properties. Because of the covalent bonding, the poor sinterability of Si_3N_4 ceramics is generally a problem during fabrication, and it is important to explore alternative processing methods that lead to improved densification at lower sintering temperatures. They are conventionally prepared by mechanical mixing of silicon nitride powder and the sintering additive [1–5]. However, this procedure does not guarantee a homogeneous distribution of the additive(s); an alternative method involves the coating of the silicon nitride

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particles with precursors of the sintering additives [6,7]. These particle coating techniques are receiving increasing attention as they not only provide a convenient means of incorporating sintering aids and dopants more uniformly than can be obtained by conventional powder mixing [8] but are well suited for the doping of Si_3N_4 with small amounts of sintering additive.

Lithium oxide has been explored previously by several authors as a densification additive for silicon nitride and sialon ceramics [9–11], but suffers from the problem of rapid volatilisation above ~1200 °C as a result of which it can be lost from a powder compact before it has had the chance to perform its densification role. For exactly this reason, Mandal [12] found that lithia was a very suitable additive for post-preparative vacuum heat treatment and in many ways it behaves in a similar way to MgO, but with enhanced volatility. This is because lithia itself, and also when present as a Li–Si–O–N liquid is extremely volatile. However, the powder coating technique is effective in keeping the Li in the sample at least up to sintering temperatures. There is nevertheless still some Li volatilisation from the resulting Li–Si–O–N liquid, and powder beds are therefore an additional necessity to restrict lithium loss.

In this study lithium-containing oxide coatings have been deposited on the surface of silicon nitride powders, with the aim of simulating grain-boundary eutectic liquid compositions for the purpose of achieving low-temperature densification. The effectiveness of this technique has been evaluated by comparing the powder properties, densification behaviour, and microstructure of coated Si_3N_4 powders with identical powders in which the additive oxide has been added in particulate form. It is concluded that the powder coating technique is an excellent method of homogeneously incorporating minor amounts of sintering additive into a powder. The coated powders have good green compact density, high green strength and densify more easily by pressureless sintering with faster densification rates, resulting in a more homogeneous microstructure, compared with materials prepared using mixed oxide powders.

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. Lithium methoxide was dissolved in methanol at a concentration of 25 g per 100 ml. Silicon nitride powder, in amounts corresponding to an overall $Li_2O/(Si_3N_4 + Li_2O)$ concentration of up to 5 w/o, was added to the solution and dispersed by magnetic stirring for 24 h, 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 and Riley [13]. After hydrolysis, the slurry was slowly stirred at 22 °C for a further 24 h, and the solvent removed by evaporation using an infra-red heater. The powder was then sieved through a 100 μm 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 h 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 1650 °C for 30 min 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 XRD and microstructures were observed using a S-2400 Hitachi Scanning Electron Microscope.

3. Results and discussion

3.1. Hot pressing of coated and mixed oxide Si_3N_4 powders

Hot-pressing was carried out at 1350, 1450 and 1650 °C for 15 min at a pressure of 30 MPa, in a powder bed of boron nitride contained in a graphite die; selected runs were also heated for longer times. Table 1 shows the densities obtained for these samples. An approximate idea of the expected maximum density can be obtained by assuming that all the lithia additive (5 w/o) has reacted with all the silica present on the silicon nitride (4 w/o) plus some silicon nitride (e.g. 1 w/o) to give 10 w/o of Li–Si–O–N glass in the final product. Assuming a density of 2.2 g cm^{-3} for the glass and 3.2 g cm^{-3} for silicon nitride, then using the relationship:

$$\frac{100}{\rho} = \frac{\text{w/o Si}_3\text{N}_4}{3.2} + \frac{\text{w/o glass}}{2.2},$$

the overall density can be calculated as 3.06 g cm^{-3}. From Table 1 it is clear that maximum density is more or less achieved at 1650 °C for the coated powder.

Also from Table 1 it can be seen that the densities for mixed samples are always lower than those for coated powders, approximately by the same amount. This point is discussed later in the context of the resulting microstructures.

Table 1
Densities of Si_3N_4 hot pressed with 5% Li_2O at various temperatures.

Temperature (°C)	Time (min)	Density (g cm^{-3})		Density (g cm^{-3})	
		Coated powder	%β	Mixed powder	%β
1250	180	2.47	8	2.24	7
1350	15	2.55	7	2.54	6
	60	2.93	8	2.88	7
1450	15	3.01	15	2.94	10
1650	15	3.04	33	2.95	29

Both time and temperature clearly play a part in determining the final density. Thus, hot-pressing for 3 h at 1250 °C does achieve some densification, which is of interest because this is below the $\alpha \rightarrow \beta$ Si_3N_4 transformation temperature (∼1410 °C), but above the eutectic temperature in the Li–Si–O–N system (approx. 1000 °C). Densification proceeds much more rapidly at 1350 °C, and again the very small $\beta{:}\alpha$ ratio shows that almost no transformation has occurred at this temperature, consistent with it still being below the eutectic value. The effect of time is particularly noticeable here, and the density value of 2.93 g cm^{-3} obtained after hot-pressing for 1 h suggests that longer time may enable full density to be reached at this temperature. 1450 °C is above the eutectic temperature, and good densities can be easily reached after short hot-pressing times. The predominantly β Si_3N_4 content of the product is further confirmation that the eutectic temperature has been exceeded. The run at 1650 °C gave a good density after 15 min as expected. It is doubtful whether improved densities could have been obtained with longer times because lithia is appreciably volatile at these temperatures. These results confirm that good densities can be achieved without the use of a lithia-containing powder bed, showing that lithia is not excessively volatile at densification temperatures. From the present results, clearly 1450 °C is the best temperature for obtaining fully dense hot-pressed samples.

3.2. *Pressureless sintering of coated and mixed oxide Si_3N_4 powders*

Compacted pellets of silicon nitride powders were pressureless sintered in the carbon sintering furnace under a nitrogen atmosphere for various lengths of time at temperatures between 1350 and 1600 °C in a powder bed made up from $Li_2O + BN + Si_3N_4$ powders.

Silicon nitride powders containing 5% Li_2O were pressureless sintered at temperatures of 1350, 1450,1500, 1550 and 1650 °C for various times in a powder bed made up from $Li_2O + BN + Si_3N_4$ powders as shown in Figs. 1–4. Clearly, using a maximum of only 5 w/o Li_2O as the additive, silicon nitride cannot be densified as easily by pressureless sintering as by hot pressing. Nevertheless, a density of up to 95% of theoretical (coated 10 min 1500 °C) was achieved as shown in Table 2 with the powder bed assisting to some extent in restricting Li volatilisation.

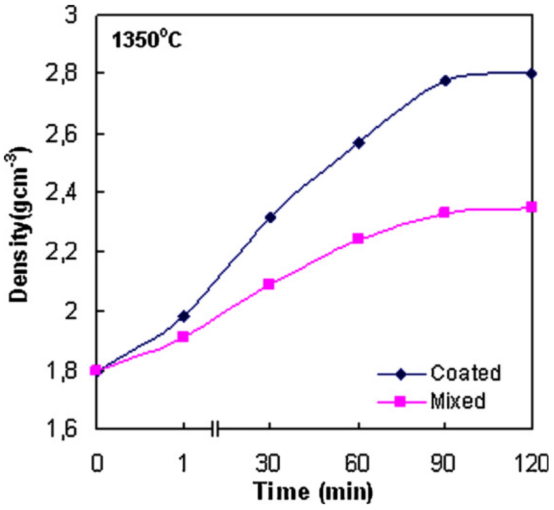

Fig. 1. Density as a function of sintering time for Si_3N_4 pressureless sintered with 5% Li_2O at 1350 °C.

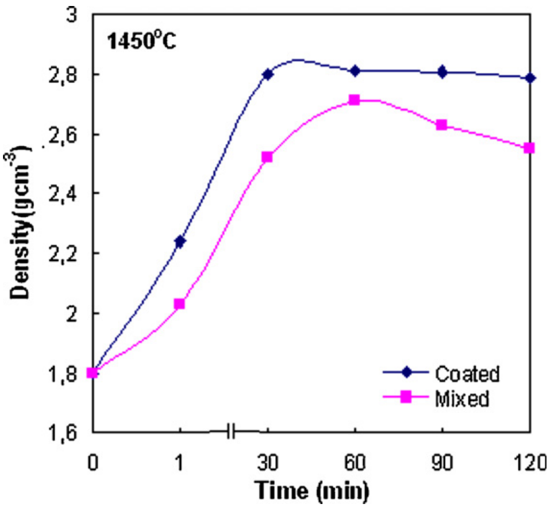

Fig. 2. Density as a function of sintering time for Si_3N_4 pressureless sintered with 5% Li_2O at 1450 °C.

Density as a function of temperature and time is plotted in Figs. 1–4 for samples densified with 5% Li_2O and shows that the coated Si_3N_4 powder densifies better than the mixed oxide powder and gives a higher final density. Densities systematically increase up to 1450 °C, showing that the liquid phase is retained satisfactorily up to this temperature (see Figs. 1 and 2). The decrease in density above this temperature is due to volatilisation as shown in Figs. 3 and 4. The main difference appears to be that increasing time does not have as beneficial an effect in increasing density for the pressureless sintered samples, and in fact increasing the time beyond 90 min at 1450 °C has a detrimental effect, presumably because of loss of gaseous species (Li, SiO, N_2) from the grain boundary Li–Si–O–N liquid.

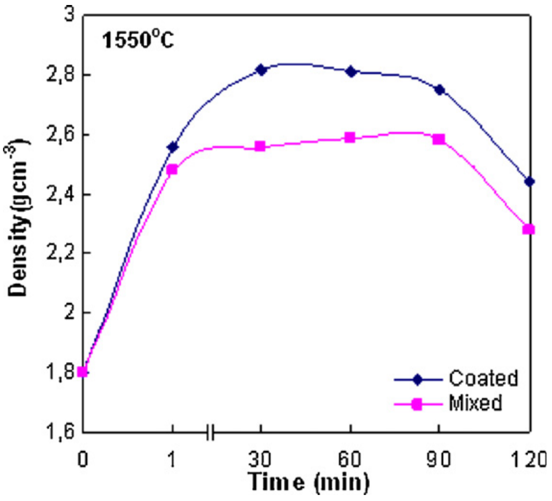

Fig. 3. Density as a function of sintering time for Si_3N_4 pressureless sintered with 5% Li_2O at 1550 °C.

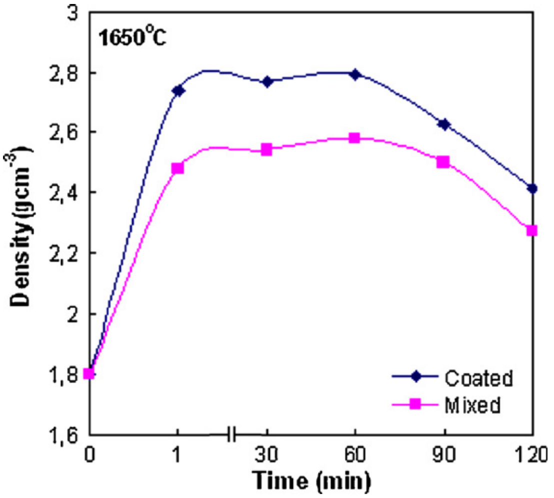

Fig. 4. Density as a function of sintering time for Si_3N_4 pressureless sintered with 5% Li_2O at 1650 °C.

The 1350 °C results are of interest in that the final density is still increasing even after 2 h of sintering time. This behaviour is consistent with the hot-pressing results, and suggests that further improvements could have been achieved if longer sintering times had been used, and also if more Li_2O had been incorporated into the powder bed.

Fig. 5 shows that density decreases with increasing temperature and weight losses also increase with increasing temperature. Nevertheless, in Fig. 6 the density increases with increasing temperature up to 1450 °C, then slightly decreases and weight losses again increase with increasing temperature. It is clear that using an appropriate packing powder prevents the loss of volatile oxides (especially MgO, Na_2O and Li_2O). The importance of using packing powder has been discussed elsewhere [14].

At both 1450 and 1500 °C, it is noticeable that densification essentially stops after a certain sintering time (≤30 min at 1450 °C, ≤10 min at 1500 °C). It would be logical to attribute this to loss of volatile species from the liquid, but it is noticeable that $\alpha \rightarrow \beta$ transformation continues after the end of densification. The results can perhaps be explained in terms of loss of lithia from the liquid, which with increasing viscosity is not able to facilitate the diffusional processes associated with densification. The latter therefore slows down and stops. Nevertheless there is still a driving force for $\alpha \rightarrow \beta$ transformation (since sintering temperatures are in excess of 1410 °C), and α grains continue to transform to β, but the resulting β may not fill up residual pores and contribute to increased densification.

Table 2
Densities of Si_3N_4 pressureless sintered with 5% Li_2O at 1500 °C.

Temperature (°C)	Time (min)	Density (g cm^{-3})	
		Coated powders	Mixed powders
1500	10	2.87	2.48
	30	2.85	2.57
	45	2.83	2.59

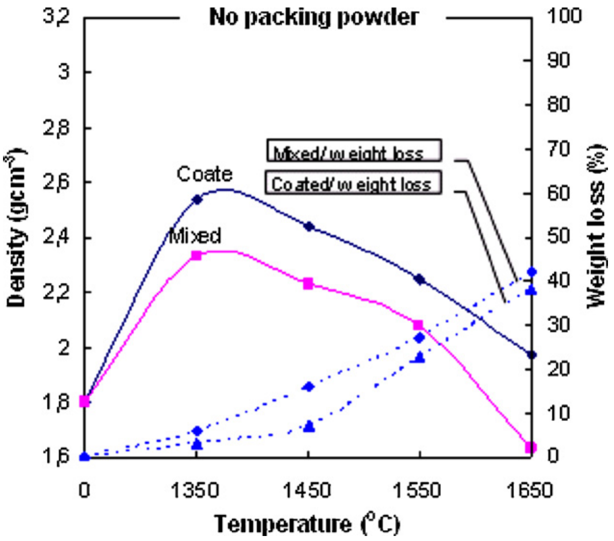

Fig. 5. Density as a function of sintering temperature for Si_3N_4 pressureless sintered using 5% Li_2O addition for 90 min (no packing powder).

4. X-ray results

The $\alpha \rightarrow \beta$ transformation data for hot-pressed (Table 1) and pressureless sintered (Fig. 7) samples shows that significant amounts of β-Si_3N_4 formed during these runs in contrast to the hot-pressed results. It is interesting that the 60 min results at this temperature gave both low density and a low β content, suggesting that these samples may have been at a lower temperature than the others. Bearing in mind that the β-Si_3N_4 content of the starting silicon nitride powder was approximately 5%, X-ray phase analysis showed that pressureless sintered, coated and mixed oxide materials were all composed of mixtures of α-Si_3N_4 and β Si_3N_4 with the amount of β increasing appreciably with increasing temperature. Fig. 7

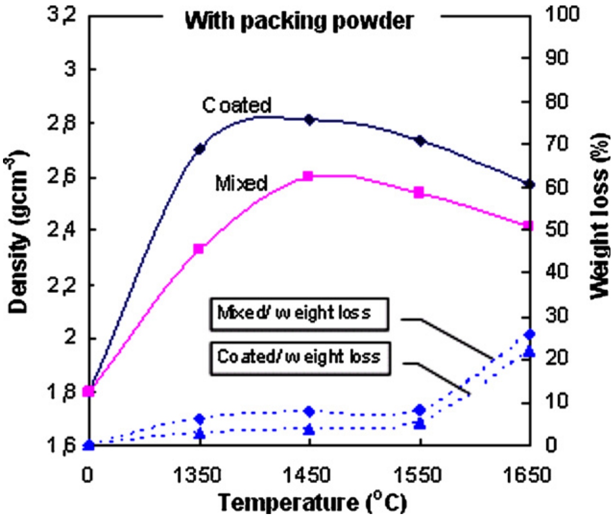

Fig. 6. Density as a function of sintering temperature for Si_3N_4 pressureless sintered using 5% Li_2O addition for 90 min (with packing powder).

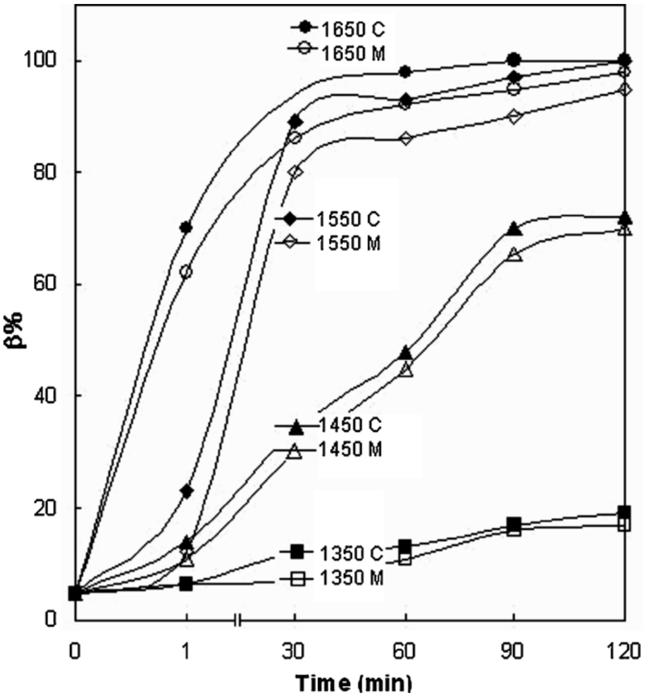

Fig. 7. %β as a function of sintering time after pressureless sintering of coated (C) and mixed (M) Si_3N_4 powders with 5% Li_2O addition.

shows that the β:α-Si_3N_4 ratio increases with increasing sintering temperature and time at 1550 and 1650 °C and more markedly so for the coated than for the mixed oxide samples. This kind of behaviour does not occur at lower temperatures (1450 °C) but increase gradually. As can be seen from Figs. 1 and 2 very little densification occurs at 1350 and 1450 °C for the first 30 min, but there is nevertheless some $\alpha \rightarrow \beta$ transformation (see Fig. 7), the amount of β-phase increasing with increasing sintering time. Increasing sintering temperature results in more liquid phase, and this combined with the further kinetics at the higher temperature promotes more rapid $\alpha \rightarrow \beta$ silicon nitride transformation.

5. Microstructural observations

SEM micrographs for pressureless sintered and hot-pressed materials are given in Figs. 8–11. As a general rule the coated materials differ from the mixed oxide ones by having no large pores. These features were observed previously in MgO-sintered materials, and were attributed to the worse distribution of the sintering additive in the mixed powder samples, the large pores forming in regions of low concentrations of additive [15]. With increasing temperature, these holes expand, as the surrounding matrix densifies around them. Fig. 8 shows that hot pressed coated and mixed materials both have similar microstructures in contrast; pressureless sintered materials at similar temperatures give lower densities. This is due to loss of

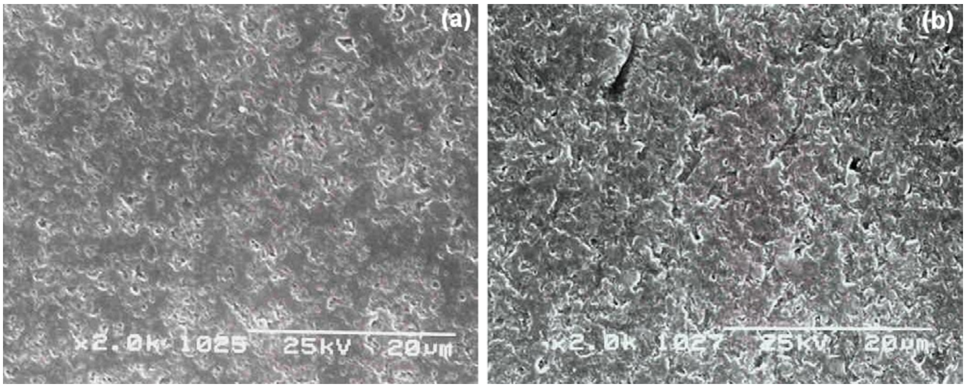

Fig. 8. SEM images of polished surfaces of Si_3N_4 hot pressed with 5% Li_2O: (a) coated and (b) mixed, at 1450 °C for 15 min.

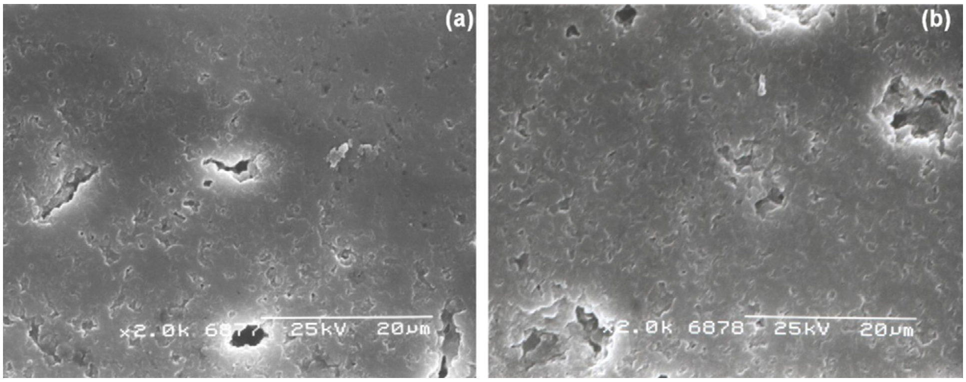

Fig. 9. SEM images of polished surfaces of Si_3N_4 pressureles sintered with 5% Li_2O: (a) coated and (b) mixed, at 1350 °C for 90 min with packing powder.

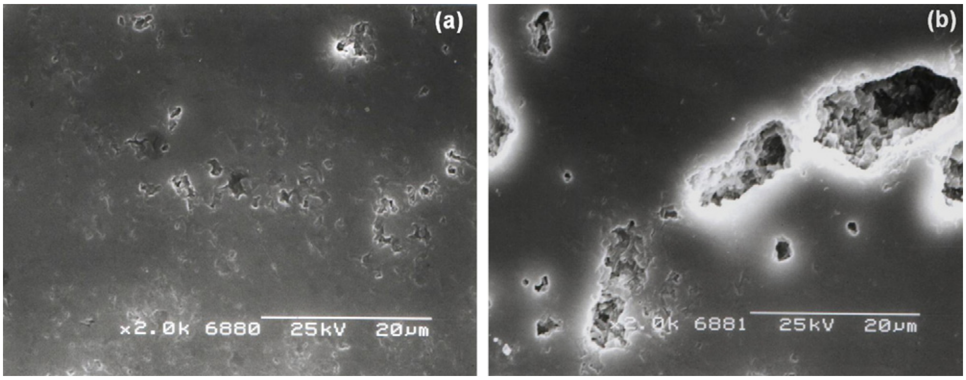

Fig. 10. SEM images of polished surfaces of Si_3N_4 pressureless sintered with 5% Li_2O: (a) coated and (b) mixed, at 1450 °C for 90 min with packing powder.

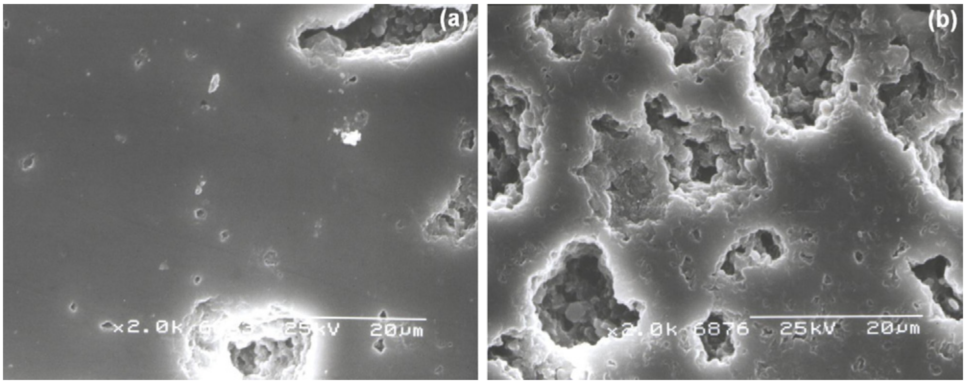

Fig. 11. SEM images of polished surfaces of Si_3N_4 pressureless sintered with 5% Li_2O: (a) coated and (b) mixed, at 1450 °C for 90 min (no packing powders).

Li during pressureless sintering, whereas the hot press can prevent loss of Li especially after short times i.e. 15 min. At lower temperatures, coated samples still show promising microstructures with pressureless sintered materials giving better densities than hot pressed samples because of the short hot-pressing time used (10–15 min). Fig. 9 shows that 1350 °C is clearly too low a temperature for the matrix to densify Fig. 10 clearly shows that 1450 °C for 90 min with packing powder (5% Li_2O + 45% Si_3N_4 + 50% BN) gave better densities (2.81 compared with 2.38 g cm^{-3}) and lower porosities compared with coated and mixed samples which were sintered without packing powder (see Fig. 11).

6. Conclusions

For pressureless sintering of silicon nitride with 5% Li_2O additions the best results were obtained for the coated powder at intermediate sintering temperatures, e.g. 1500 °C, which gave sintered densities of 2.82–2.87 g cm^{-3}. For better densities, more sintering additive would be needed, and further work would be desirable using 2–5 w/o Li_2O additions; however, the aim of the present exercise was to minimise inhomogeneity distributions of the additives by using the coating technique and this has been achieved successfully. It is very difficult to achieve full densities by pressureless sintering using volatile additives such as Li_2O. The present densities of 94% of theoretical were considered satisfactory as a basis for subsequent more detailed subsequent pressureless sintering studies.

Temperatures above 1500 °C are too high to retain the lithia in the liquid phase, and losses by volatilisation result in lower densities. At both 1450 and 1500 °C, densities of coated samples remained fairly constant with time, implying that again lithia loss is a dominant feature. To obtain the best densities by pressureless sintering, there is a choice of either sintering for long times (>3 h) at 1350 °C, or using a more lithia-rich powder bed (plus also possibly more lithia in the starting mix) and sintering for shortish (10–30 min) times at 1450–1500 °C.

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