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Comparative Study of Fabrication of Si_3N_4/SiC Composites by Spark Plasma Sintering and Hot Isostatic Pressing

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Abstract

A Si_3N_4/SiC composite with additions of La_2O_3, Y_2O_3 and SiO_2 was fabricated by spark plasma sintering (SPS). The porosity and phase formation resulting by this method are compared with those obtained by sinter/hot isostatic pressing (sinter/HIPing). The open porosity was completely eliminated by SPS in 10min of heating to 1900°C and 5min dwell time. The complete α to β transformation was achieved with the formation of elongated β Si_3N_4 grains. The same result was achieved by sinter/HIPing at 1750°C with a dwell time of 160min. There were differences in the % β transformation from α, open porosity and the presence of minor phases between the two processes. The comparison of SPS with sinter/HIP showed the former to be a rapid fabrication process for Si_3N_4 which warrants further investigation to optimise the microstructure.

1 Introduction

Spark plasma sintering (SPS) is a new process[1] which offers a means by which ceramics can be sintered very rapidly to full density. It is similar to conventional hot pressing, in that it is carried out in a graphite die, but the heating is by means of direct current of about 4000 to 8000A, pulsed by a patented power generator, applied through electrodes at the top and bottom of the die punch. The powders are heated initially by spark discharge between the particles. The temperature may be measured by an optical pyrometer focused on to the surface of the die or by means of a thermocouple placed inside the die. It has been shown that Si_3N_4 can be densified to 98–100% relative density in 15min of heating and dwell time, but the α to β transformation was not completed within this time.[2] Experience has shown[1] that SPS allows maximum density to be achieved at temperatures of 100° to 150°C lower than by hot pressing, and it is of interest to compare results from this new process with those from more established processes.

It has been found that sintering and hot isostatic pressing (sinter/HIPing) in the same cycle sinters Si_3N_4 to full density almost free of closed porosity faster than by post-sinter HIPing,[3–9] but the time required is well over one hour. In this paper the fabrication of Si_3N_4/SiC composite processed by SPS is compared with the sinter/HIPing studies reported previously.[3–5]

2 Experimental

The composition investigated consisted of $La_{0.19}Y_{0.17}Si_{2.73}O_{0.75}N_{3.50}$ with 14·6 wt% (15 vol%) SiC particles of 0·26 μm mean grain size. The composition was prepared from α-Si_3N_4 (58·4 wt%), La_2O_3 (15 wt%), Y_2O_3 (9 wt%) and SiO_2 (3 wt%) powders; the preparatory details and the description of the materials have been reported previously.[3,10] The SPS processing (Dr Sinter-SPS-2040, Sumitomo Coal Mining Co. Ltd., Kanagawa, Japan) was carried out in a vacuum ($0{\cdot}7\times10^{-2}$ Pa) by heating to the maximum temperature in 10 min, with a 5 min dwell time and cooling in about 20 min to room temperature. The pressure applied was 49 MPa from the start to the end of dwell time. The temperature was measured by means of an optical pyrometer focused on to the die surface. It has been shown that the true temperature of the powder is about 150°C higher than the measured temperature.[11] This was confirmed by placing a thermocouple tip near the sample inside the die. The listed temperature is the corrected temperature. The sinter/HIPing (Model AIP-6-30H- Sinter/HIP, AIP Ltd, OH) was carried out in a nitrogen atmosphere according to the temperature/pressure schedule shown in Fig. 1. The materials were processed between 1550–1900°C by SPS and 1400–1800°C by sinter/HIPing. During sinter/HIPing the cycle was interrupted to study the phase formation by switching off the furnace and cooling to 800°C in about 90 min. The details of the individual runs processed by SPS and sinter/HIPing are listed in Tables 1 and 2, respectively.

The open porosity of the sintered materials was determined according to AS 1774·5.[12] The X-ray diffraction (XRD) analysis was carried out on the fraction ground to <75 μm from portions of sintered materials using a Siemans D500 diffractometer with CoK_α radiation. The α and β Si_3N_4 ratio was calculated from the ratio of intensities for 102 (α) and 101 (β) reflections similar to the method used by Perera.[13] Some of the sintered materials were cross sectioned perpendicular to the flat surface, embedded in resin and diamond polished to 1 μm finish and examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

3 Results and Discussion

The open porosity values and the XRD analysis of the materials processed by SPS and sinter/HIPing are listed in Tables 1 and 2, respectively. The bulk density of the zero open porosity materials was 3·68 g cm^{-3} and the closed porosity ~ 0·3%. The variation of open porosity of the materials are plotted against temperature in Fig. 2 for materials with a dwell time of 0 to 5 min. Comparison between the two processes shows that the open porosity for a given temperature is less for materials processed by SPS.

The percentage of β transformed is plotted against temperature in Fig. 3. Given the uncertainties in the measured temperature, and the different dwell times, it appears that for short processing times the transformation rate is similar. Complete conversion occurred only at 1900°C with 5 min of SPS processing, whereas it occurred at 1750°C after 100 min of sinter/HIPing

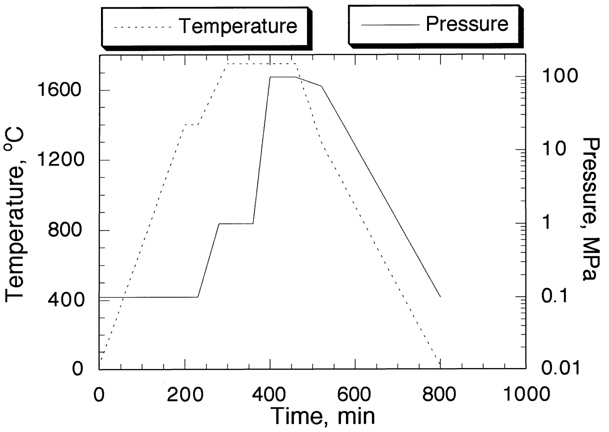


Fig. 1. Sinter/HIP temperature/pressure schedules.

Table 1. Materials processed by SPS

Max. temp. (°C)	*Dwell time (min)*	*Open porosity (%)*	*XRD analysis**
1550	5	24·1	α(85),β(15), A, N
1650	5	6·3	α(80), β(20), A, N
1750	5	0·7	α(50), β(50), A, N
1800	5	0·1	α(25), β(75), A
1850	5	0·1	α(20), β(80), A
1900	5	0·0	β(100), A, + †

*All materials contained SiC and Si_3N_4, % α and β are given in brackets. A = $Y_{3\cdot5}La_{6\cdot5}(SiO_4)_6N_2$, N = new phase (Ref. 5). †Few unidentified lines.

Note: there were no weight losses observed.

Table 2. Materials processed by sinter/HIP

Max. temp. (°C)	*Dwell time (min)*	*Open porosity (%)*	*XRD analysis**
1400	0	39.4	α(95),β(5), A(tr.), W, M
1600	5	35·0	α(90), β(10), A, N, M
1650	0	17·2	α(85), β(15), A, N, M(tr.)
1750	0	1·8	α(35), β(65), A, N, L, M(tr.)
1750	100**	0·1	β(100), A, N
1750	160†	0·0	β(100), A, N, L
1800	160†	1·6	β(100), A, L

*All materials contained SiC and Si_3N_4, % α and β are given in brackets. A = $Y_{3\cdot5}La_{6\cdot5}(SiO_4)_6N_2$, N = new phase (see Ref. 5), M = $Y_2Si_3O_3N_4$ (N-melilite), W = $Y_3Si_3O_6N_3$ (N-α Wollastonite), L = $LaSi_3N_5$, tr = trace.

**On reaching 1750°C, pressure increased to 100 MPa in 40 min and then HIPed for 60 min.

†On reaching 1750°C, held for 60 min, then pressure increased and HIPed at 100 MPa for 60 min.

Note: The weight loss of the first four runs was $<0\cdot5\%$ and of the last two runs was ~2·0%.

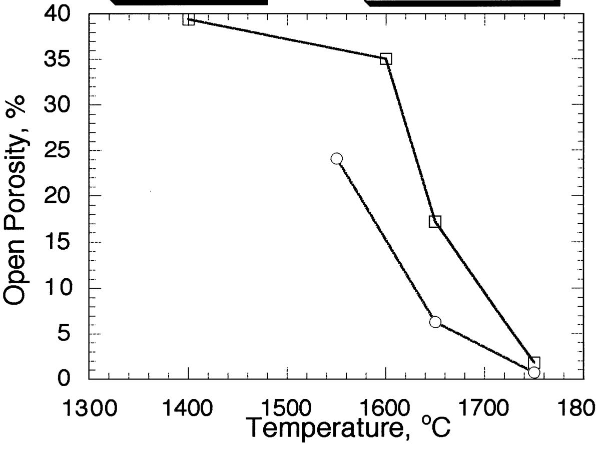


Fig. 2. Variation of open porosity with temperature of materials processed by SPS and sintered in the sinter/HIP runs for 0–5 min dwell time.

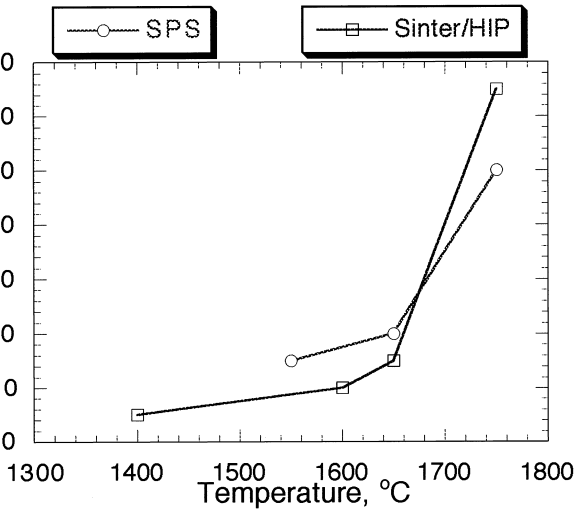


Fig. 3. Variation of β phase transformation in materials processed by SPS and sintered in the sinter/HIP cycle for 0–5 min dwell time.

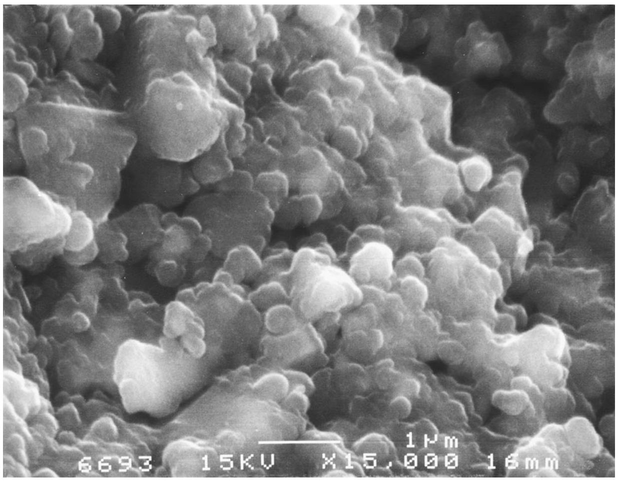
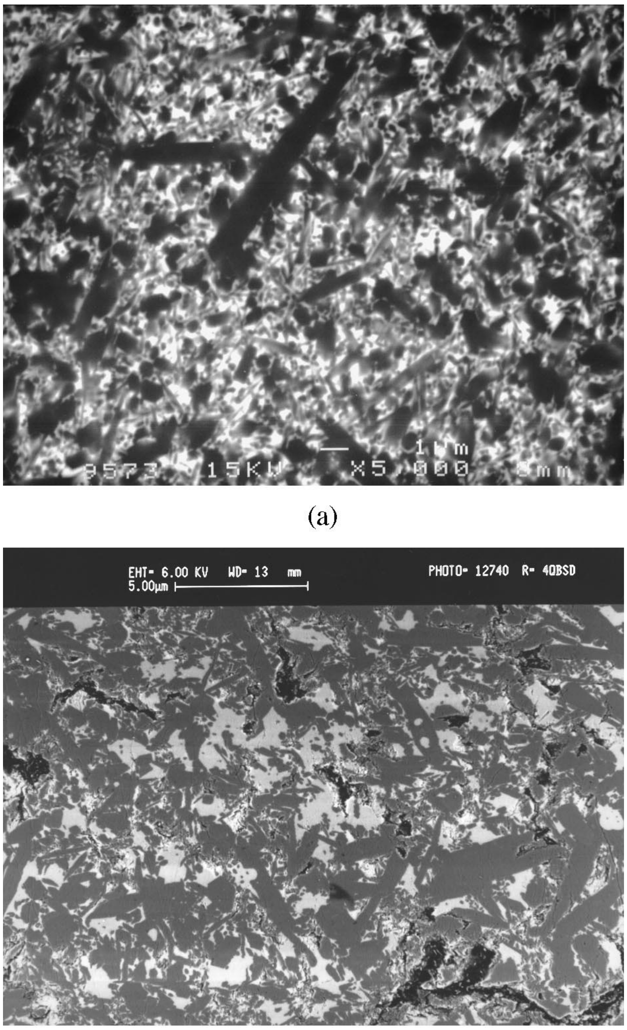


Fig. 4. SEM micrograph of the fracture surface of the material SPS processed at 1550°C.

(Tables 1 and 2), reflecting the time dependent nature of the transformation.

The XRD analysis for all the materials showed the presence of the major phases of Si_3N_4 and SiC (Tables 1 and 2). There are differences among the minor phases formed between SPS and sinter/HIPing for the same temperatures (Tables 1 and 2). A new phase (designated N) which has been indexed on a hexagonal unit-cell[5] was produced by both processes at temperatures below 1800°C. The N-apatite phase with an approximate composition of $Y_{3.5}La_{6.5}(SiO_4)N_2$[5] and the N-$\alpha$ Wollastonite phase are considered to be formed on crystallisation on cooling from the liquid phase, because the former is unstable at about 1400°C and the latter is unstable above 1600°C.[14] The rate of cooling in SPS is much faster than in sinter/HIPing, accounting for the absence of these two phases under SPS. The nitrogen rich phases N-mellilite ($Si_3N_4 \cdot Y_2O_3$) and $LaSi_3N_5$ are seen only in the sinter/HIP runs because these were carried out in a nitrogen atmosphere. No weight loss was observed at high temperatures even at 1900°C when Si_3N_4 begins to dissociate for the materials processed by SPS (Table 1). No evidence was apparent of a dissociation product on the surface of the pellet when analysed by XRD and EDS. Any condensed Si was not observed in the die walls.

The grain size of the materials processed by SPS at 1650°C was small and no elongated β Si_3N_4 grains were observed (Fig. 4). Elongated β Si_3N_4 grains were observed at 1750°C for materials sintered by both methods with 5min dwell time for SPS and no dwell time for sint/HIPed. This composition appears to be particularly effective in promoting the acicular microstructure as normally it is necessary to hold at high temperatures (~1700°C)



(a)

(b)

Fig. 5. SEM micrographs (backscattered) of polished surfaces of materials: (a) processed by SPS at 1900°C, (b) sinter/HIPed at 1800°C .White region is that of La, Y, Si, O, N glass and the dark grey grains are Si_3N_4 or SiC grains. Elongated grains are β Si_3N_4. Dark black areas are porosity.

for long times (~5 h) to form elongated grains.[15] The grain size of the β Si_3N_4 of materials processed by sint/HIP at 1800°C which had a dwell time of 160 min was similar to that of materials processed by SPS at the same temperature. The 1900°C SPS processed material had a larger grain size than the sinter/HIPed material at 1800°C (Fig. 5). It is interesting to note that this has occurred in these materials after a short time. There was no observed texture in the SPS processed material at 1900°C. Elongated grains imparts high fracture toughness and increased thermal conductivity, when aligned.[16]

4 Conclusions

These results show that Si_3N_4 can be rapidly sintered to high density by SPS processing. For example zero porosity was achieved with 10 min heating to about 1900°C with 5 min dwell time, whereas with conventional sinter/HIPing times of over 100min are required.

The composition studied here appears to be particularly effective in promoting the acicular β phase microstructure which was observed after only 5 min at 1750°C in both SPS and sinter/HIPing. There were some differences in the minor phases detected in the sintered materials, attributed to the faster cooling rate in the SPS process.

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