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The use of MgO-coated SiC powders as low temperature densification materials

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Abstract

The densification of silicon carbide powders at relatively low temperatures (i.e. 1900 °C and below) has been investigated as a means of lowering the cost of the production route for dense silicon carbide components. The work has concentrated on the use of MgO, as a coating on α-SiC powder deposited by chemical methods to allow densification by a liquid phase mechanism. Samples of SiC containing additions of MgO, both alone and as a coating on the surface of the SiC powder have been either hot pressed at temperatures between 1500 and 1750 °C or pressureless sintered at temperatures up to 1750 °C. Densification of the MgO-coated powder was observed to take place below 1650 °C and in certain cases a considerable amount of densification had taken place at temperature as low as ∼1450 °C.

Keywords: Sintering; SiC; MgO; Oxide-coating

1. Introduction

Silicon carbide (SiC) is a useful high temperature structural material because of its high strength, high hardness, and good creep resistance. For applications at temperatures below 1400 °C, the dense silicon-infiltrated varieties (REFEL, SiSiC, etc.) are often the most cost-effective choice. However, pure silicon carbide is very difficult to sinter because of its covalent nature. Prochazka[1] showed that small additions of boron and carbon achieved successful densification, but sintering temperature in excess of 1900 °C were needed. Due to the very high temperatures needed for solid state sintering of silicon carbide, there is a risk of unexpected grain growth which makes it difficult to control the microstructure and the related mechanical properties of technical materials.

In order to reduce the sintering temperature, and also to improve the mechanical properties, liquid phase sintering similar to that of silicon nitride was applied to silicon carbide. Using Al_2O_3–Y_2O_3 which is the most common additive system for Si_3N_4 the weight loss was high due to reactions of silicon carbide with the oxides at sintering temperature (approximately 1900 °C). Using an additive system consisting of Y_2O_3 and AlN, a better sintering behaviour was found. Due to the high stability of this additive system a powder bed was found to be unnecessary.[2,3]

Recently, the use of sintering additives such as Al_2O_3 plus Y_2O_3 as coatings on SiC powder by chemical methods has been reported to improve liquid phase sintering and the resulting microstructure.[4,5] The precipitation of Al and Y hydroxides often results in inhomogeneous microstructure in sintered SiC owing to the nonuniform coating of the SiC surface with the hydroxides. Furthermore, precipitation-coating is accompanied by an increase in specific surface area and a change of surface charge after the calcination of SiC powder. Sameshima et al.[6] have coated SiC powders with Al ions and densified by hot-pressing at 1650–1950 °C to achieve dense SiC materials. They concluded that if the SiC was coated uniformly with Al ions, the sample densified to 99% of relative density at 1900 °C.

Further work along these lines aimed at reducing sintering temperatures is clearly important. Magnesia was not originally used as a densification aid for silicon carbide due to the problems of volatilisation resulting from reactions with silicon carbide especially in the reducing furnace atmosphere. However, MgO is cheap, readily available and is established as a successful additive for the pressureless sintering of similar ceramics such as silicon nitride, by Terwilliger and Lange.[7] Research by Trigg and Jack[8] showed that if MgO could be retained within the compact

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Table 1
Densities of SiC coated with 5% MgO powders pressureless sintered at various temperatures and times

Temperature (°C)	Time (min)	Density (g cm^{-3})	Weight loss (wt.%)	XRD results: α-SiC always the major phase plus
1450	30	2.80	4.7 (gain)	$MgSiO_3$, α-$SiO_{2(s)}$
	120	2.84	4 (gain)	$MgSiO_3$, α-SiO_2
1550	30	3.09	7 (gain)	Mg_2SiO_4
1650	30	3.09	3.4	Mg_2SiO_4
	60	3.03	5.3	Mg_2SiO_4
1750	30	2.10	5.1	–

as part of a second phase (e.g. by addition of alumina to convert the MgO to $MgAl_2O_4$), then it was very useful as a densifying additive. However, again, quite high sintering temperatures were needed (1700 °C).

In the present study it was therefore hoped that effective densification of SiC might be promoted by providing the MgO additive as a coating, thereby enabling lower temperatures to be used for the sintering, which in conjunction with a powder bed would restrict volatilisation. The presence of MgO in a SiC powder compact is believed to provide a liquid phase at the sintering temperature by reactions with SiO_2 from the SiC powder grain surface, and also with the SiC itself. This should lower the temperature required for densification, thereby offering a more energy-efficient sintering route than provided by either the B/C or Y_2O_3/Al_2O_3 additive combinations. In Si_3N_4 sintered with MgO the liquid phase frequently does not recrystallise on cooling but forms a grain-boundary glass with a relatively low softening temperature,[9] imposing limitations on the high-temperature properties of the material (Lange et al.[10]). Similar restrictions are expected to apply to SiC materials densified with MgO.

2. Experimental

Silicon carbide coated with 5% MgO was prepared using magnesium methoxide in methanol with the coating procedure described elsewhere.[11,12] For comparison MgO powder (BDH Analar) was mixed with α-SiC (HC Starck Grade A10) powder (the latter consisting mainly of the 6H polytype with a small amount of 15R), by ball-milling for approximately 24 h, followed by drying and sieving. Cylindrical "green" pellets were formed by uniaxially pressing the powder mixtures in a steel die under a pressure of 94 MPa. The pellets were then isostatically pressed into thin discs, resulting in powder compacts typically of density 1.85 g cm^{-3}. Boot coated and mixed samples were pressureless-sintered over a range of temperatures for various lengths of time to compare the densification behaviour. The samples were sintered in packing powder containing MgO, in order to reduce weight loss by volatilisation. For each run a fresh powder bed mix of 50% BN, 45% SiC and 5% MgO was used. 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 Kα1 radiation, and microstructures were observed using a S-2400 Hitachi scanning electron microscope.

Table 2
Densities of SiC mixed with 5% MgO powder pressureless sintered at various temperatures and times

Temperature (°C)	Time (min)	Density (g cm^{-3})	Weight loss (wt.%)	XRD results
1450	30	2.05	4.0	α-SiC
	120	2.00	4.6	α-SiC
1550	30	2.01	4.1	α-SiC
1650	30	2.00	6.6	α-SiC
	60	2.03	5.3	α-SiC
1750	30	2.04	9.0	α-SiC

3. Results and discussion

Coated and mixed powder samples of SiC containing additions of 5 wt.% of MgO were pressureless sintered at temperatures between 1450 and 1750 °C shown in Tables 1 and 2. The samples were sintered in powder beds containing MgO, in order to reduce weight loss by volatilisation, and as with silicon nitride[12] a powder mix of 50% BN, 45% SiC and 5% MgO was used. The results shown in Table 1 were very surprising. What appears to have happened is that the coated samples either densify well (i.e. to a final density in excess of 90% of theoretical)

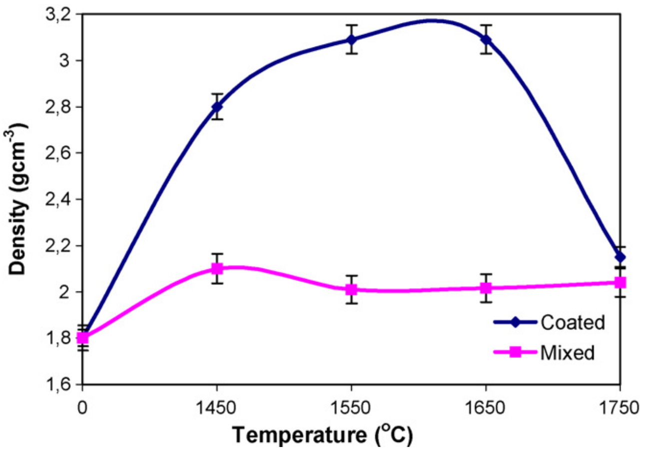

Fig. 1. Density as a function of temperature for SiC samples coated with 5% MgO pressureless sintered at various temperatures for 30 min.

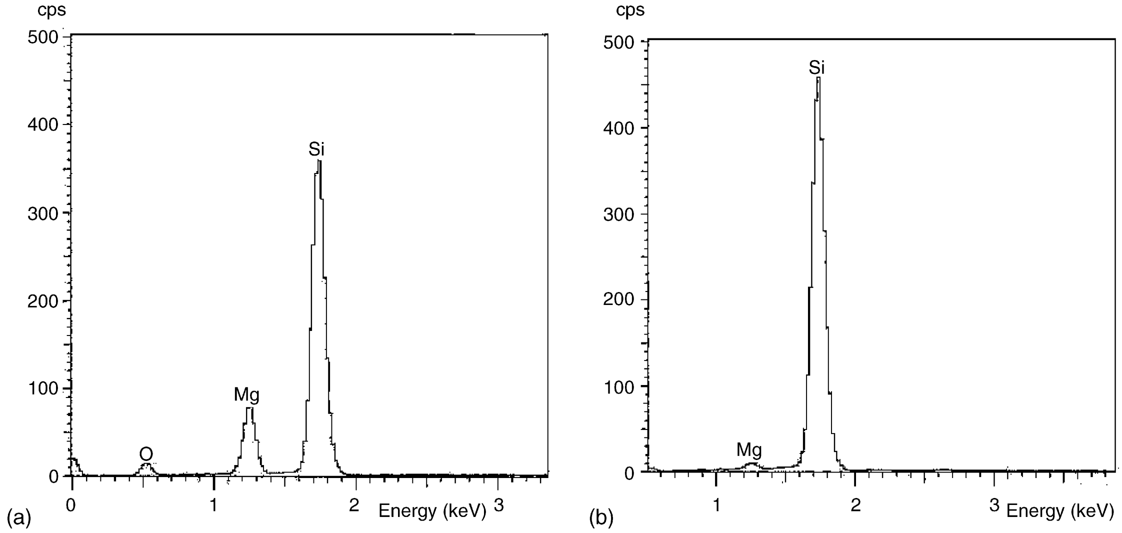

Fig. 2. EDX analyses for (a) coated and (b) mixed samples pressureless sintered at 1550 °C for 30 min.

as shown by the 1450–1650 samples, otherwise they do not densify at all (1750 °C sample). Table 2 shows that the mixed powder samples do not densify at any temperature. Fig. 1 also clearly shows that coated powders reproducibly exhibit 23–35% higher densities than particulate oxide powders up to 1650 °C temperatures when sintered under comparable conditions, the effect increasing slightly with increasing temperatures. After 1650 °C densities of both samples decrease dramatically. Weight loss would appear to play little part in influencing final density; thus 7% loss was experienced by the 3.09 g cm^{-3} coated sample sintered at 1550 °C whereas 4.1% loss was shown by the 2.01 g cm^{-3} mixed powder sample also sintered at 1550 °C. Another correlation, which is apparent from Tables 1 and 2 is that whenever crystalline oxide phases appear in the product, the density is high. It appears that MgO has reacted with SiC, and then dissolved in the liquid phase to give an enhanced amount of liquid, which has densified the sample and then crystallised during cooling to form various magnesium silicates. The absence of densification and secondary phases in the 1750 °C coated sample is probably because the volatility of magnesium at this temperature is so high that instead of dissolving in the silica liquid, the Mg released by MgO/SiC reaction has left the system; the residual SiO_2-rich liquid is then too viscous to effect densification.

In the case of the mixed powder samples, it is probable that the MgO and SiC do not react possibly because they are separated from each other by the layer of silica on the surface of the particle; moreover, the contact between the MgO and the surface silica on the SiC is at points, and this clearly promotes much slower reaction than when the MgO is present in the more active state provided by the coating process.

EDX results shown in Fig. 2, confirm that for the coated and mixed powder samples sintered at 1550 °C for 30 min, the coated samples (a) showed a strong Mg peak consistent with $MgSiO_3$, whereas the mixed powder sample (b) contained much less Mg then the coated sample. Both higher temperatures (1750 °C)

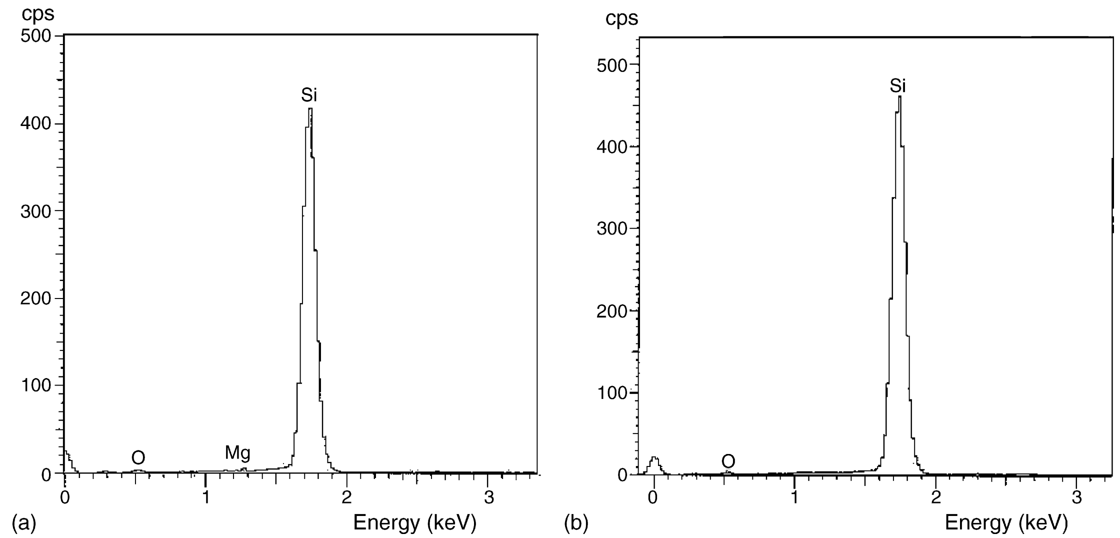

Fig. 3. EDX analyses for (a) coated and (b) mixed samples pressureless sintered at 1750 °C for 30 min.

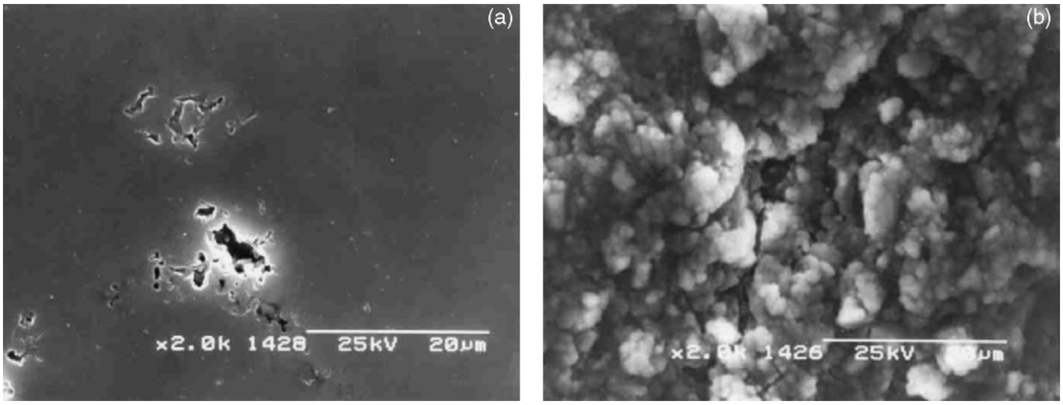

Fig. 4. SEM images of polished surfaces of (a) coated and (b) mixed SiC samples pressureless sintered with 5% MgO at 1450 °C for 30 min.

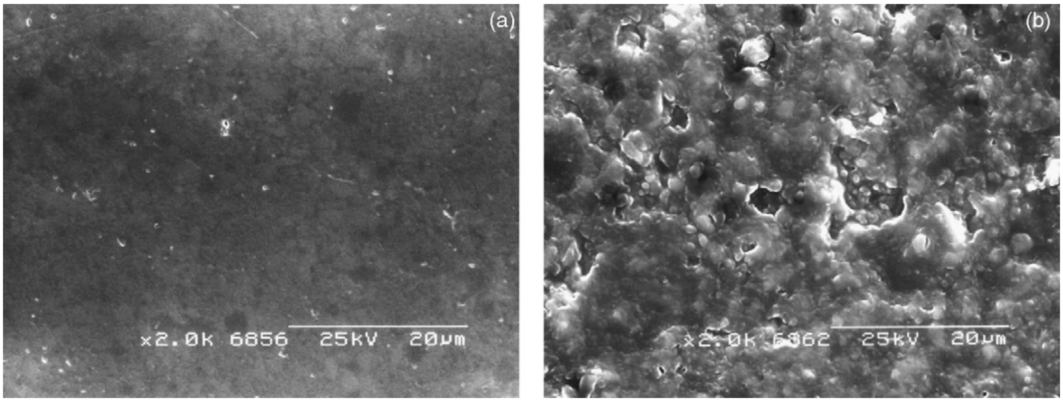

Fig. 5. SEM images of polished surfaces of (a) coated and (b) mixed SiC samples pressureless sintered with 5% MgO at 1650 °C for 30 min.

sintered samples (see Fig. 3a-coated, b-mixed) contained less Mg. In fact, EDX results indicated that these samples had lost almost all their original magnesia at the higher temperature.

Further confirmation that MgO/SiC reaction is responsible for the increase in liquid phase is provided by the X-ray results themselves. From calculations linked to the equation:

$$\mathrm{SiC(s)} + 4\mathrm{MgO} \rightarrow \mathrm{MgSiO_3(l)} + \mathrm{CO(g)} + 3\mathrm{Mg(g)} \qquad (1)$$

(and assuming that the original 1.1 w/o oxygen in the starting SiC powder doubles during processing, giving a silica content in the SiC of approx. 4%), a starting amount of 10 g of SiC plus 0.5 g MgO would generate 0.670 g of $MgSiO_3$ by direct MgO/SiO_2 reaction, and a further 0.144 g from Eq. (1), the total enstatite of 0.814 g being 8% of the final solid products. This is not inconsistent with the observed results; the simultaneous observation of cristobalite would arise if the liquid composition was more rich in silica.

The SEM micrographs shown in Figs. 4 and 5 for the α-SiC samples support the density curves shown in Fig. 1. The mixed powder samples are very porous at each sintering temperature, whilst the coated samples retain some porosity when sintered at 1450, but are essentially fully dense when sintered at 1550 and 1650 °C.

The introduction of MgO in the packing powder obviously has a beneficial effect on densification and deters weight loss by generating high partial pressures of MgO, Mg and SiO round the sample. With mixed powder samples, the effect of MgO volatilisation is too great and the powder bed is unable to prevent the escape of gaseous products.

4. Conclusion

The results described in this work show the exciting conclusion that α-SiC powders coated with 5% MgO can be densified by pressureless sintering to at least 95% of theoretical density at temperatures of 1550 °C. However, similar materials in which the MgO is present in particulate form show that no similar densification. An MgO-containing packing powder is important to avoid the MgO volatilising, but at temperatures above ∼1700 °C it is difficult to prevent MgO loss, and the final density is poor. Previous work by Trigg and Jack[8] showed that MgO reacted with SiC at sintering temperatures, and also that if the MgO remained in the liquid phase, it would promote densification. The surprise was that the process worked so well at such low temperatures.

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