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Liquid-phase sintering of SiC in presence of CaO

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Abstract

Two SiC samples S1 and S2 containing constant amount of Al_2O_3, Y_2O_3 (7 and 2 wt.%, respectively) and different amount of CaO (1 and 3 wt.%) as sintering aids were sintered to >95% of theoretical density (TD) at temperature between 1750 and 1900 °C. The densification occurred by a liquid phase formed among Al_2O_3, Y_2O_3 and CaO. A fine elongated and equiaxed grained (average grain size about ≤10 μm) microstructure was obtained. The mechanical properties in terms of hardness (HV), elastic modulus (E) and fracture toughness (K_{IC}) were also measured. Their amounts are also affected by the firing temperature and the obtained microstructure, i.e. by increasing the firing temperature, it is found that, the mechanical properties increase in S1 and S2 after firing up to 1800 °C and then decrease again at 1900 °C. These results confirm the results of densification, i.e. the maximum value of K_{IC}, HV and E were for the samples sintered at 1800 °C. Densification characteristics and microstructural development of the liquid phase-sintered β-SiC are described.

Keywords: A. Sintering; D. SiC; CaO additions

1. Introduction

Silicon carbide (SiC) is one of the promising candidate ceramics for high temperature structural components because of its excellent mechanical properties. SiC ceramics are being used in industry because they have several favorable properties such as high elastic modulus, fracture strength, toughness and hardness, good thermal and chemical stability, low thermal and electrical conductivities as well as relatively low thermal expansion coefficients [1–3].

There are two kinds of SiC powders, noncubic 6H(α)-SiC and cubic 3C(β)-SiC, which have different crystallographic structures or polytypes [4]. The mechanical strength of SiC ceramic from 6H powder is not as good as that of 3C-SiC. This is because sintered 6H-SiC consists of spherical or polyhedral grains, whereas the 3C-SiC consists of elongated grains forming an interlocked structure. This interlocking structure increases the fracture toughness of the ceramics [5].

The densification of SiC powders always needs sintering aids because of low sinterability of the covalent SiC itself. Depending on the kinds of the doped sintering aids, SiC may be densified to high density by either a solid-state or liquid-phase sintering mechanism. Sintering of SiC with B and C aids is regarded to take place by solid diffusion process [6]. This technology usually requires sintering temperatures higher than 2100 °C and easily results in exaggerated grain growth which is detrimental to mechanical properties. In contrast, the liquid-phase sintering process can be carried out at temperatures between 1850 and 2000 °C. A wide variety of rare-earth oxides, usually in combination with Al_2O_3 and/or boron compounds, could be used as sintering aids for SiC to accomplish a liquid-phase sintering process in which the oxides forms a liquid phase at a temperature as low as 2000 °C. It was recently shown that α-SiC powder with the addition of Al_2O_3 and Y_2O_3 could be sintered at lower temperatures (about 1850–2000 °C) than the conventional sintered boron- and carbon-doped SiC [7–9]. Mulla and Krstic [10] obtained dense SiC with equiaxed β grains by pressureless sintering of β-SiC powder with the addition of Al_2O_3 and Y_2O_3 at a temperature as low as 1850 °C, where the β to α transformation of SiC was suppressed. The sintering mechanism in these systems was attributed to liquid-phase sintering via the formation of an eutectic melt of Al_2O_3 and Y_2O_3 [7–10]. The objective of the present work is to study the sinterability of β-SiC ceramic materials by adding

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Table 1
Chemical impurities and physical properties as well as batch compositions of SiC starting powders

Impurities content		Physical properties		Batch composition (wt.%)		
Element	wt.% or ppm[a]			Materials	S1	S2
C	1.58	Surface area (m^2/g)	16	SiC	90	88
O	0.51	Sinter density (g/cm^3)	3.14	Al_2O_3	7	7
N	0.10	Green density (g/cm^3)	2.9	Y_2O_3	2	2
Fe	246[a]	wt. loss (%)	3.8	CaO	1	3
Ca	290[a]	Mean particle size (μm)	0.634	–	–	–
Al	105[a]	–	–	–	–	–
B	63[a]	–	–	–	–	–
Mo	39[a]	–	–	–	–	–

[a] Values given are in ppm.

Al_2O_3–Y_2O_3–CaO as a liquid phase. Elastic modulus (E), Vicker's hardness (HV) and fracture toughness (K_{IC}) and their relationship with phase composition and microstructure are also studied.

2. Materials and experimental

The starting silicon carbide powders were HSC 059 SiC (Superior Graphite Co., USA), with characteristics listed in Table 1. Ultra pure fine chemicals Al_2O_3, Y_2O_3 and CaO (Alfa Co., USA) were mixed with SiC powder as sintering aids. The batch compositions of the two prepared ceramic bodies S1 and S2 are also given in Table 1. The powder batches were ball-milled in methanol for 24 h. The resulting slurry mixtures were carefully dried and crushed by a roller in order to eliminate agglomerates in the powders. Ten grams of the mixed powder was uniaxially pressed at 50 MPa using a 1 in. diameter die and then cold isostatically pressed at 350 MPa. The specimens were packed in graphite crucible with a screwable lid. The inside packing powder sequences are graphite, SiC and Al_2O_3. Specimens were isothermally sintered at 1750, 1800 and 1900 °C in a graphite furnace (Astro Industry, Senata Rose) with flowing argon atmosphere to obtain dense ceramics. The outer skin of the specimens was removed using a 60 μm diamond impregnated net. Bulk density was measured by the Archimed's method. The relative density of sintered materials was calculated using the theoretical density of the Al_2O_3–Y_2O_3–CaO-doped SiC materials according to the rule of mixtures. The phase composition of the sintered SiC was examined by X-ray diffraction (XRD) with Cu Kα radiation (Norelco/Philips Diffractometer).

The microstructure of the polished selective surfaces were observed by a scanning electron microscope (SEM: GEOL, XL30). Fracture toughness (K_{IC}) was measured by the Vicker's indentation methods on specimens polished by 1-μm diamond paste; a 98-N load was applied. K_{IC} was

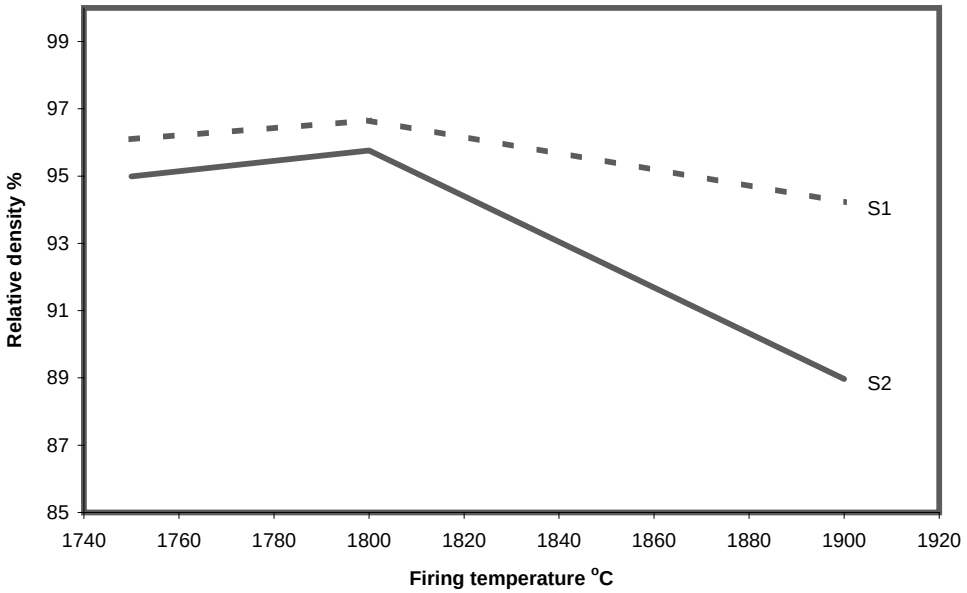

Fig. 1. Relative density of silicon carbide ceramics S1 and S2 sintered at different firing temperatures.

calculated from the following equation [11]:

$$K_{IC} = 0.016\left(\frac{E}{H}\right)^{1/2}\frac{P}{C^{3/2}}$$

where the ratio E/H of Young's modulus to hardness was obtained by the Knoop indentation method [12], P is the peak load and C is the radial crack dimension.

3. Results and discussion

3.1. Sinterability of SiC

The difficulties with the sintering of silicon carbide ceramics have been attributed to the covalent nature of its chemical bond, particularly to the low surface energy and low self-diffusion coefficient resulting from the covalent bond. Successful sintering of silicon carbide has been reported and liquid-phase promotion or additives to improve diffusivity and surface energy were usually needed for the sintering. The most promising additives for liquid phase sintering are metallic or oxide forms, such as aluminum, mixtures of alumina and yttria, and carbon and boron [13–23]. However, a problem here is that the oxides react with SiC in volatilizing SiO, Al_2O and CO gases. Complete densification is difficult by normal sintering with oxide additives. Fig. 1 shows the relative density of sintered SiC samples (S1 and S2) at different firing temperature. It can be seen that densification occurs at 1750 °C, which approaches the melting point of Al_2O_3–Y_2O_3 (YAG) [24], suggesting that sintering occurs thanks to formation of YAG liquid phase. S1 sample appeared to be more sintered than S2. The higher relative density of S1 than S2 is related to the higher CaO content in S2 which seems to increase the volatilizing of SiO, Al_2O and CO gases and consequently decrease relative density. In both samples, the relative density is generally increase after firing up to 1800 °C with a maximum relative density of about 97 and 96%, respectively and then decreases after firing up to 1900 °C. This phenomena seems to be due to increasing of volatilizing of SiO and CO with raising the firing temperature up to 1900 °C.

3.2. Phase composition and microstructure

Fig. 2 shows X-ray diffraction patterns of sintered silicon carbide S1 and S2 after firing at 1750 and 1800 °C. From this analysis, β-SiC peaks with relatively higher intensity in S2 than S1 are evidenced. Both samples exhibit a peak of $Al_5Y_3O_{12}$ (YAG). By increasing the amount of CaO as going form S1 to S2, a new oxide phase (CaY_2O_4) appeared. Also, few amounts of α-SiC were detected in both samples. Their amount is higher in S2 than S1 and increases with increasing sintering temperature. This amount of α-SiC is produced from transformation of β-SiC.

The existence of $Al_5Y_3O_{12}$ and CaY_2O_4 as liquid phases, seems to enhance the sintering at 1800 °C by activation of a rapid diffusion path at the grain boundary [6].

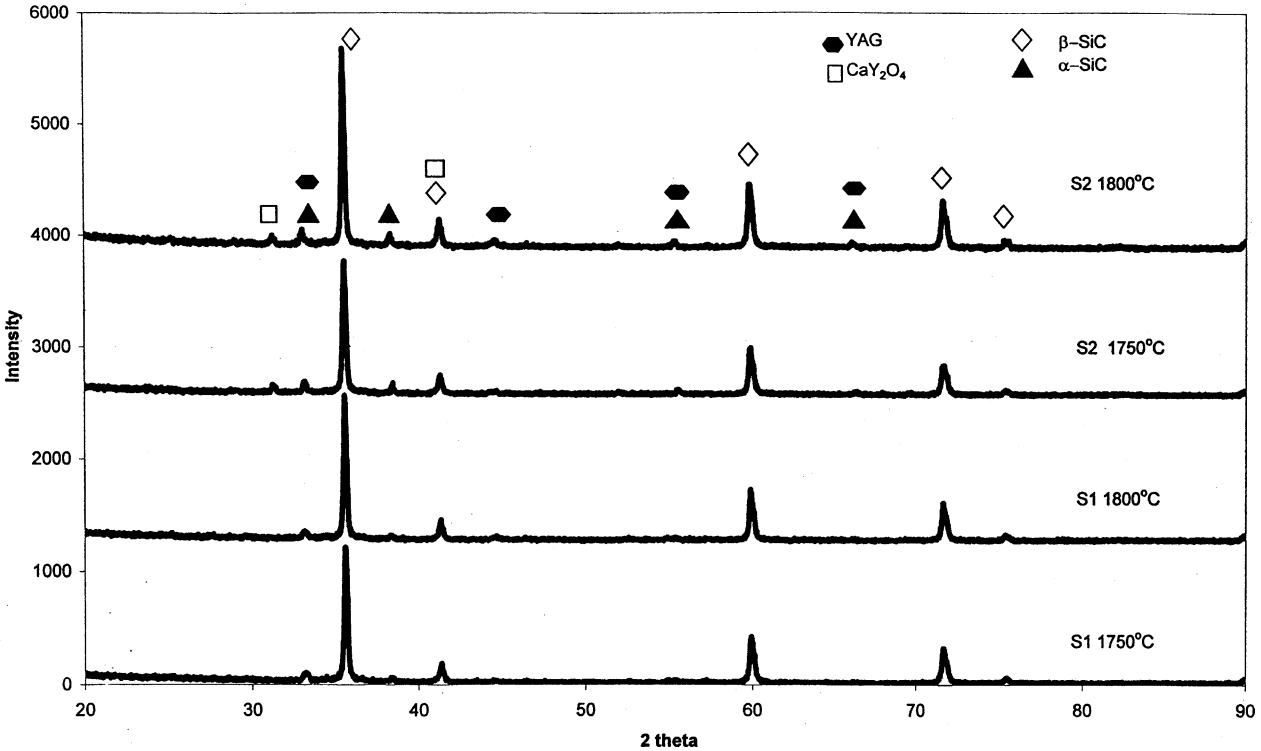

Fig. 2. XRD of silicon carbide ceramics S1 and S2 sintered at 1750 and 1800 °C.

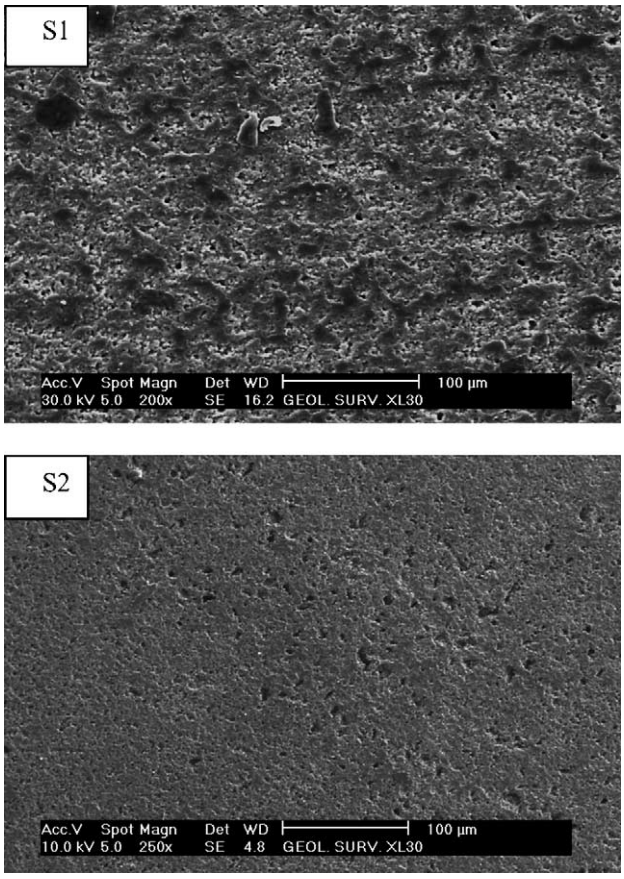

Fig. 3. Microstructure of silicon carbide ceramics S1 and S2 sintered at 1800 °C.

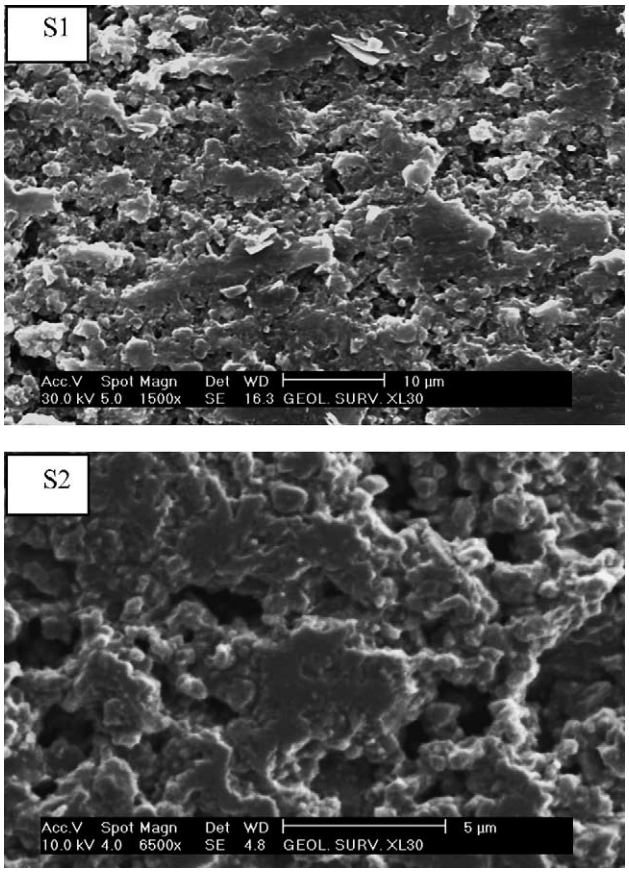

Fig. 4. SEM of the fracture surfaces of silicon carbide ceramics S1 and S2 sintered at 1800 °C.

The microstructures of silicon carbide ceramics (S1 and S2) sintered at 1800 °C are shown in Fig. 3. The use of low sintering temperatures and short sintering times allows submicron grain size to be retained with moderate grain growth. Both S1 and S2 show a fine grain size of about $\leq$10 and $\leq$5 μm, respectively. The micrographs show also the presence of fine elongated grains in S1 and equiaxed grains in S2, each covered with a very thin layer of grain-boundary phase.

The fractographs (Fig. 4) show that the fracture mode of specimens S1 and S2 was a mixture of intergranular (majority) and transgranular (minority) fracture due to a weak interface resulting from thermal expansion mismatch between liquid phase and matrix on cooling after sintering [25,26]. As shown in Fig. 3, the sintering additives (Al_2O_3–Y_2O_3–CaO) seem to reside at the grain boundaries and constitute the grain boundary phases. It is known that [6] the difference in the grain boundary chemistry (oxide versus non-oxide) would lead to the differences in the thermoelastic properties of the grain boundary phases themselves and the chemical bonding strength between the SiC grains and the grain boundary phases, which results in different interfacial strength. A strong interface would hinder the occurrence of interfacial debonding, which is a basic premise for the crack bridging process.

3.3. Mechanical properties

It has been reported that K_{IC} of liquid-phase-sintered SiC were generally higher than that of boron- and carbon-doped SiC due to the toughening effects of crack deflection that resulted from a weak interface [25–27].

Some authors [10] showed that the presence of α-SiC type weaken the material. Also the fraction toughness of SiC ceramic depends on its type (β- or α-) and grain morphology, i.e. main grain size and porosity of the sintered specimens [28,29]. Table 2 summarizes mechanical properties, i.e. Vickers hardness (HV), Young's modulus (E), and fracture toughness (K_{IC}) of S1 and S2 sintered at different firing temperatures. It appears generally that the mechanical prop-

Table 2
Fracture toughness (K_{IC}), hardness (HV) as well as elastic modulus (E) of the sintered SiC at different temperatures

Properties	Firing temperature (°C)					
	1750		1800		1900	
	S1	S2	S1	S2	S1	S2
K_{IC} (MPa m$^{1/2}$)	4.1	3.9	5.7	4.2	4.5	4.0
HV (GPa)	20.7	19.2	23.2	22.12	22.6	20.0
E (GPa)	290	280	410	380	330	310

erties are more elevated for a firing temperature of 1800 °C, then decrease at 1900 °C. This agrees with the densification trend, suggesting that the mechanical properties depend essentially on the porosity of the sintered ceramics. Also the overall mechanical properties (hardness and fracture toughness) of S1 are higher than those of S2 in spite of the relatively higher grain size of S1. This can be attributed, again, to the higher densification of S1 and also to the presence of relatively fine elongated grain in this sample. It was found that, the combination of Al_2O_3 and Y_2O_3 as additives have attracted particular attention in recent years because of their ability to provide an in situ toughened material by crack bridging or deflection [30] with a microstructure consisting of elongated SiC grains [17,30].

4. Conclusions

It has been found that a silicon carbide containing Al_2O_3, Y_2O_3 and CaO can be sintered to above 95% of theoretical density at a temperature as low as 1800 °C due to liquid phase formation. Silicon carbide ceramic containing 1% CaO (S1 sample) showed higher relative density than that containing 3% CaO (S2 sample). This seems to be due to the higher volatilizing of SiO, Al_2O and CO in S2 sample. Doping with Al_2O_3, Y_2O_3 and CaO as additive to β-SiC starting powder resulted in a fine microstructure with grain size of about 10 μm for the sample containing 1% CaO and 5 μm for that containing 3% CaO. The porosity and microstructure of the sintered bodies affected the mechanical properties, namely Young's modulus, Vickers hardness and fracture toughness. The maxims of such properties occurred at a sintering temperature of 1800 °C.

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