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The Spark Plasma Sintering of Silicon Carbide Ceramics Using Alumina

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SiC ceramics were fabricated by spark plasma sintering technique with the use of Al_2O_3 additive. The sintering process was carried out at three different temperatures in the range of 1700–1800 °C applying two different pressures 40 and 80 MPa under vacuum atmosphere. The effect of additive, different temperatures and pressures on densification behaviour, density, Vickers hardness, fracture toughness, and microstructure were examined. The hardness and fracture toughness of the samples were evaluated by the Vickers indentation technique. Microstructure of spark plasma sintered SiC samples were characterized by using scanning electron microscopy technique. The highest value of fracture toughness 5.9 ± 0.2 MPa $m^{1/2}$ was achieved with the addition of 5 vol.% Al_2O_3.

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1. Introduction

Silicon carbide is a very interesting ceramic material due to its properties like high hardness, low bulk density, high oxidation resistance, excellent mechanical strength, and thermal stability which made SiC useful for a wide range of industrial application [1, 2]. One of the greatest drawbacks in the manufacture of SiC is the difficulty in sintering dense samples without the use of additives. This is because the covalent nature of the Si–C bonds and the low self-diffusion coefficients require very high sintering temperatures and pressures [3]. Depending on the kinds of doped sintering aids, SiC may be densified to high density by either a solid-state or liquid phase sintering mechanisms. Sintering of SiC with the aid of B and C is regarded to take place by solid-state diffusion process. This technology requires sintering temperatures of more than 2100 °C and easily results in exaggerated grain growth, which is hazardous to the mechanical properties [4].

In the recent years, liquid phase silicon carbide has been developed as a material with a higher fracture toughness than the solid phase sintered SiC but with a similar hardness. The use of yttria or other rare earth oxides and Al_2O_3 or AlN as sintering additives, which form together with the SiO_2 existing on the surface of the starting SiC-powder, a liquid phase during the sintering, promotes the densification and microstructural development [5, 6]. Liquid phase sintering allows densification of SiC at temperatures close to 1900 °C without the use of external pressures. These temperatures are much lower than the close to 2200 °C required by the conventional solid-state sintering [3]. The liquid-phase sintered SiC ceramics have high fracture toughness compared with solid phase sintered SiC, because the elongated grains can form during liquid-phase sintering [7]. However, a major problem associated with sintering of silicon carbide in the presence of oxide additives is the reaction between the silicon carbide and the oxides. The major weight loss in the $SiC–Al_2O_3–Y_2O_3$ system during sintering is a result of the formation of gaseous CO, SiO, Al_2O, and Al [5].

The objective of this work is to rapidly densify SiC powders with the use of Al_2O_3 additive and investigate the influence of the additive and the spark plasma sintering (SPS) temperature and pressure on the microstructure, densification behaviour and some mechanical properties.

2. Experimental procedure

The samples were prepared starting from α-SiC powder (UF-10 H.C. Starck, Germany) with its average particle size of 0.7 μm and 5 vol.% α-Al_2O_3 (Inframat Advanced Materials) with its average particle size of 100 nm as additive. The oxygen content in the starting powder was 0.74 wt%. The powders were wet-mixed in ethanol with SiC balls in a plastic bottle to ensure homogeneity. Then, the slurry was dried at 100 °C for 24 h in an oven and ethanol was removed. After drying and sieving to 150 μm, a graphite die with a 50 mm inner diameter was filled with the powder, and they were sintered by the SPS technique (SPS-7.40MK-VII, SPS Syntex Inc.) under a vacuum atmosphere by applying 40 and 80 MPa of pressure. The sintering process was carried out at three different temperatures in the range of 1700–1800 °C with a heating rate of 100 °C/min under a vacuum atmosphere.

In order to compare the densification behaviour of $SiC–Al_2O_3$ ceramics with monolithic SiC ceramics, the α-SiC powder (UF-10 H.C. Starck, Germany) was prepared with the same powder preparation procedure and spark plasma sintered at four different temperatures in the range of 1800–1950 °C under two different pressures, 40 MPa and 80 MPa with a heating rate of 100 °C/min under a vacuum atmosphere without using sintering additives.

The temperature of the SPS process was measured with an optical pyrometer that was focused on the surface of the die. The current was controlled manually. Linear shrinkage of the specimens during the SPS process was continuously monitored by displacement of the punch rods. After soaking the powder at a desired temperature for 5 min, the applied current was reduced, the pressure was released, and the specimen was cooled down to room temperature. The densified samples were in the form of disks 50 mm in diameter and 5 mm thick and sand-blasted to remove the graphitic sheet.

The densities of the sintered bodies were measured by Archimedes' method in distilled water. Samples were polished by using diamond polishing solution. The hardness and fracture toughness (K_{IC}) of the samples were evaluated by the Vickers indentation technique at a load of 49 N (Struers, Duramin A300). Fracture toughness values were determined by measuring the half-length of a crack formed around the indentations and calculated by using the following equation:

$$K_{\mathrm{IC}} = 0.016(E/H)^{1/2} \times (P/C^{3/2}), \qquad (1)$$

where K_{IC} is the fracture toughness, E is the elastic modulus, H is the hardness, P is the load and $2C$ is the full crack length produced by the Vickers HV indentation. The hardness and fracture toughness data were averaged over ten measurements. Microstructural investigation was performed by a scanning electron microscope (SEM, model JSM 7000F, JEOL, Japan) on a fracture surface.

3. Results and discussion

The densification of specimens during the SPS process was evaluated by the displacement of punch rods due to the shrinkage of samples. Figure 1 shows the effect of the sintering pressure and temperature on the displacement of the monolithic SiC ceramics SPSed at 1800 °C under a pressure of 40 MPa (Fig. 1a), SPSed at 1950 °C under a pressure of 80 MPa (Fig. 1b), and Al_2O_3 added SiC ceramics SPSed at 1800 °C under a pressure of 40 MPa (Fig. 1c) under a pressure of 80 MPa (Fig. 1d) with a 5 min soaking time under a vacuum atmosphere.

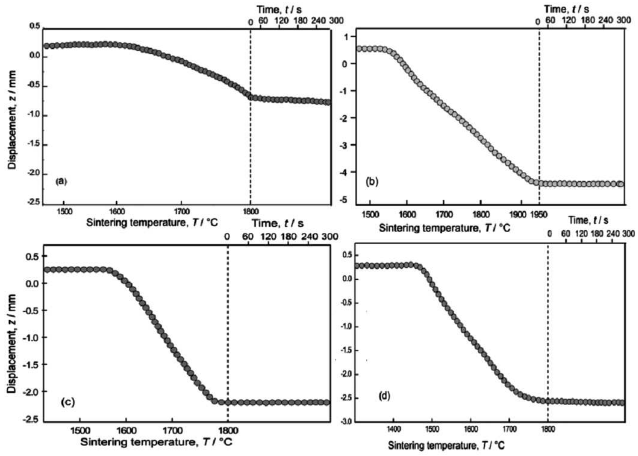

Fig. 1. Effect of sintering temperature on the displacement of the SiC ceramics (a) SPSed at 1800 °C under a pressure of 40 MPa, (b) SPSed at 1950 °C under a pressure of 80 MPa, (c) SiC+5 vol.% Al_2O_3 SPSed at 1800 °C under a pressure of 40 MPa, (d) SiC+5 vol.% Al_2O_3 SPSed at 1800 °C under a pressure of 80 MPa.

The monolithic SiC ceramic heated to 1800 °C while applying 40 MPa of pressure began to shrink at 1637 °C, and shrinking was completed at 1800 °C, whereas the specimen SPSed at 1950 °C while applying 80 MPa of pressure started to shrink at 1530 °C, and shrinking was completed at 1950 °C. An increase in the applied SPS temperature and pressure decreased the starting temperatures of shrinkage. Moreover, the higher the applied pressure during SPS treatment, the higher the densification process. For the sample containing 5 vol.% Al_2O_3 additive and SPSed at 1800 °C under a pressure of 40 MPa the shrinkage started at 1540 °C. An increase in the applied pressure from 40 to 80 MPa decreased the starting temperature of shrinkage to 1490 °C. The addition of 5 vol.% Al_2O_3 resulted in a decrease in the shrinkage starting temperature from 1637 °C to 1540 °C for the sample SPSed at 1800 °C under a pressure of 40 MPa.

For the monolithic SiC samples, as the sintering temperature and pressure were increased from 1800 °C to 1950 °C and 40 MPa to 80 MPa, respectively, the relative density of the bulk compact increased from 87% to 99.7% due to the pore elimination and expedited rearrangement of the grains. Higher sintering temperatures resulted in higher densification rates of spark plasma sintered SiC ceramics, which led to a decrease in porosity. The highest relative density value obtained was approximately 99.7% for the sample SPSed at 1950 °C while applying 80 MPa of pressure, revealing that the sintering pressure has a significant influence on the relative density of the SiC ceramics in case of the solid state sintering. The use of Al_2O_3 as a sintering additive, which reacts with the SiO_2 existing on the surface of the starting SiC-powder, forms a liquid phase during the sintering process and the liquid promotes the densification. The addition of 5 vol.% Al_2O_3 resulted in an increase in relative density from 87% to 97.7% for the samples SPSed at 1800 °C under a pressure of 40 MPa. This result is in a good correlation with the liquid phase sintering which enhances the densification.

Figure 2 shows the SEM images of the fracture surfaces of both monolithic and the samples containing 5 vol.% Al_2O_3 additive. Both liquid phase and solid state sintering mechanisms can be observed under the same SPS conditions (Fig. 2a–c). Homogeneous and fine-grained microstructures were obtained by liquid phase sintering (Fig. 2c,d).

Additionally, a slight increase in grain size can be observed in the samples SPSed at relatively higher temperatures (Fig. 2b). More pores were investigated on the fracture surface of the ceramic SPSed at 1800 °C while applying 40 MPa of pressure. Correspondingly, the relative density of the ceramic SPSed with these parameters is only 87.2%. Few pores were detected on the fracture surface of the ceramic SPSed at 1950 °C while applying 80 MPa pressure; increasing the sintering temperature and pressure results in a decrease in porosity, producing a sample with almost the full density (99.7%).

The Vickers hardness value of 10.2 GPa was attained in the sample spark plasma sintered at 1800 °C under an applied pressure of 40 MPa; however, increasing the sinter-

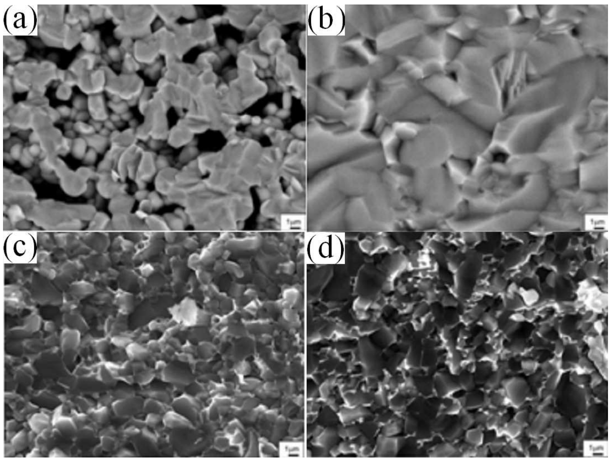

Fig. 2. SEM images of fracture surfaces of SiC ceramics (a) SPSed at 1800 °C under a pressure of 40 MPa, (b) SPSed at 1950 °C under a pressure of 80 MPa, (c) SiC+5 vol.% Al_2O_3 SPSed at 1800 °C under a pressure of 40 MPa, (d) SiC+5 vol.% Al_2O_3 SPSed at 1800 °C under a pressure of 80 MPa.

ing temperature to 1950 °C caused it to reach 31.9 GPa. It was concluded that a higher sintering temperature and pressure led to an increase in the Vickers hardness of the SiC ceramics due to accelerated densification results in the value of the relative density. The addition of 5 vol.% Al_2O_3 increased the Vickers hardness from 10.2 to 26.8 GPa for the samples SPSed at 1800 °C while applying 40 MPa of pressure (Table).

TABLE

Relative density, Vickers hardness and fracture toughness values of the SPSed ceramics.

Samples	SPS parameters [°C, MPa, min]	Relative density [%]	Vickers hardness [GPa]	Fracture toughness [MPa $m^{1/2}$]
SiC+5vol.% Al_2O_3	1700, 40, 5	97.7	26.4	4.6 ± 0.2
	1750, 40, 5	97.7	26.7	4.7 ± 0.3
	1800, 40, 5	97.8	26.9	5.8 ± 0.5
	1700, 80, 5	97.5	26.2	5.7 ± 0.2
	1750, 80, 5	98.2	28.6	5.5 ± 0.4
	1800, 80, 5	98.3	28.9	5.9 ± 0.2
monolithic SiC	1800, 40, 5	87.2	10.2	–
	1950, 80, 5	99.7	31.9	3.6 ± 0.3

The fracture toughness that could be achieved, 3.6 ± 0.3 MPa $m^{1/2}$, was with the sample SPSed at 1950 °C while applying 80 MPa of pressure. For the monolithic SiC ceramic SPSed at 1800 °C while applying 40 MPa of pressure, fracture toughness cannot be determined because of its lower density. The addition of 5 vol.% Al_2O_3 increased the fracture toughness value to 5.8 ± 0.5 MPa $m^{1/2}$ for the sample SPSed at 1800 °C under an applied pressure of 40 MPa. The mechanical properties of ceramics are largely dependent on the microstructure. The liquid phase sintered ceramics have high fracture toughness compared with the solid-phase sintered SiC, because the elongated grains can form during liquid phase sintering [7].

4. Conclusions

SiC ceramics were consolidated by both solid state and liquid phase sintering mechanisms using spark plasma sintering technique. The results of this study showed that relative density of approximately 99% was obtained for the solid state sintered monolithic SiC ceramic. Increased sintering temperature and pressure led to an increase in the relative density, Vickers hardness and fracture toughness of the monolithic SiC ceramics. The use of Al_2O_3 as a sintering additive which reacts with the SiO_2, forms a liquid phase during the sintering process and the liquid enhances the densification. Hence, the addition of 5 vol.% Al_2O_3 resulted in an increase in relative density and Vickers hardness from 87.2% to 97.7% and 10.2 to 26.8 GPa, respectively, for the samples SPSed at 1800 °C under a pressure of 40 MPa. Moreover, the addition of 5 vol.% Al_2O_3 decreased the densification temperature and increased the fracture toughness value to 5.8 ± 0.5 MPa $m^{1/2}$ for the samples SPSed at 1800 °C under a pressure of 40 MPa. Increase in applied pressure did not have a significant effect on the relative density, Vickers hardness and fracture toughness values for the samples containing 5 vol.% Al_2O_3.

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