

Sintering of nano crystalline α silicon carbide doping with aluminium nitride

M S DATTA, A K BANDYOPADHYAY* and B CHAUDHURI

Department of Metallurgical Engineering, Jadavpur University, Kolkata 700 032, India

*College of Ceramic Technology, Kolkata 700 010, India

MS received 1 October 2001; revised 8 February 2002

Abstract. Sinterable silicon carbide powders were prepared by attrition milling and chemical processing of an acheson type α -SiC. Pressureless sintering of these powders was achieved by addition of aluminium nitride together with carbon. Nearly 99% sintered density was obtained. The mechanism of sintering was studied by scanning electron microscopy and transmission electron microscopy. This study shows that the mechanism is a solid state sintering process.

Keywords. Sintering mechanism; silicon carbide; aluminium nitride; polytype.

1. Introduction

Silicon carbide found many applications in the high temperature field. Due to the amount of covalent bonding in silicon carbide, it is not possible to obtain high densities with pure material by using a normal sintering process. The hot pressing technique with additions of small amounts of boron, aluminium among others (Alliegio *et al* 1956) is well known but is limited to the production of rather simple shape. Hot pressing may be used for fabrication of more complicated geometrics.

Pressureless sintering of silicon carbide was reported by Prochazka (1975) who synthesized β silicon carbide in the submicron range which was sintered after addition of boron and carbon at 2050°C to 2150°C to densities of 95 to 96% of theoretical density in argon atmosphere. Three years later, Coppola and Mcmurty (1976) achieved sintering of the more readily accessible alpha-silicon carbide powder in a mixture with boron and carbon containing additives. However, in both boron doped sintered alpha-silicon and beta-silicon carbides, exaggerated grain growth was observed (Johnson and Prochazka 1977) if the sintering temperature exceeded a critical limit. The microstructure of boron doped SiC sintered at >2075°C usually contains large tabular grains, which may act as stress concentrators and seriously degrade the strength properties.

In this paper, we report studies of sinterability of nano crystalline alpha silicon carbide with addition of aluminium nitride, its effect on microstructure and the mechanism of sintering.

2. Experimental

2.1 Powder preparation and characteristics

A commercially available acheson type alpha silicon carbide powder of grade 1000 from M/s Grindwell Norton Ltd, India, with a silicon carbide content of 98.7% and a specific surface area of 1.5 m²/g (measured by Surface Analyser, Micromeritics, USA) was used as a starting material. After milling in an attrition mill (Model PRIS of M/s Metisch Feinmath Technik GmbH) with a special active agent for oxygen removal for 12 h at a pH of 9, the iron wear was removed by a treatment with hydrochloric acid. An excess carbon in the powder was burnt off in air at 700°C. Since a slight oxidation of the silicon carbide powder occurs under these conditions, the powder was treated with hydrofluoric acid to remove the silica formed on the surface of the powders. The powder's characteristic is given in table 1 and the particle size distribution was measured using a particle size analyser Malvern Autosizer 2C (M/s Malvern Instruments Ltd, UK) and is shown in figure 2 and the particles were also seen using a transmission electron microscope (figure 1). The final processed powder has a mean size of 37 nm.

2.2 Sintering additives

Aluminium nitride was used as sintering aid along with phenolic resin which was used as a source for carbon. Phenolic resin pyrolyzes at high temperature with carbon yield of 47%.

2.3 Sample preparation

The silicon carbide and the additives were mixed under acetone and 1 wt% of oleic acid was added in solution as

*Author for correspondence

pressing aid. After drying of the slurry at 80°C, the mixture was passed through a sieve of mesh 60 and compacted isostatically at a pressure of 270 MPa to a green density of 62% of the theoretical density of silicon carbide.

2.4 Sintering

Sintering was carried out on bars of 50 × 10 × 20 mm and on pellets of size 10 mm in diameter × 10 mm in thickness in vacuum (3 mbar) atmosphere in an Astro Furnace (Model No. 1000-3600-FP-20-F8204025 of M/s Thermal Technology Inc, USA) at the temperature of 2050°C for 15 min.

2.5 Sample preparation for TEM study

For TEM study, cylindrical specimen of 3 mm diameter and 1 mm high, a size suitable for the fabrication of TEM specimens, was cut directly from the bulk sintered pellets of alpha silicon carbide. Specimens were prepared from these samples by mechanical thinning to $\approx 75 \mu\text{m}$, followed by dimpling and subsequent low-energy (5 to 6 kV) and low angle (15°) Ar⁺ ion beam milling. The

Table 1. Powder characteristics.

Phase composition		Mainly α -SiC
Total carbon	Wt%	30.27%
Free carbon	Wt%	1%
Impurities		
Al		125
Fe	PPM	130
Ca		150
Specific surface area	m ² /s	40.5
Equivalent particle size	nm	37

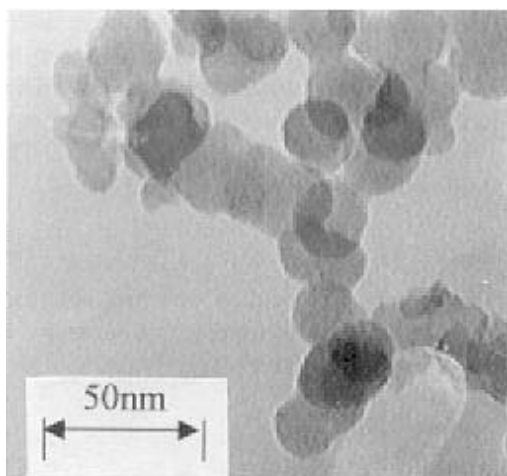


Figure 1. Transmission electron micrograph of processed α -SiC powder.

films were examined in transmission electron microscope operated at an accelerating voltage of 100 kV.

3. Results and discussion

Nano crystalline particles were developed by attrition grinding as is evident from figures 1 and 2.

The change in bulk density of sintered body as a function of aluminium nitride concentration was measured in terms of different sintering temperatures. The results obtained are shown in figure 3, where one can see that the maximum sintered density is obtained at 2 wt% AlN concentration at each temperature from 2000–2100°C. These results were obtained at constant amount of carbon addition (1 wt%). Above 2 wt% AlN concentrations, density decreases from its peak value.

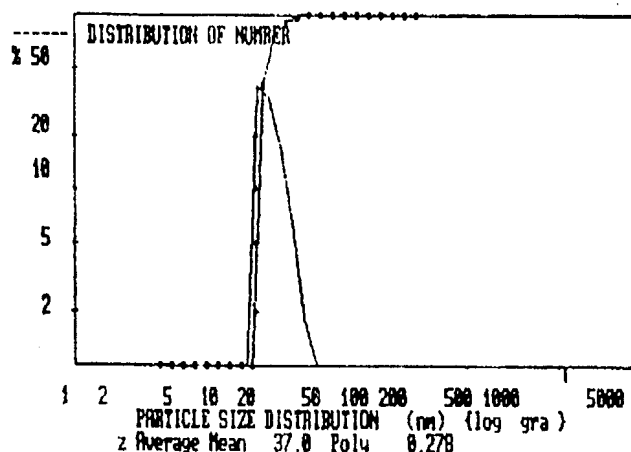


Figure 2. Particle size distribution.

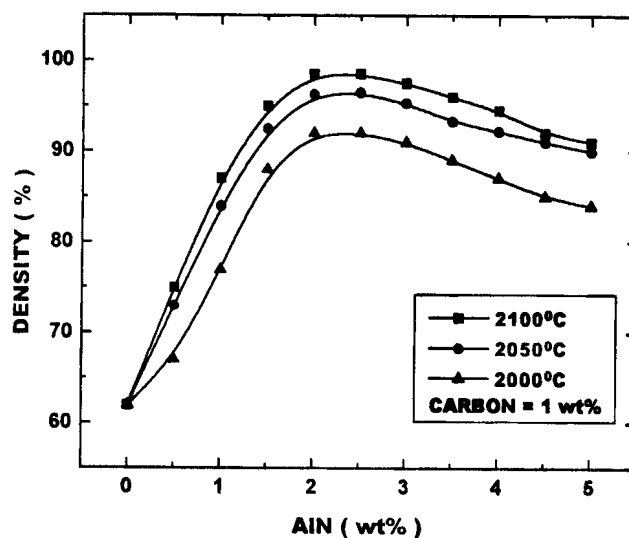


Figure 3. Effect of aluminium nitride content on sintered density.

It is a significant result that sintered density changes from 62% theoretical density to 99% theoretical density at 2 wt% AlN at a temperature of 2100°C at time of 15 min under vacuum (3 mbar). This suggests that the solid solubility of Al in SiC may be 1 wt% from 2000–2100°C. As a matter of fact, the body having 99% TD exhibits a dense microstructure with relatively fine grains, the average size of which is around 5.7 μm . Two types of porosity could be identified in the microstructure which are (i) between grain-boundaries and (ii) within the bulk crystal. The latter were developed during grain growth of the original submicron size SiC grain. The needlelike growth of grains of SiC pointed out to the fact that the rate of crystallization from the original rather spherical particles produced by grinding and leaching etc has been very fast, favouring growth in a particular direction according to energy consideration. Due to growth from 0.037 μm to 5.7 μm (figure 4), it is suggested that a group of grains after sintering should have the grain boundaries with relatively low energy.

To examine the effect of carbon on sintered density, experiments were made with the compositions containing a constant amount of AlN (2 wt%) and varied amounts of carbon from zero to 5 wt% (figure 5).

In figure 5, the effect of carbon content on densification is shown in which the maximum density is obtained at 1 wt% carbon at each temperature from 2000–2100°C. The curves shown in figure 5 also demonstrate that the addition of carbon is quite effective for enhancing the sintered density. For instance, at zero% carbon, the sintered density is 2.15 g/cm^3 , which is only an increase of 7.5% from green density of 2 g/cm^3 . The density increases almost linearly with increasing carbon content up to 1 wt% and above 1 wt%, it becomes almost saturated. The role of carbon during sintering of silicon carbide is primarily to be (i) the de-oxidation of SiO_2 films origi-

nally developed on silicon carbide grains, (ii) to coat the surface of silicon carbide to lower the free energy of the surface and consequently lowering the surface vapour energy and (iii) to decrease the diffusivity of C atom to match with diffusivity of Si atom essential for effective sintering. One of the roles of carbon during sintering of SiC was examined by measurement of grain size of the sintered body. It was found that grain size decreases with increasing carbon content. This means that carbon is a surface vapour energy and thus prevents vapour surface transport responsible for grain growth.

In figure 3, the sintering density of α -SiC samples with aluminium nitride addition are shown. In order to achieve high sintered density the simultaneous addition of carbon is necessary like in the case of boron addition. The density increases with an increasing aluminium nitride content up to a maximum of 3.16 g/cm^3 or 98.4% of theoretical density through an addition of aluminium nitride of 2 wt%. On molar basis, this corresponds almost to the same amount which was found as an optimum concentration in the case of boron addition. A further increase in the aluminium nitride concentration lowers the sintered density again. The effect of carbon has also been studied. At zero carbon content, the density did not increase. With the increase of carbon content at constant aluminium nitride content of 2 wt%, the density was found to increase, which attained a maximum at the carbon content of 1 wt% (figure 5). A further increase of carbon content has not produced any change in sintered density.

In figure 4, the microstructure of a sintered α -SiC specimen is shown with a starting composition of 97 wt% α -SiC, 2 wt% AlN and 1 wt% C. The grain size is in the range 5–10 μm . The grain size is smaller compared to the sample doped with boron as sintering aid. To study the sintering mechanism, the grain boundary regions have been thoroughly studied using transmission electron

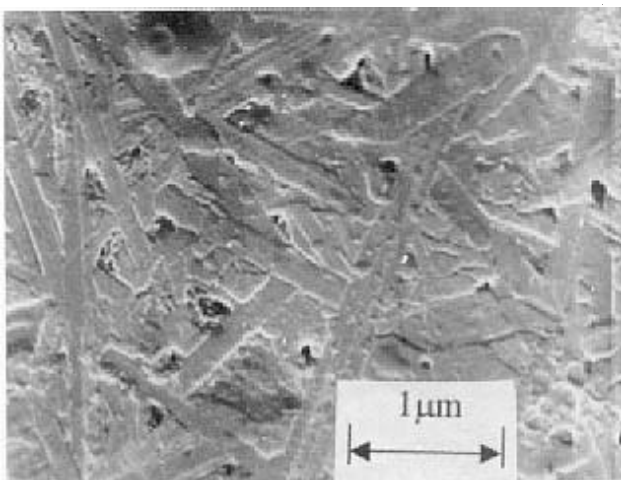


Figure 4. Microstructure of sintered α -SiC (2 wt% AlN + 2 wt% C) at a sintering temperature of 2100°C for 15 min.

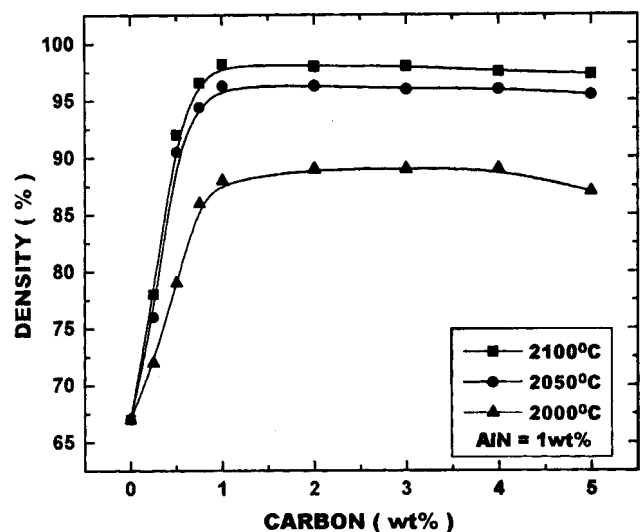
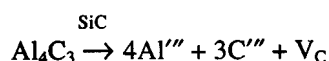
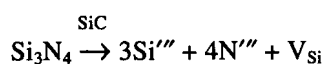
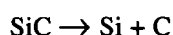


Figure 5. Effect of carbon content on sintered density.

microscopy (figure 6). No liquid phase was found. From the electron diffraction pattern (figure 7), it is also found that aluminium has entered into the structure of silicon carbide. Thus, it may be concluded that the sintering of silicon carbide is a solid state process involving 6H to 4H polytype transformation for which some evidences are presented subsequently in the paper.

Through transmission electron microscopy study, no intergranular phase was observed at the grain-boundary, as shown in figure 6. Therefore, we can conclude that sintering process of silicon carbide through aluminium nitride doping is found to be a solid state one.

We propose the following mechanism for enhancement of diffusion



AlN and SiC form solid solution for a limited range. When aluminum enters into Si site, Al_4C is likely to form leading to creation of carbon vacancy, whereas when nitrogen enters into carbon site, Si_3N_4 is likely to be formed which leads to a silicon vacancy. Thus vacancies are created which leads to the increase in diffusion coefficient of silicon and carbon. In argon atmosphere carbon diffusion coefficient is two orders of magnitude larger than that of silicon. But in carbon rich atmosphere, carbon diffusion coefficient is less than the diffusion

coefficient of silicon and also enhancement of diffusion coefficient of silicon occurs as reported by Rijswijk and Shanefield (1982). Here carbon also prevents the formation of Al_3C_4 structure and also decreases the vacancies of carbon. Thus it lowers the diffusion coefficient of carbon as reported earlier. Chemical analysis of both β -SiC and 6H- α -SiC single crystals by three different Laboratories have found the crystals to be silicon-rich. The ratio of silicon to carbon of both β -SiC and 6H SiC were reported to be 1.049 and 1.032, respectively (Nagatomo *et al* 1979; Shaffer 1980). The excess silicon must result from carbon vacancies. The low diffusion coefficient, high activation energy and large pre-exponential term for silicon and carbon preclude high concentration of carbon vacancies, a conclusion supported by high value of the calculated Schottky energy (Vechten 1975). It is found that self-diffusion rate of each element is enhanced by the presence of other elements, because of the generation of vacancies. Thus, carbon atmosphere would equalize the ratio of Si to C to unity or less than unity in silicon carbide thereby creating silicon vacancies and thus increasing bulk diffusion of silicon. Addition of boron in silicon carbide creates further vacancies of silicon and carbon which enhance the bulk diffusion. If atom is associated with a vacancy, it always has an adjacent site to jump into such that atomic diffusion coefficient is similar to vacancy diffusion rather than the lattice diffusion, i.e. increased by many orders of magnitude. By this process with addition of boron which create, bulk diffusion of silicon and carbon increases by many orders of magnitude and become equal to grain boundary diffusion coefficient of both silicon and carbon vacancies. For densification to occur, the mass transport of silicon and carbon should be equal. Without addition of aluminium nitride and carbon, the mass of silicon and carbon are not equal and also low and densification does not occur. Thus the addition of aluminium nitride increases the diffusion coefficient and the carbon creates partial carbon

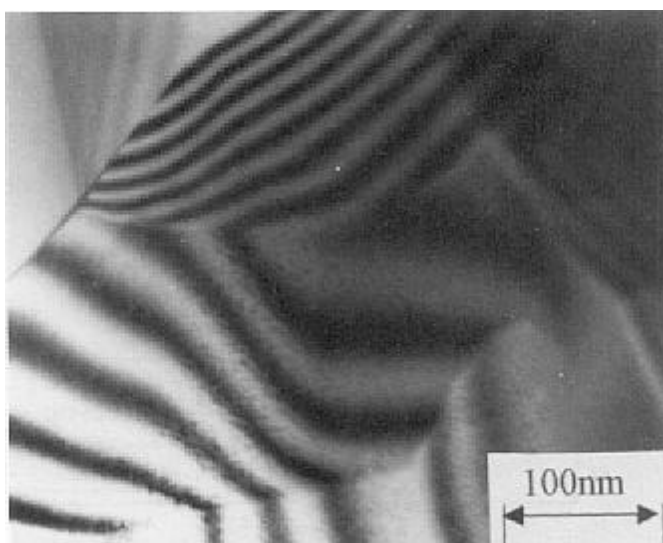


Figure 6. Transmission electron micrograph of sintered α -SiC.

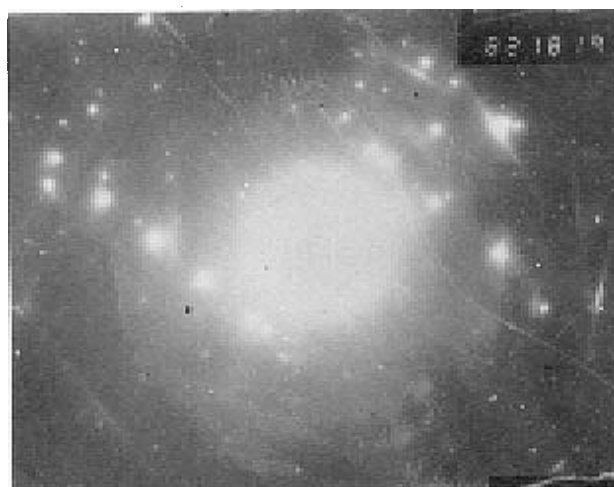


Figure 7. Electron diffraction pattern at the grain boundary.

atmosphere which makes the diffusion coefficient equal. The difference of covalent radius between Al and Si is 0.08 Å, whereas, the difference of covalent radius between N and C is - 0.07 (Raghavan 1974).

Formation of Al_4C_3 increases the cell dimension. During sintering, the cell containing the structure of Al_4C_3 begin to coalesce by layer displacement mechanism, not by screw dislocation as it would require clockwise as well as anti-clock wise movement in the transformation which is possible. The cells become disordered and strained and thus structure began to recrystallize as 4H polytype leading to increase of entropy.

The polytype transformation from 6H to 4H might result from suitable layer displacements caused by the nucleation and expansion of stacking faults in individual close-packed double layers of Si and C. This process is governed by thermal diffusion such as grain boundary diffusion since the nucleation of a stacking fault would require the migration of atoms inside the crystal. This layer displacement is likely to occur in such a manner as to minimize the free energy and take the structure towards the more stable one. If the stable state happens to be one with a different order such an order will tend to result. Such a mechanism was also suggested by Verma and Krishnan. During sintering by addition of B_4C and carbon and the increase of temperature, vacancies would be created and atoms would become free to migrate within the crystal and to the surface by diffusion. If number of vacancies come closer together, it will become possible for neighbouring atoms to move into "B" sites thereby nucleating a fault. Within the region the atoms are in "B" sites while the rest of atoms are in 'A' sites causing a partial dislocation to bind the faults. This partial dislocation glides causing the fault to expand until the entire layer of atoms is displaced into 'B' sites and the partial dislocation moves out of the crystal. The entire layer is then displaced from 'A' to 'B' orientation. By the same mechanism, displacements occur for other layers throughout the structure in such a manner as to result in a new structure. By this mechanism transformation proceeds through a one dimension disorder

caused by the nucleation of stacking faults and is expected to exhibit considerable one-dimension disorder as observed by the needle-like crystals of 4H polytype.

4. Conclusions

- (I) Nanocrystalline alpha silicon carbide powder of 37 nm, equivalent size can be produced by attrition grinding from 0.39 μm silicon carbide particles.
- (II) Sintering of nanocrystalline alpha silicon carbide powders can be achieved with a nearly theoretical density by the addition of aluminium nitride along with carbon.
- (III) Sintering could not be possible without the addition of carbon.
- (IV) Fine grained microstructure of the samples has been obtained with addition of aluminium nitride.
- (V) Sintering of silicon carbide is a solid state sintering process as no liquid phase was found at the grain boundary.
- (VI) 6H to 4H polytypic transformation occurs during sintering.

References

- Alliegio R A, Coffin L B and Tinklepaugh J R 1956 *J. Am. Ceram. Soc.* **39** 386
- Coppola J A and McMurty C E 1976 *Mater. symp. on ceramics in the service of Man* (Washington: Carnegie Institute)
- Johnson C A and Prochazka S 1977 *Ceramic microstructure, VIth Proc. int. mater. symp.* (Boulder, Colorado: Westview Press) p. 366
- Nagatomo M, Ishiwara H and Furukawa S 1979 *Jpn. J. Appl. Phys.* **18** 76
- Prochazka S 1975 *Special ceramic* (ed.) P Popper (New York: Academic Press) **Vol. 6**, p. 171
- Rijswijk W Van and Shanefield J Daniel 1982 *J. Am. Ceram. Soc.* **73** 148
- Raghavan V 1974 *First course in material science* (New Delhi: Prentice-Hall of India Pvt Ltd) p. 68
- Shaffer P T B 1980 *Mater. Res. Bull.* **16** 699
- Vechten J A van 1975 *J. Electrochem. Soc.* **122** 419
- Verma A R and Krishnan in *Polymorphism and polytypism in crystal* (New York: John Wiley and Sons Inc.) p. 261