JOURNAL OF MATERIALS SCIENCE 26 (1991) 4813–4817

Preparation and mechanical properties of SiC–AlN ceramic alloy

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Fine-grained SiC–AlN ceramic alloys were synthesized by the reaction of silicon nitride and aluminium nitride powders with additions of carbon and CaO. X-ray diffraction and STEM–EDX analysis showed that they are single phase solid solutions. The SiC–AlN alloys were sintered without additives to full density by hot isostatic pressing at 2173 K and 200 MPa for 2 h. The flexural strength, microhardness and fracture toughness were measured and it was found that SiC–AlN alloys have double the strength and slightly higher fracture toughnesses than conventional monolithic SiC.

1. Introduction

It is well known that silicon carbide has high strength and good oxidation resistance even at a temperature of 1873 K [1]. But compared with silicon nitride, the fracture toughness and room temperature strength are rather lower and this disadvantage prevents the practical application of silicon carbide as a high performance structural material. Even though some methods have been attempted to improve both strength and toughness, no effective method has been found to toughen silicon carbide while keeping its high strength at higher temperatures.

Cutler *et al.* [2] found that a solid solution is formed in 2H–SiC and AlN systems in a wide range of composition because they both have the same structure and their lattice parameters are very close. Rafaniello *et al.* [3] prepared SiC–AlN alloys by the carbothermal reduction of silica and alumina, and sintered them to high density by hot pressing. According to their results, the fracture toughness of SiC–7.5 wt % AlN and SiC–15 wt % AlN alloys, with relative densities of about 95% and 99%, respectively, were higher than that of SiC. However, it is not known whether the toughening is a real effect due to the solutioning of AlN or an apparent effect due to lower density. Ruh and Zangvil [4] hot-pressed SiC and AlN powder mixtures in the temperature range of 1973–2573 K and found that 2H solid solution was formed from 35–100 wt % AlN. However, their flexural strengths were quite low probably due to inhomogeneous mixing. Recently, some studies of the microstructure and phase relationship of the SiC–AlN alloy have been done in detail [5–7] and there are also a few reports about its synthesis [8, 9].

The authors [10] have recently confirmed that fine-grained SiC–AlN solid solution can be formed by the chemical reaction above 2073 K in the mixture of Si_3N_4, AlN, carbon black and CaO, as suggested by Dobson [8]. It was found that the reaction process has two steps: above 1873 K, Si_3N_4, AlN and CaO react to form alpha–sialon; above 2073 K, carbon reduces it to form SiC–AlN alloy. The following two-step chemical reaction formulae have been proposed [10]

$$Si_3N_4 + x\mathrm{AlN} + m\mathrm{CaO} \rightarrow \mathrm{Ca}_m\mathrm{Si}_{12-x}\mathrm{Al}_x\mathrm{O}_y\mathrm{N}_{16-y} \quad (1)$$

$$\mathrm{Ca}_m\mathrm{Si}_{12-x}\mathrm{Al}_x\mathrm{O}_y\mathrm{N}_{16-y} + (3+y)\mathrm{C} \rightarrow 3\mathrm{SiC}{:}x\mathrm{AlN} + y\mathrm{CO(g)} + \mathrm{N_2(g)} + m\mathrm{Ca(g)} \quad (2)$$

It can be postulated that the alloying mentioned above is effective for the improvement of the mechanical properties of SiC, as is usually the case in metallic alloys.

The objectives of the present work were to prepare a dense SiC–AlN alloy and investigate the effect of the solid solutioning of AlN on the mechanical properties of the alloy. For this purpose, SiC–AlN solid solutions were synthesized by high temperature reaction. They were then sintered to full density by subsequent hot isostatic pressing (HIP). Their mechanical properties, such as flexural strength, fracture toughness and microhardness were measured.

2. Experimental procedures

2.1. Synthesis of SiC–AlN ceramic alloy

The commercial Si_3N_4 powder (Toshiba Ceramics Co. Ltd, Tokyo), AlN powder (Toyo Aluminum Co. Ltd, Tokyo), carbon black and $Ca(NO_3)_2 4H_2O$ were weighed according to the pre-determined compositional ratios based on the above reaction (Equations 1 and 2) and mixed for 12 h in ethanol solution in a polymer container with nylon-coated steel balls. The mixed powders were dried at 400 K, heated to 1073 K in hydrogen for the decomposition of $Ca(NO_3)_2 4H_2O$ to CaO and then compacted at a pressure of 100 MPa.

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The green bodies were placed in a BN crucible and heated in nitrogen in a tungsten mesh resistance furnace at 2123 K for 5.4–10.8 ks for the synthesis reaction to yield porous reaction products. The heating and cooling rates were about 20 K min^{-1}. The furnace temperature was controlled to ± 10 °C with a W–Re thermocouple placed near the specimen.

2.2. Phase characterization and composition analysis

The porous reaction products were smashed and analysed by X-ray diffraction. In all cases, Ni-filtered CuK_α radiation was used. The microanalysis of the composition was performed on HIP-densified specimen. A thin disc sample of 3 mm diameter for transmission electron microscopy was sliced from the HIPed specimen and diamond ground to 0.1 mm thick. The disc samples were then thinned to perforation by the argon-ion thinning method. The samples were observed for elemental analysis on a scanning transmission microscope (STEM) equipped with an energy dispersive X-ray spectrometer (EDX).

2.3. Hot isostatic pressing

The smashed reaction product was compacted to a cylindrical form of 10 mm diameter and 30 mm height. The green compact was inserted into a vycor glass tube with BN powders as a barrier layer to prevent the reaction between the specimen and the glass during HIP, then vacuum encapsulated at 1673 K. The encapsulated samples were HIP-sintered for 7.2 ks in the temperature range 2123–2223 K and at an argon pressure of 200 MPa. For comparison, SiC powder was also HIP-sintered with a 0.5 wt % B_4C addition.

2.4. Measurement of mechanical properties

The four-point bending test was used to measure the strength of the HIP-sintered specimens. Rectangular specimens of 23 mm × 2 mm × 1.5 mm in size were cut from the HIP-sintered bodies using a diamond wheel and their tensile surfaces polished with a 3 μm diamond paste to achieve a mirror-like surface finish. A part of the specimens was annealed in air at 1473 K for 2 h to heal the grinding damage [11]. The four-point bending tests were conducted with upper and lower spans of 20.0 and 10.0 mm, respectively, at a crosshead speed of 0.5 mm min^{-1}, fracture toughness were measured by utilizing the Vickers indentation microfracture technique under a load of 49 N, and the values were calculated using the equation proposed by Niihara *et al.* [12]. Vickers microhardness values were also measured under a load of 4.9 N. The average values were taken from at least five measured points.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the starting powders and the reaction product with a composition of 25 mol % AlN. Only one sharp peak for the (1 0 0) plane was detected with peak broadening as seen in the figure. Considering that the 2θ values for the (1 0 0) plane of SiC and AlN are 33.6° and 33.2°, respectively, the single peak for the (1 0 0) plane shows the formation of a single phase solid solution. The formation of a solid solution will be confirmed in more detail by the STEM–EDX analysis of densified specimens as described later.

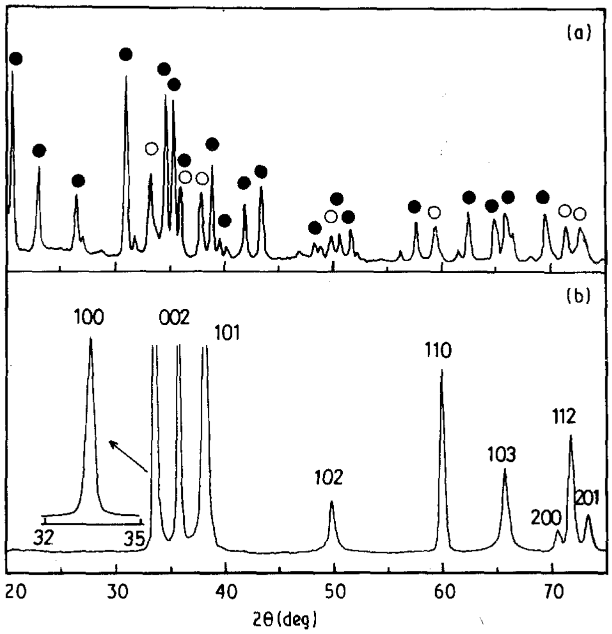

Figure 1 X-ray diffraction patterns of (a) the starting powders, and (b) reaction product with composition of SiC–25 mol % AlN. (●) Si_3N_4, (○) AlN.

Fig. 2 shows the scanning electron micrographs of the starting powders and the reaction product of SiC–5 mol % AlN. It can be seen that the grain size of the reaction product is much finer than those of the starting powders. The average grain size of the reaction-formed SiC–5 mol % AlN was measured by the BET method to be about 0.36 μm, while those of the original Si_3N_4 and AlN powders were 0.88 and 1.39 μm, respectively. The other reaction products with different compositions have similar fineness. No shrinkage was observed during the reaction sintering, presumably due to a large amount of vapour evolution, indicated in the reaction formulae in the preceding section.

Fig. 3 shows the relation between the HIP-sintering temperature and the final density for the three reaction products and the commercial alpha-SiC powders with and without B_4C addition. The commercial alpha-SiC powder has an average grain size of 0.37 μm, which is nearly equal to that of the reaction products. While this SiC powder was sintered to 93% theoretical density at 2223 K, the SiC–AlN alloy powders were sintered to full density at a lower temperture. This result indicates that the sinterability of SiC was enhanced by the solutioning of AlN as is the case of SiC with B_4C. This is supposed to be due to the increase in the volume diffusion coefficient with the solutioning of AlN, which is also suggested from the diffusion enhancement in Al-doped SiC [13].

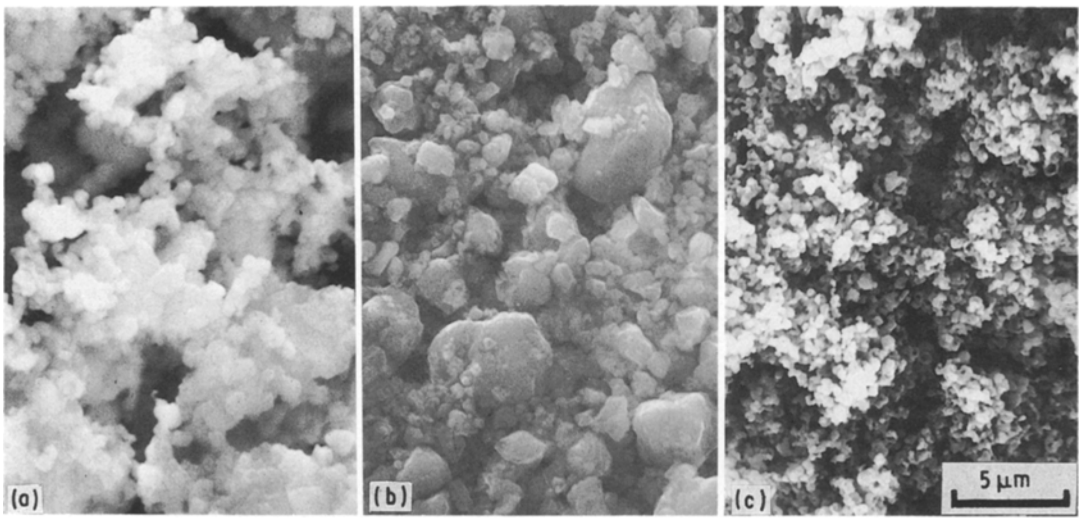

Figure 2. Scanning electron micrographs of the starting powders: (a) Si_3N_4, (b) AlN, and (c) the reaction product with the composition of SiC–5 mol % AlN.

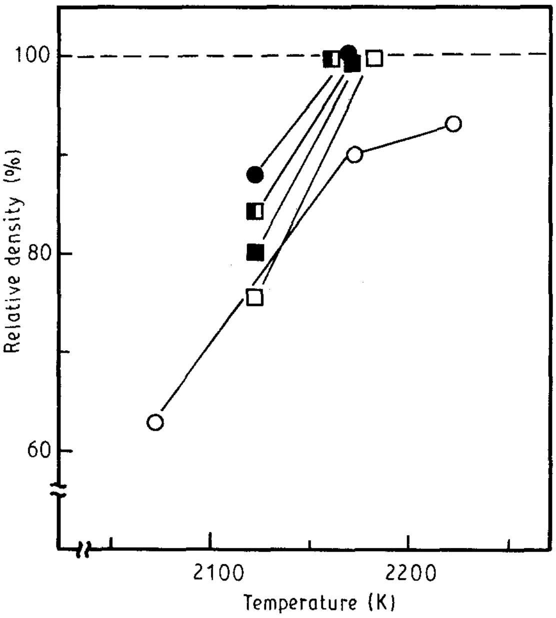

Figure 3 Density change as a function of HIP-sintering temperature, with an HIP-pressure of 200 MPa. (○) SiC, (●) SiC + 0.5 wt % B_4C, (□) SiC–5 mol % AlN, (■) SiC–10 mol % AlN, (◧) SiC–25 mol % AlN.

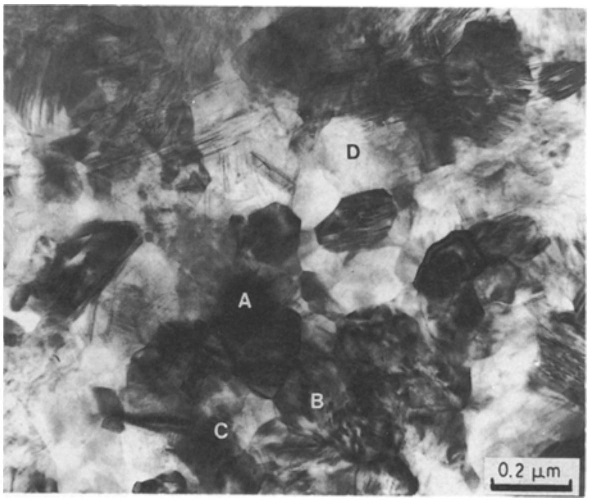

Figure 4 Transmission electron micrograph of SiC–25 mol % AlN alloys, the composition is SiC–19 mol % AlN at A, SiC–25 mol % AlN at B, SiC–21 mol % AlN at C, and SiC–23 mol % AlN at D.

Fig. 4 shows the typical transmission electron micrograph of the HIP-sintered compact with the nominal composition of SiC–25 mol % AlN. The indicated areas were analysed by selected area analysis. The average compositions of the areas indicated were identified to be SiC–23 mol % AlN with a small scattering in the values. This result indicates that a uniform solid solution was formed. It was confirmed by the same method that the reaction products of the other compositions (SiC–5 mol % AlN and SiC–10 mol % AlN) were also homogeneously solid solutioned.

Table I summarizes the Young's modulus and microhardness values of the present SiC and the SiC–AlN alloys. The Young's modulus decreases with increasing AlN content, which should be due to the mixing of low stiffness material. The Young's modulus values of the present SiC and AlN were 439 and 300 GPa, respectively, and the measured values of the SiC–AlN alloy are nearly equal to the calculated values from the linear mixing rule. High hardness was achieved in the SiC–AlN alloys. The hardness value at 5 mol % AlN is higher than that of SiC, probably due to the grain-refinement in the SiC–AlN alloy as shown later, in Fig. 7. The hardness of the SiC–AlN decreases with increasing low-hardness phase AlN.

TABLE I Young's modulus and Vickers hardness of SiC and the SiC–AlN alloys

Specimens	Young's modulus (GPa)	Vickers' hardness (GPa)
SiC	439	29.8
SiC–5 mol % AlN	414	31.9
SiC–10 mol % AlN	408	29.5
SiC–25 mol % AlN	380	28.3

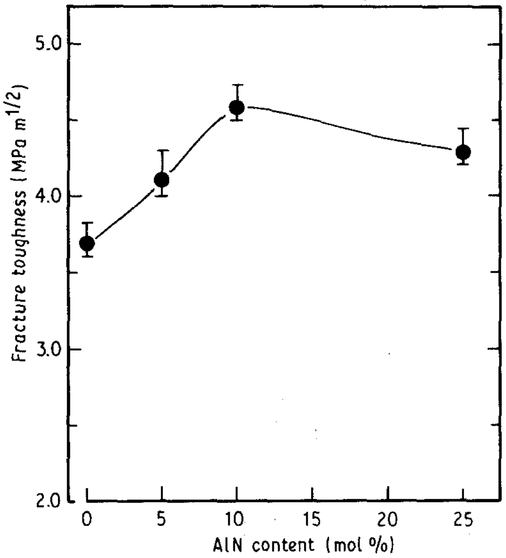

Figure 5 Fracture toughness as a function of AlN content.

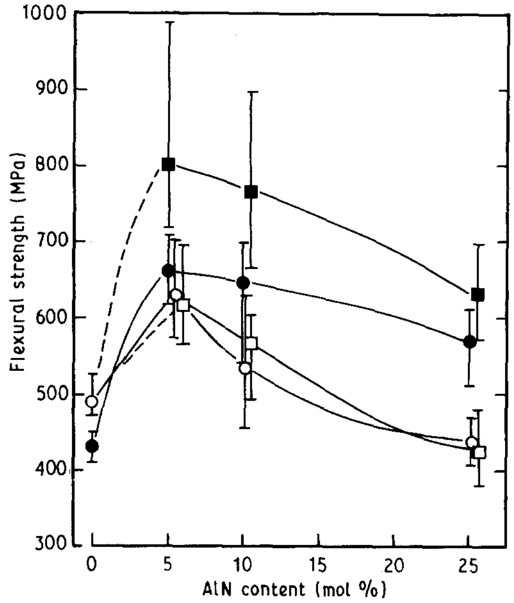

Figure 6 Flexural strength as a function of AlN content. (○, □) As-polished specimens HIPed at 2173 K, (●, ■) specimens annealed in air after surface-polishing (HIPed at 2223 K).

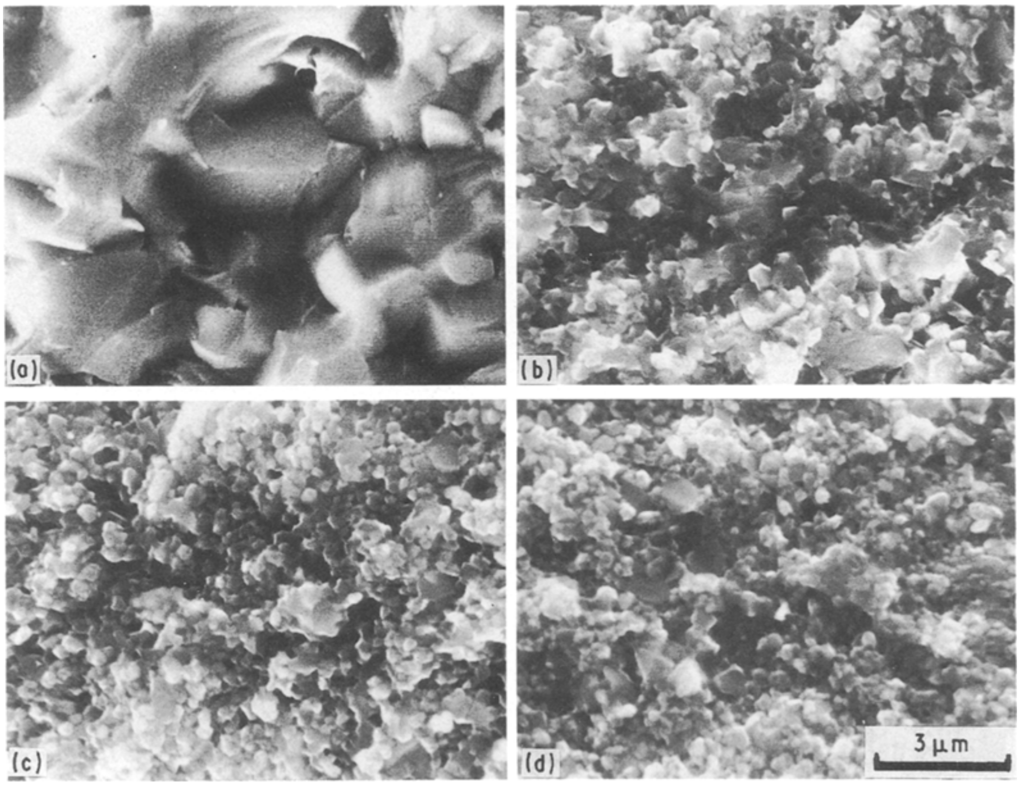

Figure 7 Scanning electron micrographs of the fracture surfaces of SiC and SiC–AlN alloys. HIP-sintered at 2173 K: (a) SiC + 0.5 wt % B_4C, (b) SiC-5 mol % AlN, (c) SiC-10 mol % AlN, (d) SiC-25 mol % AlN.

Fig. 5 shows fracture toughness as a function of AlN. The fracture toughnesses of the SiC–AlN alloys are higher than that of SiC over the composition range. The toughening of SiC by the alloying of AlN can be attributed to the formation of several kinds of atomic bonding. In the SiC–AlN solid solution, four bonds such as Si–C, Si–N, Al–C and Al–N will be formed, compared with only one Si–C bond in SiC. In addition, the SiC–AlN alloys have 2H structure, and their stacking fault density is considered to be higher than that of the alpha-SiC (6H structure). These specific features are considered to cause the increase in fracture energy and to result in the increase in fracture toughness.

Fig. 6 shows the flexural strength of the present SiC and SiC–AlN alloys. Both the data for the as-polished and the annealed specimens are shown. The SiC–AlN alloys generally have much higher flexural strength than monolithic SiC. In all cases, the flexural strength showed the maximum value at 5 mol % AlN. It is remarkable that the strength of SiC–5 mol % AlN, HIP-sintered at 2223 K and annealed in air, has the highest strength with the maximum value of about 1 GPa. It is to be noted here that the annealing in air caused considerable increase in strength for the SiC–AlN alloys, while weight gain due to oxidation was below 0.08% for all specimens. From this result, it is considered that the oxidation resistance of the SiC–AlN alloys is comparable to SiC. The increase in strength by annealing treatment is considered to be due to the healing of grinding damage caused during surface-machining as suggested by Dutta [11]. On the other hand, no strength increase was measured for monolithic SiC, probably because the initial fracture origin (such as the large grains and the inhomogeneous mixing of the sintering aid) was larger than the grinding damage, or that the B_4C addition caused non-uniform oxidation.

Fig. 7 shows scanning electron micrographs of the fractured surfaces of the SiC and SiC–AlN specimens. The SiC sintered with B_4C addition has much larger grains than those of the SiC–AlN alloys which have grain size of submicrometre order. This fact indicates that the solutioning of AlN suppresses grain growth effectively. The refinement of the grains in the SiC–AlN alloys is considered to be very effective for the improvement of strength, allowing that the increase of fracture toughness also leads to some increase of strength according to the Griffith's theory.

4. Conclusion

SiC–AlN alloys with compositions of 5, 10 and 25 mol % AlN were synthesized by the reaction of the mixture of Si_3N_4, AlN, carbon and CaO at 2073 K. They were confirmed to be single-phase solid solution by X-ray diffraction and STEM–EDX analysis. The synthesized powders were HIP-sintered to full density without additives at 2173–2223 K and the sintered alloys had uniform microstructure with submicrometre-sized grains. The flexural strength of all the HIP-sintered SiC–AlN alloys were higher than that of SiC. The maximum flexural strength of 1 GPa for SiC–5 mol % AlN was obtained. The improvement of strength is thought to be due to the fine-grained microstructure of the SiC–AlN alloy. The fracture toughness was measured by using the Vickers indentation method, which showed that the SiC–AlN alloys had slightly higher toughnesses than SiC over the range of composition investigated. The microhardness of SiC–5 mol % AlN alloy is found to be higher than that of SiC.

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Received 2 January
and accepted 29 October 1990