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].

Dobson [8]. It was found that the reaction process has two steps: above 1873 K, Si3N4, 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]

\[ \text{Si}_3\text{N}_4 + x\text{AlN} + m\text{CaO} \rightarrow \text{Ca}_m\text{Si}_{12-x}\text{Al}_x\text{O}_y\text{N}_{16-y} \]

\[ \text{Ca}_m\text{Si}_{12-x}\text{Al}_x\text{O}_y\text{N}_{16-y} + (3 + y)\text{C} \rightarrow 3\text{SiC} + y\text{CO(g)} + N_2(g) + mz\text{Ca(g)} \]

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 Si3N4 powder (Toshiba Ceramics Co. Ltd, Tokyo), AlN powder (Toyoo Aluminum Co. Ltd, Tokyo), carbon black and Ca(NO3)2·4H2O were weighed according to the pre-determined compositional ratios based on the 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(NO3)2·4H2O to CaO and then compacted at a pressure of 100 MPa.
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 CuKα 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 % B₄C 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 x 2 mm x 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 was 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 20 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.

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 Si₃N₄ 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 B₄C 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 temperature. This result indicates that the sinterability of SiC was enhanced by the solutioning of AlN as is the case of SiC with B₄C. 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 1 X-ray diffraction patterns of (a) the starting powders, and (b) reaction product with composition of SiC–25 mol % AlN. (●) Si₃N₄, (○) AlN.