Texture development of surface-modified SiC prepared by EPD in a strong magnetic field

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Silicon carbide is a very important material for various applications and its properties are expected to be improved by controlling the crystallographic orientation. It was difficult to simultaneously consolidate SiC powder and sintering additives by electrophoretic deposition (EPD) because of the different electrophoretic mobility. When using the alumina-coated SiC by the sol–gel method, it is possible to deposit SiC and sintering additives by EPD at the same time.

In this study, we demonstrated that the c-axis alignment of SiC was controlled by EPD and a strong magnetic field, and we investigated the effect of the surface-modification on the microstructure and the degree of orientation. The dilute solution and the large number of repeated coating times prevent the oxide phase from precipitating at the multiple grain junctions and enhance grain growth. The grain growth promoted the degree of orientation in the textured SiC prepared by EPD in a strong magnetic field.

Key-words: c-Axis orientation, Al₂O₃, Grain growth

1. Introduction

Silicon carbide is one of the most important ceramics used as a structural material due to its high elastic modulus, high chemical stability, high thermostat and good wear resistance. Furthermore, SiC is also a very attractive ceramic used as a functional material suitable for high power devices in extreme environments. Controlling the density and designing the microstructure of the sintered bodies are very important for high performance ceramics. The high covalent bonding nature of SiC requires a very high temperature and suitable additives for densification. Al₂O₃ is very effective for obtaining the dense SiC, because Al₂O₃ additives interact with the SiO₂ on the surface of the SiC to form a liquid phase at elevated temperature that enhances the SiC densification. Other oxide additives often make an inhomogeneous microstructure in the sintered SiC due to the non-uniform dispersion of powders in the slurry. Colloidal processing is a very useful technique for controlling a high density green compact and the uniform microstructure of the sintered bodies. It has been shown that the use of surface modification methods for addition of sintering additives improves the densification properties of SiC over those achieved with conventional mixing techniques. Electrostatic adsorption of a small amount of Al ions was applied to coat uniformly the surface of SiC particle in an Al(NO₃)₃ solution. Other surface coating techniques using controlled hydrolysis of Alalkoxide and adsorption of colloidal Al₂O₃ sol were reported. Electrophoretic deposition (EPD) is a colloidal processing technique wherein ceramics bodies are directly shaped from a stable colloid suspension by a dc electric field. This technique exhibits very interesting cost effectiveness. Complex shaped ceramics and coating of the metallic substrate can be easily attained. The production of SiC/graphite laminated composites by EPD was achieved to overcome the brittle properties due to introducing weak interlayers that deflect cracks. Many studies on the dispersion and EPD of silicon carbide have been reported. Although the EPD method can be applied to the shaping of a SiC powder, it is essential to consider how the sintering aid should be added. This is because a simple mixture of SiC and sintering additives in a colloidal suspension is not appropriate due to the different electrophoretic mobility. However, we achieved the forming of SiC particles by EPD due to the surface modification of the SiC particles using the sol–gel method. When the surface of SiC is coated with Al₂O₃, the modified surface leads to stable dispersion in an aqueous suspension and SiC particles are deposited to the cathode without damaging metal ions due to the positive surface charge.

Tailoring of the crystallographic orientation in ceramics is very effective for the improvement of their properties, because the mechanical and functional properties depend on the crystal axis. The mechanical properties of SiC single crystals depended on the crystal planes. Development of texture in SiC by hot forging and the Templated Grain Growth method has been reported. On the other hand, the crystallographic orientation even in feeble magnetic ceramics, such as Al₂O₃ and AlN, etc., can be controlled by a colloidal processing under a magnetic field. When a strong magnetic field was applied to the particles with an anisotropic susceptibility in stable suspensions during colloidal processing, the particles were rotated to an angle minimizing the system energy by a magnetic torque generated from the interaction between the magnetic anisotropy and the applied magnetic field. This orientation processing could be applied to the SiC and the c-axis of the SiC became aligned parallel to the magnetic field.

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Therefore, we demonstrate in this study that control of the crystallographic orientation in SiC was achieved by EPD in a strong magnetic field using the surface-modified SiC powder, and the effect of the surface modification on the microstructure was investigated.

2. Experimental procedure

A commercially available silicon carbide powder (OY-20, Yakushima Denko Co., Ltd., Japan) with the average particle sizes of 0.55 μm was used as the starting powder. The powder contains impurities of SiO₂ (1.3 mass%), C (0.63 mass%), Fe (0.027 mass%) and Al (0.020 mass%). Aluminum tri-isopropoxide [Al(OCH₃)₃] was used to modify the surface of the SiC particles. Aluminum tri-isopropoxide was dissolved in isopropyl alcohol to prepare a 2.5 or 5 mM solution, and then 20 g of SiC powder was added to the solution. The number of coating times was 4 and 2 for the 2.5 and 5 mM solutions, respectively. Distilled water of pH 11 adjusted with ammonium hydroxide was then dropwise added to the suspension to hydrolyze the aluminum tri-isopropoxide followed by further stirring for 1 h to ensure the hydrolysis. The stoichiometric molar ratio of water to Al-alkoxide was 3:1; however, 5–10 times the level of water was added to ensure a complete hydrolysis reaction. The amount of the alumina precursor, more accurately aluminum hydroxide, on the SiC powder was altered by repeating the coating process and/or changing the concentration of the aluminum tri-isopropoxide solution. The zeta potential of the surface-modified SiC and uncoated SiC powder in isopropyl alcohol were measured as a function of the pH by the laser Doppler Velocimetry method.

After the coating, polyethyleneimine (PEI) and poly (vinyl butyral) (PVB) were added to the isopropyl alcohol suspension as a dispersing agent and a binder, respectively. The solid loading of the suspension was fixed at 0.6 vol%. The suspensions of the surface-modified SiC were then consolidated by EPD in a strong magnetic field of 12 T at room temperature. A palladium sheet was used as the cathodic substrate to absorb hydrogen produced by electrolysis of the solvent and then the electrical field at a constant voltage of 200 V was applied. The direction of the magnetic field was parallel to the electric field. A schematic illustration of the apparatus is shown in Fig. 1. The SiC green compacts were sintered by pseudo-HIP using BN powder as the pressure transmitting medium in an argon atmosphere at 2000°C and 40 MPa. The crystallographic orientation was analyzed by X-ray diffraction (XRD) and the microstructures of the sintered samples were observed by scanning electron microscopy (SEM). The sintered samples were polished using diamond suspensions and plasma etched with CF₄ for the SEM observations.

3. Results

The hydrolysis reaction proceeds by the sequential steps. In the first step, the adsorption of aluminum alkoxide to the SiC surface occurs by reacting with Si-OH groups on SiC, and then the alkoxide reacts with other aluminum alkoxide through hydrolysis and condensation. The amounts of Al on the SiC powder were analyzed by ICP-AES as shown in Fig. 2. The total amount of the aluminum in SiC particles increased linearly with the increasing the number of coating times and the concentration of the Al(OCH₃)₃ solution. It is found in Fig. 3 that the shape of the particles was isotropic and the surface-modified and uncoated particles were almost similar in appearance.

Figure 4 shows the zeta potential of the surface-modified SiC with a double coating from a 5 mM solution and uncoated SiC powder in isopropyl alcohol as a function of the pH. The isoelectric point (i.e.p.) of the uncoated SiC was around pH 5. In contrast to the uncoated SiC, the i.e.p. of the surface-modified
SiC was around pH 9. This value was confirmed to be similar to the i.e.p. of alumina in the isopropyl alcohol. Furthermore, the zeta potential was around 70 mV at a pH less than 8. From this result, pH was determined to be 5 for EPD.

Figure 5 illustrates the XRD profiles of the specimens prepared by EPD in a strong magnetic field followed by sintering at 2000°C. The 006 reflection at 2θ = 35.6 is extremely high in the surface perpendicular to the applied magnetic field. This demonstrates that a crystalline orientation with the c-axis parallel to the magnetic field had been developed by EPD in the strong magnetic field for the surface-modified SiC powder. This orientation is consistent with the uncoated SiC prepared by slip casting in a strong magnetic field described in previous reports.\textsuperscript{24, 25} The modification to the SiC surface did not prevent the particle from rotation in the suspension due to the magnetic field. The degree of orientation was estimated by the Lotgering factor calculated from the XRD intensities.\textsuperscript{27} The Lotgering factors for the samples coated from the 2.5 and 5 mM solutions were 0.87 and 0.77, respectively.

Figure 6 shows the microstructure of the textured SiC prepared by EPD in a strong magnetic field for the surface-modified SiC particles followed by sintering at 2000°C. The dark spots in the grains were uneven surface attributed to the plasma etching. The average grain size parallel and perpendicular to the magnetic field was determined to be 1.56 times the average linear intercept length of the grains along each direction. The average grain sizes perpendicular to the magnetic field, d⊥, were 2.3 and 2.0 μm in the sintered SiC using the powder coated from the 2.5 and 5 mM solutions, respectively.

White particles precipitated along the grain boundaries and at the multiple grain junctions in the sintered SiC using the powder coated from the 5 mM solution as shown in Fig. 6. EDS analyses of the sintered SiC prepared from the 5 mM solution are shown in Fig. 7. In the grey matrix (point 1), only C and Si were detected, whereas C, O, Al and Si were detected in the white grain (point 2). This provided evidence that the white grains were Al-Si-O phases in the microstructure of SiC using the twice coated powder from the 5 mM solution. No white precipitation grains were observed in the SiC using the 4-time coated powder from the 2.5 mM solution.

4. Discussion

Figure 2 and Fig. 4 show that the surface of the SiC particles was successfully modified and the zeta potential was sufficient for dispersion and electrophoresis. The surface-modified powder showed a stable positive mobility at low pH, and this phenomenon was similar to alumina powder. The Al contents were 0.98 and 0.95 mass % in the SiC powder coated from the 2.5
and 5 mM solutions, respectively. Although the amounts of Al were similar in both samples, the oxide phase precipitated in the SiC using the 5 mM solution. When the amount of one coating was significant, a thick layer could be generated by the hydrolysis reaction. White grains precipitated from the thick layer during sintering. When using a dilute solution, a thin and homogeneous layer could be coated by a large number of coatings and no precipitation grains were observed at the multiple grain junctions. The total amounts of Al were same in the both solutions after the hydrolysis and the content of Al coated with SiC particles were similar to each other. Consequently there were similar amount of Al in both slurries. The white particles were observed in only the sintered samples using the 5 mM solution. This indicates that the aluminum hydroxide did not deposit at the same time as deposition of SiC if the unadhered particles would remain in the solution.

The density of the sintered SiC prepared from the 2.5 and 5 mM solutions were 93.5 and 92.5% of the theoretical value (3.21 g/cm³), respectively. The 0.95 mass% Al on the surface of the SiC corresponded to 1.8 mass% of Al₂O₃. When using other methods to add Al for sintering additives, the amount of Al₂O₃ was less than the present study in order to densify SiC. It is possible to reduce the amount of Al additive by optimizing the concentration of the solution and the coating time.

The ratios of d₁ to the grain sizes parallel to the magnetic field, d₁/m, were 1.45 and 1.41 in the samples prepared from the 2.5 and 5 mM solutions, respectively. The c-axis was aligned parallel to the magnetic field; hence, the direction of the a and b axes of the SiC grains were elongated greater than that of the c-axis and the d₁ was greater than d₂. The ratios of both SiCs were similar to each other for these average grain sizes. In the case of alumina, the ratio of d₁ to d₂ increased with the increasing d₁. It is expected that the ratio will increase with the increasing grain growth at higher temperature during sintering or annealing than the present study, and the platelet grains will be aligned perpendicular to the magnetic field.

The grain growth rate of the sample prepared from the 5 mM solution was slightly slower than that of the sample prepared from the 2.5 mM solution because the oxide particles prevent grain growth due to the pinning effect at the grain boundaries and the multiple grain junctions. The degree of orientation estimated from the Lotgering’s factor of the sample prepared from the 2.5 mM solution was higher than that of the sample prepared from the 5 mM solution in Fig. 5. This is because the development of a crystallographic orientation is promoted by the grain growth during sintering.

5. Summary

The preparation of the textured SiC was achieved by EPD in a strong magnetic field when using the surface modified SiC powder by the sol–gel method. When using the dilute solution, a large number of coatings prevented the oxide grains from precipitating at the multiple grain junctions. When the precipitated oxide particles prevented the grain growth due to the pinning effect, the degree of orientation decreased compared to the sample without the precipitate oxide grains from the dilute solution.

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References
18) S. Horii, A. Ishihara, T. Fukushima, T. Uchikoshi, H. Ogino,