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Fabrication of dense silicon carbide through aqueous slurries containing well-dispersed carbon as a sintering aid

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Tetramethyl ammonium hydroxide (TMAOH) has no fluidizing effect on carbon particles, because of their hydrophobic surface properties. On the other hand, styrene/maleic copolymer (SM) enhanced the fluidity of two kinds of carbon slurries in the basic pH range, where the particle diameters of carbon #2650 and MA100 were 13 and 22 nm, respectively. High-density sintered bodies of silicon carbide containing carbon and boron carbide as sintering aids were obtained by controlling the pH of ∼10–11 with TMAOH and by addition of SM: i.e., 9.5 and 5.5 wt% of SM were added to #2650 and MA100, respectively, in the dry weight base of the carbon. The highest sintered density product with more than 98% was obtained by intimate dispersion of the finer carbon particles in the silicon carbide slurries.

1. Introduction

Silicon carbide materials are prime candidates for structural ceramic parts, such as gas turbine engines, heat exchangers, wear-resistant seals, and diffusion furnace parts for semiconductor manufacture [1–3]. The forming process for the materials as well as the preceding silicon carbide powder preparation process are very important in the fabrication of ceramic parts as defects introduced in this process will normally remain in the product even after a successful sintering process. Aqueous slip casting [4, 5] is especially important in terms of ecology, safety, and cost. In slip casting, enhancement of the dispersion and fluidity of the silicon carbide slurry, is a key technique for fabricating structural silicon carbide parts.

We have reported previously that a silicon carbide body of high sintered density can be obtained through the slip casting process using aqueous slurries containing SM and TMAOH at a pH of ∼10–11 [6, 7]. In these previous reports, analysis of the flow curves and flow point data indicated that the dispersion and fluidity of silicon carbide slurries were effectively enhanced by the addition of TMAOH, as the surface of silicon carbide powder consists of an oxide film and colloidal stability of silicon carbide behaves like SiO_2; the absolute zeta potential of this powder showed large values in the basic region [8, 9]. Usually, boron carbide and carbon powders have been used as sintering aids [10]. We reported previously that boron carbide had no effect on the fluidity of aqueous silicon carbide slurries [6]. However, enhancement of the dispersion and fluidity of carbon particles as a sintering aid are key concerns for slip casting of aqueous slurries, because carbon powder has a hydrophobic surface and high specific surface area. Generally, silicon carbide powder has free carbon as one of the mainly contaminants [11]. We considered that the colloidal stability of these total carbon powders (i.e., additive carbon as a sintering aid and free carbon in silicon carbide) in the slurries is a key factor to obtain a silicon carbide fired body with high density. However, it is difficult to control dispersion and fluidity of silicon carbide with carbon, because the amount of free carbon in silicon carbide powder is dependent on powder processing history.

The present study was performed to determine suitable processing conditions to obtain a silicon carbide body with high sintered density using high-purity silicon carbide powders with lower contents of free carbon (<0.3 wt%) as a starting material. We examined how polyelectrolytes and alkaline bases function in silicon carbide and carbon powder in multi-particle slurries.

2. Experimental procedures

2.1. Materials

Silicon carbide (β-SiC, F, Central Glass Co., Tokyo, Japan) was used to prepare the slurries. Two kinds of carbon powders (MA100 and #2650, Mitsubishi Chemical Co., Tokyo, Japan) and boron carbide (Denka Boron #1200, Denki Kagaku Kogyo Co., Tokyo, Japan) were used as sintering aids. Table I shows the characteristics of the powders supplied by the manufacturers shown. Aqueous styrene/maleic copolymer (SM: average M.N. = 1,900, Acros Organics, Geel, Belgium) solution with tetramethyl ammonium hydroxide (TMAOH: Aldrich Chemical Co., Milwaukee,

TABLE I Characteristics of the powders

	SiC	Carbon		B_4C
	F	MA100	#2650	#1200
Mean particle size (μm)	0.5	0.022	0.013	1.2
Specific surface area (m^2/g)	15	134	320	18–20

WI) was used as a dispersant. The pH of the slurries was adjusted with TMAOH and HNO_3.

2.2. Slurry preparation and sintering

Slurries containing water, SM, silicon carbide, carbon, and boron carbide, which were added to the slurries in fixed amounts on a dry-weight basis (dwb) for the silicon carbide or carbon powders, were prepared by ball milling with silicon carbide balls for 24 h at room temperature. After ball milling, the slurries were stirred and degassed in a vacuum. The slurries were cast into a plaster mold on a vibration board to produce the green body. The specimen size was approximately 50 × 50 × 5 mm. Dried green bodies were pressureless sintered in an Ar atmosphere at 2,150°C for 1 h.

2.3. Measurements

The flow and wet point measurements were conducted to evaluate the effectiveness of TMAOH and SM for the carbon slurries [12, 13]. The amount of carbon powder used was 4 g. The carbon powder was mixed with dispersant solution at various concentrations. Water was added from a burette and kneaded, and the amount of water required to form a lump was read as the wet point. On further addition of water, the amount of water at which the suspension began to flow was read as the flow point. The rheological behavior of the slurries was determined from shear rate-shear stress curves, using a controlled-stress rheometer (RS50, Haake, Karlsruhe, Germany) at 25°C. The green and sintered densities were determined from the size and weight of the specimen and by the Archimedes method, respectively.

3. Results and discussion

3.1. Fluidity of carbon slurry

Fig. 1 shows the changes in the flow and wet points of the #2650 powders with various amounts of TMAOH. The flow and wet points did not change with addition of TMAOH up to 80 wt% (dwb of #2650 powders). These observations suggested that TMAOH was not effective as a dispersing and fluidizing agent for the carbon slurries. On the other hand, increasing the amount of SM for the #2650 and MA100 powders reduced the flow point and wet point values as shown in Fig. 2. The flow point showed a minimum value at about 10 and 6 wt% SM on dwb of the #2650 and MA100 powders, respectively.

Fig. 3 shows the changes in apparent viscosity as a function of SM concentration. Although the solid loading of the #2650 and MA100 slurries differed, both slurries were dispersed and fluidized by the addition of SM. The optimum amounts of SM on dwb for #2650 and MA100 powders were 9.5 and 5.5 wt%, respectively. The difference in the optimum amount for the two kinds of carbon was attributed to the differences in specific surface area of these particles as the amount required to improve the hydrophobic surface of the particles increases gradually as the specific surface area of the particles increases. SM has both hydrophobic and hydrophilic functional groups in its structure. The hydrophobic group of SM should adsorb on the hydrophobic surface of carbon, and the hydrophilic group

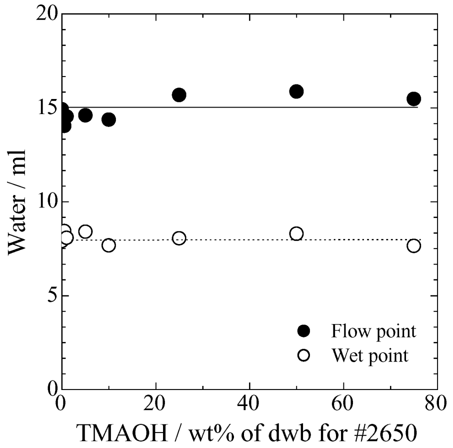

Figure 1 Flow and wet points of #2650 particles with various amounts of TMAOH.

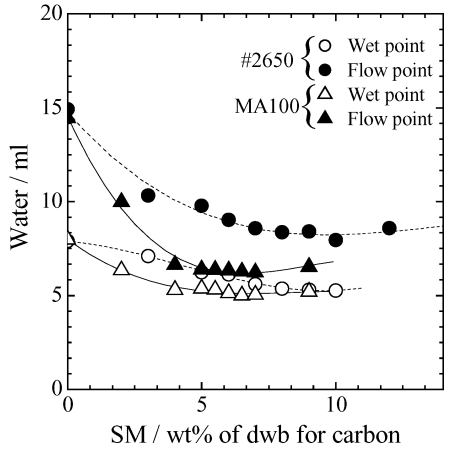

Figure 2 Flow and wet points of #2650 and MA100 particles with various amounts of SM.

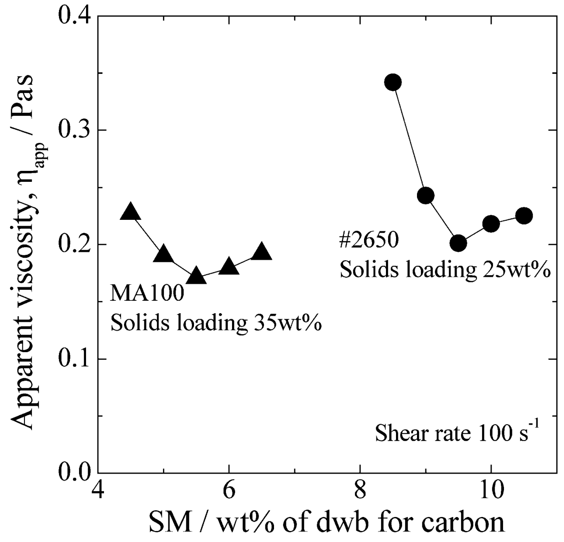

Figure 3 Apparent viscosity for #2650 and MA100 slurries with various amounts of SM.

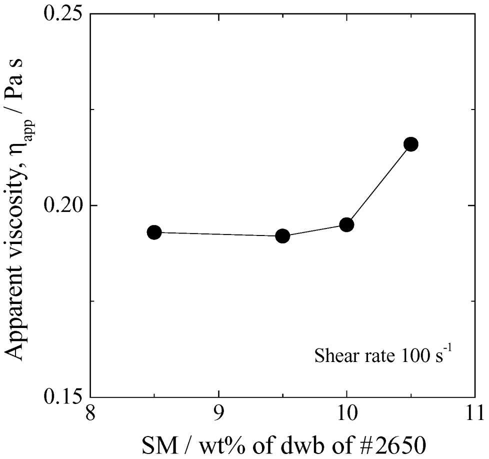

Figure 4 Apparent viscosity for 70 wt% silicon carbide slurries containing 2 wt% #2650 in the presence of various amounts of SM.

should enhance the affinity for aqueous media, because the electrostatic repulsive potential overcame the van der Waal's attractive potential. As a result, the addition of SM to carbon promotes fluidization of the carbon slurries in aqueous media. SM worked on the carbon surfaces and the coexistent base worked on the dissociation of the carboxyl group in SM.

3.2. Suitable processing condition

The results of our previous studies [6, 7] and this report showed that TMAOH and SM play important roles in governing the dispersion and fluidity of silicon carbide and carbon slurries, respectively. On the other hand, the fluidization of silicon carbide slurries with carbon powders should be evaluated, because silicon carbide slurries with sintering aids are needed to carry out slip casting of silicon carbide and to obtain the sintered body of silicon carbide. Thus, it is important to evaluate the role of SM in mixed slurries of silicon carbide and carbon powders. Silicon carbide slurries containing carbon were prepared using silicon carbide powders with 0.35 wt% TMAOH (dwb for silicon carbide) and 2 wt% #2650 (dwb for silicon carbide) with various amounts of SM (dwb for the #2650 powders).

Fig. 4 shows the apparent viscosity for 70 wt% silicon carbide slurries with 2 wt% #2650 (dwb for silicon carbide) in the presence of various amounts of SM. Well-dispersed silicon carbide slurries with #2650 were obtained at 8.5–10 wt% SM (dwb for #2650 powders). This optimum amount of SM for silicon carbide slurry with #2650 was equal to that for the #2650 slurry, as mentioned above. These observations indicated that TMAOH works on the silicon carbide surface silanol groups, that have dissociated to form SiO^-, and SM works on the surface of carbon preferentially in the mixed slurry of silicon carbide and carbon. Furthermore, these results indicated that with the addition of the optimum amounts of TMAOH (dwb for silicon carbide) and SM (dwb for carbon) in the silicon carbide slurry with carbon, a well-dispersed and fluidized silicon carbide slurry with carbon can be obtained easily, even if the characteristics of the silicon carbide and/or carbon powders and mixed ratio of these powders are different.

The green body and sintered bodies were obtained by the silicon carbide slurries with carbon and boron carbide (dwb for silicon carbide) prepared in this process. Fig. 5 shows the densities of the green and sintered bodies using MA100 and #2650 as a function of amount of boron carbide added. The green density values of both MA100 and #2650 did not change, and were 62–63% of the theoretical density (Th. D.) of silicon carbide (Th.D. 3.21 g/cm^3). The sintered density value of silicon carbide with MA100 increased markedly up to addition of 0.3 wt% boron carbide, showed a slight increase at 0.3–0.5 wt%, and the maximum value was 96.5% Th.D. with addition of 0.5–0.6 wt% boron carbide. On the other hand, the sintered density value of silicon carbide with #2650 increased up to addition of 0.3 wt% boron carbide with a higher value at 0.3–0.6 wt% boron carbide, reaching a maximum value of 98.3% of Th.D. With the addition of 0.2–0.6 wt% boron carbide, the sintered density value of the silicon carbide with #2650 was higher than that of the silicon carbide with MA100.

Fine carbon powder is generally associated with segregation of carbon. Segregation results in a concentration gradient in the green body and leads to a density gradient, high residual stresses, and cracking during firing. In this experiment, however, green and fired silicon carbide bodies containing nano scale carbon showed very high densities. Especially, the sintered density of the silicon carbide body with finer carbon powder

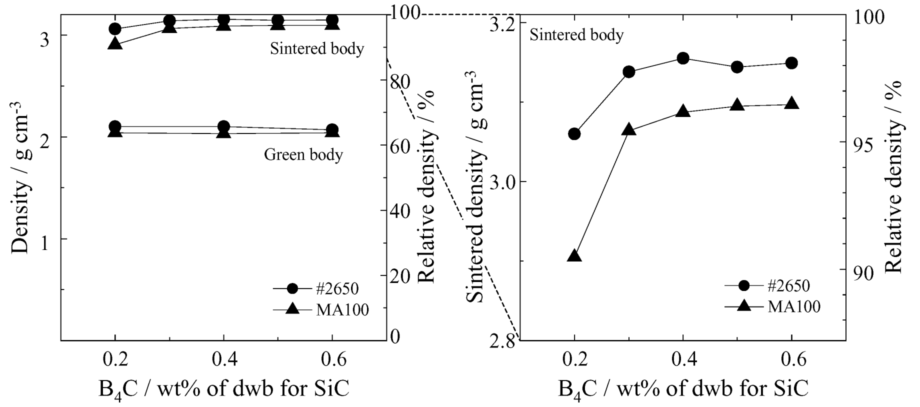

Figure 5 Green and sintered densities for silicon carbide slurries with 2 wt% #2650 or MA100 as a function of amount of boron carbide added.

(mean particle diameter, 13 nm) was equivalent to that of the silicon carbide body using phenolic resin and pitch tar as a carbon source [14].

These results indicated that carbon and boron carbide as sintering aids could be distributed homogeneously in the silicon carbide slurries and a green body obtained through this process, even if nano scale carbon powder was used as a sintering aid. Thus, this process is suitable to promote the dispersion and the fluidization of silicon carbide slurries containing carbon and boron carbide.

4. Conclusions

The addition of SM to carbon promoted the fluidization of carbon slurries in aqueous media. The enhancement of the fluidity of the aqueous silicon carbide slurry with carbon indicated that TMAOH and SM worked mainly on silicon carbide and carbon, respectively. A well-dispersed and fluidized silicon carbide slurry with carbon was easily obtained by adding the optimum amount of TMAOH (dwb for silicon carbide) and that of SM (dwb for carbon) to the slurry. The green and sintered bodies cast by the silicon carbide slurries with carbon and boron carbide prepared in this process showed high densities. Using carbon with higher specific surface area, the sintered density was high with addition of 0.3–0.6 wt% boron carbide, reaching a maximum value of 98.3% Th.D.

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