

# Aqueous Processing, Hot-Pressing and Mechanical Properties of Silicon Carbide with $\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$

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アルミナとイットリアを添加した炭化ケイ素の水系プロセッシング，加圧焼結及び力学特性

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Submicrometer-sized  $\alpha$ -SiC powder was mixed in an aqueous solution at pH 5.0 with the following  $\text{Al}_2\text{O}_3$  (1–2 vol% against SiC)– $\text{Y}_2\text{O}_3$  (0.94–1.6 vol%) sintering additives: sample A– $\text{Al}_2\text{O}_3$  powder plus  $\text{Y}_2\text{O}_3$  powder, sample B– $\text{Al}_2\text{O}_3$  powder plus  $\text{Y}_2\text{O}_3$  powder and polyacrylic acid dispersant, sample C– $\text{Al}_2\text{O}_3$  powder plus  $\text{Y}^{3+}$  ion adsorbed and sample D– $\text{Y}^{3+}$  ion adsorbed. The prepared suspensions were consolidated by filtration through a gypsum mold. Green compacts were densified to a 96.2–99.3% relative density at 1800–1950°C under a pressure of 39 MPa for 2 h in an Ar or reduced atmosphere. The sinterability of SiC became higher in the following order: sample D < sample C < sample A  $\approx$  sample B. The sinterability of samples A and B was comparable to that of SiC hot-pressed with  $\text{Al}_2\text{O}_3$ . Dense SiC with  $\text{Y}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  plus  $\text{Y}_2\text{O}_3$  showed the following excellent mechanical properties: average four-point flexural strengths of 565–719 MPa, fracture toughness of 5.0–6.2  $\text{MPa} \cdot \text{m}^{1/2}$ , Weibull modulus of 5.4–11.4 and Vickers hardness of 19–22 GPa. Suppression of grain growth in SiC enhanced the mechanical properties.

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## 1. Introduction

Silicon carbide (SiC) is widely useful as a high temperature structural material because of its excellent high temperature strength, good oxidation resistance, high thermal shock resistance, and high hardness. However, it has been impossible to densify a submicrometer-sized SiC powder without sintering additives because of its strong covalent bonding character. Alliegro et al.<sup>1)</sup> were the first researchers who recognized in 1956 that a silicon carbide powder with an additive could be densified under a pressure. Their extensive study on the sintering additives in the hot-pressing of SiC suggested that aluminum (either in elemental form or as an oxide) is a highly effective additive to densify SiC above 98% of theoretical. Lange<sup>2)</sup> obtained in 1975 dense SiC ceramics by hot-pressing with  $\text{Al}_2\text{O}_3$  as a sintering additive at 1950°C. The added  $\text{Al}_2\text{O}_3$  reacted with the  $\text{SiO}_2$  present at the SiC surfaces, and formed an eutectic melt below the melting point of  $\text{Al}_2\text{O}_3$ . The densification of SiC was achieved by the liquid phase sintering. Recently the chemical methods for the addition of sintering additives such as  $\text{Al}_2\text{O}_3$  plus  $\text{Y}_2\text{O}_3$  to SiC powder have been studied to control the liquid phase sintering and the resultant microstructures of SiC ceramics.<sup>3)–8)</sup> Liden et al.<sup>4)</sup> mixed 0.45  $\mu\text{m}$ -SiC powder with 2 mass%  $\text{Al}_2\text{O}_3$  (50 nm) powder–1 mass%  $\text{Y}_2\text{O}_3$  (10 nm) powder in aqueous solutions and sintered the dried green compact of 51% of theoretical density to 99.7% relative density at 1880°C for 4 h in an Ar atmosphere. Sciti and Belloso<sup>9)</sup> studied the densification of SiC powder of a specific surface area of 11.6  $\text{m}^2/\text{g}$  by the hot-pressing under a pressure of 30 MPa at 1880°C in vacuum. The SiC powder, 2.2–4.8 vol%  $\text{Al}_2\text{O}_3$  powder and 1.6–2.6 vol%  $\text{Y}_2\text{O}_3$  powder were mixed in ethylalcohol. The prepared suspension was dispersed by pulsed ultrasonic vibration and dried at 80°C using a rotary evaporator. The dried and sieved powder started the densification at 1470–1520°C and was sintered to a density higher than 98% at

1880°C.

The densification of  $\text{Al}_2\text{O}_3$  plus  $\text{Y}_2\text{O}_3$ -doped SiC ceramics proceeds by the liquid phase sintering with a dissolution–precipitation mechanism of SiC in the eutectic liquid of the  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  system.<sup>10)–13)</sup> The  $\text{SiO}_2$  component forms slightly on the surface of SiC powder. The sinterability of the SiC– $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  compact depends on the amount and ratio of  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  system.<sup>14)–16)</sup> Uniform addition of a small amount of sintering additives to SiC is effective to increase the sinterability. The chemical methods of SiC with the sintering additives are expected to provide the following advantages: (1) a homogeneous distribution of the additives around SiC particles, (2) the increased densification rate by the well-distributed liquid and (3) the decrease of the amount of additives.<sup>17)</sup>

In our previous papers,<sup>7),10)</sup> we studied the interaction of the submicrometer-sized SiC particles– $\text{Al}_2\text{O}_3$  (0.2  $\mu\text{m}$ )– $\text{Y}_2\text{O}_3$  (0.1  $\mu\text{m}$ ) system in the aqueous suspensions at pH 3–10. The isoelectric points of SiC,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  were pH 2.5, 8.0 and 7.5, respectively. The processing in the heterocoagulation region at pH 5 gave the superior properties (high strength, high fracture toughness, and high Weibull modulus) after the hot-pressing of the consolidated powder compacts at 1800°C. In the SiC– $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  system at pH 5.0, the negatively charged SiC particles are well dispersed by their strong repulsive interaction. On the other hand, positively charged  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  particles are adsorbed on the negatively charged SiC particles by their electrostatic attractive forces to form a network structure of heterocoagulated particle clusters. We also reported the interaction between SiC surfaces and Al or Y ion (added as  $\text{Al}(\text{NO}_3)_3$  or  $\text{Y}(\text{NO}_3)_3$ ) to adsorb uniformly the sintering additives.<sup>18),19)</sup> The neutral SiC surface near the isoelectric point ( $\sim$ pH 3) adsorbed no  $\text{Al}^{3+}$  ions or just a trace. The negatively charged SiC surface at pH 4 adsorbed 0.030 mg  $\text{Al}^{3+}$  ions/ $\text{m}^2$  in a 3.7 mM– $\text{Al}(\text{NO}_3)_3$  solution. In the pH

range from 5 to 8, negatively charged SiC particles coexisted with positively charged  $\text{Al}(\text{OH})_3$  precipitate. The amount of  $\text{Y}^{3+}$  ions adsorbed on the SiC particles increased with an increase of pH. In a 0.3 M- $\text{Y}(\text{NO}_3)_3$  solution at pH 5,  $\text{Y}^{3+}$  ions of 0.854 mg were adsorbed on the SiC surface of  $1 \text{ m}^2$ . In this paper, the sinterability and mechanical properties of SiC were compared for the sintering additives of  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ - $\text{Y}_2\text{O}_3$  and  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  systems. The green compacts were formed from the corresponding aqueous SiC suspensions containing the oxide additives or metal ion and hot-pressed at 1600–2050°C in an Ar atmosphere.

## 2. Experimental procedure

### 2.1 Preparation and consolidation of SiC suspension

In this experiment, four kinds of SiC compacts were formed from the aqueous SiC suspensions at pH 5. Sample A—An  $\alpha$ -SiC powder with the following characteristics, supplied by Yakushima Electric Industry Co., Ltd., Kagoshima, was used: chemical composition, SiC 97.5 mass%,  $\text{SiO}_2$  1.75 mass%, C 0.65 mass%, Al 0.025 mass%, Fe 0.027 mass%, median size 0.65  $\mu\text{m}$ , and a specific surface area of 13.4  $\text{m}^2/\text{g}$ . As-received  $\alpha$ -SiC powder was mixed with  $\alpha$ - $\text{Al}_2\text{O}_3$  of a median size 0.2  $\mu\text{m}$  and a specific surface area 10.5  $\text{m}^2/\text{g}$  ( $\text{Al}_2\text{O}_3 > 99.99$  mass%, Sumitomo Chemical Industry Co., Ltd., Tokyo) and  $\text{Y}_2\text{O}_3$  of a specific surface area 15.0  $\text{m}^2/\text{g}$  ( $\text{Y}_2\text{O}_3 > 99.9$  mass%, Shinetsu Chemical Industry Co., Ltd., Tokyo). The SiC/ $\text{Al}_2\text{O}_3$ / $\text{Y}_2\text{O}_3$  (1/0.020/0.016 volume ratio) mixed powders were dispersed at 30 vol% in an aqueous solution at pH 5.0 for 5 h.<sup>7),10)</sup> The pH of suspension was adjusted using 0.1M- $\text{NH}_4\text{OH}$  solution. Sample B—Polyacrylic acid (PAA, average molecular weight 10000, Daiichi Kogyo Seiyaku Co., Kyoto) of 0.5  $\text{mg}/\text{m}^2$ -SiC surface was added to the SiC suspension with  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  powders. From the measurement of viscosity of the SiC- $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  suspensions with PAA of 0–0.7  $\text{mg}/\text{m}^2$ , the saturated amount of PAA adsorbed on the surfaces of SiC,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  was estimated to be 0.5  $\text{mg}/\text{m}^2$  because of the minimum apparent viscosity.<sup>20)</sup> Sample C—As-received  $\alpha$ -SiC powder was mixed with 0.2  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder (SiC/ $\text{Al}_2\text{O}_3$  = 1/0.012 volume ratio) and dispersed at 30 vol% solid in a 0.3 M- $\text{Y}(\text{NO}_3)_3$  aqueous solution at pH 5 for 12 h to adsorb  $\text{Y}^{3+}$  ions on the negatively charged SiC surface.<sup>12),18),21)</sup> No adsorption of  $\text{Y}^{3+}$  ions on the positively charged  $\text{Al}_2\text{O}_3$  surface was measured in the previous experiment.<sup>11),13)</sup> From the measurement of the amount of  $\text{Y}^{3+}$  ions adsorbed, the volume ratio of the SiC/ $\text{Al}_2\text{O}_3$ / $\text{Y}_2\text{O}_3$  (as  $\text{Y}^{3+}$  ions) components was adjusted to 1/0.0117/0.0094 (1/0.0145/0.0145 mass ratio). Although the SiC supplier of sample C was same as that of samples A and B, the SiC purity of as-received powder was slightly higher than the powder of sample A: SiC 98.90 mass%,  $\text{SiO}_2$  0.66 mass%, C 0.37 mass%, Al 0.004 mass%, Fe 0.013 mass%, median size 0.8  $\mu\text{m}$ , specific surface area 13.4  $\text{m}^2/\text{g}$ . Sample D—PAA of 0.40  $\text{mg}/\text{m}^2$ -SiC surface (saturated amount)<sup>12),18),21)</sup> was added to a 30 vol% SiC suspension with  $\text{Y}^{3+}$  ions (SiC/ $\text{Y}_2\text{O}_3$  = 1/0.010 volume ratio). The used SiC powder was same as that of sample C. The sinterability and mechanical properties of the above four kinds of SiC compacts were compared with the previously reported data of the SiC compacts with  $\text{Al}_2\text{O}_3$  additive (samples E and F). Sample E—The SiC with 0.2  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  (purity  $> 99.99$  mass%) at the volume ratio SiC/ $\text{Al}_2\text{O}_3$  = 1/0.035 was dispersed at 30 vol% in an aqueous solution at pH 10.0.<sup>5)</sup> The used SiC was same as that of sample A. Sample F—As-received  $\alpha$ -SiC powder (same as that of sample A) was dispersed at 30 vol% solid in a 0.28 M- $\text{Al}(\text{NO}_3)_3$  aqueous solution at pH 5 to adsorb  $\text{Al}^{3+}$  ions on the negatively charged

SiC surface (SiC/ $\text{Al}_2\text{O}_3$  = 1/0.002 volume ratio).<sup>22)</sup>

The rheological properties of the colloidal SiC suspensions (samples A–D) were measured by a cone and plate type viscometer at room temperature in a shear rate range from 1 to 400  $\text{s}^{-1}$  (Visconic EMD, EHD type, Tokyo Keiki Co., Tokyo). The prepared each suspension was formed into a rectangular green compact with 38 mm length, 25 mm width and 20 mm height by filtration through a gypsum board at room temperature. Bakelite molds were set on a thick flat gypsum board to shape the suspension into the rectangular compact.

### 2.2 Hot-pressing and mechanical properties of SiC

The consolidated green compacts were hot-pressed under a pressure of 39 MPa at 1600–2050°C for 2 h in an Ar flow. The heating and cooling rates were 10°C/min. The densities of the hot-pressed compacts were measured by the Archimedes method using kerosene. The surface of hot-pressed SiC sample was polished with 1  $\mu\text{m}$  diamond paste and etched with the mixture of  $\text{NaCl}/\text{NaOH}$  = 85/15 (molar ratio) at 600°C for 5 min in air to observe the microstructure by scanning electron microscope (SM300, Topcon Technologies, Inc., Tokyo). The hot-pressed SiC was cut into the specimens with sizes of 3 mm height, 4 mm width, and 38 mm length. The specimens were polished with SiC papers of Nos. 600 and 2000 and diamond paste of 6 and 1  $\mu\text{m}$ . The Vickers hardness of the hot-pressed SiC was measured at the load of 9.8 N (model MVF, Akashi Seisakusho Co., Ltd., Tokyo). The flexural strength of hot-pressed SiC was measured at room temperature by the four-point flexural method over spans of 30 mm (lower span) and 10 mm (upper span) at a crosshead speed of 0.5 mm/min. The fracture toughness was evaluated by single-edge V-notch beam (SEVNB) method (samples A–D, F) or single edge precracked beam (SEPB) method (sample E). A thin diamond blade 1 mm thick, where the tip of V-notch had a curvature radius of 20  $\mu\text{m}$ , was used to introduce V-notch of  $a/W$  = 0.1–0.6 ( $a$ : notch length,  $W$ : width of the beam). The strengths of the notched specimens (samples A–D, F) and sample E precracked by a Vickers indenter of 98 N to induce microcracks, were measured by three-point loading over a span 30 mm at a crosshead speed of 0.5 mm/min. Equation (1) provides the fracture toughness for the SEVNB method and equation (2) indicates the shape factor ( $Y$ ) of crack at  $S/W$  = 7.5.  $S$ ,  $P$ , and  $B$  in Eqs. (1) and (2) are the span width, applied load and thickness of beam, respectively.

$$K_{\text{IC}} = \frac{3PS}{2BW^2} Y\sqrt{a} \quad (1)$$

$$Y = 1.964 - 2.837\lambda + 13.711\lambda^2 - 23.250\lambda^3 + 24.129\lambda^4 \quad \left( \lambda = \frac{a}{W} \right) \quad (2)$$

## 3. Results and discussion

### 3.1 Rheological properties of SiC suspensions

Figure 1 shows the influence of additives on the apparent viscosity of 30 vol% SiC suspension at pH 5. The rheological behavior of the SiC suspensions was similar to a Bingham flow. The apparent viscosity of samples A, C, and D was similar each other and became higher than that of monolithic SiC suspension. The addition of a small amount of  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{Y}^{3+}$  ions enhanced the formation of a network structure of heterocoagulated particle clusters in the concentrated SiC suspension, resulting in the increased apparent viscosity.<sup>7),13),18),21)</sup> PAA addition (sample B) decreased the apparent viscosity of the SiC- $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  suspension, indicating that the dispersibility of the colloidal SiC,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$

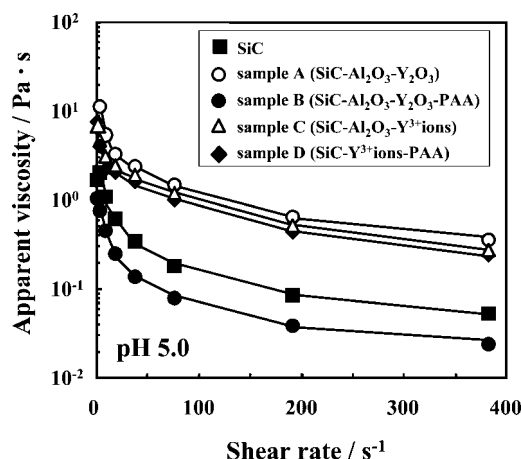


Fig. 1. Effect of addition of  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Y}^{3+}$  ions and PAA on the apparent viscosity of 30 vol% SiC suspension at pH 5.0.

particles was increased by the adsorption of PAA. PAA  $[-\text{CH}_2-\text{CH}(\text{COOH})-]_n$  releases  $\text{H}^+$  ions and produces negatively charged polymer at pH higher than 3.<sup>23)</sup> The negatively charged PAA is adsorbed on the positively charged  $\text{SiOH}_2^+$  sites of the thin  $\text{SiO}_2$  layer.<sup>12),18),21),24)</sup> The number of  $\text{SiOH}_2^+$  sites is greatly smaller than that of  $\text{SiO}^-$  sites. The increased zeta potential of SiC to negative values with addition of PAA indicates the adsorption of negatively charged PAA on the positively charged  $\text{SiOH}_2^+$  sites. However, the effect of PAA addition was small on the viscosity of SiC- $\text{Y}^{3+}$  ions suspension. Apparently,  $\text{Y}^{3+}$  ion addition and PAA addition have an opposite influence on the viscosity of the SiC suspension. In sample D, the coagulation effect by  $\text{Y}^{3+}$  ions became larger than the dispersion effect by PAA.

### 3.2 Hot-pressing of SiC compact

The 30 vol% SiC suspensions (samples A–D) were consolidated by filtration through a gypsum mold. The relative density of the powder compact after the calcination at  $1000^\circ\text{C}$  in an Ar atmosphere was as follows: sample A–47%, sample B–56%, sample C–53%, sample D–51%. The suspension of lower apparent viscosity (Fig. 1) gave the higher packing density. Similarly, the packing density for samples E and F after  $1000^\circ\text{C}$  calcination was measured to be 56 and 47%, respectively. Figure 2 shows the relative density of SiC hot-pressed at  $1600$ – $2050^\circ\text{C}$  for 2 h under a pressure of 39 MPa in an Ar flow. The sinterability of SiC became higher in the following order of the sintering additives: sample D < sample C < sample F < sample E < sample A  $\approx$  sample B. The mixed  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  interact with the  $\text{SiO}_2$  on the surface of SiC to form a liquid phase. Only the addition of  $\text{Y}_2\text{O}_3$  (as  $\text{Y}^{3+}$  ions, sample D) needed a higher heating temperature for the densification. On the other hand,  $\text{Al}_2\text{O}_3$  component enhanced the sinterability of SiC compact through the formation of the liquid of the  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$  system (samples E and F). The addition of the  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  components had also a great effect on the densification of SiC (samples A, B and C). The above result suggests that the liquids of the  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$  system and  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  system are more useful than that of the  $\text{SiO}_2$ – $\text{Y}_2\text{O}_3$  system for the decrease of sintering temperature. According to Omori and Takei,<sup>25)</sup> the sinterability of SiC shows a maximum at the mass ratio of  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3 \approx 50/50$ . She and Ueno<sup>3)</sup> reported a high sinterability of SiC at the mass ratios of  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3 = (50\text{--}75)/(25\text{--}50)$ . These results indicate that  $\text{Al}_2\text{O}_3$  rich composition of the  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  additives is more useful than  $\text{Y}_2\text{O}_3$

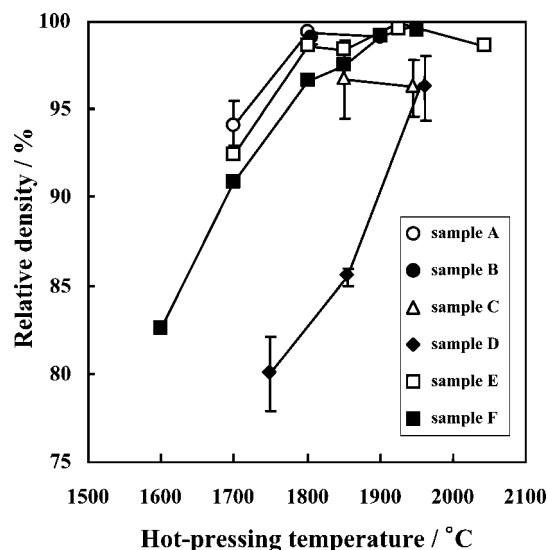


Fig. 2. Relative density of the SiC compact with  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  additives as a function of hot-pressing temperature.

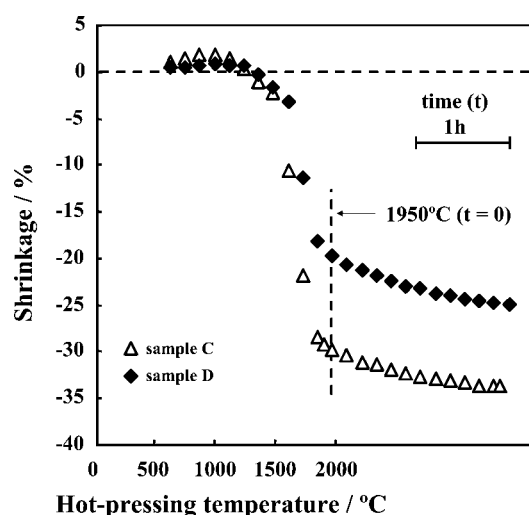


Fig. 3. Shrinkage curves of samples C and D during the hot-pressing at  $1950^\circ\text{C}$  (See Table 1 for samples).

rich composition for the densification of SiC. In this experiment, the compositions of the  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  additives in samples A, B and C were slightly enriched with  $\text{Al}_2\text{O}_3$ .

Figure 3 shows the shrinkage curves of samples C and D during the heating under a pressure of 39 MPa. The shrinkage of both the samples with a similar packing density after  $1000^\circ\text{C}$  calcination ( $52 \pm 1\%$ ) started at about  $1400^\circ\text{C}$ . The liquid formation temperatures of the  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  system and the  $\text{SiO}_2$ – $\text{Y}_2\text{O}_3$  system at the given compositions, are  $1400$  and  $1775^\circ\text{C}$ , respectively, in the phase diagrams. During the heating up to the temperatures higher than  $1500^\circ\text{C}$ , sample C showed a greater shrinkage than sample D. That is, the  $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$  liquid enhanced the densification of SiC than the  $\text{SiO}_2$ – $\text{Y}_2\text{O}_3$  liquid in the temperature range from  $1500$ – $1950^\circ\text{C}$ . The X-ray diffraction patterns for samples A–D hot-pressed at  $1850$ – $1950^\circ\text{C}$  corresponded to 6H- and 4H-type SiC and no secondary phases were identified.

Figure 4 shows the microstructures of dense SiC compacts

hot-pressed at 1800–1950°C for 2 h. The average grain size, measured on 200 grains, was (a) 2.8  $\mu\text{m}$  for sample A hot-pressed at 1800°C, (b) 2.0  $\mu\text{m}$  for sample B hot-pressed at 1800°C, (c) 2.9  $\mu\text{m}$  for sample C hot-pressed at 1850°C, (d) 2.4  $\mu\text{m}$  for sample D hot-pressed at 1950°C. The grain size distributions in the present four samples were narrow. In our previous experiments,<sup>5),22)</sup> sample E hot-pressed at 1850°C and sample F hot-pressed at 1950°C provided the microstructures of average grain sizes of 5.8 and 5.2  $\mu\text{m}$ , respectively. The addition of Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> additives suppressed the grain growth of SiC particles rather than the addition of Al<sub>2</sub>O<sub>3</sub> additive. Enhanced dispersion of colloidal particles in the aqueous suspension by PAA addition (sample B) was effective to achieve the fine SiC microstructure.

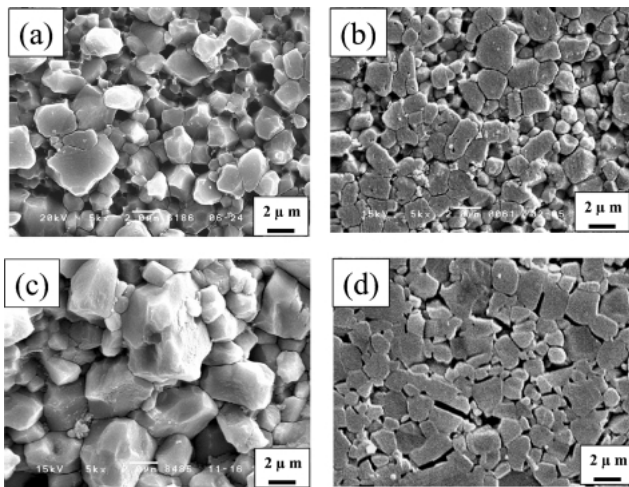


Fig. 4. Microstructures of (a) sample A hot-pressed at 1800°C, (b) sample B hot-pressed at 1800°C, (c) sample C hot-pressed at 1850°C, and (d) sample D hot-pressed at 1950°C.

### 3.3 Mechanical properties of densified SiC

Figure 5 shows the Weibull distribution plots of the flexural strengths for the dense SiC hot-pressed at 1800–1950°C. The strength at 50% fracture probability and Weibull modulus were summarized in Table 1. The average strength increased in the following order: sample C2 (1950°C hot-pressing) < sample B < sample A ≈ sample C1 (1850°C hot-pressing) < sample D. Addition of a small amount of Y<sub>2</sub>O<sub>3</sub> (1 vol%, sample D) was more effective than the addition of Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> system (samples A–C) to increase the strength of SiC. The decrease of the amount of Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> additives gave no significant influence on the strength of SiC hot-pressed at 1800–1850°C (samples A and B: 2.0 vol% Al<sub>2</sub>O<sub>3</sub>, 1.6 vol% Y<sub>2</sub>O<sub>3</sub>, sample C1: 1.2 vol% Al<sub>2</sub>O<sub>3</sub>, 0.94 vol% Y<sub>2</sub>O<sub>3</sub>). The

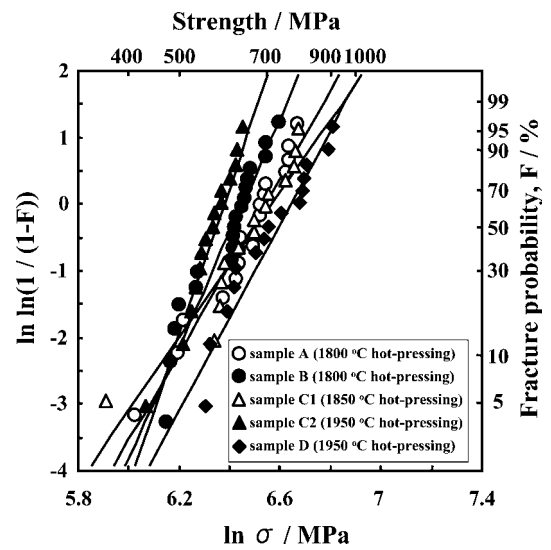


Fig. 5. Weibull distribution plots for flexural strengths of dense SiC.

Table 1. Mechanical Properties of SiC Hot-Pressed at 1800–1950°C under a Pressure of 39 MPa in an Ar Atmosphere

Processing and properties	Sample						
	A <sup>10)</sup>	B <sup>20)</sup>	C1	C2	D <sup>12)</sup>	E <sup>5)</sup>	F <sup>22)</sup>
Al <sub>2</sub> O <sub>3</sub> (vol%)	2.0	2.0	1.2	1.2	—	3.5	0.20
Y <sub>2</sub> O <sub>3</sub> (vol%)	1.6	1.6	0.94	0.94	1.0	—	—
PAA (mg/m <sup>2</sup> )	—	0.5	—	—	0.4	—	—
Hot-pressing temperature (°C)	1800	1800	1850	1950	1950	1850	1950
Relative density (%)	99.3 ± 0.3	99.0 ± 0.3	96.6 ± 2.3	96.2 ± 1.6	96.2 ± 1.8	98.3	99.8
Average grain size (μm)	2.8	2.0	2.9	3.5	2.4	5.8	5.2
Weibull modulus	6.6	8.2	5.4	11.4	6.7	—	—
Average strength (MPa)	647	615	666	565	719	390	357
Fracture toughness (MPa·m <sup>1/2</sup> )	5.0 ± 0.44	5.8 ± 1.11	6.2 ± 1.10	5.4 ± 0.50	6.2 ± 1.30	4.9 ± 0.30	4.2 ± 0.24
Vickers hardness (GPa)	21.8 ± 1.9	21.9 ± 1.2	21.0 ± 3.0	19.0 ± 1.0	19.9 ± 0.5	—	—

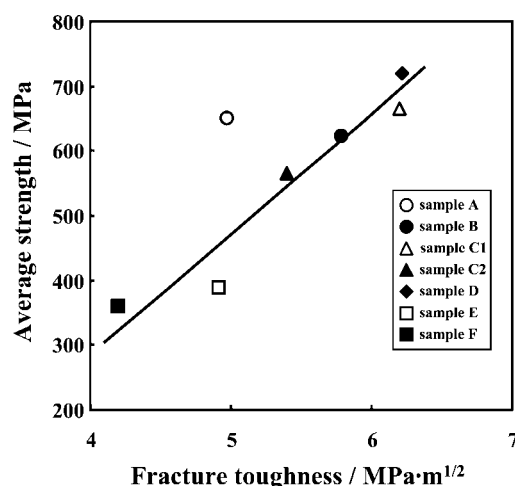


Fig. 6. Relationship between average strength and fracture toughness for the dense SiC hot-pressed at 1800–1950°C.

increase of the hot-pressing temperature of sample C from 1850° to 1950°C improved the Weibull modulus but decreased the strength. As compared with the SiC with Y<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> additive, the dense SiC with Al<sub>2</sub>O<sub>3</sub> (samples E and F, Table 1), showed a lower strength (360–390 MPa).

The strength ( $\sigma$ ) of brittle ceramics is dominated by fracture toughness ( $K_{IC}$ ) and size of flaw ( $a$ ) by Eq. (3),

$$\sigma = \frac{K_{IC}}{Y\sqrt{a}} \quad (3)$$

where  $Y$  is the shape factor of flaw. Figure 6 shows relationship between the average strength and fracture toughness of the hot-pressed SiC. The strength increased with an increase of fracture toughness. The addition of Y<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> increased the fracture toughness of SiC than the addition of Al<sub>2</sub>O<sub>3</sub>. As seen in Table 1, the fracture toughness was sensitive to the average grain size of SiC and increased when the grain growth was suppressed. From the viewpoints of processing (a small amount of sintering additives, low processing temperature, high bulk density and fine microstructure) and mechanical properties (high Weibull modulus, high strength and high fracture toughness), sample B may be the most attractive SiC. Addition of PAA to sample C is also expected to provide the superior microstructure and mechanical properties. On the other hand, the following mechanical properties are reported for the pressureless-sintered SiC. Mulla and Krstic<sup>26,27)</sup> sintered  $\beta$ -SiC with 10 mass% Al<sub>2</sub>O<sub>3</sub> to 97–98% theoretical density at 2050°C for 30 min. The obtained dense SiC provided 600  $\pm$  50 MPa of the flexural strength and 6.0  $\pm$  0.3 MPa·m<sup>1/2</sup> of the fracture toughness. The SiC pressureless-sintered with 6 vol% Al<sub>2</sub>O<sub>3</sub> and 1.6 vol% Y<sub>2</sub>O<sub>3</sub> at 1900–2000°C by She and Ueno,<sup>3)</sup> showed 530–625 MPa of flexural strength and 6.8–7.2 MPa·m<sup>1/2</sup> of fracture toughness. Rixecker et al.<sup>28)</sup> mixed  $\alpha$ -SiC with 6 vol% AlN and 4 vol% Y<sub>2</sub>O<sub>3</sub> and formed green compacts by isostatic pressing of 240–600 MPa. They densified the SiC in a graphite-heated gas pressure furnace at 1950°C for 30 min under a N<sub>2</sub> pressures of 10 MPa. The obtained fully dense SiC provided 607  $\pm$  80 MPa of the flexural strength and 4.4  $\pm$  0.2 MPa·m<sup>1/2</sup> of the fracture toughness. As compared with the above reported data, the present SiC hot-pressed was characterized by (1) the comparable strength (average strengths of 565–719 MPa after the hot-pressing of 1850–1950°C) and fracture toughness (5.0–6.2 MPa·m<sup>1/2</sup>),

and (2) the lower amount of sintering additives (1.2–2.0 vol% Al<sub>2</sub>O<sub>3</sub>, 0.94–1.6 vol% Y<sub>2</sub>O<sub>3</sub>). The Vickers hardness at 9.8 N of the present SiC was independent of the strength and fracture toughness. The hardness was affected by the bulk density and reached 22 GPa in samples A and B of 99.0–99.3% relative density.

#### 4. Conclusions

(1) The addition of a small amount of Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> powders (1–2 vol% Al<sub>2</sub>O<sub>3</sub>, 0.94–1.6 vol% Y<sub>2</sub>O<sub>3</sub>) or Al<sub>2</sub>O<sub>3</sub> powder (0.2–3.5 vol%) provided a great effect on the densification of SiC during the hot-pressing at 1800–1850°C. Only the addition of Y<sub>2</sub>O<sub>3</sub> (as Y<sup>3+</sup> ions) needed a higher hot-pressing temperature (1950°C) for the densification.

(2) Addition of a small amount of Y<sub>2</sub>O<sub>3</sub> was more effective than the addition of Al<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> additives to increase the strength of dense SiC (average strength 719 MPa). The SiC densified with Al<sub>2</sub>O<sub>3</sub> plus Y<sub>2</sub>O<sub>3</sub> showed 565–666 MPa of average strength. Only the addition of Al<sub>2</sub>O<sub>3</sub> resulted in the strength lower than 400 MPa.

(3) The strength and fracture toughness depended on the grain size of SiC. Suppression of grain growth of SiC enhanced the strength and fracture toughness.

(4) Addition of PAA in the SiC suspension with Al<sub>2</sub>O<sub>3</sub> plus Y<sub>2</sub>O<sub>3</sub> decreased the grain size of hot-pressed SiC and enhanced the Weibull modulus and fracture toughness.

#### References

- Alliegro, R. A., Coffin, L. B. and Tinklepaugh, J. R., *J. Am. Ceram. Soc.*, Vol. 39, pp. 386–389 (1956).
- Lange, F. F., *J. Mater. Sci.*, Vol. 10, pp. 314–320 (1975).
- She, J. H. and Ueno, K., *Mater. Chem. Phys.*, Vol. 59, pp. 139–142 (1999).
- Liden, E., Carlstrom, E., Eklund, L., Nyberg, B. and Calsson, R., *J. Am. Ceram. Soc.*, Vol. 78, pp. 1761–1768 (1995).
- Hirata, Y., Hidaka, K., Matsumura, H., Fukushige, Y. and Sameshima, S., *J. Mater. Res.*, Vol. 12, pp. 3146–3157 (1997).
- She, J. H. and Ueno, K., *Mater. Res. Bull.*, Vol. 34, pp. 1629–1636 (1999).
- Wang, X. H., Shirakawa, R., Hirata, Y., Hatate, Y. and Ijichi, K., *J. Ceram. Proc. Res.*, Vol. 4, pp. 265–270 (2003).
- Magnani, G., Minoccarri, G. L. and Pilotti, L., *Ceram. Inter.*, Vol. 26, pp. 495–500 (2000).
- Sciti, D. and Bellosi, A., *J. Mater. Sci.*, Vol. 35, pp. 3849–3855 (2000).
- Wang, X. H. and Hirata, Y., *J. Ceram. Soc. Japan*, Vol. 112, pp. 22–28 (2004).
- Hidaka, N. and Hirata, Y., *Ceram. Trans.*, Vol. 152, pp. 109–118 (2004).
- Tabata, S. and Hirata, Y., *Ceram. Trans.*, Vol. 152, pp. 119–128 (2004).
- Hidaka, N., Hirata, Y. and Sameshima, S., *J. Ceram. Proc. Res.*, Vol. 3, pp. 271–277 (2002).
- Wang, L. M. and Wei, W. C., *J. Ceram. Soc. Japan*, Vol. 103, pp. 434–443 (1995).
- Lee, S. K. and Kim, C. H., *J. Am. Ceram. Soc.*, Vol. 77, pp. 1655–1658 (1994).
- Mulla, M. A. and Krstic, V. D., *Am. Ceram. Soc. Bull.*, Vol. 70, pp. 439–443 (1991).
- Hirata, Y. and Shih, W. H., *Advances in Science and Technology 14, Proceedings of 9th CIMTEC—World Ceramics Congress, Ceramics: Getting into the 2000's—Part B, 1999*, Ed. by P. Vincenzini, Techna Srl., Faenza, pp. 637–644.
- Hirata, Y., Tabata, S. and Ideue, J., *J. Am. Ceram. Soc.*, Vol. 86, pp. 5–11 (2003).
- Hirata, Y., Miyano, K., Sameshima, S. and Kamino, Y., *Colloids and Surface A*, Vol. 133, pp. 183–189 (1998).
- Wang, X. H. and Hirata, Y., *Ceram. Inter.* (2004) in press.
- Tabata, S., Sameshima, S. and Hirata, Y., *J. Ceram. Proc.*

- Res.*, Vol. 3, pp. 29–33 (2002).
- 22) Sameshima, S., Miyano, K. and Hirata, Y., *J. Mater. Res.*, Vol. 13, pp. 816–820 (1998).
- 23) Hirata, Y., Kamikakimoto, J., Nishimoto, A. and Ishihara, Y., *J. Ceram. Soc. Japan*, Vol. 100, pp. 7–12 (1992).
- 24) Hirata, Y., Nakagama, S. and Ishihara, Y., *J. Mater. Res.*, Vol. 5, pp. 640–646 (1990).
- 25) Omori, M. and Takei, H., *J. Am. Ceram. Soc.*, Vol. 65, pp. C92–C92 (1982).
- 26) Krstic, V. D., *Mater. Res. Soc. Bull.*, Vol. XX, pp. 46–49 (1995).
- 27) Mulla, M. A. and Krstic, V. D., *Acta Metal. Mater.*, Vol. 42, pp. 303–308 (1994).
- 28) Rixecker, G., Wiedmann, I., Rosinus, A. and Aldinger, F., *J. Eur. Ceram. Soc.*, Vol. 21, pp. 1013–1019 (2001).