

Consolidation behavior of nanometer-sized SiC particles with phenylalanine through pressure filtration at 1 MPa

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The consolidation behavior of two kinds of colloidal SiC particles (30 and 330 nm diameters) with and without phenylalanine dispersant ($\text{C}_6\text{H}_5\text{CH}_2\text{CHNH}_3^+\text{COO}^-$) at pH 7 was examined using a developed pressure filtration apparatus at 1 MPa of applied pressure. The height of 5 vol %–30 nm SiC suspension with and without phenylalanine as a function of filtration time was well simulated by a filtration model developed for a flocculated suspension rather than a traditional filtration model for a dispersed suspension. The result with phenylalanine is related to the colloidal phase transition from well dispersed particles to flocculated particles under an applied pressure of 1 MPa. The consolidation time became longer as the amount of phenylalanine added exceeded 0.1 mg/m²-SiC. However, the packing density of 30 nm SiC particles after consolidation increased from 35% for no addition of phenylalanine to 37–42% for 0.1–1 mg phenylalanine/m²-SiC. The consolidation behavior of 20 vol %–330 nm SiC suspension with and without phenylalanine was also well expressed by the filtration model for a flocculated suspension. A longer consolidation time was also measured for the addition of phenylalanine above 1 mg/m²-SiC. However, the packing density (49%) of 330 nm SiC particles increased scarcely to 52% by the addition of phenylalanine (2.68×10^{-2} –2.85 mg/m²-SiC).

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1. Introduction

Wet forming method of ceramic powders such as filtration, pressure filtration,^{1)–3)} electrophoretic deposition^{4)–6)} or doctor blading^{7)–9)} provides more uniform microstructures of green compacts rather than dry forming processes. Among these wet forming methods, pressure filtration can shorten consolidation time of colloidal suspensions and produce dense compacts. The applied pressure of pressure filtration can be as high as 80 MPa when stainless steel equipment is used.¹⁰⁾ However, the filtration process of ceramic particles at a high pressure has been scarcely analyzed. In past five years, our group analyzed the consolidation behavior of aqueous suspensions of hydroxyapatite, silicon carbide, 8 mol % yttria-stabilized zirconia, and alpha alumina powders in a size range from 20 to 800 nm using a newly developed pressure filtration apparatus up to 19 MPa (Fig. 1).^{11)–17)} In this apparatus, gravity effect causing sedimentation of particles can be minimized.

The suspension height of electrosterically stabilized SiC particles (30 and 800 nm median sizes) with polyacrylic ammonium dispersant (PAN, molecular weight 10,000) were measured at a constant crosshead speed of piston and at a constant applied pressure. From the relation between applied pressure (ΔP_f) and volume of dehydrated filtrate (V_f), it was found that a phase transition from dispersed state to flocculated state occurs at a critical applied pressure (ΔP_{tc}).^{17)–19)} The ΔP_{tc} value had a similar value for 30 and 800 nm SiC particles without PAN. The solution in the flocculated particle clusters without PAN was easily filtrated at a low applied pressure. The adsorption of PAN on 30 and 800 nm SiC particles at pH 7 suppressed the colloidal phase

transition.^{18),19)} As a result, a high pressure was needed to eliminate the solution through the PAN layers compressed in the small spaces among SiC particles. The packing density of SiC particles after calcination at 1000°C became higher for PAN addition than for no PAN addition. This increase of packing density was caused by the change of conformation of PAN during drying. The decrease of molecular weight of dispersant causes the decrease of the distance between two particles consolidated, leading to the increased packing density due to the electrosteric stabilization effect and change of conformation of dispersant during drying. In our previous paper,²⁰⁾ pressure filtration of aqueous suspensions of 800 nm SiC particles with 0.05–5 mass % phenylalanine ($\text{C}_6\text{H}_5\text{CH}_2\text{CHNH}_3^+\text{COO}^-$, molecular weight 165.2) was investigated at a constant crosshead speed of piston. Addition of phenylalanine with equal numbers of COO^- and NH_3^+ groups to negatively charged SiC particles at pH 7 caused (1) increase of zeta potential to negative value, (2) little change of the apparent viscosity and (3) adsorption of phenylalanine on SiC surfaces (0.1–0.2 mg/m²). The adsorbed and free phenylalanine in the SiC suspension suppressed the colloidal phase transition to flocculated state during pressure filtration. A high packing density (64–65%) after calcination at 1000°C was achieved by the addition of a small amount of phenylalanine (0.05–0.5 mass %). Based on the above results, this paper reports the influence of phenylalanine on (1) filtration of 30 and 330 nm SiC particles at a constant pressure (1 MPa) and (2) packing density after calcination at 1000°C in an Ar atmosphere. The above results were coupled with the data for 800 nm SiC particles to discuss the relation between the sizes of dispersant and particles in colloidal pressure filtration.

2. Experimental procedure

A plasma CVD-processed β -SiC powder (SiC B) supplied by Sumitomo Osaka Cement Co., Ltd., Tokyo, has the following

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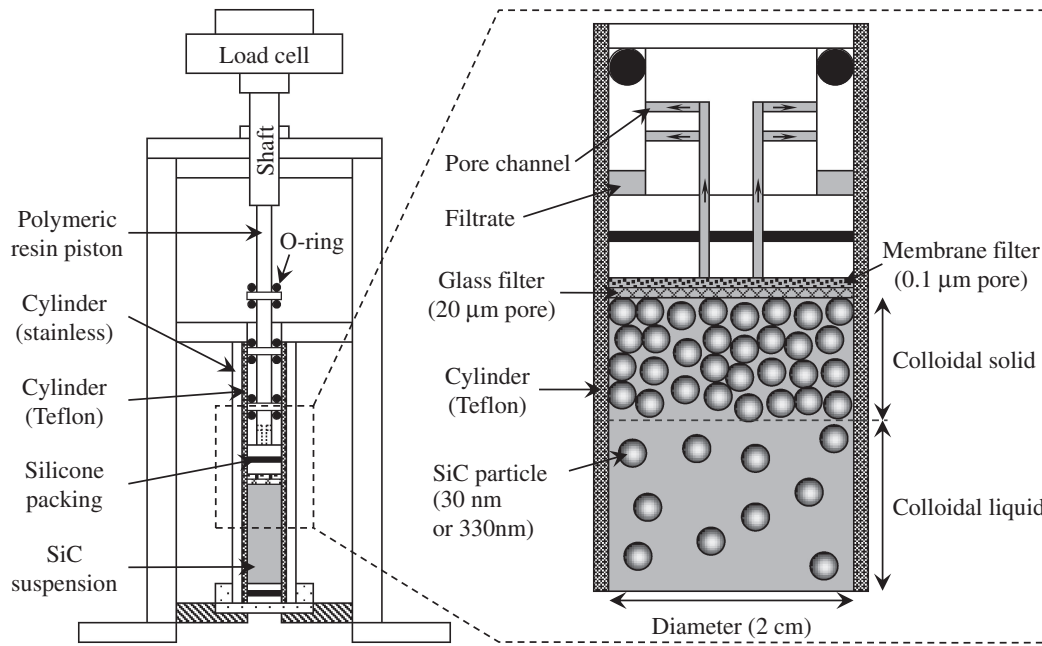


Fig. 1. Schematic illustration of pressure filtration apparatus recording the applied load and suspension height.

characteristics: chemical composition-SiC 95.26 mass %, SiO₂ 0.97 mass %, C 3.76 mass %, median size 30 nm, aspect ratio 1.21, true density 3.10 g/cm³, specific surface area 50.4 m²/g. Another β-SiC powder (SiC C) was supplied by Ibiden Co. Ltd., Gifu, Japan: chemical composition-SiC 97.35 mass %, SiO₂ 0.29 mass %, C 2.13 mass %, median size 330 nm, aspect ratio 1.42, true density 3.15 g/cm³, specific surface area 18.5 m²/g. As-received SiC B and C powders were dispersed at 5 and 20 vol %, respectively, in aqueous solutions with phenylalanine (C₆H₅CH₂CHNH₃⁺COO⁻, molecular weight 165.2) of 0.05–5 mass % against SiC powders (9.63 × 10⁻³–1.03 mg/m²-SiC B and 2.68 × 10⁻²–2.85 mg/m²-SiC C) at pH 7. The saturated amount of phenylalanine adsorbed on 800 nm SiC particles (SiC A) was 0.1–0.2 mg/m² in our previous experiment.²⁰ SiC A powder (α-SiC) supplied by Yakushima Electric Industry Co., Ltd., Kagoshima, Japan has following characteristics: chemical composition-SiC 98.90 mass %, SiO₂ 0.66 mass %, Al 0.004 mass %, Fe 0.013 mass %, free C 0.37 mass %, median size 800 nm, aspect ratio 1.24, true density 3.23 g/cm³ and specific surface area 13.4 m²/g. The zeta potential of SiC A, B and C particles was measured at a constant ionic strength of 0.001 M-NH₄NO₃ (Rank Mark II, Rank Brothers Ltd., Cambridge, UK).^{20–22} The rheological behavior of aqueous SiC suspensions with and without phenylalanine was measured by a cone and plate type viscometer (DV-II+Pro, Brookfield Eng. Lab., Massachusetts, USA). The SiC suspensions were consolidated through a glass filter with a 20 μm pore diameter and three sheets of a membrane filter with a 0.1 μm pore diameter, which were attached to the bottom of the piston (polymeric resin) moving at a constant pressure (1 MPa, Fig. 1). The applied load and the height of piston were continuously recorded (Tensilon RTC, A&D Co., Ltd., Tokyo, Japan). The consolidated SiC compacts were taken out of the cylinder and dried at 100°C in air for 24 h. The dried compacts were heated at 1000°C in Ar atmosphere for 1 h to give an enough strength for the measurement of bulk density by the Archimedes method using kerosene. The microstructures of calcined compact were observed by field

emission scanning electron microscope (S-4100H, Hitachi High-Technologies Co., Tokyo, Japan).

3. Filtration model

The filtration theories of dispersed and flocculated suspensions were reported in our previous papers.^{16–19} A filtration process for well dispersed particles, shown in Fig. 2(a), was analyzed by Aksay and Schilling.²³ The relation of piston height (h_t)–filtration time (t)–applied pressure ($\Delta P_t = P_t - P_0$) is approximated by Eq. (1),

$$\Delta P_t t = \frac{\eta \alpha_c}{2n} (H_0 - h_t)^2 \quad (1)$$

where η is the viscosity of filtrate, α_c the specific resistance of porous consolidated layer, H_0 the initial suspension height, n the system parameter ($\equiv (1 - C_0 - \varepsilon_c)/C_0$, ε_c is the volume fraction of voids in the consolidated layer, C_0 the initial particle concentration).

A phase transition from a dispersed suspension to a flocculated suspension occurs at a critical applied pressure (ΔP_{tc}).¹⁷ Figures 2(c) and 2(d) show a schematic structure of flocculated suspension and the hydraulic pressure profile across the mold, consolidated layer and flocculated suspension. The relation between suspension height and filtration time at a constant pressure, $\Delta P_s (= P_t - P_i)$, for an initially flocculated suspension is presented by Eq. (2),^{16–19}

$$\begin{aligned} \Delta P_s t &= \eta B S^2 (H_0 C_0)^2 \int_{H_0}^{h_s} \frac{h_s^2}{(h_s - H_0 C_0)^3} dh_s \\ &= \eta B S^2 (H_0 C_0)^2 \left\{ \frac{1}{2} \left[\frac{h_s^2}{(h_s - H_0 C_0)^2} - \frac{H_0^2}{(H_0 - H_0 C_0)^2} \right] \right. \\ &\quad + \left[\frac{h_s}{(h_s - H_0 C_0)} - \frac{H_0}{(H_0 - H_0 C_0)} \right] \\ &\quad \left. + \ln \left(\frac{H_0 - H_0 C_0}{h_s - H_0 C_0} \right) \right\} \quad (2) \end{aligned}$$

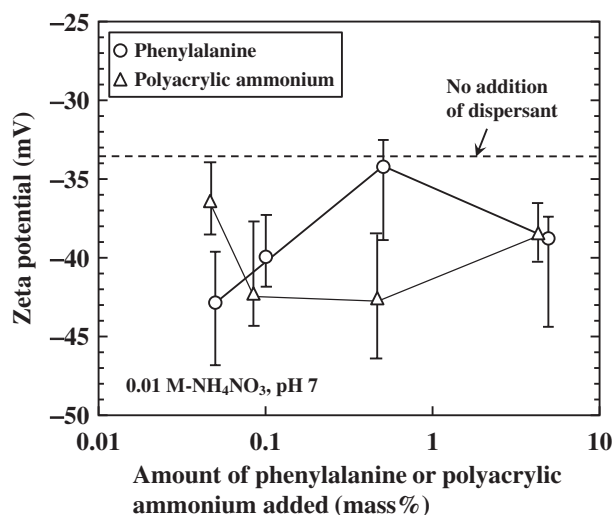


Fig. 4. Zeta potential of SiC powders with phenylalanine and polyacrylic acid in 0.01 M-NH₄NO₃ solution at pH 7.

than that of negatively charged SiO⁻ sites. The opposite case occurs at a pH above the isoelectric point. Phenylalanine (C₆H₅CH₂CHNH₂COOH) is charged positively below pH 2.61 (C₆H₅CH₂CHNH₃⁺COOH) and has both charged groups of NH₃⁺ and COO⁻ in the pH range from 2.61 to 9.18 (C₆H₅CH₂CHNH₃⁺COO⁻).²⁵ In the high pH range above 9.18, phenylalanine is charged negatively (C₆H₅CH₂CHNH₂COO⁻). When the SiC suspension is prepared at pH 7, two types of interaction occur between phenylalanine and SiC surfaces: (1) NH₃⁺ group...SiO⁻ site, (2) COO⁻ group...SiOH₂⁺ site.

Figure 4 shows the zeta potential of SiC A powder in 0.01 M-NH₄NO₃ solution at pH 7.²⁰ The SiC powder without phenylalanine was charged -33.7 mV. Addition of 0.05 or 5 mass % phenylalanine to the SiC increased slightly the zeta potential toward the negative values. However, no change of zeta potential was measured for 0.5 mass % addition of phenylalanine. When 0.05 mass % phenylalanine is added, the SiOH₂⁺ sites are covered with neutral phenyl group through the adsorption of COO⁻ group of phenylalanine, resulting in the increased total potential to negative value. With the further addition of phenylalanine (0.05–0.5 mass %), the negatively charged SiO⁻ sites are covered with neutral phenyl group through the electrostatic interaction of NH₃⁺ group. As a result, the covered SiC surface is changed from negative one (SiO⁻ site) to neutral one (phenyl group), increasing the total surface potential to the positive value with addition of phenylalanine. At 0.5 mass % phenylalanine, the competitive reactions (SiOH₂⁺ site...COO⁻ group, SiO⁻ site...NH₃⁺ group) reach a steady-state. When the zeta potential of SiC surface is shifted to a positive value, the adsorption of COO⁻ group on SiOH₂⁺ site becomes easily. As a result the SiC surface is again charged negatively (>0.5 mass % phenylalanine) because of the shield effect of phenylalanine adsorbed. The zeta potential of SiC A with PAN at pH 7 is also shown in Fig. 4. The saturated amount of polyacrylic acid (PAA) adsorbed through the interaction between SiOH₂⁺ site and COO⁻ group at pH 7 was measured to be 0.29 mg/m² in our previous papers.^{26),27)} When PAN of 0.05–5 mass % (2.68 × 10⁻²–2.85 mg/m²-SiC) was added, the zeta potential of SiC particles shifted from -33.7 mV for no PAN addition to more negative values in a wide range of PAN concentration (for example, -43.3 mV for 0.5 mass % PAN). This result indicates that negatively charged

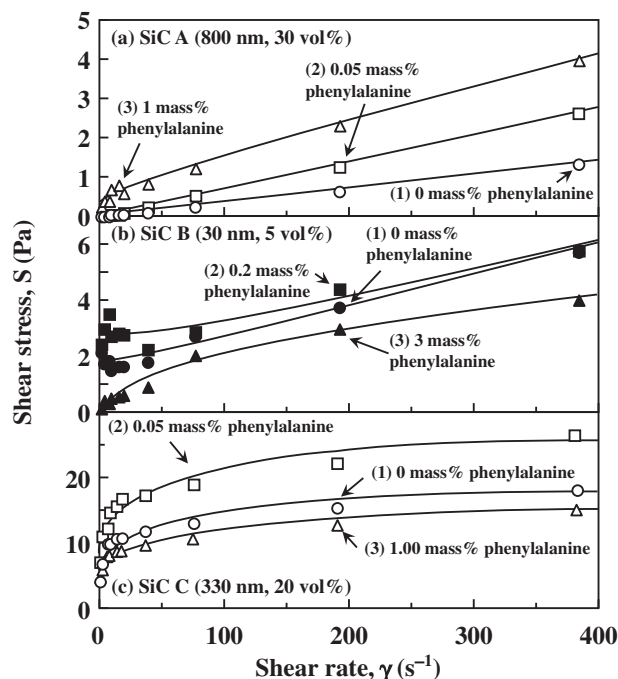


Fig. 5. Typical shear rate–shear stress relations for aqueous suspensions of SiC powders with and without phenylalanine.

COO⁻ groups of PAN were adsorbed on SiOH₂⁺ sites of SiC surfaces. As discussed above, the adsorption characteristic of phenylalanine is different from that of PAN.

4.2 Rheology of SiC suspensions

Figure 5 shows typical shear rate–shear stress relations for SiC suspensions of 5–30 vol % solid at pH 7. When SiC particle size became smaller, it was difficult to prepare fluid concentrated suspensions. Addition of a small amount of phenylalanine (<0.2 mass %) to SiC A, B and C suspensions increased the shear stress (apparent viscosity), suggesting the formation of weak bridging of particles through the interaction between adsorbed and free phenylalanine. However, decrease of apparent viscosity was measured for the 5 vol % suspensions of 30 nm SiC [Fig. 5(b)] and 20 vol % suspension of 330 nm SiC [Fig. 5(c)] when 1–3 mass % phenylalanine was added, suggesting the dispersion effect of low molecular weight electrolyte on nanometer-sized particles.

According to our recent study, the critical surface potential of SiC particles causing a colloidal phase transition (dispersed particles → flocculated particles) is calculated to be 34.1 mV for 30 nm diameter, 18.2 mV for 100 nm diameter and 12.8 mV for 500 nm diameter at 1 atm.^{19),28)} That is, the surface potential of SiC B particles without phenylalanine at pH 7 (Fig. 3) was lower than or comparable to the critical surface potential, increasing the probability of flocculation due to thermal energy. The addition of phenylalanine (>1 mass %) to SiC B suspensions prevents the flocculation of SiC particles because of the increased zeta potential and steric stabilization effect (Fig. 5). On the other hand, SiC A particles with zeta potential higher than the critical surface potential (Figs. 3, 4) are located in a colloidal liquid region in the proposed colloidal phase diagram as functions of surface potential and solid content.^{19),28)} That is, it was possible to make a fluid suspension of 30 vol % SiC particles [Fig. 5(a)]. The rheology of the SiC suspensions is affected by the state of

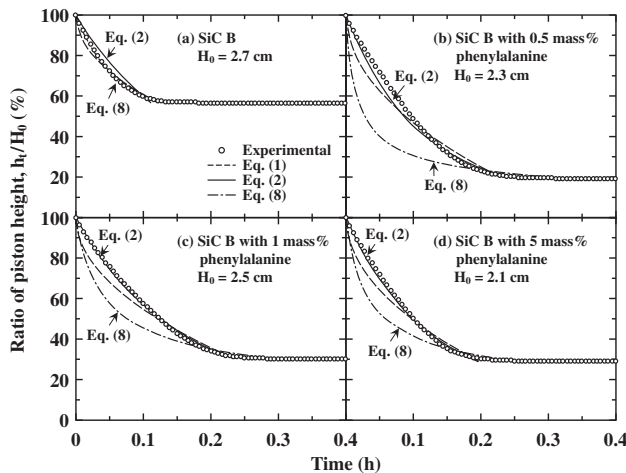


Fig. 6. Relation between height of piston (h_t) and filtration time of the SiC B suspensions with and without phenylalanine at pH 7 at 1 MPa.

colloidal suspension and solid content which is related to the average distance between dispersed particles. The increased solid content of dispersed suspension reduces the distance between charged particles and increases the repulsive interaction energy, leading to the increased shear stress.

4.3 Filtration kinetics of SiC suspension at a constant pressure

Figure 6 shows the relation between height of piston (h_t) and filtration time for SiC B suspensions at 1 MPa. All the h_t values decreased nonlinearly within 0.2 h. The consolidation behavior was analyzed by Eqs. (1), (2) and (8). The piston height of SiC B suspension without dispersant [Fig. 6(a)] was well fitted by Eq. (8) rather than by Eq. (1), indicating the filtration of a flocculated suspension. This result was in accordance with the discussion of rheological properties of SiC B suspension in Section 4.2. However, the filtration process of SiC with phenylalanine (0.05–5 mass %) was expressed by Eq. (2). Therefore, it is understood that (1) SiC B particles dispersed by the addition of phenylalanine (>1 mass %) were flocculated promptly when 1 MPa of filtration pressure was applied, and (2) flocculated particles worked as a filter with specific resistance depending on suspension height [Eq. (3)]. As seen in Fig. 6, the final height of colloidal cake became lower when phenylalanine was mixed, indicating the formation of dense powder compact. This result is discussed in a latter section. The flocculation of SiC B particles with phenylalanine occurred at 1 MPa of applied pressure. The consolidation time to reach the final height of colloidal cake became longer for the addition of phenylalanine as seen in Fig. 6. This result is analyzed in Section 4.4 and due to the slow increase of specific resistance during filtration (Figs. 8, 9). The deformation rate of flocculated particle clusters was reduced with addition of phenylalanine and controlled the dehydration rate.

Figure 7 shows the relation between h_t and filtration time for SiC C suspension at 1 MPa. All the experimental data were well fitted by Eq. (2). Addition of phenylalanine increased the filtration time as mentioned before. This result is discussed in a next section. The zeta potential of SiC C particles was comparable to the critical surface potential to form a flocculated suspension at 1 atm (Fig. 3) and the SiC suspension changed easily to a flocculated suspension under 1 MPa of applied pressure.

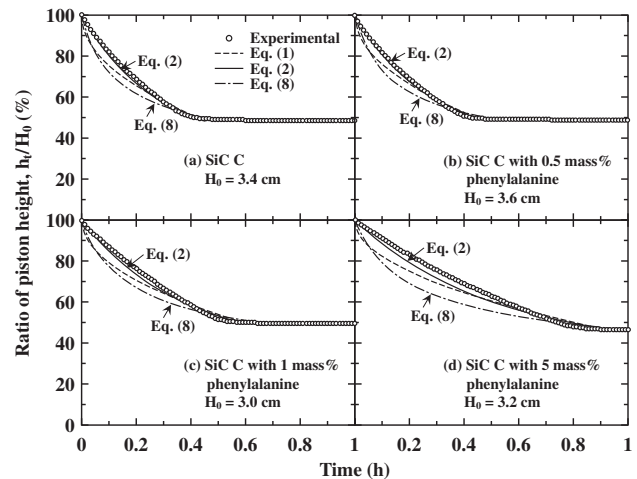


Fig. 7. Relation between height of piston (h_t) and filtration time of the SiC C suspensions with and without phenylalanine at pH 7 at 1 MPa.

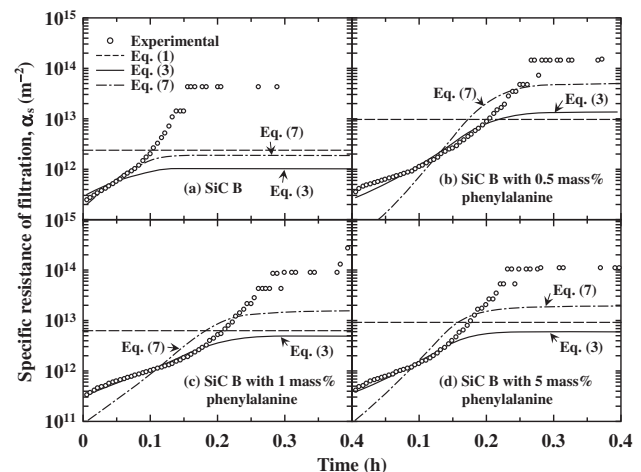


Fig. 8. Relation between filtration time and specific resistance of filtration for SiC B suspensions with and without phenylalanine.

4.4 Specific resistance of filtration and packing density of consolidated cake

Figure 8 shows the relationship between filtration time and specific resistance of filtration for SiC B suspensions at 1 MPa. The experimental specific resistance (α_s) was determined by Eq. (9) at the interval $\Delta t = 40$ s. On the other hand, the theoretical resistance was determined by Eqs. (1), (3) and (7). The n value in Eq. (1) was calculated using the final packing density after filtration. As seen in Fig. 8, the measured α_s increased gradually with increasing filtration time. However, α_s value in Eq. (1) was treated as a constant value and was not in accordance with the measured tendency. On the other hand, Eqs. (3) and (7) can represent time dependence of α_s using the measured h_t value. The simulation with Eq. (3) provided a good agreement of α_s values except for the final region of filtration. As seen in Fig. 8, the slope of α_s with filtration time decreased with addition of phenylalanine. This result indicates that the relaxation of structure of flocculated particles needs a longer time when phenylalanine coexists in a SiC suspension. The attractive interaction between adsorbed and free phenylalanine through COO^- and NH_3^+ groups may reduce the deformation rate of flocculated particle clusters. Figure 9 shows the α_s - t relation for

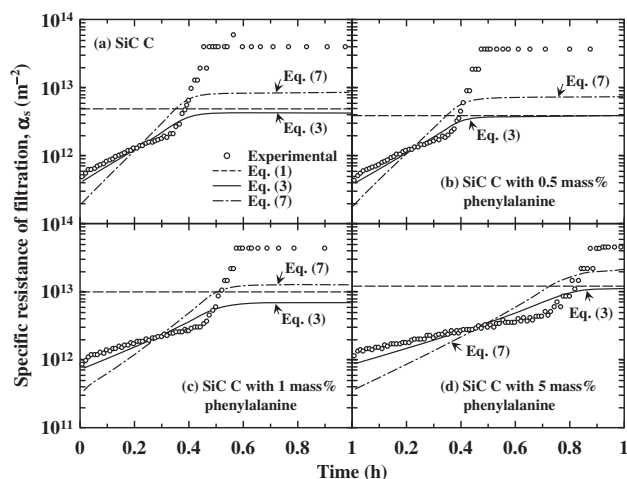


Fig. 9. Relation between filtration time and specific resistance of filtration for SiC C suspensions with and without phenylalanine.

SiC C suspensions. The measured α_s values were well expressed by Eq. (3). The deformation rate of flocculated particle clusters, which was reflected in the slope of $d\alpha_s/dt$, decreased with addition of phenylalanine.

At a longer filtration time approaching the final stage of consolidation (Figs. 8 and 9), the observed α_s value increased rapidly with a small increase in filtration time and reached a constant value. In this paper, the filtration of a flocculated suspension was analyzed by Eq. (3) at a constant BS^2 value. However, the B and S values depend strongly on the structure of flocculated particles in the final stage of filtration. The actual flocculated particles forms a dense structure in the final stage of filtration as compared with the structure defined by a constant BS^2 value. This discussion is supported by the larger α_s value by Eq. (7) whose S value increases with decreasing suspension height. That is, the difference of α_s values between the experiment and theory [Eq. (3)] becomes larger when the structure of flocculated particles changes to denser one in the final consolidation stage.

Figure 10 shows (a) the packing density of SiC B and C compacts after calcination at 1000°C in an Ar atmosphere and (b) BS^2 value in Eq. (3). The packing density of SiC B powder increased from 35% for no addition of phenylalanine to 37–42% for 0.1–1 mg phenylalanine/m²-SiC. On the other hand, the packing density of SiC C powder increased scarcely from 49 to 52% for the addition of 2.68×10^{-2} –2.85 mg phenylalanine/m²-SiC. The applied pressure affects the phase transition of colloidal suspension and controls the packing behavior of particles in final colloidal cake. This packing behavior depends mainly upon the particle size. When the particle size became smaller, the influence of low molecular dispersant on packing behavior became larger. The results for SiC B compacts suggest that a slow deformation of flocculated particles with phenylalanine dispersant is effective to promote the dense packing during filtration. A faster consolidation of SiC B particles without phenylalanine freezes the randomly packed porous structure, resulting in the decreased packing density. This type effect of phenylalanine was small on 330 nm SiC particles.

Packing density of SiC A particles (800 nm) consolidated at 1 MPa of applied pressure and calcined at 1000°C was measured in Ref. 18, and increased from 58 to 62% for the addition of 0.27 mg PAN/m²-SiC. Similarly, packing density of SiC B

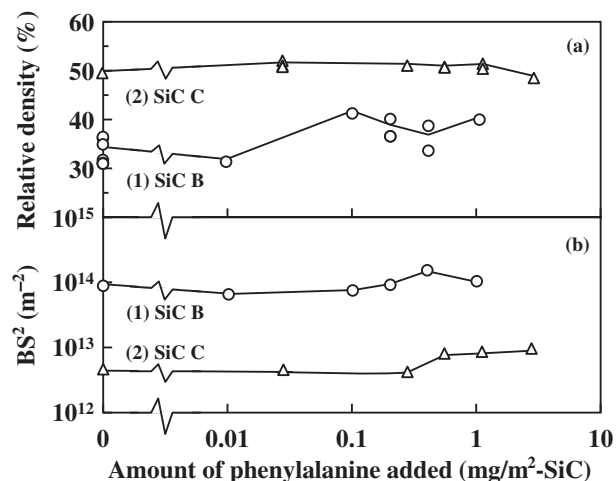


Fig. 10. (a) Packing density after calcination at 1000°C and (b) BS^2 value of Eq. (3) for SiC B and C suspensions with and without phenylalanine.

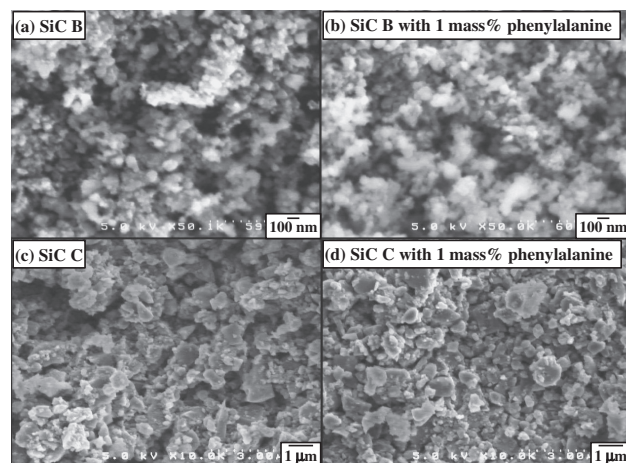


Fig. 11. Microstructures of SiC B (a, b) and SiC C (c, d) compacts after calcination at 1000°C in an Ar atmosphere. Phenylalanine of 1 mass % was added in the SiC suspensions of (b) and (d).

particles increased from 30 to 37% for the addition of 0.75 mg PAN/m²-SiC at 1 MPa of applied pressure.¹⁸⁾ Therefore, both the low and high molecular dispersants are effective to increase the packing density of 30 nm SiC particles. For the suspensions of SiC C particles (330 nm), high molecular dispersant may be effective to increase the packing behavior but low molecular dispersant gave small influence on the packing density.

The BS^2 value dominating the specific resistance of filtration was higher for SiC B particles than for SiC C particles. This result is closely related to the pore size formed among SiC particles. Larger pores in SiC C compact reduce the resistance of migration of solution during filtration. This BS^2 value showed a slight tendency to increase when the amount of phenylalanine was increased. The adsorbed and free phenylalanine in the open spaces among SiC particles increases the filtration resistance of solution. In addition, the relaxation of particles under an applied pressure proceeds slowly with addition of phenylalanine.

Figure 11 shows the microstructures of SiC B and C compacts after calcination at 1000°C in an Ar atmosphere. The consolidated SiC compacts with 2.5–3.4 cm height were cut at three parts (top, middle and bottom) along the direction of height. No

significant difference was observed for the microstructures along the direction of height. As seen in Figs. 11(a) and 11(b), the microstructures of SiC B compacts became denser with addition of phenylalanine (1 mass %). A similar change was also observed for SiC C compacts [(c) and (d)]. The above observation indicates that uniform microstructures are achieved by the addition of low molecular dispersant for 30 and 330 nm particles.

5. Conclusions

SiC particles (30 and 330 nm median sizes) with -18 to -21 mV of zeta potential at pH 7 were flocculated promptly when 1 MPa of filtration pressure was applied. Flocculated particles worked as a filter with specific resistance which increased with decreasing suspension height. This filtration process under 1 MPa was well expressed by the proposed filtration theory which contained a filtration resistance depending on suspension height. The deformation rate of flocculated particle clusters was reduced with addition of phenylalanine and a longer filtration time was needed to consolidate the particles with phenylalanine. This dispersant effect promoted the packing density of 30 nm SiC particles but was small for the packing density of 330 nm SiC particles. The microstructures of consolidated SiC compacts became more uniform when phenylalanine was added.

References

- 1) P. C. Kapur, S. Laha, S. Usher, R. G. deKretser and P. Scales, *J. Colloid Interface Sci.*, **256**, 216–222 (2002).
- 2) E. Vorobiev, *Chem. Eng. Sci.*, **61**, 3686–3697 (2006).
- 3) S. Raha, K. C. Khilar, P. C. Kapur and Pradip, *Int. J. Miner. Process.*, **84**, 348–360 (2007).
- 4) J. Will, M. K. M. Hruschka, L. Gubler and L. J. Gauckler, *J. Am. Ceram. Soc.*, **84**, 328–332 (2001).
- 5) B. D. Hatton and Y. Sakka, *J. Am. Ceram. Soc.*, **84**, 666–668 (2001).
- 6) Y. C. Wang, I. C. Leu and M. H. Hon, *J. Am. Ceram. Soc.*, **87**, 84–89 (2004).
- 7) J. X. Zhang, D. L. Jiang, S. H. Tan, L. H. Gui and M. L. Ruan, *J. Am. Ceram. Soc.*, **84**, 2537–2541 (2001).
- 8) S. Uchida, S. Sameshima and Y. Hirata, *J. Ceram. Soc. Japan*, **109**, 100–105 (2001).
- 9) A. I. Kontos, A. G. Kontos, D. S. Tsoukleris, M. C. Bernard, N. Spyrellis and P. Falaras, *J. Mater. Process. Technol.*, **196**, 243–248 (2008).
- 10) F. F. Lange and K. T. Miller, *Am. Ceram. Soc. Bull.*, **66**, 1498–1504 (1987).
- 11) Y. Hirata, M. Nakamura, M. Miyamoto, Y. Tanaka and X. H. Wang, *J. Am. Ceram. Soc.*, **89**, 1883–1889 (2006).
- 12) K. Kishigawa and Y. Hirata, *J. Eur. Ceram. Soc.*, **26**, 217–221 (2006).
- 13) K. Kishigawa and Y. Hirata, *J. Ceram. Soc. Japan*, **114**, 259–264 (2006).
- 14) Y. Hirata and Y. Tanaka, Proceedings of 6th Pacific Rim Conference on Ceramic and Glass Technology (CDR), The American Ceramic Society (2006).
- 15) Y. Hirata, Y. Tanaka and Y. Sakamoto, *Adv. Sci. Technol.*, **45**, 471–479 (2006).
- 16) Y. Tanaka, Y. Hirata, N. Matsunaga, M. Nakamura, S. Sameshima and T. Yoshidome, *J. Ceram. Soc. Japan*, **115**, 786–791 (2007).
- 17) Y. Hirata and Y. Tanaka, *J. Am. Ceram. Soc.*, **91**, 819–824 (2008).
- 18) Y. Hirata, Y. Tanaka, S. Nakagawa and N. Matsunaga, *J. Ceram. Process. Res.*, **10**, 311–318 (2009).
- 19) Y. Hirata, N. Matsunaga and S. Sameshima, *Ceram. Trans.*, **223** (2010) in press.
- 20) S. Baba, Y. Hirata, N. Matsunaga and S. Sameshima, *Ceram. Trans.*, **219**, 105–110 (2010).
- 21) N. Hidaka and Y. Hirata, *J. Ceram. Soc. Japan*, **113**, 466–472 (2005).
- 22) Y. Hirata, N. Suzue, N. Matsunaga and S. Sameshima, *J. Eur. Ceram. Soc.*, **30**, 1945–1954 (2010).
- 23) I. A. Aksay and C. H. Schilling, “Forming of Ceramics,” Advances in Ceramics, Vol. 9, Ed. by J. A. Mangels and G. L. Messing, The American Ceramic Society, Columbus, Ohio (1984) pp. 85–93.
- 24) Y. Hirata, K. Hidaka, H. Matsumura, Y. Fukushima and S. Sameshima, *J. Mater. Res.*, **12**, 3146–3157 (1997).
- 25) Y. Hirata, H. Takahashi, H. Shimazu and S. Sameshima, *Ceram. Trans.*, **152**, 1–10 (2004).
- 26) Y. Hirata, S. Tabata and J. Ideue, *J. Am. Ceram. Soc.*, **86**, 5–11 (2003).
- 27) Y. Hirata, S. Tabata and J. Ideue, *Adv. Sci. Technol.*, **30**, 545–554 (2003).
- 28) Y. Hirata and Y. Tanaka, *J. Ceram. Process. Res.*, **9**, 362–371 (2008).