

# Rheology and pressure filtration of aqueous SiC suspensions of nanometer-sized bimodal particles

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## Abstract

The consolidation behavior of mixed SiC particles (30 and 800 nm diameters) at pH 7 was examined using a developed pressure filtration apparatus at a constant crosshead speed of a piston. The addition of 30 nm SiC to 800 nm SiC changed the rheological properties of colloidal suspension from Newtonian to pseudoplastic flow through Bingham flow with increasing amount of 30 nm SiC. A phase transition from a well dispersed suspension to a flocculated suspension occurred when the applied pressure exceeded a critical pressure ( $\Delta P_{ic}$ ). The  $\Delta P_{ic}$  value decreased with increasing amount of 30 nm SiC. The packing density of bimodal SiC particles was analyzed based on the partial molar volume of each powder. The larger particles were more densely packed than the smaller particles in the mixed powder compact.

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## 1. Introduction

Pressure filtration can reduce the consolidation time of a colloidal suspension of nanometer-sized particles with high filtration resistance as compared with the filtration method using a gypsum mold. In our previous papers [1–3], 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 was analyzed using a newly-developed pressure filtration apparatus at a constant pressure or at a constant crosshead speed of piston. From a comparison between applied pressure ( $\Delta P_t$ ) at a constant crosshead speed and volume of dehydrated filtrate ( $V_f$ ), it was found that a phase transition from a dispersed state to a flocculated state occurs at a critical applied pressure ( $\Delta P_{ic}$ ). Based on the colloidal phase transition, a new filtration theory was developed to explain the  $\Delta P_t - h_t$  (height of piston) relation for a flocculated suspension [4,5]. Good agreement was shown between the theory developed and experimental results of electrostatically-stabilized suspensions. Our next interest is to study the consolidation behavior of bimodal particles system. The quantitative analysis of the degree of particle mixing in two-

component powder compacts is important to understand the sintering behavior, mechanical properties or electrical properties of the composite materials such as  $\text{Al}_2\text{O}_3\text{--ZrO}_2$  [6],  $\text{Al}_2\text{O}_3\text{--TiC}$  [7],  $\text{Al}_2\text{O}_3\text{--Ni}$  [8],  $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{--ZrO}_2\cdot \text{SiO}_2$  [9] or  $\text{Al}_2\text{O}_3\text{--ITO}$  (indium tin oxide) [10–12]. In a two-component system of A–B, three types of particle contact of A–A, A–B and B–B are formed in the microstructure of the powder compact [13,14]. The particle connection provides the geometrical feature of the microdomain. In this paper, the rheological properties and consolidation behavior of bimodal SiC particles (30 and 800 nm diameters) at pH 7 were examined and the resultant packing density was analyzed using partial molar volumes of fine and large particles.

## 2. Fractional collision frequency and DLVO theory of SiC suspension

When the motion of colloidal particles is dominated by diffusion, Smoluchowski has given Eq. (1) for the number ( $b_{ij}$ ) of collisions per unit time for any particles in the system [15],

$$b_{ij} = 4\pi C_i C_j D_i r_i (r_i + r_j) \left( \frac{1}{r_i} + \frac{1}{r_j} \right) \\ = 4\pi C_i C_j D_i r_i \left\{ 4 + \left[ \left( \frac{r_i}{r_j} \right)^{1/2} - \left( \frac{r_j}{r_i} \right)^{1/2} \right]^2 \right\} \quad (1)$$

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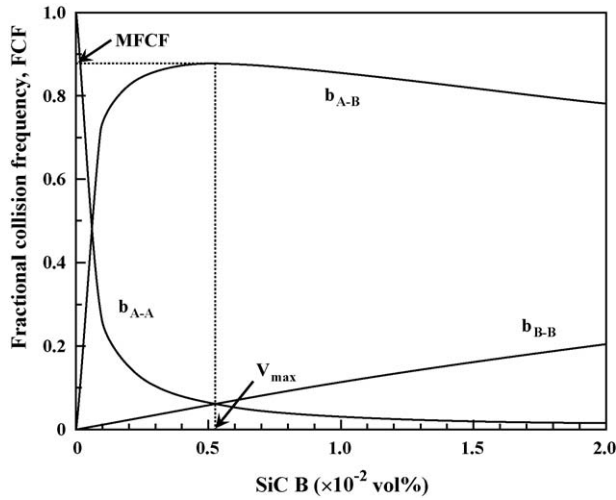


Fig. 1. Fractional collision frequency for bimodal particles system of 800 nm SiC (SiC A)–30 nm SiC (SiC B).

where  $C_i$ ,  $D_i$  and  $r_i$  are the particle number concentration, diffusion coefficient and radius of  $i$  particle, respectively. The diffusion coefficient is inversely proportional to the radius of particle, as indicated by the Stokes' law ( $D = kT/6\pi\eta r$ ,  $k$ : Boltzmann constant,  $\eta$ : viscosity). Collision frequency has a minimum at  $r_i = r_j$  and becomes higher at larger difference of particle sizes. The fractional collision frequency between particles  $i$  and  $j$ ,  $(FCF)_{ij}$ , is defined by Eq. (2).

$$(FCF)_{ij} = \frac{b_{ij}}{b_{ii} + 2b_{ij} + b_{jj}} \quad (2)$$

Fig. 1 shows the fractional collision frequency of the bimodal SiC particles system with  $r_{\text{SiC A}} = 400$  nm and  $r_{\text{SiC B}} = 15$  nm. The collision frequency of SiC A–SiC A particles decreases drastically with the addition of SiC B particles. The fractional collision frequency of SiC A–SiC B particles increases rapidly to 0.878 at SiC B fraction of  $5.2 \times 10^{-3}$  vol% and decreases gradually at a higher SiC B fraction. The collision of SiC B–SiC B particles is also accelerated with the increase of SiC B fraction. The maximum fractional collision frequency (MFCF) and corresponding volume fraction ( $V_{\text{max}}$ ) of SiC B for the collision of SiC A–SiC B are presented by Eqs. (3) and (4), respectively [14],

$$MFCF = \frac{(1+x)^2}{(1+x)^2 + 4x} \quad (3)$$

$$V_{\text{max}} = \frac{1}{1+x^3} \quad (4)$$

where  $x$  is the particle size ratio of  $r_A$  (large particle)/ $r_B$  (small particle). The substitution of  $x = 400 \text{ nm}/15 \text{ nm} = 26.67$  for Eqs. (3) and (4) results in  $MFCF = 0.878$  and  $V_{\text{max}} = 5.27 \times 10^{-3}$  vol%, respectively. The above calculation suggests the high collision frequency between SiC A–SiC B particles and SiC B–SiC B particles at SiC B fractions above 0.01 vol%. When two particles collide, the possibility of formation of flocculated particles is controlled by the interaction

energy between charged particles. Eqs. (5)–(9) represent the van der Waals energy ( $E_a$ , Eqs. (5) and (6)) and repulsive energy ( $E_r$ , Eqs. (7)–(9)) to calculate the interaction energy ( $E_i = E_a + E_r$ ) [16]. Eqs. (5), (7) and (8) are applied to calculate the interaction energy between same kinds of particles (A–A particles and B–B particles). Eqs. (7) and (8) are effective for the conditions of  $D$  (particle diameter)  $\gg 1/\kappa$  (double layer thickness) and  $D \ll 1/\kappa$ , respectively. Eqs. (6) and (9) are used to calculate the interaction energy between different kind of particles (A–B particles).

$$E_a = -\frac{A}{12} \left[ \frac{D^2}{H^2 + 2DH} + \frac{D^2}{(H+D)^2} + 2 \ln \frac{H^2 + 2DH}{(H+D)^2} \right] \quad (5)$$

$$E_a = -\frac{Ar_1r_2}{6(r_1 + r_2)H} \quad (6)$$

$$E_r = 32\pi\epsilon\epsilon_0 \left( \frac{D}{2} \right) \left( \frac{RT}{ZF} \right)^2 \tanh^2 \left( \frac{ZF\varphi}{4RT} \right) \ln \{ 1 + \exp(-\kappa H) \} \quad (7)$$

$$E_r = \frac{\pi\epsilon\epsilon_0 D^2 \varphi^2}{H+D} \exp(-\kappa H) \quad (8)$$

$$E_r = \frac{\pi\epsilon\epsilon_0 r_1 r_2}{r_1 + r_2} (\varphi_1^2 + \varphi_2^2) \left[ \frac{2\varphi_1 \varphi_2}{\varphi_1^2 + \varphi_2^2} \ln \left\{ \frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)} \right\} + \ln \{ 1 - \exp(-2\kappa H) \} \right] \quad (9)$$

The symbols in above equations express the following meaning:  $A$  the Hamaker constant,  $r_1$  and  $r_2$  the radius of particles 1 and 2, respectively,  $H$  the distance between particles 1 and 2,  $\epsilon$  the relative dielectric constant of solution (78.3 for  $\text{H}_2\text{O}$  at 25 °C),  $\epsilon_0$  the permittivity of vacuum ( $8.8542 \times 10^{-12}$  F/m),  $\varphi$  the surface potential (approximated by zeta potential) of charged particles,  $R$  the gas constant,  $F$  the Faraday constant,  $Z$  the charge number of electrolyte (assumed to be +1) and  $T$  the temperature (assumed to be 298 K). The double layer thickness ( $1/\kappa$ ) was calculated to be about 100 nm for a typical electrolyte condition ( $Z = +1$ ) of  $10^{-5}$  mol/l. The interaction energy between SiC A–SiC A particles ( $D = 800$  nm,  $A = 10.9 \times 10^{-19}$  J [17],  $\varphi = -34.2$  mV [2]) was calculated from Eqs. (5) and (7) ( $D \gg 1/\kappa$ ). The interaction energy between SiC B–SiC B particles ( $D = 30$  nm,  $A = 10.7 \times 10^{-19}$  J [18],  $\varphi = -29.8$  mV [2]) was calculated from Eqs. (5) and (8) ( $D \ll 1/\kappa$ ). Similarly, Eqs. (6) and (9) were used to calculate the interaction energy between SiC A and SiC B ( $A = \sqrt{A(\text{SiC A})} \sqrt{A(\text{SiC B})} = 10.8 \times 10^{-19}$  J) [19].

Fig. 2 shows three kinds of interaction energies,  $E_a + E_r$ , for the bimodal particles system of SiC A and SiC B. A small interaction energy was calculated between SiC B and SiC B or between SiC A and SiC B, as compared with the interaction energy between SiC A and SiC A. The formation of flocculated particles is accelerated under the condition of  $E_i(\text{max}) < 15kT$  ( $=6.17 \times 10^{-20}$  J at 298 K) [16]. The  $E_i(\text{max})$  values for the interaction of SiC B–SiC B particles and SiC A–SiC B particles were calculated to be  $4.02 \times 10^{-20}$  J ( $H(\text{max}) = 6.15$  nm) and

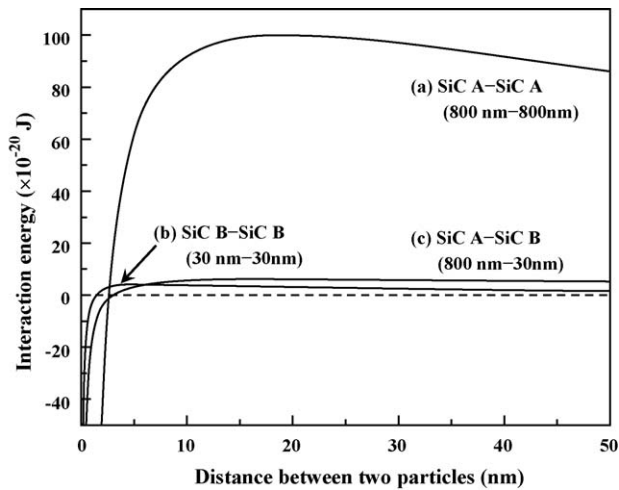


Fig. 2. Interaction energy of SiC-SiC particles as a function of distance between two particles.

$6.32 \times 10^{-20}$  J ( $H(\max) = 21.7$  nm), respectively. These values were comparable to the above condition for the formation of flocculated particles. The calculated results in Figs. 1 and 2 lead to the following prediction. In a solution at pH 7, SiC A particles are well dispersed because of the strong repulsive interaction. Addition of a small amount of SiC B to SiC A increases the collision frequency between SiC B-SiC B particles and SiC A-SiC B particles. The collision between particles form flocculated particles because of the significantly weak repulsive interaction energy. As a result, the above bimodal particles system forms a flocculated suspension through the bridging effect of SiC B particles.

### 3. Experimental procedure

A high purity  $\alpha$ -SiC powder (powder A) supplied by Yakushima Electric Industry Co. Ltd., Kagoshima, Japan (specific surface area  $13.4 \text{ m}^2/\text{g}$ , median size 800 nm, true density  $3.23 \text{ g/cm}^3$ ) and a plasma CVD-processed  $\beta$ -SiC powder (powder B) supplied by Sumitomo Osaka Cement Co. Ltd., Tokyo, Japan (specific surface area  $50.9 \text{ m}^2/\text{g}$ , median size 30 nm, true density  $3.10 \text{ g/cm}^3$ ) were used in this experiment. Powders A and B were mixed at an interval of 10 vol% SiC B. These mixed particles were dispersed at 5 vol% solid in an aqueous solution at pH 7.0. The zeta potential of powders A and B was measured at a constant ionic strength of 0.01 M  $\text{NH}_4\text{NO}_3$  (Rank Mark II, Rank Brothers Ltd., Cambridge, UK). The rheological behavior of the mixed powder suspensions was measured by a cone and plate type viscometer (DV-II + Pro, Brookfield Eng. Lab., MA, USA). The prepared suspensions were consolidated through a plastic filter with a  $20 \mu\text{m}$  pore diameter and three sheets of a membrane filter with a  $0.1 \mu\text{m}$  pore diameter, which were attached to the bottom of the piston (polymeric resin, cross-sectional area  $3.14 \text{ cm}^2$ ) moving at a constant crosshead speed of  $0.2 \text{ mm/min}$ . When the suspension in a closed cylinder was compressed by the piston, the filtrate flowed into and through the pore channels formed in the upper piston. The applied load

and the height of the piston were continuously recorded (Tensilon RTC, A & D Co. Ltd., Tokyo, Japan). The consolidated SiC compact was taken out of the cylinder and dried at  $100^\circ\text{C}$  in air for 24 h. The dried compact was heated at  $1000^\circ\text{C}$  in Ar atmosphere for 1 h to give an enough strength for the measurement of bulk density by the Archimedes method using kerosene.

## 4. Results and discussion

### 4.1. Rheology of SiC suspensions of bimodal particles system

Fig. 3 shows typical shear rate-shear stress relations for the suspensions of bimodal SiC particles of 5 vol% solid. The measured shear stress increased with increasing shear rate and with the volume fraction of SiC B. This result was well understood by the calculated tendency in Figs. 1 and 2. The well dispersed SiC A suspension provided the very low shear stress but the agglomerated SiC B suspension needed a higher shear stress at a similar shear rate. The measured shear rate ( $\dot{\gamma}$ )-shear stress ( $S$ ) relations were analyzed by the following equations.

$$\text{Newtonian flow } S = k\dot{\gamma} \quad (k > 0) \quad (10)$$

$$\text{Bingham flow } S = S_0 + k\dot{\gamma} \quad (k > 0) \quad (11)$$

$$\begin{aligned} \text{Pseudoplastic flow } S \\ = S_0 + k_1\dot{\gamma}^{1/2} + k_2\dot{\gamma} \quad (k_1 > 0, k_2 \neq 0) \end{aligned} \quad (12)$$

$S_0$  and  $k$  are constants. The condition of  $k_1 = 2k_2^{1/2}S_0^{1/2}$  in Eq. (12) provides Eq. (13) known as Casson's equation.

$$S^{1/2} = S_0^{1/2} + k_2^{1/2}\dot{\gamma}^{1/2} \quad (13)$$

The solid lines in Fig. 3 correspond to Eq. (12) and express well the nature of the measured data. The correlation coefficient of the curve in Fig. 3 was 0.987–0.999.

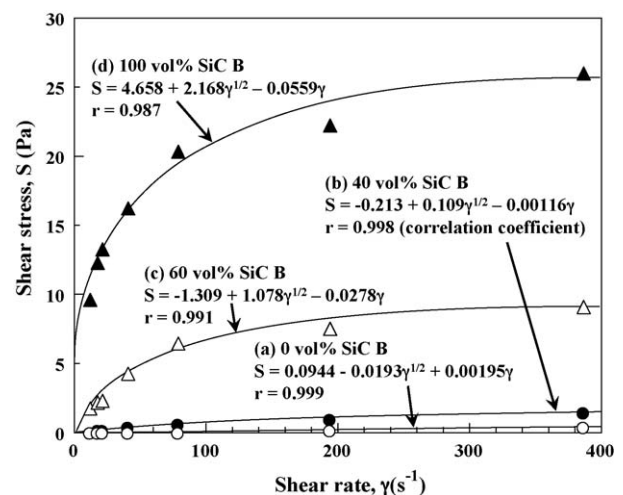


Fig. 3. Typical shear rate-shear stress relations for mixed powder SiC suspensions. The solid lines represent Eq. (12) for pseudoplastic flow.

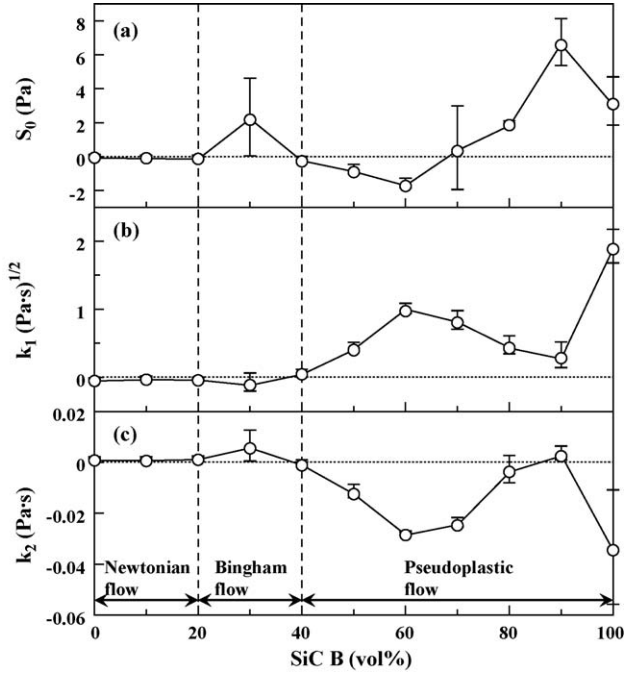


Fig. 4. Experimental constants  $S_0$ ,  $k_1$  and  $k_2$  of Eq. (12) for pseudoplastic flow.

Fig. 4 shows  $S_0$ ,  $k_1$  and  $k_2$  in Eq. (12) as a function of volume fraction of SiC B. The flow behavior of the bimodal particles suspension was divided in three regions. The region I at 0–20 vol% SiC B can be identified as Newtonian flow because  $k_1$  and  $S_0$  were close to 0. In region II at 20–40 vol% SiC B,  $k_1$  was close to 0 but  $S_0$  and  $k_2$  had positive values, corresponding to Bingham flow. The rheological behavior in region III at 40–100 vol% SiC B is interpreted as a pseudoplastic flow.

#### 4.2. Pressure filtration of SiC suspensions of bimodal particles

Fig. 5(A) shows the relationships between applied pressure ( $\Delta P_t$ ) and normalized filtrate volume ( $V_f/V_0$ , where  $V_f$  is the volume of filtrate during the period time of  $t$ ,  $V_0$  the volume of initial suspension) for bimodal SiC particles. The following four regions appeared [4]. Region I: a very low applied pressure at the initial stage of compression of the suspension. Region II: a linear increase of  $\Delta P_t$  with increasing  $V_f$ . Region III: an almost plateau region of  $\Delta P_t$  with increasing  $V_f$ . Region IV: a rapid increase of  $\Delta P_t$  with a small increase of  $V_f$ . The consolidation behavior of bimodal SiC particles was analyzed based on the following filtration model of dispersed particles [4,20].

$$\Delta P_c = \left( \frac{\eta \alpha_c v}{nA} \right) V_f = \left( \frac{\eta \alpha_c v}{n} \right) (H_0 - h_t) \quad (14)$$

$\Delta P_c$  in Eq. (14) is the pressure drop across the consolidated cake of dispersed particles,  $\eta$  the viscosity of the filtrate,  $\alpha_c$  the specific resistance of the consolidated cake,  $v$  the crosshead speed of piston,  $n$  the system parameter ( $= (1 - C_0 - \varepsilon_c)/C_0$ ,  $C_0$ : initial volume fraction of colloidal particles,  $\varepsilon_c$ : porosity of the

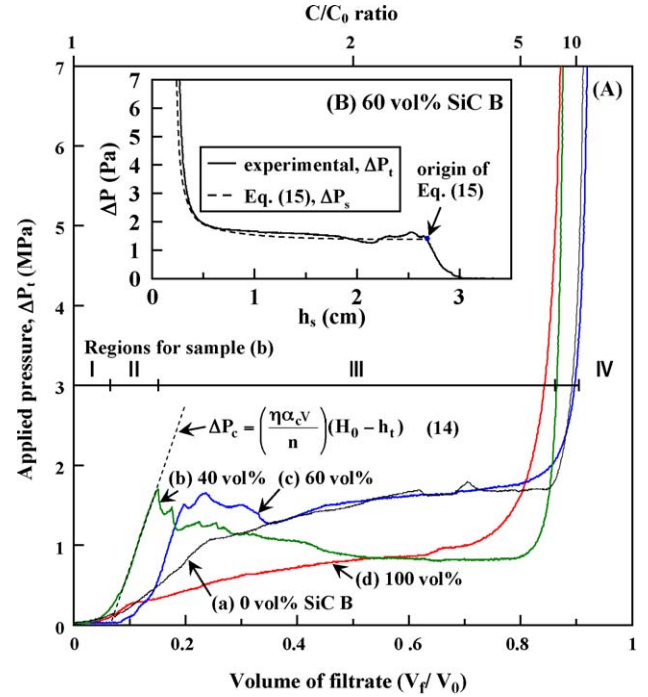


Fig. 5. Applied pressure ( $\Delta P_t$ ) as a function of volume of filtrate of mixed powder SiC suspension.  $\Delta P_c$  in (A) represents the theoretical pressure drop across the consolidated cake during the pressure filtration of well dispersed particles. (B) The comparison between experimental result ( $\Delta P_t$ ) and theoretical pressure drop ( $\Delta P_s$ , Eq. (15)) for the consolidation of flocculated suspension.

consolidated cake),  $A$  the cross-sectional area of the piston,  $H_0$  the initial height of the piston,  $h_t$  the height of the piston (summation of  $h_c$  (height of the consolidated cake) and  $h_s$  (height of the colloidal suspension containing dispersed particles at time  $t$ )). When only the solution was compressed at the crosshead speed of  $v = 0.5$  mm/min, the pressure drop across the filters ( $\Delta P_m$ ) was  $5 \pm 5$  kPa. This value of  $\Delta P_m$  was very small as compared with the experimental pressure range  $\Delta P_t$  ( $= \Delta P_c + \Delta P_m$ ) = 0.1 – 19 MPa, and  $\Delta P_m$  can be neglected to  $\Delta P_c$ . The small  $\Delta P_c$  in region I reflects a small  $\alpha_c$  for a thin consolidated layer. The linear increase of  $\Delta P_c$  with  $V_f$  in region II is well interpreted by Eq. (14). However, the slope of the  $\Delta P_t - V_f$  curve decreased when the consolidation process shifted to region III. No leak of the filtrate at the filters of the apparatus was recognized. The critical applied pressure corresponding to the start of region III was determined as a pressure at the boundary of regions II and III. In our previous papers [4,5], it was clarified that a phase transition from a dispersed suspension to a flocculated suspension occurs at a critical applied pressure ( $\Delta P_{tc}$ ) for nanoparticles 20–800 nm in size. The pressure drop  $\Delta P_s$  for the consolidation of an initially flocculated suspension is calculated by Eq. (15)

$$\Delta P_s = \eta v B S^2 (H_0 C_0)^2 \int_{H_0}^{h_s} \frac{h_s}{(h_s - H_0 C_0)^3} dh_s \quad (15)$$

where  $B$  is the ratio of the shape factor to the tortuosity constant and  $S$  the ratio of the total solids surface area to the apparent



volume of the consolidated system. The integration of the right term, named as  $T(h_s)$ , is given by Eq. (16).

$$T(h_s) = \frac{1}{2} \left[ \frac{H_0}{H_0^2(1-C_0)^2} - \frac{h_s}{(h_s-H_0C_0)^2} + \frac{1}{H_0(1-C_0)} - \frac{1}{h_s-H_0C_0} \right] \quad (16)$$

Fig. 5(B) shows the comparison of  $\Delta P_t - h_t$  relation between experimental result and Eq. (15) for 40 vol% SiC A–60 vol% SiC B suspension. The origin ( $H_0$ ) of Eq. (15) was shifted to the height ( $h_{sc}$ ) of the suspension corresponding to  $\Delta P_{tc}$ . The height of  $h_{sc}$  was calculated by  $h_{sc} = V_{fc}/nA$ , where  $V_{fc}$  was the critical volume of filtrate at  $\Delta P_{tc}$  and  $n$  was estimated from the final packing density of particles at 19 MPa. The measured  $\Delta P_t - h_t$  curve was well fitted by Eq. (15) for the flocculated suspension model. Therefore, the consolidation behavior of bimodal particles system was well explained by the combination of two filtration models for well dispersed particles in early stage and for flocculated particles in latter stage.

#### 4.3. Phase transition pressure and packing density of bimodal SiC particles

Fig. 6 shows phase transition pressure ( $\Delta P_{tc}$ ), concentration at  $\Delta P_{tc}$  and packing density of bimodal particles after calcination at 1000 °C in Ar atmosphere.  $\Delta P_{tc}$  was almost constant in the fraction range of SiC B at 0–60 vol% ( $\Delta P_{tc} = 0.72$ –1.11 MPa) and at 60–100 vol% ( $\Delta P_{tc} = 0.11$ –0.58 MPa), respectively. This result suggests that the phase transition to a flocculated suspension occurs under a low

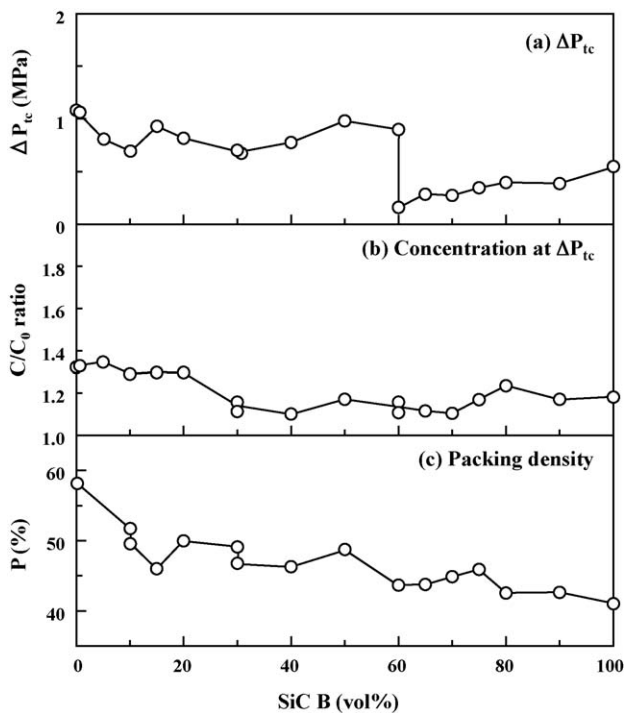


Fig. 6. (a) Phase transition pressure ( $\Delta P_{tc}$ ), (b) concentration at  $\Delta P_{tc}$  and (c) packing density for mixed powder system.

applied pressure in a SiC B-rich suspension (SiC B > 60 vol%). The concentration at  $\Delta P_{tc}$  decreased at a higher content of SiC B particles but almost constant in a wide range of SiC B from 30 to 100%. The comparison between rheological behavior in Fig. 4 and  $\Delta P_{tc}$  in Fig. 6(a) suggests that  $\Delta P_{tc}$  becomes a lower value for a pseudoplastic flow suspension rather than for a Newtonian flow or Bingham flow suspension. As explained for the result of Fig. 2, the bridging effect of SiC particles in a pseudoplastic flow suspension becomes significant, resulting in the decreased  $\Delta P_{tc}$ . After the phase transition to a flocculated suspension, the particle concentration of the suspension increases during the filtration. Packing density of calcined compacts decreased at a higher fraction of SiC B particles. The packing behavior of mixed SiC particles was analyzed by applying the concept of partial molar volume for the mixed powder system. The partial molar volume ( $\bar{V}$ ) of each powder is given by Eqs. (17) and (18),

$$\bar{V}_A = V - X_B \left( \frac{dV}{dX_B} \right) \quad (17)$$

$$\bar{V}_B = V + (1 - X_B) \left( \frac{dV}{dX_B} \right) \quad (18)$$

where  $X_B$  is the molar fraction of powder B in the mixed powder system and  $V$  the molar volume of mixed powder compact which can be determined from bulk density. Fig. 7 shows the molar volume of bimodal SiC particles consolidated. The measured data were fitted by the polynomial approximation by Eq. (19),

$$V = a + bX_B + cX_B^2 + dX_B^3 + eX_B^4 \quad (19)$$

where  $a$ – $e$  are experimental constants. As seen in Fig. 7, the two intercept values of tangent line for an arbitrary composition of SiC B correspond to  $\bar{V}_A$  and  $\bar{V}_B$ . Fig. 8(a) shows  $\bar{V}_A$  and  $\bar{V}_B$  as a function of  $X_B$ .  $\bar{V}_B$  was larger than  $\bar{V}_A$  and approached a constant value at  $X_B = 0.5$ –1.0. As compared with  $\bar{V}_B$ ,  $\bar{V}_A$  was not sensitive to  $X_B$ . This analysis indicates that (1) molar

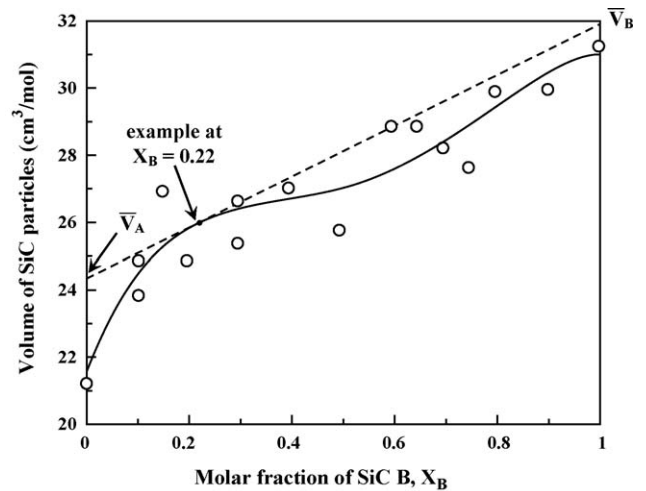


Fig. 7. Analysis of partial molar volume of SiC A and SiC B particles in the mixed powder compact after calcination at 1000 °C.

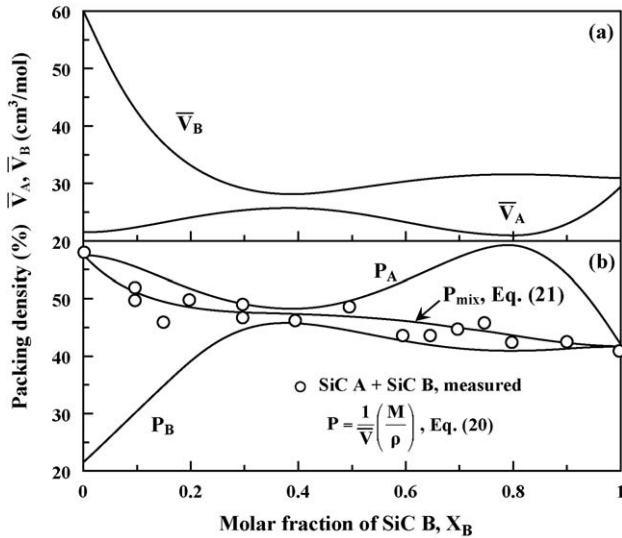


Fig. 8. Partial molar volume (a) and packing density (b) of SiC particles A and B in the mixed powder compact.

volume of SiC depends on particle size and (2) finer particles of 1 mol SiC occupy a large volume in the mixed powder system. The packing density ( $P$ ) of each powder in the mixed powder compact is related to  $\bar{V}$  by Eq. (20),

$$P = \frac{1}{\bar{V}} \left( \frac{M}{\rho} \right) \quad (20)$$

where  $M$  is the molecular weight and  $\rho$  the true density of particles. Fig. 8(b) shows  $P$  values of SiC A and SiC B particles.

It is apparent that the larger particles are densely packed than smaller particles in the mixed powder system. The packing density of bimodal particles system ( $P_{mix}$ ) is given by Eq. (21),

$$P_{mix} = \frac{1}{\rho_m} \frac{1}{(X_A/P_A\rho_A) + (X_B/P_B\rho_B)} \quad (21)$$

where  $\rho_m$  is the true density of mixed powders. The measured density of mixed powder system was well expressed by Eq. (21) based on the partial molar volume of each powder. The structure formed by the connection between larger particles is dense but that formed by the connection between smaller particles is porous. These characteristics of packing structures are reflected in the measured density of mixed powder system.

Fig. 9 shows the schemes of structures estimated from packing density shown in Fig. 8(b). The structure of SiC A particles is close to simple cubic packing (density 52.4%) at  $X_B = 0.2$ . The fine SiC B particles are packed in the pores formed by SiC A particles or cover the surfaces of SiC A particles. Further addition of SiC B particles (30–40 mol% SiC B) expands the structure of SiC A particles, resulting in the decreased packing density of A particles,  $P_A$ . The increased number of SiC B particles changes the porous structure (Fig. 9(a)) to dense one (Fig. 9(b)). In the range of  $X_B = 0.5–0.8$ ,  $P_A$  was in the range of 0.498–0.593. This packing density reflects the mixed structure of simple cubic packing and random close packing (calculated density of random close packing: 63.7%) or body-centered cubic packing (theoretical packing density: 68.0%).  $P_B$  value is around 0.41 and SiC B particles are porously packed. Further addition of SiC B particles ( $X_B = 0.9$ ) leads to the decreased packing density of SiC A particles. Little change of packing density was measured

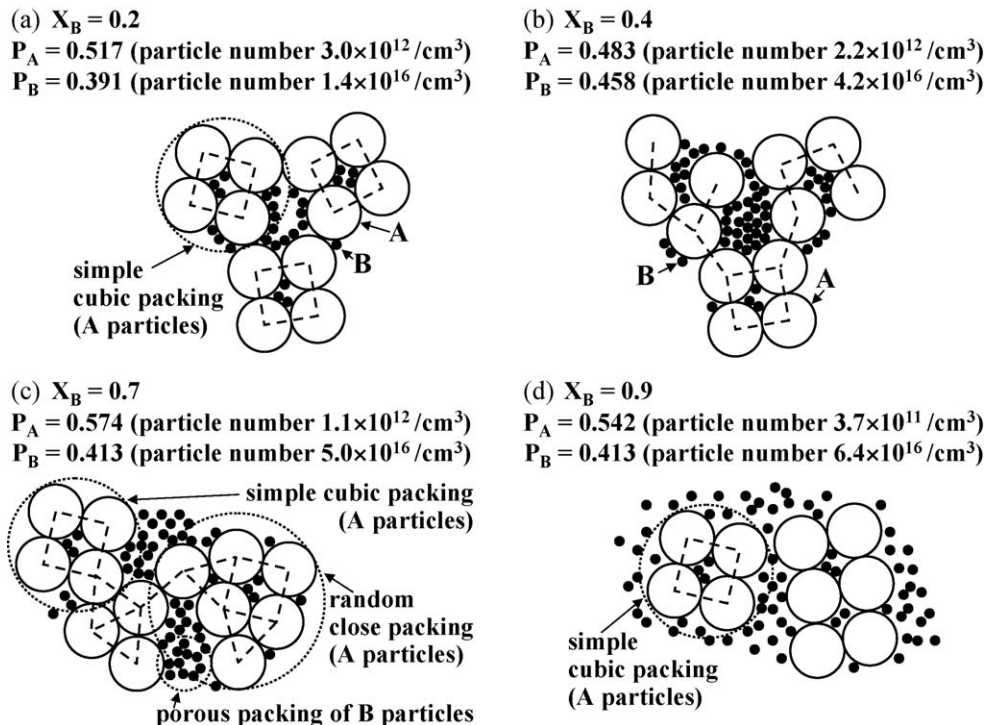


Fig. 9. Schematic structures estimated from packing density of SiC particles A and B.

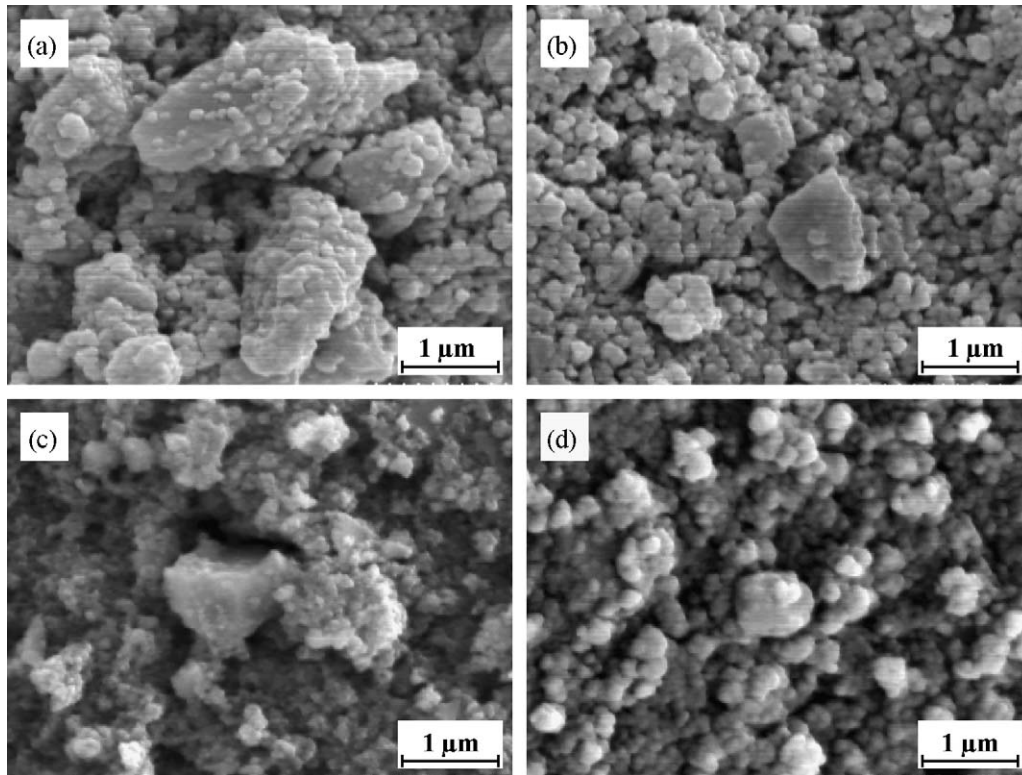


Fig. 10. Microstructures of SiC compacts with (a) 20 vol% SiC B, (b) 40 vol% SiC B, (c) 70 vol% SiC B and (d) 90 vol% SiC B after calcination at 1000 °C in Ar atmosphere.

for SiC B particles. As reported in Fig. 9, the packing structure formed by SiC A particles or SiC B particles is influenced by each other.

Fig. 10 shows the microstructures of SiC compacts after calcination at 1000 °C. At the composition of 20 vol% SiC B (Fig. 10(a)), the small SiC B particles were attached to the surface of large SiC A particles. This result is understood by the calculated interaction energy shown in Fig. 2. The observed microstructure was basically similar to the schematic structure shown in Fig. 9(a). In the microstructure for 40 vol% SiC B composition, it was difficult to see directly large A particles. The increased fraction of SiC B particles separates SiC A particles connected in Fig. 9(b). In addition, SiC B particles formed particle clusters because of the weak repulsive energy as shown in Fig. 2. When the fraction of SiC B particles is increased to 70 vol%, large SiC A particles were embedded in the matrix of SiC B particles. A similar microstructure was also observed for 90 vol% SiC B composition. From Fig. 10(d), it was difficult to see the structure formed by the connection between SiC A particles.

## 5. Conclusions

- (1) The rheological behavior of the suspensions of bimodal SiC particles (800–30 nm) changed as follows with increasing fraction of 30 nm SiC particles: Newtonian flow → Bing-Bingham flow → pseudoplastic flow.
- (2) Colloidal phase transition from dispersed to flocculated suspension occurred at a critical applied pressure ( $\Delta P_{tc}$ )

during the pressure filtration of the mixed powder suspensions. The  $\Delta P_{tc}$  and final packing density decreased with an increase of the fraction of 30 nm SiC.

- (3) Partial molar volume of large SiC particles was smaller than that of small SiC particles. Therefore, large SiC particles were more densely packed than small SiC particles in all the range of mixing.
- (4) Understanding of the packing characteristics of small and large SiC particles assists an observer in interpreting the microstructures of SiC compacts.

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