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Preparation of SiC Particles Coated with Alumina Hydrate: Effect of Reaction Condition on Particle Coalescence

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Abstract

Alumina-hydrate-coated SiC particles were prepared via a homogeneous precipitation method using urea, and the conditions for uniform coating and less coalescence of the particles were investigated. Coalescence of coated particles could be said to occur by collision and agglomeration followed by deposition of alumina hydrate on the agglomerated particles. Coalescence of coated particles was suppressed by use of low reaction temperature, low concentration of aluminium sulfate, high concentration of urea, intensive stirring, and a flow reactor. © 1996 Elsevier Science Limited

1 Introduction

Recently, composite particles in which a core particle is coated by another phase have attracted attention from various viewpoints. The main objectives of applying the coating are the improvement of chemical stability and/or surface character[1-5] and uniform addition or mixing of a second phase.[6-10] Such composite particles were also useful to improve sinterability.[11]

In the preparation of composite particles, uniform coating and suppression of particle coalescence are essential. To achieve these, fine control of the deposition rate of the second phase is necessary. Thus, many researchers have used alkoxide as a starting material for composite particles, because of the ease of control of its precipitation rate, to prevent the formation of coagulated particles. On the other hand, inorganic salts can also be used as a starting material,[12-18] mostly via the homogeneous precipitation method which is also characterized by easy control of precipitation rate.

In the preparation of composite particles from inorganic precursors with the homogeneous precipitation method, it is not easy to prevent the coalescence of particles. A number of efforts have been made to prevent the coalescence. Matijevic and co-workers prevented coalescence of particles by using dilute dispersions and/or adding surfactants.[13,14] De Jonghe and co-workers also used surfactants.[16,17] However, it is still rather difficult to prevent the coalescence, especially when coating layers are thick and dispersions are concentrated. In the present study, we prepared alumina-hydrate-coated SiC particles and investigated the effects of reaction conditions on the coalescence of composite particles. The reaction conditions investigated were reaction temperature, aluminium sulfate and urea concentrations, stirring rate, and reactor type.

2 Experimental Procedure

A batch or a flow reactor was used as a reactor (Fig. 1). SiC particles (Ibigawa Electric Industry Co., Ltd; median diameter = 0·6 μm as shown in Fig. 2) were dispersed in distilled water and then aluminium sulfate (reagent grade, Wako Pure Chemical) was dissolved in it, and followed by supersonic agitation for 15 min. The dispersion was heated to a given temperature. During heating, the dispersion was stirred (batch reactor) or was made to flow (flow reactor). Then, urea (reagent grade, Wako Pure Chemical) was added to start the reaction. The amount of reacting solution was 100 ml for the batch reactor and 250 ml for the flow reactor. During the reaction, the suspension was stirred with a wing-type stirrer (batch reactor) or circulated (flow reactor). The pH

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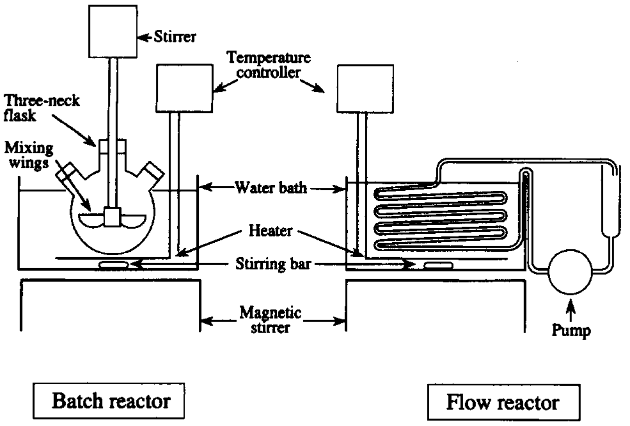

Fig. 1. Schematic illustrations of reactors.

of the dispersion was measured and the reaction was stopped at pH = 7·0, where the deposition of alumina hydrate was complete. The precipitate was filtered and washed with distilled water and finally with ethanol. The precipitate was dried *in vacuo* at 70°C. The alumina hydrate deposited was amorphous.

To evaluate the degree of coalescence of coated particles, the particle size distributions of the powders were measured. A small amount (1–2 mg) of the as-coated powder was dispersed in 5 ml of ethanol using ultrasonic agitation, and one drop of the dispersion was dropped on a glass plate for observation under a scanning electron microscope (SEM). The particle size distributions were measured from the SEM photographs. In this measurement, particles which were hardly discriminated from aggregates were omitted. The as-coated powder was also characterized using an X-ray microanalyser (XMA). Zeta-potential measurements were performed on a few samples using the electrophoresis method.

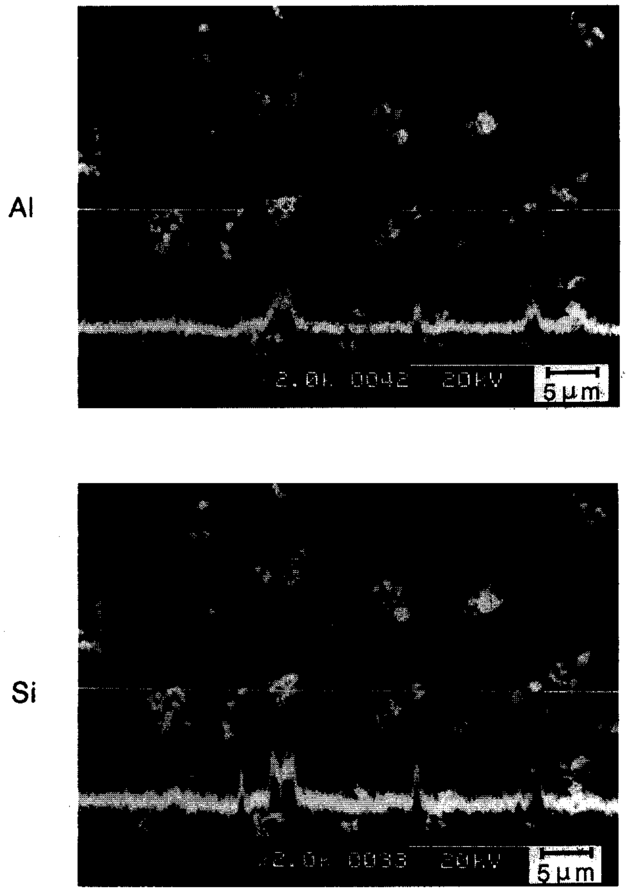

Fig. 3. Distribution of Al and Si elements. [$Al_2(SO_4)_3$] = 0·075 mol l^{-1}, [SiC] = 9·0 g l^{-1}, [urea] = 10·8 mol l^{-1}, reaction temperature = 70°C, stirring rate = 3000 rev min^{-1}, batch reactor.

3 Results

Figure 3 shows the distributions of silicon and aluminium elements in the alumina-hydrate-coated SiC particles. Good coincidence in the distributions of both elements indicates that SiC

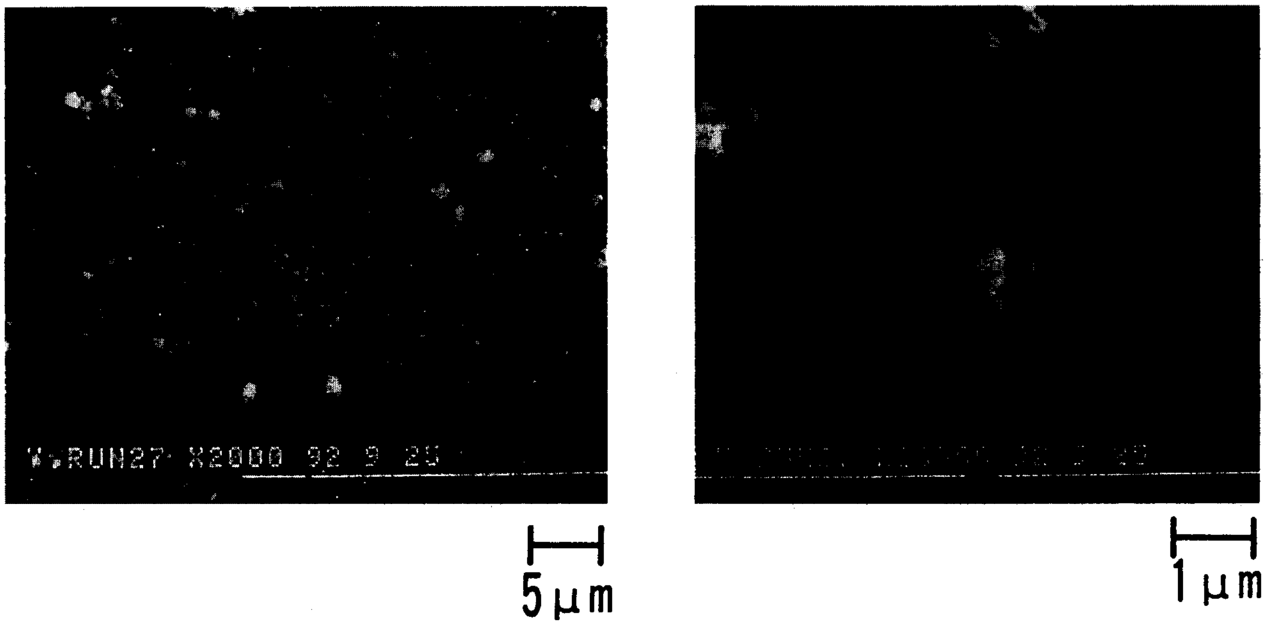

Fig. 2. SiC particles.

particles are coated uniformly with alumina hydrate and that there is little formation of separately precipitated alumina hydrate particles. Another important parameter, the degree of particle coalescence, was evaluated from the size distribution of coated particles.

3.1 Effects of reaction temperature and urea concentration on coalescence of composite particles

The deposition rate of the alumina hydrate is considered to affect the coalescence of coated particles. The deposition rate is governed by the hydrolysis rate of urea. The hydrolysis rate of urea depends on reaction temperature and concentration of urea according to the following formula.[18]

$$r=6{\cdot}5\times10^{15}[\text{urea}]\exp(-1{\cdot}3\times10^{5}/RT)\ [\text{mol l}^{-1}\ \text{min}^{-1}]$$

where [urea] is the concentration of urea (mol l^{-1}), R is the gas constant (8·31 J (mol^{-1} K^{-1})) and T is absolute temperature. The effect of deposition rate of alumina hydrate on the coalescence of composite particles was investigated by using batch reactor under different reaction temperatures and urea concentrations. Other reaction conditions were: aluminium sulfate concentration ($[Al_2(SO_4)_3]$) = 0·075 mol l^{-1}, dispersion amount of SiC particles ([SiC]) = 9·0 g l^{-1}, stirring rate = 170 rev min^{-1}. The ideal diameter of a coalescence-free composite particle for this $[SiC]/[Al_2O_3]$ ratio was calculated to be 1·0 μm. Figure 4 shows the effect of reaction temperature under [urea] = 10·8 mol l^{-1}. The degree of coalescence decreases slightly with decrease in reaction temperature (i.e. decrease in hydrolysis rate of urea). Figure 5 shows the effect of urea concentration on the coalescence of particles. The coalescence of composite particles tends to be suppressed by increasing urea concentration.

3.2 Effect of stirring rate on coalescence of composite particles

Stirring rate was found to have a remarkable effect on the coalescence of composite particles during coating as shown in Fig. 6. The ideal diameter of a coalescence-free composite particle at the $[SiC]/[Al_2O_3]$ ratio used is calculated as 1·0 μm. Figure 6 shows that the coalescence of composite particles is suppressed significantly under a high stirring rate above a few thousand rev min^{-1}. Particle size distributions were also measured by a laser diffraction light scattering method (MICROTRAC model 7995-30, Leeds & Northrup Instruments). A result is illustrated in Fig. 7 for the effect of stirring rate. Both Figs 6 and 7 show that SEM and the light scattering method give close results, although the size distribution curves by the latter method are shifted slightly to the finer side.

3.3 Effect of aluminium sulfate concentration on coalescence of composite particles

The concentration of aluminium sulfate also affects the coalescence of composite particles; the results are summarized in Table 1. With decreasing aluminium sulfate concentration, i.e. with decreasing thickness of alumina hydrate coating, the observed diameters of composite particles

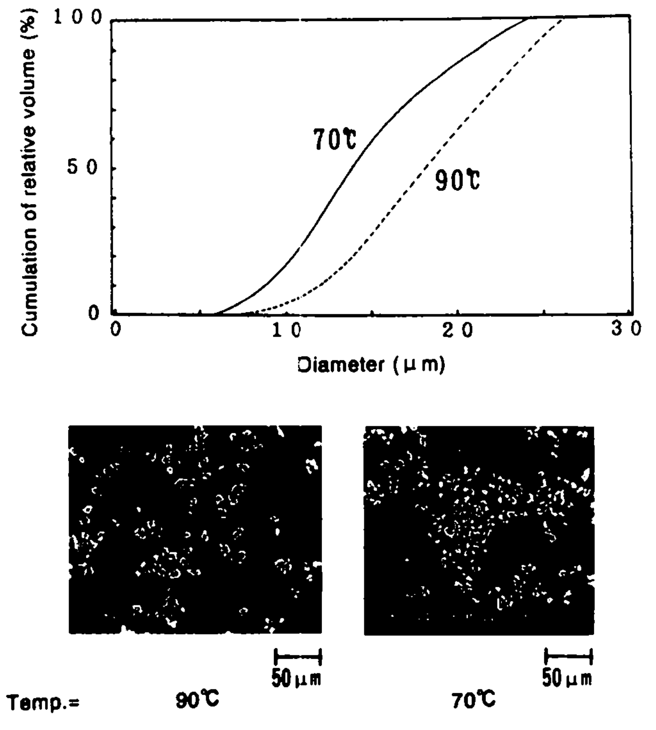

Fig. 4. Effect of reaction temperature on coalescence of particles. $[Al_2(SO_4)_3]$ = 0·075 mol l^{-1}, [SiC] = 9·0 g l^{-1}, [urea] = 10·8 mol l^{-1}, stirring rate = 170 rev min^{-1}, batch reactor.

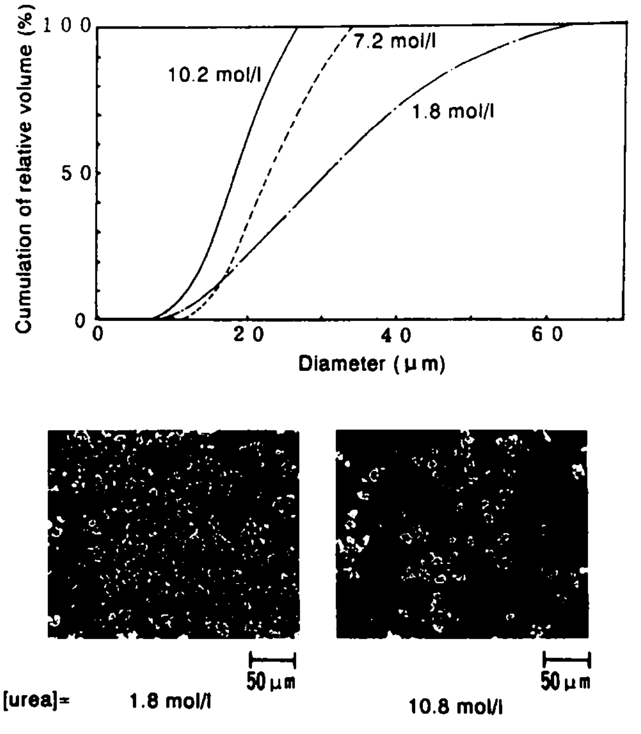

Fig. 5. Effect of urea concentration on coalescence of particles. $[Al_2(SO_4)_3]$ = 0.075 mol l^{-1}, [SiC] = 9.0 g l^{-1}, reaction temperature = 90°C, stirring rate = 170 rev min^{-1}, batch reactor.

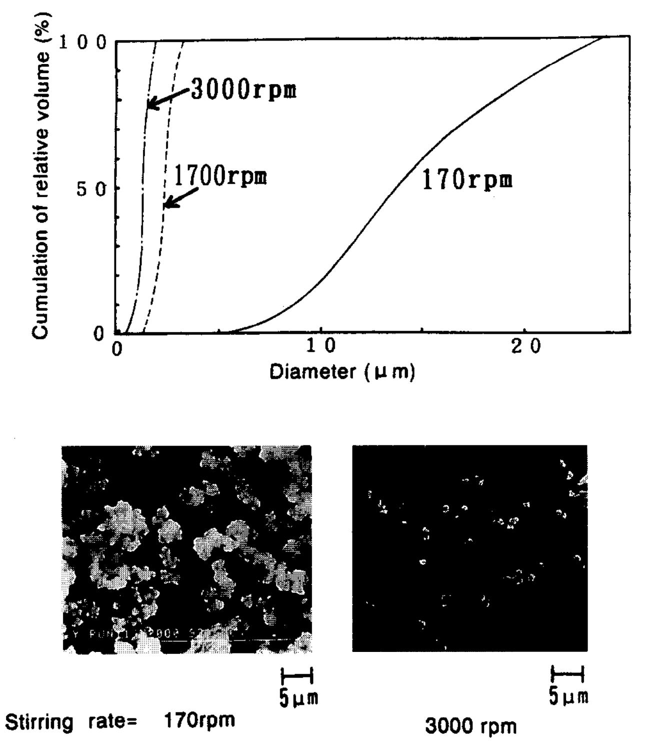

Fig. 6. Effect of stirring rate on coalescence of particles (measured from SEM photographs). [$Al_2(SO_4)_3$] = 0·075 mol l^{-1}, [SiC] = 0·9 g l^{-1}, [urea] = 10·8 mol l^{-1}, reaction temperature = 70°C, batch reactor.

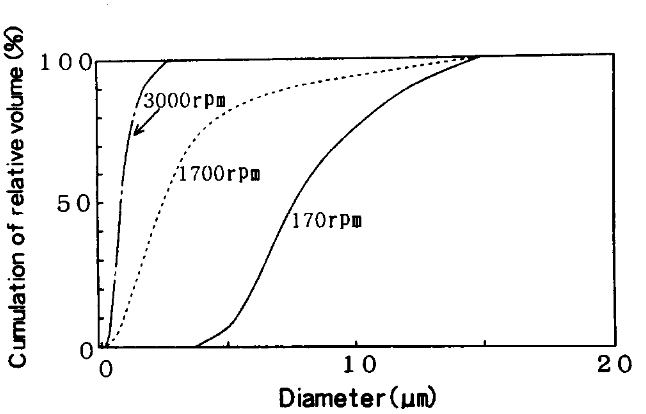

Fig. 7. Effect of stirring rate on coalescence of particles (measured by laser diffraction light scattering method). The samples measured are shown in Fig. 6.

become close to the value calculated on the assumption of no coalescence. Typical examples of composite particles are shown in Fig. 8.

3.4 Effect of reactor type on coalescence of composite particles

The results described above were obtained using the batch reactor. Composite particles were also prepared using the flow reactor shown in Fig. 1. In the flow reactor method, the reacting solution containing suspended SiC particles was circulated at a flow rate which resulted in almost laminar flow (Reynold's number was 2 × 10^3). As shown in Fig. 9, the flow reactor gave less coagulated particles comparable to the particles obtained at 1700 rev min^{-1} stirring rate using the batch reactor. Although further investigations are required to determine the optimum reaction condition, one can say that use of a flow reactor may aid in the preparation of coalescence-free composite particles.

Table 1. Ideal and median diameters of composite particles[a]

No.	*[$Al_2(SO_4)_3$] (mol l^{-1})*	*Ideal diameter[b] (μm)*	*Median diameter (μm)*	*Median diameter/ ideal diameter*
1	0·0047	0·65	0·6	0·9
2	0·0063	0·66	1·1	1·6
3	0·0094	0·69	1·3	1·9
4	0·019	0·76	1·8	2·3
5	0·038	0·87	2·3	2·6
6	0·075	1·04	3·2	3·1

[a] Reaction conditions: [SiC] = 9·0 g l^{-1}, [urea] = 10·8 mol l^{-1}, reaction temperature = 70°C, stirring rate = 1700 rev min^{-1}, batch reactor.

[b] Ideal diameter was calculated on the assumptions: original SiC diameter = 0·6 μm, uniform coating of alumina hydrate on SiC particles, and no coalescence of composite particles.

4 Discussion

Coalescence of composite particles would occur by collision of coated particles followed by deposition of alumina hydrate on the agglomerates in a similar manner as in the formation of alumina-hydrate-coated SiC whiskers.[18] The coalescence process is shown schematically in Fig. 10. The coalescence may depend on the probability of formation of agglomerates and the deposition rate of alumina hydrate. The probability of formation of agglomerates is thought to be affected by the collision frequency of particles and the probability of cohesion. The deposition rate of alumina hydrate depends on the hydrolysis rate of urea.

As described above, coalescence of composite particles was suppressed by (1) intensive stirring, (2) use of a flow reactor, (3) low reaction temperature, (4) high concentration of urea, and (5) low concentration of aluminium sulfate. These conclusions are the same as those drawn on the formation of alumina-hydrate-coated SiC whiskers.[18] It was also observed in the formation of YSZ-coated SiC particles that intensive stirring suppressed particle coalescence.[19]

Intensive stirring is considered to suppress the coalescence of composite particles by breaking agglomerated composite particles before further deposition of alumina hydrate, which strengthens the agglomerated structure to form the coagulated particles. Williams *et al.* also reported that the degree of particle aggregation in dispersion

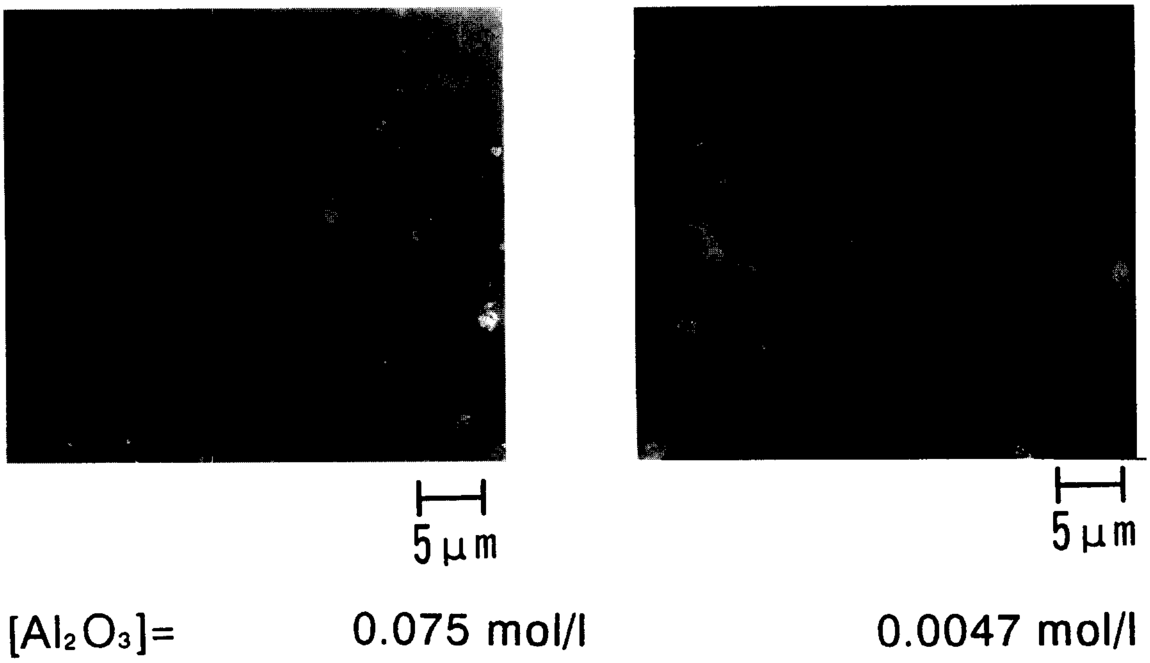

Fig. 8. Typical example of the effect of thickness of coating layer on coalescence of particles. [SiC] = 9·0 g l^{-1}, [urea] = 10·8 mol l^{-1}, reaction temperature = 70°C, stirring rate = 1700 rev min^{-1}, batch reactor.

decreased with increasing stirring rate.[20] Use of a flow reactor under a laminar flow condition my suppress the coalescence by decreasing the collision frequency of dispersion particles. Suppression of the formation of coalesced particles by decrease in reaction temperature may be mainly due to the decrease in the deposition rate of alumina hydrate, thereby increasing the chance of breakage of agglomerated particles.

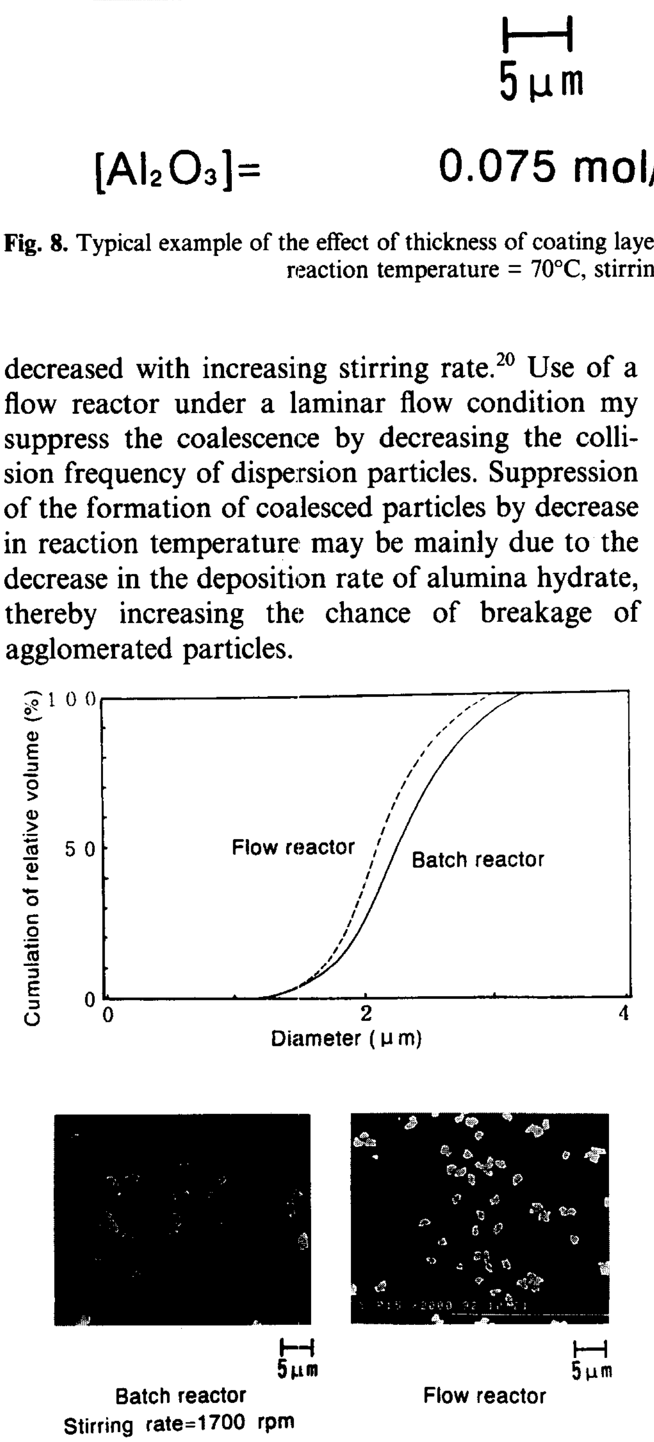

Fig. 9. Effect of reactor type on coalescence of particles. [$Al_2(SO_4)_3$] = 0·075 mol l^{-1}, [SiC] = 9·0 g l^{-1} [urea] = 10·8 mol l^{-1}, reaction temperature = 70°C.

The effect of urea concentration is complex. From the viewpoint of deposition rate of alumina hydrate alone, the increase in urea concentration should enhance the coalescence as described above. However, this observation was not the case. Thus, there are some strong functions of urea other than the increase in hydrolysis rate itself. Vincent *et al.* reported that the surface charge of AgI increased in the presence of absorbed neutral substances.[21] Thus, zeta-potentials of the as-coated powders were measured at 25°C under different urea concentrations (1.8 or 10·2 mol l^{-1}) in the presence of aluminium sulphate (0·075 mol l^{-1}). The zeta-potentials were +2 mV for 1·8 mol l^{-1} urea concentration and +8 mV for 10·2 mol l^{-1} urea concentration. Both values are in the range of zeta-potential where colloids are commonly accepted as unstable. In addition to the change of zeta-potential, the following functions of urea may be considered. One can suppose (1) a steric effect — urea molecules are adsorbed on the alumina hydrate coating and decrease the probability of cohesion between coated particles; (2) the formation of a complex with Al^{3+}-carrying species in solution which modifies the deposition rate of alumina hydrate; (3) the increase in viscosity of the solution decreases the collision frequency of particles and/or increases the shear force to redisperse aggregated particles. In the hydrolysis of $TiOSO_4$, the presence of urea also has a remarkable effect on the formation of discrete spherical titania particles even under conditions of negligible hydrolysis of urea.[22]

For the decrease of particle coalescence under low concentration of aluminium sulfate, there

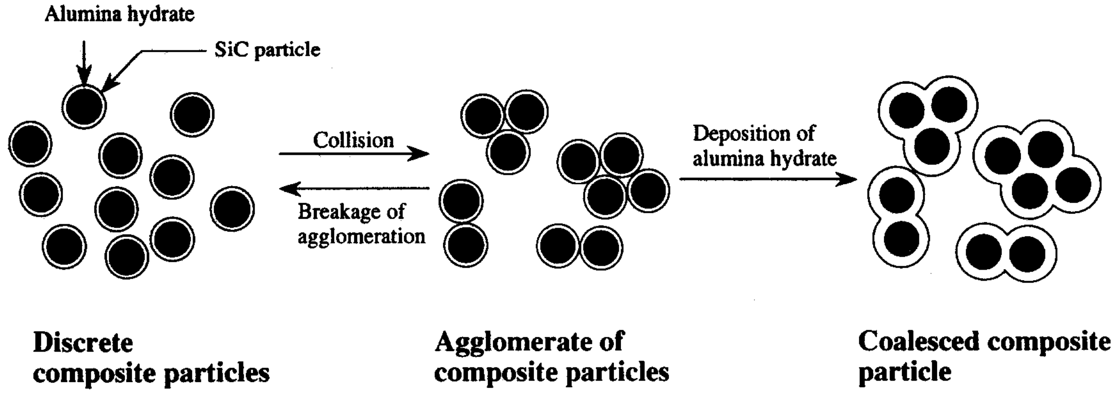

Fig. 10. Schematic representation of coalescence process of particles.

are many reasons to be taken into account. With thinning of the coating layer, (A) the collision frequency of composite particles will decrease following a decrease in collision cross-section, and (B) the cohesion probability at collision will decrease following a decrease in neck cross-section formed with cohesion of two particles (Fig. 11). Both multivalent Al^{3+} and SO_4^{2-} ions have a high flocculation power. That is, (C) a decrease in the concentration of aluminium sulfate gives a low ionic strength of the reacting solution which may increase the thickness of the electric double layer, resulting in a decrease in the collision frequency of composite particles. (D) Decrease in coating duration at low aluminium sulfate concentrations may decrease the chance for coalescence. In order to reveal the dominant factor, concentrations of the raw materials (i.e. [SiC] and $[Al_2(SO_4)_3]$) were changed under fixed $[SiC]/[Al_2(SO_4)_3]$ ratio. Other conditions were equal to those in Table 1. The ratio of observed to ideal particle diameters is shown in Table 2. Under a fixed $[SiC]/[Al_2(SO_4)_3]$ ratio, a higher concentration of raw materials results in a higher ionic strength of the reacting solution, longer reaction time, and thus more frequent collisions. In Table 2, in spite of the large difference in concentration of raw materials [four times for no. 7/no. 4, nine times for no. 8/no. 3; average particle distance varies inversely with the cube root of the number of particles (i.e. concentration)], the ratios of both diameters are equal or very close. These results show that the increase in collision frequency (A) resulting from the increased concentration of SiC particles does not affect the particle coalescence under the conditions examined and that the change of the concentration of aluminium sulfate (C and D) does not affect the particle coalescence under the same ratio of $[SiC]/[Al_2(SO_4)_3]$. Consequently, it can be said that (B), the decrease of cohesion probability, is the main reason for the decrease of coalescence under low concentration of aluminium sulfate.

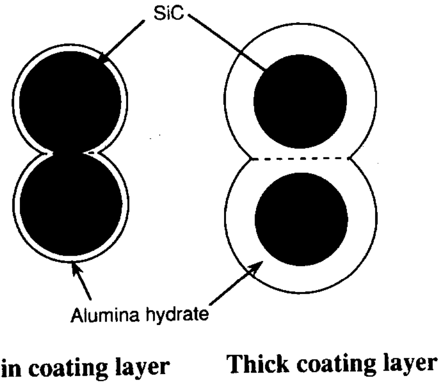

Fig. 11. Effect of coating layer thickness on cohesion area.

5 Conclusions

Alumina-hydrate-coated SiC particles were prepared by homogeneous precipitation using urea. It

Table 2. Effect of raw material concentration on particle coalescence

No.	*[SiC]* $(g\ l^{-1})$	$[Al_2(SO_4)_3]$ $(mol\ l^{-1})$	$[SiC]/[Al_2(SO_4)_3]$ $(g\ mol^{-1})$	*Ideal diameter*[a] *(μm)*	*Median diameter (μm)*	*Median diameter/ideal diameter*
4	9·0	0·019	470	0·76	1·8	2·3
7	36	0·075			1·8	2·3
3	9·0	0·0094	950	0·69	1·3	1·9
8	72	0·075			1·5	2·2

[a] Ideal diameter was calculated on the assumptions: original SiC diameter = 0·6 μm, uniform coating of alumina hydrate on SiC particles, and no coalescence of composite particles.

can be said that coalescence of coated particles occurred by collision and agglomeration followed by deposition of alumina hydrate on the agglomerated coated particles. Coalescence of coated particles was suppressed under the conditions of intensive stirring, thin coating layer, low reaction temperature, high urea concentration and a use of flow reactor.

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