Computer Simulation on Aggregated Structure of Fine Particles in Slurry

Takatoshi Kimura, Masafumi Arakawa Kiyoshi Hirota and Hitoshi Murata
Faculty of Eng.& Design, Kyoto Institute of Technology*

Abstract

The property of a shaped body by slip casting in ceramic processing greatly depends on the dispersive state in the slurry.

The agglomerate process in a high densed slurry we studied by three dimensional computer simulation. The movement of particles was determined by cohesion probability between particles. The aggregative and this process was discussed from the view points of the aggregation rate, the coordination number and the aggregative ratio by using cohesion probability.

The experimental results from the measurement of viscosity and SEM observational dried slurries supported this simulation well.

1. Introduction

Slip casting is a method of moulding ceramics which has been practised since old times and uses slurry containing fine particles as raw material dispersed in a medium at a high concentration. As well known, the dispersion aggregation state of the fine particles as raw material in slurry not only exerts large influence over rheological behaviors of the slurry but causes changes in the structure of the moulded or fired products too. Accordingly, it is important to be acquainted with the aggregation state of particles in slurry. However, it is difficult to observe directly the aggregate structure or aggregation process of the particles dispersed at a high concentration in the slurry. Till now, for explanation of aggregate structures, many studies using computer-simulation of the aggregation of particles in slurry have been carried out. In a large part of the studies, the simulation dealt with two-dimensional aggregation and dilute slurry systems. Accordingly, it is impossible to adapt the results of such studies to high densed slurry systems.

In this study, three dimensional computer-simulation of aggregation was carried out to explain the aggregation process of particles. Water-alumina slurry systems which are employed for practical slip casting were used, and the viscosities were measured. The freeze-dried slurries were observed by SEM. Based on the test results, the aggregate structure and the aggregation process in the slurries were examined. A good agreement between the results of the computer simulation and those of the measurement and observation has been obtained.

2. Experimental Procedures

2.1 Simulation of Aggregation

As to the initial state defined for the simulation, 805 model particles, which are uniform in shape and size, were packed into a cube, in which each side is 10 times long as the size of one particle so that the volume concentration of the particles becomes 42...
The particles were given numbers and optional movement directions. The particles were then, moved to a distance of $\frac{3}{100}$ of the particle size along the movement directions. In order to ensure the Brownian movement, the movement directions of the particles were changed with a certain probability. The probability, in which the particles collided and aggregate with each other is defined as cohesion probability. Pseudo-random numbers in the range of 0 to 1, are generated every time whenever the collision occurs, and they are compared with the cohesion probability. As shown in Fig. 1, in the case where the random number is smaller than the cohesion probability, the particles are aggregated. Thereafter, the aggregate is considered as a unit of movement for calculation. On the other hand, in the case where the random number is larger than the cohesion probability, the particles are rebounded and the movement directions are changed. Fig. 2 illustrates the flow chart of this program. For all the particles, this operation is repeatedly run and the calculation is conducted until the run times reaches 100. Under different aggregation conditions, that is, at different cohesion probabilities of 100%, 50%, 30%, 10% and 5%, the changes in aggregate structure and aggregation process of the particles were examined.

Also, the above-described simulation was carried out at a particle volume concentration of 30 vol.% and 5 vol.% respectively.

### 2.2 Preparation of Slurry

As a powdery sample, alumina with easy sintering properties and a low soda content (AL-160SG modified-4 true specific gravity 3.93g/cm$^3$; BET specific surface area 5.5m$^2$/g;
manufactured by Showa Denko KK), as previously reported, was used. To the alumina, water and one dispersant (ammonium salt of polyacrylic acid) were added so that the volume ratio of the alumina based on the water became 42 vol.%. To the mixture, alumina balls were added and vibrated for 30 minutes. Thereafter, the mixture was deaerated under vacuum and was used as experimental slurry.

The relationships between the addition amounts of the dispersant and the apparent viscosities of the slurries suggest there are essentially three different regions, namely region(a) where the slurry isn’t enough the dispersant; region(b) where the amount of the dispersant is appropriate; and region(c) in which the amount of the dispersant is excessive and with different aggregation states. In this study, three slurry systems (a), (b), and (c) have been considered as representative of the above mentioned regions (a), (b), and (c); the addition amounts of the dispersant are: 0.18 g for the system (a), 0.30 g for the system (b), and 1.00 g for the system (c), based on 100 g of the alumina, were prepared. The slurry systems (a), (b), and (c) are defined as a strong aggregation system, a dispersion system, and a weak aggregation system, based on their flow curves, respectively.

### 2.3 Viscosity Measurement of Slurry

In order to measure the viscosity of the slurries, a rotary viscometer was used. The measurements of the viscosity were recorded on a recorder so that the time-dependent, changes in viscosity of the slurries were examined. The rotation speed of the rotor was set to 3 rpm so that fine changes in the viscosity could be detected. The measurement was conducted immediately after the slurries were deaerated.

### 2.4 SEM Observation of Freeze-Dried Slurry

In order to get detailed information of the real aggregate structures of the slurries, the freeze-dried slurry samples were observed by SEM. To obtain a sample for the observation, each slurry system was placed on a copper mesh, then dipped and freeze-dried quickly in isopentane (−140 °C) cooled with liquid nitrogen so as to avoid the crystal growth of the water. Thereafter, the slurry was dried under vacuum with cooling at −15 °C.

### 3. Result and Discussion

Fig. 3 illustrates the relationships between the number of aggregates and the number of run times at particle volume concentration of 42%, at different cohesion probabilities. In Fig.3 N0 is the initial number of the aggregates (805), and N is the total number of aggregates and dispersed particles at the t-th run time. Table 1 shows the ratios of the gradients (k) of the straight lines in Fig.3 to that of the straight line at cohesion probability of 100%. As shown in Fig.3, the decrement ratio (k) of the particles increases with the cohesion probability, that is, there exists correlation between the cohesion probability and the aggregation rate. As generally recognized, the aggregation process of a monodispersion system at the initial stage is in accordance with the quadratic process represented by the Smoluchowski’s solution. The total number N, of particles is expressed as follows:

\[ N = N_0 \times (1 + k \times \text{run times})^2 \]
\[
\frac{dN_t}{dt} = \frac{4kT}{3\eta}N_t^2
\]

(1)

Table 1 Comparison between cohesion probability and \(k_1\)

| Cohesion probability | \(k_1\)  | \(k_1/k_{1100}\% \times 100\) |
|----------------------|--------|-------------------------------|
| 100%                 | 0.094  | 100.0                         |
| 50                   | 0.057  | 60.6                          |
| 30                   | 0.041  | 43.6                          |
| 10                   | 0.014  | 14.8                          |
| 5                    | 0.008  | 8.0                           |

In which \(k\) is the Boltzman constant, \(T\) is the absolute temperature, and \(\eta\) is the viscosity of a medium. The Smoluchowski’s solution has been experimentally demonstrated to reveal its adaptability to diluted slurry systems\(^3\). However, as a result of the simulation, the aggregation of the particles which proceeds according to the linear process has been observed as clearly shown in Fig. 3. In such dense slurry systems as simulated in this study, the volume concentrations of particles are large, so that the number of collision times between the particles is very high. That is, the number of collision times of the particles per unit time is very high. Accordingly, it is speculated that the assumed initial stage of the aggregation by the Smoluchowski’s solution is completed in a very short time, so that no aggregation process by the quadratic process is presented. Therefore, in this study, the simulation was conducted at different concentrations of the particles in order to elucidate effects of the differences in concentration, that is, in number of collision times of the particles, on the reaction process. Fig. 4 shows the results. In the simulation, the cohesion probability is set to 100\%. In Figs. 4(A), 4(B) and 4(C), the volume concentrations of particles are 42 vol.%, 30 vol.% and 5 vol.% respectively. The changes in number of the aggregates, on the assumption that the aggregation proceeds according to the quadratic and linear processes represented by the formulae (2), (3) are plotted as ordinates in the graphs.

Quadratic process:

\[
\frac{1}{N_t} \frac{1}{N_{t-1}} = k_t
\]

(2)

\[
\text{Linear process:}
\]

\[
\text{Quadratic process:}
\]

\[
\text{Linear process:}
\]

\[
\text{Quadratic process:}
\]

\[
\text{Linear process:}
\]

Fig.4 Change in number of aggregates in different concentration
\[ \frac{dN_i}{dt} = k_iN_i \]
\[ \ln\left( \frac{N_i}{N_o} \right) = -k_i \cdot t \]

In which \( K_i, k_i, K, \) and \( k \) represent proportional constants. In Fig. 4, \( n \) represents the degrees. As shown in Fig. 4 (A), the aggregation proceeds substantially not according to the quadratic but to the linear process. The aggregation rate decreases remarkably in the latter half of the aggregation process, following the linear process, because the number of aggregates becomes very small. In Fig. 4 (B), in the initial period, the aggregation proceeds according to the quadratic process, but from the number of run times of about 40 it departs from the quadratic process. Accompanied with the departure, the aggregation proceeds partially according to the linear process. In Fig. 4 (C), the entire aggregation proceeds according to the quadratic process. In this figure, the straight line has an X intercept, not passing through the origin, because the particles, excluding particles of which the inter-particle distances are small, are packed, so that the particles begin to collide with each other at certain time after the start of the simulation. Based on the foregoing description, when the concentration of particles is low, the aggregation proceeds according to such quadratic process as represented by the Smoluchowskis’ solution in the overall simulation range. On the other hand, as the concentration of particles is increased, the aggregation rate is enhanced, so that the aggregation by the quadratic process ceases before the completion of the simulation. Moreover, at a high concentration of 42 vol.%, the aggregation by the quadratic process is completed in a very short time, so that the aggregation can hardly be observed. In the case of relatively high concentrations, the number of collision times of particles is high, resulting in the formation of large aggregates. Probably, this causes the aggregation to depart from the assumption for the Smoluchowski’s solution that the particle sizes are not significantly different. This simulation assumes that all the movement distances of the movement units are equal. It is supposed that this is not sufficiently compatible with the assumption of the Smoluchowski’s solution. At present, the authors consider effects of the condition that the movement distance changes with the number of particles constituting one movement unit, on the simulation.

Fig. 5 shows the relationship between the average coordination number of aggregates and the number of run times at different cohesion probabilities, at a volume concentration of particles of 42 vol.%. The average coordination number is the average number of coordinating particles in the aggregates excluding aggregates with a coordination number of 0, that is, the dispersed particles. At any of the cohesion probabilities, the average coordination number increases with the numbers of run times. Particularly, in the case of the relative high adhesion probabilities, the increase of the average coordination numbers ceases at a certain number of run times and thereafter is kept constant. As to this figure, even at the same number of run times, the aggregation rates are different depending on the cohesion pro-
abilities, so that the numbers of aggregates are different. Accordingly, by Fig. 5, no knowledge of effects of the cohesion probabilities on the coordination numbers can be obtained. Fig. 6 shows the relationship between the number of aggregates and the average coordination number of respective aggregates. As understood in Fig. 6, when the numbers of aggregates are equal, the average coordination number at the lower cohesion probability is high than that at the higher cohesion probability. This is because that when the cohesion probability is low, the number of collision times of particles increases and the probability of forming aggregates having high coordination number is enhanced. By the model experiment using white alumina by Arakawa, it has been confirmed that when the cohesion becomes low, the coordination number increases. It is suggested that the cohesion probability in this simulation corresponds not only to the aggregation rate but also to the cohesion itself.

Fig. 6 Relation between coordination number and aggregate number

Fig. 7 shows the relationship between the volume ratio of aggregates and the number of run times at particle volume concentration of 42%. For clear understanding of the aggregation process, an aggregate composed of 2 to 5 particles is defined as a small aggregate, and an aggregate composed of at least 6 particles is considered as a large aggregate.

Fig. 7 The effect run times on aggregate ratio
The cohesion probabilities are set to 100% for Fig. 7 (A), 30% for Fig. 7 (B), and 5% for Fig. 7 (C). As understood in these figures, the aggregation proceeds like a successive reaction. With the advancement of the run, the collision of the dispersed particles forms small aggregates and increases the volume ratio of the small aggregates irrespective of the cohesion probabilities. However, the small aggregates repeatedly collide against each other to grow into large particles, so that the volume ratio of the small aggregates slowly increases and then decreases. On the other hand, with the reduction in number of small aggregates, the number of large aggregates increases step by step. As to the aggregates obtained in this simulation, these results show that, the dispersed particles grow into small aggregates and then large aggregates.

According to the authors’ speculation, when the cohesion probability is high, the aggregation rate is high and large aggregates are instantaneously formed. On the other hand, when the cohesion probability is low, small aggregates are formed with difficulty. Accordingly, the dispersed particles repeatedly collide against each other, so that small aggregates having high coordination numbers are formed as described above. Also, it is difficult for the produced small aggregates to be converted to large ones, and the small aggregates would remain as they are.

Table 2 shows the volume ratios of the aggregates at the number of run times of 100 to be compared with the distributions of the aggregates. As understood in Table 2, when the cohesion probability is low, the volume ratios of the dispersed particles and the small aggregates increase. In other words, if the cohesion, that is, the cohesion probability, is low in a dispersion system of particles at a high concentration, small aggregates with large coordination numbers are present together with few large aggregates, at certain time after the start of the simulation. On the other hand, if the cohesion probability is low in the dispersion system, large aggregates with low coordination numbers exist together with few small aggregates.

Fig. 8 shows the schematic models of the aggregation process. When the cohesion probability is high, the dispersed particles quickly move from the step(1) to the step(II), so that small aggregates with low coordination numbers are formed. The small aggregates, by collision against each other, are formed into large aggregates. In contrast, when the cohesion probability is low, the dispersed particles at the step(1) relatively slowly move to the step(II) where, by repeated collision, small aggregates with high coordination numbers are formed. Thereafter, the movement from the step(II) to the step(III) occurs with difficulty, and the small aggregates remain unchanged except one part of the small aggregates that move to the step(III).

### 3.2 Viscosity Measurement of Slurry

Fig. 9 shows the changes in viscosity of the slurries with time. As the viscosities of the slurries measured 5 minutes after the preparation, the strong aggregation system(a) is highest, followed by the weak aggregation system(c) and then the dispersion system(b). The viscosity of the system(c) increases with time and 40 minutes after the preparation, becomes equal to that of the system(a). Thereafter, the viscosity continues to increase, exceeding that of the system(a). The viscosity of the system(a) remains substantially unchanged with the progress of time. In the case of the system(c) having a weak cohesion, the cohesion probability is low and the aggregation rate is low. Probably, this causes the aggregation to proceed slowly and the viscosity to increase time-dependently. As to one of the causes of the fact that the viscosity of the system(c) becomes higher than the system(a) 40 minutes after the preparation, it is...
probable that aggregates with higher coordination numbers and closer structures, as compared with the aggregates in the system (a), exist in the system (c) immediately after the preparation. In the case of the system (a) having a strong cohesion, the cohesion probability is high and the aggregation rate is high. Probably, this causes the aggregation to reach an equilibrium five minutes after the preparation, and the viscosity remains unchanged since the equilibrium has been reached.

The above-described experimental results present a good agreement with those of the simulation.

3.3 Observation of Freeze-Dried Slurries

Fig. 10 shows the SEM photographs of freeze-dried slurries. The letters (A), (B) and (C) designate the SEM photographs of the strong aggregation system (a), the dispersion system (b), and the weak aggregation system (c), respectively. In the photograph (B), a large number of small aggregates with an even particle size are shown. Large aggregates are shown in the photographs (A), (C) and the size of the aggregates in the system (a) is larger if compared with those in the system (c). Fig. 11 shows the aggregate size distributions of the aggregates obtained in the SEM photographs of the freeze-dried slurries in order to clearly present the above-described differences. The aggregate size distribution for the system (a) is most narrow. That of the system (c) is wider than that of the system (a). In the case of the system (c), the cohesion is low and the aggregation rate is low, so that a large number of small aggregates exist, substan-
large particles. Table 3 shows the mean aggregate sizes calculated by using the distribution curves and the densities of the aggregates calculated from the settling speeds. The system(b) has a mean aggregate size almost equal to that of the dispersed particles and a density substantially equal to that of the powder sample. The system(a) has a relatively large mean aggregate size and a smaller density than the system(c). In contrast, the system(c) has a relatively small mean aggregate size and a higher density than the system(a). Based on these experimental results: for the strong aggregation system(a), relatively large aggregates are formed but the structures of the aggregates are sparse with low coordination numbers. In the weak aggregation system(c), small aggregates are formed but their structures are relatively dense and the coordination numbers are high. These results coincide with those of the simulation.

Table 3 Aggregate size and density of sample

| System | Mean aggregate size (μm) | Density (g/cm²) |
|--------|-------------------------|-----------------|
| (a)    | 10.0                    | 1.04            |
| (b)    | 3.5                     | 1.23            |
| (c)    | 1.3                     | 3.57            |
5. Conclusion

The aggregation process obtained by the simulation is a linear process when the concentration of the particles is high, which departs from the Smoluchowski's solution often used to elucidate aggregation behaviors. As revealed above, this is because an aggregation region in which the aggregation proceeds according to the Smoluchowski's solution is very short, since the high concentration of the particles increases the number of collision. When the concentration is increased to reduce the number of collision times of the particles, The region in which the aggregation proceeds according to the Smoluchowski's solution becomes large. In this study, the movement distance of the movement unit is set to a constant value. Probably, this exerts some influences over the simulation. At present, the authors consider influences by the movement distance in detail. Also, as revealed here, the cohesion probability used in the simulation has a relationship to the cohesion and the coordination number, in addition to the aggregation rate. In the case of the small cohesion probability, the aggregation proceeds with difficulty and a large number of small aggregates with relatively dense structures are present. In contrast, at the high cohesion probability, the aggregation proceeds fast and large aggregates with relatively sparse structures are formed.

The above simulation results were examined by the viscosities of the slurries and the SEM observation of the freeze-dried slurries. In all the cases, good agreement has been obtained. The adaptability of this simulation has been recognized.

Nomenclature

\[ N_0 : \text{initial number of particles} \]  
\[ N_i : \text{number of aggregate} \]  
\[ k : \text{Boltzmann constant} \]  
\[ T : \text{temperature} \]  
\[ \eta : \text{viscosity} \]  
\[ K_1,K_2,k_1,k_2 : \text{constant} \]

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