Simulation of Aggregate Packing and Analysis of Aggregating Process of Ultra-Fine Powder by Brownian Dynamic Method

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Abstract

Dense and uniform packing of ultra-fine powders, the primary particle size which ranges from 1 nm to 0.1 μm, is very difficult because of strong and sparse aggregation. In this paper, the aggregating process of ultra-fine powder is examined by Brownian dynamic methods, and the effects of interaction between the primary particles and the initial concentration on aggregate shape and size is analyzed quantitatively by Fractal dimension and Weibull's distribution function. Furthermore, the packing of aggregates, which are of various shapes and are composed of different numbers of particles, is investigated by computer simulation. The effect of the geometrical characteristics and size distribution of aggregates on the porosity and distribution of micropore diameters in a packed bed is analyzed. When many aggregates consist of hundreds of particles, the porosity exceeds 94%. The porous structure is obtained by bridging between several aggregates. The wide spaces in ultra-fine powder composed by bridging are confirmed experimentally by mercury porosimetry. The effect of shape and size distribution of aggregates on packed bed structures is remarkable in the case of weakly aggregated powder, which means that the number of constituent particles is below 10.

Introduction

Inorganic system ultra-fine powders of primary particle size 100 nm or less are expected to be of use as functional material powders or easy-to-sinter raw materials for structural ceramics, but problems may be involved in homogeneous dispersion or densification of packed beds and compacts since ultra-fine powders form strong and sparsely aggregated structures. With respect to the aggregating process of ultra-fine powders, an analysis using the diffusion model has been carried out in the fields of aerosols, etc. On the other hand, with respect to the aggregate's shape and structure which affect the packed bed structure, simulations in which particles are made to adhere one by one to a seed particle have been carried out. In particular, the Diffusion Limited Aggregation model (DLA model), in which particles are allowed to move through a Brownian motion by pseudo-random numbers, is coupled with Fractal science and has been attracting the attention of researchers and the industry. Meakin and Kolb et al. almost at the same time carried out simulations by extending the DLA model and allowing all particles generated in a space to adhere and aggregate by pseudo Brownian motion and investigated the changes in aggregate structures by the Fractal dimension. In addition, Mountain et al. eliminated the restrictions arising from the methods of Meakin and Kolb et al., who advocated that particles move on the square lattice points, and carried out simulations representing a near actual Brownian motion, and called these methods Brownian Dynamics methods. The method advocated by Mountain et al. is used for the analysis of the aggregation and destruction processes in the shear flow but since a large number of particles requires a very long calculating time, many of the studies primarily deal with few hundreds of

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particles. The methods advocated by Meakin, Kolb, etc. are believed to be effective when the number of particles is of the order of several thousands or more, but they have been adopted only for the analysis of particle growth by sintering catalyst particles. No systematic investigation of the effects of interaction between particles on the aggregate shape and structure has yet been undertaken. For the packing characteristics of powders, simulations in which rigid single ball are packed one by one have been carried out, but investigations in which the relationship between aggregate structures and packed bed structures are studied using particles which cause aggregation, such as ultra-fine powders, have scarcely been reported.

In this paper, allowing the interactions between particles to be represented by adhesive probability and varying the initial concentration of the primary particles, clusters of various shapes and a wide range of distribution of the constituent particles have been formed by the Brownian Dynamics method which is similar to the techniques of Meakin, Kolb, etc. The effects of interaction between particles and their concentration on the aggregation process as well as on the aggregate's shape and distribution of constituent particles were quantitatively analyzed using Fractal dimension and Weibull's distribution function. In addition, simulations of packing clusters obtained were carried out and an analysis of the relationship between the ultra-fine powder packed bed structures and aggregate structures was performed. Lastly, ultra-fine powder compacts were experimentally analyzed by mercury porosimetry and the adequacy of the simulation results was investigated with special emphasis placed on the distribution of micropore diameters.

1. Simulation and Experiment

1.1 Simulation of aggregation

Figure 1 (a) shows schematically the aggregation simulation method. The simulation was carried out in two-dimensions. The space was divided into square cells of side A and it was assumed that particles were generated and aggregated in the same manner in all cells. The space for which the simulation was performed was one of these cells. It was assumed that particles were generated in this cell randomly and the particles (i) leaving the cell by pseudo-Brownian motion entered the cell in the opposite direction. This square cell was divided into square lattices, one side of each of which was equal to the particle diameter (dp) to be generated and particles were assumed to be circles moving on lattice points. For the Brownian motion of primary particles, it was assumed that the particles moved by unit lattice in either one of the four directions, up, down, right, or left, according to one calculation loop using pseudo random numbers (R [0, 1]). On the other hand, it was assumed that the Velocity of Brownian motion decreased as the aggregate grew and the movement was restricted in accordance with the Einstein equation, in which the mean displacement of a particle per unit time (Δx/t) through the Brownian motion is proportional to the primary particle diameter (dp) to the power -1/2.

\[ \Delta x \propto (D_B)^{1/2} \propto d_p^{1/2} \]  

(1)

The representative diameter of the aggregate (dpag) was considered to be the square of the mean distance from the center of gravity of the aggregate to each particle in Eq. (2) and the displacement was considered to be proportional to dpag to the power 1/2.

\[ d_{\text{dpag}} = 2R_g = 2\left( \frac{1}{N} \sum_{i=1}^{N} r_i^2 \right)^{1/2} \]  

(2)

All particles composing the aggregate were assumed to move by unit lattice in either one of the four directions, up, down, right, or left, only when the relationship between pseudo random numbers newly generated and Eq. (3) was satisfied.

\[ \frac{1}{(d_{\text{dpag}})^{1/2}} > R[0, 1] \]  

(3)

where, \( D_B \) is the coefficient of diffusion, \( r_i \) is the displacement from the i-th particle to the center of gravity of the aggregate, and \( N \) is the number of constituent particles in each aggregate. Whenever other particles came above, below, right, or left of each particle through the pseudo Brownian motion and the generated pseudo random number was greater than the first assumed adhesive probability for the aggregation process (P_a), adhesion aggregation occurred and if it were small, the particles moved in
a direction away from other particles in the next calculation loop. For calculation conditions, the magnitude of various repulsive forces between particles such as repulsion by electric double layers in the liquid were represented by the adhesive probability ($P_a$). The aggregates with various types of structures and distribution of constituent particles were prepared by varying the initial concentration of primary particles ($n_0$) and the adhesive probability. The target cell size ($A$) was fixed at 180 times the primary particle diameter.

1.2 Packing simulation

Figure 1 (b) outlines the packing simulation method of aggregates. The horizontal direction ($x$) of the plane being simulated was assumed to be an infinitely repeated width ($B$) in the same manner as in the aggregation simulation, and the vertical direction ($y$) was considered to extend infinitely upward with the origin fixed. Prior to packing aggregates, clusters of particles obtained through the aggregation simulation were ranked, and the aggregate of the rank closest to the product of the total number of aggregates by pseudo random number $R [0, 1]$ was designated as a generated aggregate. After rotating the selected aggregate through an angle of $2\pi R [0, 1]$ about the center of gravity ($x_{ag}, y_{ag}$), it was moved laterally so that they y coordinate of the center of gravity did not come in contact with the packed particles ($y_{max} + r_{max}$) while the $x$ coordinate remained at a distance equal to the product of the newly generated pseudo random number $R [0, 1]$ and the cell width ($B$). Then, all particles forming the aggregate were allowed to settle per unit lattice. Whenever one of the aggregate constituent particles came into contact with the packed particles, the aggregate was allowed to adhere to the packed bed if the adhesive probability for the packing process ($P_c$) previously assumed was greater than the newly generated pseudo random number.

Fig. 1 Schemes of simulated methods
Whenever the adhesive probability was high, more than several hundreds of aggregates were able to be linked even through one-point contact. For particles of several hundreds of nm in diameter, the adhesive force between particles may reach tens of thousands of times the dead weight of the particle, and these conditions were assumed to exist actually. When particles did not adhere and there was no particle of packed bed one lattice below all the aggregate composing particles, the aggregate was allowed to settle in one further lattice. Whenever any packed particle existed, the aggregate was allowed to move horizontally and settle at a position where there was no packed particle one lattice below while moving by one lattice either right or left by random numbers. Every time a particle settled, adhesion judgment was made, and when the generated random number became greater than the adhesive probability ($P_a$) or the aggregate entered the packed bed and was unable to move downward, the aggregate adhered to the packed bed. For simulation purposes, the adhesive probability of the packing process ($P_c$) was defined as being either 1 or 0.

From the obtained packed bed, the porosity and micropore diameter distribution were determined.

1.3 Experiment by mercury porosimetry

As a comparison with the packing simulation results, the micropore diameter distribution was measured by mercury porosimetry (Micrometrics Inc., Poresizer 9310). Table 1 shows powder samples used for the experiment. The micropore diameter distribution was measured at a maximum uniaxial pressure of 414 MPa by cutting out a small piece assuming that powder packed beds are filled into a 20-mm-diameter mold and formed under pressures ranging from 12 to 30 MPa.

2. Results and Discussion

2.1 Aggregation simulation results

Figure 2 shows one example of the results. In order to investigate the effect of the initial concentration of primary particles ($n_0$) defined by the ratio of the total area of generated circular particles to the area of square cells of side ($A$), in Figures 2 (a) and (b), the adhesive probability ($P_a$) was fixed at 1.0 and the generated concentration was varied between 0.185 and 0.077, respectively. Figures 2 (b) - (d) show cases in which the initial concentration ($n_0$) was fixed at 0.077 and the adhesive probability ($P_a$) was varied between 1.0 and 0.005. The numerals in the figure ($\Delta x/d_p$) represent the ratio of the overall displacement of individual particles ($\Delta x$) to the diameter of the primary particle ($d_p$), which indicates the nondimensional elapsed time counted from the generation of the particle and corresponds to the number of calculation loops in the simulation of this report.

A comparison of Figures 2 (a) and (b) indicates that in the case of the higher the particle concentration ($n_0 = 0.185$), the faster is the aggregating speed, and the gel condition in which all particles are bonded is produced at $\Delta x/d_p = 528$. The shape of the aggregate tends to become denser as the concentration increases. A comparison of Figures 2 (b) - (d) indicates that a lowering of the adhesive probability decreases the aggregating speed and at the same time, and the aggregate shape changes from a coarse structure with many branches to a mass. The primary particles or small aggregates with comparatively small numbers of constituent particles have a high probability of coming into contact at the tip end of large aggregates first through Brownian motion. Consequently, when the adhesive probability is high, the particle or aggregate is caught at the tip end of the large aggregate and cannot move deeper inside, whereas in the case of a low adhesive probability, the particles or aggregates do not adhere even when they are in the vicinity of the tip end and are allowed to move deeper inside, where they may produce a mass structure.

In order to quantitatively determine the change of the aggregate's shape as a function of the conditions, an analysis by Fractal dimension (D) was carried out. Figure 3 (a) shows one example of the analysis results. This figure shows the relationship between the mean radius ($R_g$) of an aggregate found from Eq. (2) and the number of particles in a cluster or aggregate (N), with respect to every aggregate having 10 or more constituent particles (N) obtained through the aggregation process. The Fractal dimension (D) is given by the following equation.
Fig. 2 Effect of initial concentration ($n_0$) and adhesion probability ($P_a$) on aggregating process

(a) $n_0 = 0.185$, $P_a = 1.0$
(b) $n_0 = 0.0772$, $P_a = 1.0$
(c) $n_0 = 0.077$, $P_a = 0.1$
(d) $n_0 = 0.0772$, $P_a = 0.005$
Figure 3 (a) is determined for all conditions with initial concentration of primary particles ($n_0$) and adhesive probability ($P_a$) varied. The Fractal dimension (D) is calculated using Eq. (4), and the results are shown in Figure 3 (b). It has been quantitatively confirmed that the higher the initial concentration of primary particles and the smaller the adhesive probability, the higher the Fractal dimension (D), and the dense structure of the aggregate was obtained. The tendency of the Fractal dimension to increase due to lowered adhesive probability differs depending on the initial concentration of primary particles. In the case of $n_0 = 0.185$, the Fractal dimension increases gradually, whereas in the case of $n_0 = 0.0077$, it increases only when $P_a = 0.005$. Consequently, it has been determined that the aggregate structure varies in a complicated manner depending on the conditions.

Next, in order to quantitatively investigate the effect of the initial concentration of primary particles and of the adhesive probability on the aggregating speed, Figures 4 (a) and (b) were drawn to show one example of a decreasing process of monodisperse particles. The abscissa represents the number of calculation loops and the ordinate represents the concentration of monodisperse particles (n) expressed as a ratio to the initial concentration ($n_0$). The curve in the figure is approximated by Eq. (5), which is
deduced from the Smoluchowski's equation \( \frac{dn}{dt} = -K_{80}n^2 \) of the aggregating speed.

\[
\frac{n}{n_0} = \left( 1 + K_{80}n_0t \right) \left\{ 1 + \frac{1}{K_{80}D_p\Delta x} \right\} \quad (5)
\]

where \( K_{80} \) corresponds to the coefficient \( K_{80} \) when time \( t \) is replaced by the nondimensional time \( \Delta x/d_p \). The Smoluchowski's equation is a relation which holds true for the initial aggregation stage of monodisperse particles in the three-dimensional space, but it was assumed to apply to a quantitative comparison of the aggregation process since it can be satisfactorily approximated by Eq. (5) in the range of \( \Delta x/d_p < 1000 \) even in two-dimensional conditions. Therefore, parameter \( K_{80} \) was estimated by the nonlinear least square method, the results of which are shown in Figure 5. Figure 5 (a) shows the results of plotting \( K_{80} \) versus the initial concentration of primary particles, and indicates that \( K_{80} \) exhibits a concentration dependency when the adhesive probability is particularly high. Conventionally, the Smoluchowski's equation was believed to hold true for the initial stage of the aggregation of monodisperse particles, but in the case of a high adhesive probability, the aggregation takes place immediately after the particle is generated as the particle concentration increases, and the particle becomes a polydisperse aggregating particle, possibly invalidating the Smoluchowski's equation.

Figure 5 (b) shows the variation of constant \( K_{80} \) with respect to the adhesive probability. Under the condition of an adhesive probability of 0.1 or lower, the constant increases almost proportionally with the adhesive probability. In the Smoluchowski's equation, the number of collisions between particles per unit time (\( N_B \)) is related to Eq. (6), and the deceasing rate of monodisperse particles' is found by assuming that two monodisperse particles are eliminated per collision.

\[
N_B = 8\pi D_p D_p n^2 = K_B n^2 \quad (6)
\]

where, \( K_B \) is the coefficient corresponding to

(a) Effect of initial concentration \( n_0 \)

(b) Effect of adhesion probability \( P_a \)

Fig. 5 Parameter \( (K_{80}) \) in Smoluchowski's equation obtained by Brownian dynamics method
Consequently, in the case of P of which the adhesive probability is lower than 1, the frequency of adhesion aggregation in all collisions becomes the frequency found by multiplying Eq. (6) by \( P_a \), and therefore, the decreasing rate of monodisperse particles' is given by Eq. (7).

\[
\frac{dn}{dt} = -2K_0 \cdot P_a \cdot n^2 = -K_{so}(P_a) \cdot n^2 \tag{7}
\]

Consequently, assuming that the number of collisions does not change if the frequency of the collisions is not varied even if the number of adhesion collisions varies, if coefficient \( K_{so}(P_a) \) of the Smoluchowski's equation satisfied the conditions of monodisperse particles at the initial aggregation stage, it becomes proportional to the adhesive probability. Figure 5 (b) shows a case in which aggregating particles are not generated in a large quantity at the initial stage and the coefficient is nearly proportional to the adhesive probability, thus proving the adequacy of this simulation.

Figure 6 (a) shows one example of the aggregation process arranged with special emphasis on the change in the distribution of the number of constituent particles of the aggregate. This figure represents the distribution of the number of mass-based constituent particles in cluster or aggregate (Q) using the two-parameter Weibull's distribution when the initial concentration of primary particles is \( n_0 = 0.0077 \) and the adhesive probability is 1.0.

\[
Q = 1 - \exp\left(-\left(\frac{N}{N_c}\right)^m\right) \tag{8}
\]

On the Weibull’s distribution graphic paper, the distribution of the constituent particles is approximated to an almost straight line, and the distribution can be represented by the scale parameter (\( N_c \)) which represents the number of constituent particles at a cumulative probability of 63.2% and the shape parameter (m) which represents the width of the distribution. Under the conditions used in the recent investigation, the scale parameter (\( N_c \)) increases almost proportionally with time except during the last stage of the aggregation in which the number of aggregates increases as shown in Figure 6 (a), while the shape parameter (m) remains nearly constant, with a slight variation. In order to investigate the effect of the calculation conditions, the scale and shape parameters are plotted in Figure 6 (b) against the adhesive probability to find the mean value of m. The figure indicates that when the adhesive probability is close to 1, m is about 3 but as the adhesive probability decreases, m decreases and the distribution of the constituent particles expands. Analyzing the distribution with particle concentration taken into account, the same results as those of the Fractal dimension are obtained in the case of a concentration of 0.185. The distribution monotonously decreases as the adhesive probability decreases, but at \( n_0 = 0.077 \) a significant decrease is observed at an adhesive probability of 0.03 or lower. Consequently, it may be assumed that there is a correlation.
between the distribution of constituent particles and the aggregate structure.

2.2 Packing simulation results and discussion

A packing simulation was carried out using clusters with different distributions of constituent particles and structures obtained through an aggregation simulation. First, an example of the results is shown in Figure 7 where the adhesive probability \( P_c \) during packing is fixed at 1. At a high adhesive probability, the aggregates were considered to grow large, and clusters of ultra-fine particles of which the scale parameter \( N_c \) of the distribution of constituent particles was of the order of several hundreds were assumed for the packing process. Regarding the conditions during aggregation, the adhesive probability \( P_a \) was fixed at 1, and Figure 7 (a) shows the result of packing clusters when the particle concentration \( n_0 \) is 0.185 and \( \Delta x/d_p = 1000 \), while Figure 7 (b) shows the result when \( n_0 \) is 0.185 and \( \Delta x/d_p = 200 \). In both cases, large spaces are generated since the aggregates form bridging structures, resulting in extremely sparse structures having a porosity of over 90%. In the case of ultra-fine powders formed by an actual vaporization process, there exist cases with more numerous constituent particles, suggesting the possibility of a simulation of packed beds with a higher porosity and with a further increase in the number of constituent particles.

In order to investigate the effect of the number and structure of aggregate constituent particles on the packed bed structure, Figure 8 is used to show the porosity when clusters obtained under various conditions are packed at an adhesive probability \( P_c \) fixed at 1.0. The abscissa represents the scale parameter \( N_c \) of the distribution of the constituent particles of 0.077 and \( \Delta x/d_p = 1000 \), while Figure 7 (b) shows the result when \( n_0 \) is 0.185 and \( \Delta x/d_p = 200 \). In both cases, large spaces are generated since the aggregates form bridging structures, resulting in extremely sparse structures having a porosity of over 90%. In the case of ultra-fine powders formed by an actual vaporization process, there exist cases with more numerous constituent particles, suggesting the possibility of a simulation of packed beds with a higher porosity and with a further increase in the number of constituent particles.

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**Fig. 7** Structure of high porosity packed bed obtained by packing simulation. Adhesion probability \( (P_c) \) on packing process is fixed 1.0. Aggregates which composed mean particle's number is more than 100 are used.
the aggregate and the ordinate represents the porosity of the packed bed. Under the condition of $P_c=1$, the effect of the number of constituent particles on the porosity is comparatively small as compared to that at a low adhesive probability which is discussed later. An analysis of the effect of the aggregate's structure indicates that even at the same $N_c$ value, the porosity tends to decrease as the Fractal dimension ($D$) increases and the shape parameter ($m$) of the distribution of constituent particles decreases.

Figure 9 shows one example of the results of packing at an adhesive probability ($P_c$) fixed at 0 when aggregates settle to enter the packed bed and are unable to move further. Figure 9 (a) shows the results of packing aggregate clusters similar to those used in Figure 7 (a). Compared to the porosity of 0.941 indicated in Figure 7 (a), the porosity slightly decreases to 0.910 when the adhesive probability during packing is fixed at 0, but a large bridging structure exists, resulting in an extremely high porosity. Figure 9 (b) shows the result of packing clusters at the initial aggregation stage ($\Delta x/d_p$) =50 under the same aggregation conditions as those of Figure 9 (a). A scale parameter of 15.9 and fine powders of about 1 nm with lower aggregation capabilities than those of ultra fine powders of several tens of nm used in (a) are used here, but the porosity has dropped to 0.688. However, through they are still smaller than those found in Figure 9 (a), pores with diameters equivalent to dozens of particles are present. These pores may still remain even after compression forming or sintering, and may result in nonhomogeneous structures of sintered compacts. Figures 9 (c) and (d) show cases in which the adhesive probability ($P_c$) is set at 0.005 while the Fractal dimension and shape parameter of the distribution of constituent particles are varied. Indicating the results of packing clusters at the stage of $\Delta x/d_p$ =5000 and 1500, respectively, in which a scale parameter nearly similar to that of Figures 9 (a) and (b) can be achieved. Lowering the adhesive probability during aggregation increases the Fractal dimension, makes the aggregate structure denser, and expands the distribution of the constituent particles, thus lowering the porosity below that of (a) and (b).

To confirm this tendency, aggregates prepared under various conditions were packed at an adhesive probability of $P_c=0$, the results of which are summarized in Figure 10. This figure is a plotting of the relationship between the scale parameter ($N_c$) of the distribution of constituent particles of clusters used for packing and the porosity, similar to that of Figure 8. When $N_c$ is 100 or less the porosity rapidly decreases, and the adhesive probability during the packing of clusters shown with solid and dotted lines, the aggregate's shape at the initial concentration of primary particles as well as the Fractal dimension ($D$) and the shape of the distribution of the constituent particles ($m$) have more effects on the porosity than in the case of $P_c$=1. When $N_c$ exceeds 100, the effects of the shape of the aggregates and those of the adhesive probability during aggregation and packing decrease, resulting in about 90% porosity under any condition.

In order to investigate in detail the effect of the adhesive probability ($P_c$) during packing, $P_c$ was varied from 0 to 1 for clusters of $N_c$ =395 and 15.9, respectively, which were used in Figure 9 (a) and (b), and packing was carried out. The corresponding results are shown in Figure 11. In the case of clusters with a large scale parameter $N_c$ =395, the change in porosity is minor. On the other hand, in the case of clusters with a comparatively small scale parameter $N_c$=15.9, the porosity rapidly decreases in the range from $P_c=0.1$ to 0.01.

Finally, Figure 12 shows the measurement results of the distribution of micropore diameters as a comparison between the structure of the packed bed obtained by simulation and that of actual ultra-fine powder packed compacts. Figure 12 (a) shows the measurement results of
Fig. 9 Structures of packed bed. Adhesion probability ($P_a$) on packing process is fixed 0.
Fig. 10 Relations between porosity of packed bed and scale parameter. Adhesion probability \( P \) on packing process is fixed 0.

Fig. 11 Effect of adhesion probability at packing simulation on porosity of packed bed

Micropore diameter distribution of ultra-fine silica powder packed beds and compacts molded at a pressure of 30 MPa by a uniaxial press using mercury porosimetry. For comparison purposes, results of silicon nitride compacts using 0.18 \( \mu \)m-diameter powders are shown. The micropore diameter \( D_p \) represented on the abscissa is made dimensionless by dividing it by the primary particle size \( d_p \) and the cumulative pore volume \( V \) represented on the ordinate is made dimensionless by dividing by the cumulative pore volume \( V_{cp} \) at a micropore diameter equal to the primary particle diameter. In the silica particle packed bed of a primary particle size of 20 nm and a porosity of 99%, micropores larger than 1000 times the particle size exist, and even if the bed is formed at 30 MPa to lower the porosity to 76%, micropores larger than 100 times the particle size remain. On the other hand, in the silicon nitride compacts with a primary particle size of 180 nm, only micropores several times the particle size are observed. A comparison of this result with that of the packed bed analysis by simulation shown in Figure 12 (b) indicates that the distribution profile of micropore diameters is quite similar to that obtained in the experiment. Consequently, it is confirmed that large pores formed by the bridging structures of aggregates, which have been identified by simulation, exist in actual ultra-fine powder packed beds, leading to packed beds with a porosity as high as 90% or above. However, the simulation space used in this investigation enables only the reproduction of micropores of several hundred times the primary particle diameter. In order to reproduce micropores structures in which the pores are larger than 100 times the particle size.
obtained with ultra-fine silica powders of primary particle diameters of 20 nm, the simulation space must be expanded and three-dimensional simulation of clusters of a larger number of constituent particles is necessary. On the other hand, when the number of constituent particles is about 10, no micropores of which the diameter exceeds 10 times the particle size have been observed. Such micropores are nearly similar to those in silicon nitride powders. Consequently, even in packed beds and compacts of powders of size of the order of about submicrons, aggregates form small bridging structures, resulting in pores about several times the primary particle size, though such size is smaller than that formed with ultra-fine powders.

In future, in order to determine the mechanism at the preparation stage or pressure-forming and sintering stage of ultra-fine powders, the Brownian dynamics method shall be applied in the study of the behavior of the molecular level, the simulation shall be extended to the forming and sintering processes using the packed bed structure obtained in this report, and the results shall be analyzed and compared with the experimental results.

3. Conclusion

Using the Brownian Dynamics Methods, the aggregation process of ultra-fine powders was simulated by computer, the aggregation process and aggregates’ shapes were analyzed, and the following conclusions were reached.

(1) From a quantitative analysis of the aggregates’ shapes by Fractal dimension (D), it was discovered that by lowering the adhesive probability (P_a) during aggregation from 1 to 0.005 the Fractal dimension increased from 1.5 to 1.7, resulting in aggregates of dense structure. This increasing method differed depending on the initial concentration of primary particles (n_o).

(2) The aggregation process was analyzed using Eq. (5) based on the Smoluchowski’s equation (d(n)/dt = -K_a0n^2) with special emphasis on the process of decreasing the initial concentration of primary particles. It was observed that the coefficient K_a0^−", when time (t) was replaced by the non-dimensional time (∆x/d_p), exhibited a concentration dependency, in particular, when the adhesive probability (P_a) is close to 1.

(3) The distribution of the constituent particles of an aggregate can be expressed by the two-parameter Weibull’s distribution. The change due to the aggregation conditions was expressed by the scale parameter (N_c) and shape parameter (m).

Packing simulation was carried out for a cluster which had obtained a distribution of constituent particles and shape, and the results were compared with those of the analysis of ultra-fine powder packed beds using mercury porosimetry, and the following conclusions were reached.

(4) Following the packing of clusters having a scale parameter of 100 or larger, packed bed structures with a porosity exceeding 90%, which may be equated to that of ultra-fine powders of a size smaller than submicrons, could be reproduced. It was determined that this high porosity structure is attributed to the bridging structure formed by aggregates, which leads to the formation of large pores. When clusters of constituent particles numbering about 10 were packed, dispersed micropores of about 10 times the primary particle size, forming an extremely nonhomogeneous structure were observed.

(5) The results of the analysis of the micropore distribution in a packed bed of ultra-fine powder having a mean particle size of 20 nm measured by mercury porosimetry were compared with those of the distribution of micropore diameters of packed beds obtained by simulation and a similar distribution profile was obtained. In packed bed structures having a porosity of 90% of higher, micropores larger than 100 times the primary particle size were observed both in the experiment and through simulation, thus proving the adequacy of the ultra-fine powder packed bed structure obtained by simulation.

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Nomenclature

\( A \) : length of side of square plane used on aggregating simulation \([\text{m}]\)

\( B \) : width of rectangle plane used on packing simulation \([\text{m}]\)

\( D \) : Fractal dimension of aggregate \([-\text{ }]\)

\( D_s \) : pore diameter in packed bed \([\text{m}]\)

\( D_B \) : coefficient of diffusion \([-\text{ }]\)

\( d_p \) : diameter of primary particle \([\text{m}]\)

\( d_{agg} \) : representative diameter of cluster and aggregate \([\text{m}]\)

\( H \) : height of rectangle plane used on packing simulation \([\text{m}]\)

\( i \) : number of particle in aggregate \([-\text{ }]\)

\( K_B \) : parameter of number of collided times with particles by Brownian motion \([-\text{ }]\)

\( K_{B0} \) : parameter in Smoluchowski’s equation \([-\text{ }]\)

\( K_{B0}^{*} \) : parameter in Eq. (5) \([-\text{ }]\)

\( m \) : shape parameter in Weibull’s distribution function \([-\text{ }]\)

\( N \) : numbers of particle in cluster or aggregate \([-\text{ }]\)

\( N_B \) : numbers of collided times with particles \([-\text{ }]\)

\( N_c \) : scale parameter in Weibull’s distribution function \([-\text{ }]\)

\( n \) : concentration of primary particle \([-\text{ }]\)

\( n_0 \) : initial concentration of primary particle \([-\text{ }]\)

\( P_a \) : adhesive probability on aggregating process \([-\text{ }]\)

\( P_c \) : adhesive probability on packing process \([-\text{ }]\)

\( p \) : pressure at uniaxial press test of packed bed \([\text{MPa}]\)

\( Q \) : cumulative probability of particle number in cluster or aggregate \([-\text{ }]\)

\( R_{[0,1]} \) : pseudo-random number between zero and unity \([-\text{ }]\)

\( R_{x} \) : mean radius of cluster or agglomerate \([\text{m}]\)

\( r_1 \) : displacement between \(i\)-th particle and gravity center of aggregate \([\text{m}]\)

\( r_{max} \) : maximum radius of aggregate \([\text{m}]\)

\( V \) : cumulative pore volume \([\text{m}^3]\)

\( V_{dp} \) : cumulative pore volume at \(D_s=d_p\) \([\text{m}^3]\)

\((x_{agg}, y_{agg})\) : center gravity coordinate of aggregate \([\text{m}]\)

\( y_{max} \) : maximum height of previous packed bed \([\text{m}]\)

\( \Delta x \) : moving displacement of primary particle by Brownian motion \([\text{m}]\)

\( \epsilon \) : porosity ratio of packed bed \([-\text{ }]\)

Literature cited


13) Sutherland, D.N.: *J. Colloid Interface Sci.*, **25**, 373 (1967)

