The Aggregate Structure of Fine Particles and Compacting Process

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Abstract

The compacting characteristic of fine particles is greatly affected by the aggregate structure of particles. Several kinds of silicon nitrides, which are different from each other in particle shape, size and bulk density, were compacted in a uniaxial direction under various conditions, and the behavior of the particles during compaction was analyzed and compared by using Cooper's equation. It was found that the difference in the kind of samples and the condition of their pretreatment resulted in considerably different behaviors during compaction, and that the apparent volume reduction rate under pressure was remarkably different at low and high pressures.

The aggregate structure of each sample was estimated based on the above results together with the result of the measurement of the compaction structure of the molded bodies.

1. Introduction

Although many formulas have been proposed to represent the compaction characteristics of powders, strongly-cohesive fine particles assume an aggregate structure of such a high order and so complicated a phenomenon during compaction that the existing formulas are not readily applicable to such powders. Guided by the applicability of Cooper's formula, in which particle deformation is considered, to the compaction of the fine particles under study, the authors, through a study of silicon nitrides with respect to changes in the compacting characteristics caused by pretreatment, pointed out that a wetted powder containing a suitable quantity of liquid medium exhibits an improvement in its compacting characteristic. "Compacting characteristic" refers to the degree of ease with which a powder material can be compacted, that is, the quality of a powder material that permits the material to be compacted into a dense homogeneous body.

In this paper, the effect of pretreatment, under various conditions, on the compacting characteristic is studied with respect to several kinds of industrially used silicon nitrides. These nitrides differ from each other in their method of fabrication, particle size, and shape etc. By analyzing the behavior of powders under compaction, the aggregate structure that fine particles assume can be estimated.

2. Experiments

2.1 Samples

Table 1 lists the physical properties and methods of fabrication with respect to the silicon nitrides that were employed in the present experiments.

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The particles of Sample A each resembled a thick rectangular plate in shape and had a fairly broad particle size distribution, whereas those of Sample D were each an amorphous mass. They were also the most irregular in particle size of all the samples employed. The particles of all three samples of the U series

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were each almost cube-shaped and were virtually uniform in particle size.

Butanol was used as the wetting medium.

2. Method and apparatus

Each of the cylindrical molds with a cross-sectional area of 0.5 cm² was filled with a sample in the form of dry powder or with a wet preparation of a sample prepared by mixing it with butanol at a suitable volume percentage and by kneading the two together. The sample in the mold was compacted under a pressure of up to 1,000 kg/cm² by means of an Autograph S-500 to form a cylindrical specimen several centimeters long. The relationship between the applied pressure and the apparent volume during compaction was analyzed using Cooper's formula. The cylindrical specimen was also longitudinally divided into three approximately equal parts, and the pore distribution of each part was measured by means of a mercury porosimeter so as to determine the degree of homogeneity of the compacted body.

To mix a sample with the liquid medium, a laboplastomill and a biaxial continuous kneader were used. The degree to which the kneading was performed was shown by the time with respect to the use of the batch-based laboplastomill (hereafter abbreviated as LPM) or by the number of times of repeated kneading with respect to the use of a continuous biaxial kneader (hereafter abbreviated as KRC).

3. Results

3.1 Optimum volume percentage of the wetted powder

The optimum percentage of volume of a wetted powder was determined in the following manner. A dry sample powder was kneaded by stirring in the LPM with the gradual addition of butanol in small quantities as a liquid medium, and the relationship of the kneading torque to the content of the liquid medium was obtained as shown in Fig. 1. The kneading torque changed only slightly while the powder was dry or while the aggregates of the particles with the liquid medium were so small as to be able to move freely. However, the kneading torque increased as the aggregates became so large as to exceed the interval between the stirring vanes. This is because of the need to deform and break the aggregates. The torque reached its peak when all the particles assumed their most close-packed structure in which the pores were filled with the liquid medium, and it then decreased as the content of the liquid was increased further. This happened because the volume of the pores (filled with the liquid medium) in which particles could move freely increased. Assuming that the conditions for obtaining a dense, homogeneous compacted body were for the aggregates of particles to be capable of being deformed and for the porosity to be minimal, as previously reported, the optimal content of the liquid was considered to be the volume percentage that was slightly larger than the content at the peak of the kneading torque. Samples wetted at differing volume percentages about the optimal value were compacted, and the respective mean pore
size was obtained from the pore distribution, as shown in Fig. 2. The volume percentage of the liquid medium at which the mean pore size was the smallest was regarded as the optimal content.

Samples wetted with butanol at the optimal volume percentage were kneaded well in a mortar, LPM, or KRC, and then compacted into specimens of various thicknesses by the application of 1,000 kg/cm² of pressure. Of all the specimens thus prepared, those kneaded by KRC showed the packing fraction to be highest and the changes with column length to be relatively small. Therefore, KRC was mainly employed for kneading in the present experiments.

3.2 Behavior of particles during compaction

A. R. Cooper divided the behavior of powder particles during compaction into two stages, one characterized by the packing of particles and the other characterized by the deformation of the individual particles that causes disappearance of the pores. Equation (1) was then proposed.

\[
\frac{V_0 - V}{V_0 - V_s} = \alpha_1 e^{k_1/P} + \alpha_2 e^{k_2/P}
\]

where \(V_0\) and \(V\) represent the apparent volume of a powder before and at the application of pressure \(P\), respectively, and \(\alpha_1\), \(\alpha_2\), \(k_1\), and \(k_2\) are constants.
are experimentally obtainable constants. $V_s$ represents the specific volume of a material, i.e. the volume that particles assume when they have become consolidated into a single solid mass with no pores through deformation of the particles by compaction. Since, however, it is hardly possible for inorganic fine particles to be deformed by compaction under general conditions, $V_s$ is dealt with in this paper as the apparent volume of a group of most close-packed (to a porosity of 0.26) uniform globular particles.

Changes in the apparent volume reduction rate $(V_0 - V)/(V_0 - V_s)$ under pressure (hereafter referred to as the “Cooper plot”) obtained with respect to each sample listed in Table 1 are represented by straight lines each deflected at a certain pressure, as shown in Fig. 4, that corroborate Eq. (1). The slopes $k_1$ and $k_2$ of these straight lines vary with changes in the kind of sample, and kneading conditions, etc.

3.3 The relationship to column length

Changes in the Cooper plot of the compacted bodies for differing column lengths were examined for differing samples and for differing kneading machines. Figure 5 shows an example of the results. With respect to Sample A, consideration of the changes in $k_1$ and $k_2$ in relationship to the column length shows that, as seen in Fig. 6, $k_2$ mainly assumes a larger value with an increase in the column length until eventually $k_1$ and $k_2$ coincide, i.e. $k_1$ and $k_2$ are then represented by a straight line. With respect to the samples in which $k_1 > k_2$, such as the samples of the U series, little change is observed, but a parallel relationship is maintained, as shown in Fig. 7.

4. Discussion

The Cooper plots of silicon nitrides, as shown in Figs. 4 and 5, can be classified into the three types — Type A ($k_1 < k_2$), Type B ($k_1 > k_2$), and Type C ($k_1 = k_2$) — illustrated in Fig. 8. The pressure dependency of the apparent volume reduction rate is represented key $k_1$ and $k_2$, $k_1$ corresponding to the com-
paction of particles under low pressure and $k_2$ to the compaction of particles under high pressure.

The particles of a fine powder have a relatively strong tendency to aggregate and necessarily form aggregates of particles under normal conditions. An aggregate of such particles can be considered to act as a unit of motion, where motion occurs under a low force. Such particles not only form aggregates by primary aggregation, but in many cases they also form secondary or tertiary aggregates. The present experiments however, besides dealing with primary particles, are concerned also with tightly clustered secondary aggregates, considering the effect of the kneading given to the samples. The differing stages of $k_1$ and $k_2$ in a Cooper plot signify the occurrence of two distinctly different phenomena, for example, the stage at which secondary aggregates of particles are packed without being modified and the stage at which primary particles resulting from the disintegration of particle aggregates are packed.

Type B corresponds to a case in which when one phenomenon under low pressure is finished, and another phenomenon occurs under a higher pressure. Type C is a case in which two different phenomena occur concurrently under low pressure and, at the point of deflection, one of the phenomena terminates but the phenomenon signified by $k_2$ continues. Type A signifies continuation of the same process during compaction for the changing pressures in the full range.

A practical example of Type B is the packing of particles that are in part sintered between particles and form aggregates that are fairly firm but somewhat fragile. The aggregates are packed under low pressure without disintegrating but, after being packed to the greatest density, the aggregates disintegrate under pressure into primary particles during subsequent compaction. If the reduction in the volume when a shift occurs from $k_1$ to $k_2$ is less than one half the volume in the most close-packed state, it is considered that the aggregates of particles as units of motion in the compacted bodies are so large that the particles in a unit volume are small in number, and the pores between particles amount to a large volume. Type C is considered to show a case in which the particles interact with each other so as to form weakly clustered aggregates that concurrently undergo both disintegration and packing of the resulting primary particles. When the disintegration of the aggregates of particles terminates and only primary particles continue to be packed subsequently, the particles are packed close to the greatest density, and the subsequent reduction in the volume is at a low rate. Type A is typified by relatively small but firmly clustered aggregates of particles that are presumed to undergo compaction without involving disintegration of the aggregates to any significant degree. Although it may be con-
Considered reasonable for primary particles not in the aggregates form to assume Type A, the present experiments can hardly consider that notion, since, as shown in Figs. 4 and 5, it is observed that particles may shift from Type B to Type A or from Type A to Type C depending on the degree of kneading to which they are subjected, but the particles do not shift in the reverse order. The reason in that unless it is presupposed that the shift of B → A caused by kneading does not signify the disintegration of firmly clustered particles at a stroke into unit particles but means disintegration into smaller aggregates of particles, there is no explanation with respect to the shift of A → C. The shift of A → C is presumed to occur because an aggregate of particles the momentum of which balances the interaction between particles disintegrates into finer unit particles, and the particles in a unit volume increase in number. As a result, the interaction between them is enhanced, and the behavior peculiar to aggregate particles is seen.

Closer and more accurate observations of such behavior of particles may be possible, if, for example, the pore size distributions of compacted bodies obtained by the application of various degrees of pressure are examined. However, since compacted bodies with low strength easily collapse, it is very difficult to carry out such examination. A method of overcoming this difficulty is now under study.

On the other hand, it is observed, for example, that in Fig. 5 the Cooper plot of Sample A by the column length shows that the ratio $k_2/k_1$ becomes smaller with column length and approaches that of Type A. This phenomenon may be explained by the observation that since pressure is applied in only one downward direction in uniaxial compaction, the relaxation of particle stress caused by internal friction or friction against the wall surface becomes large with an increase in the quantity of particles and in the thickness of the compacted body. Also, the stress distribution in the longitudinal direction broadens so that the two-stage change appears continuous. In the case of the Type A sample, such as Sample D in Fig. 4, it is considered that the $k_1/k_2$ ratio does not change with column length because the aggregates of particles easily disintegrate when packed and, therefore, the internal stress is small, and the pressure is easily transmitted. These phenomena do not contradict our observations with respect to the aggregate structure of particles and their behavior under compaction.

The pore size distributions of compacted bodies for differing methods of kneading, examined with respect to the top, middle, and bottom parts, respectively, by means of a mercury porosimeter, are observed to be broader and less densely filled toward the bottom, as shown in Fig. 9. However, compacted bodies of a sample well kneaded by KRC show pores to be densely and evenly distributed throughout, as shown in Fig. 10.

In this way, compacted bodies can be estimated with respect to their pore size distribution, which is dependent on the particle size of the sample powder. The samples U-02, -05,
and -10 are characterized by the shape of the particles, which is virtually cubic, and narrow particle size distributions with the mean particle sizes as shown in Table 1. The pore size distributions of the compacted bodies of these samples show uniformity, as seen in Fig. 11, and they correspond to the mean particle sizes calculated from the specific surface areas. Since the mean particle size based on the specific surface area reveals the size of primary particles independent of the aggregate structure, a uniaxial compaction of the order in view, if fine particles are processed, is shown to produce compacted bodies that are densely and evenly packed. An increase in particle size makes it more difficult to obtain an evenly compacted body. It is considered that the particles then becomes less cohesive, and the internal friction increases.

5. Conclusion

Wetted samples of five kinds of industrially used, silicon nitride powders which differed from each other in particle shape, particle size, and method of fabrication, were subjected to simple uniaxial compaction, and the compacting characteristics of the specimens were analyzed using Cooper's formula. The specimens showed three different types of particle behavior depending on the method of fabrication of the samples, and the conditions of kneading them with a dispersion medium volume percentage, etc. The aggregate structures of particles of each specimen were capable of being estimated.

Furthermore, by measuring the pore size distributions of the compacted bodies using a mercury porosimeter, the optimal wetting conditions, with respect to volume percentage, kneading method, and compacting conditions, were determined. It was found that since the pore size of the compacted body was more or less relative to the size of the primary particles of the sample powder, fine particles, such as the samples, are capable of being compacted into densely and evenly compacted bodies by controlling the compacting conditions.

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Reference

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