The Estimation of Packing Characteristics by Centrifugal Compaction of Ultrafine Particles †

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Abstract

At present, there is no reliable method available for determining the compaction characteristics of ultrafine particles, the sizes of which ranges from several to one hundred nanometers. In this paper, the authors propose the centrifugal compaction method to evaluate the compaction characteristics of the ultrafine particles by applying the self-compressive stress by centrifugal force in a packed powder bed. With such a system, compressive strains can be determined with good reproducibility as a function of centrifugal force. The relationships between compressive strain and centrifugal force for ten kinds of ultrafine particles, such as Fe, Co, Al, SiO₂, Al₂O₃, and TiO₂, were found to be divided into two categories. One category can be written as a linear relationship between the logarithm of compressive strain and the logarithm of centrifugal force, while the other can be described by a linear relationship between compressive strain and the logarithm of the centrifugal force.

1. Introduction

Ultrafine particles whose sizes range from several nm to one hundred nm have a large number of particles per unit weight, greater specific surface area and stronger adhesive and cohesive forces as compared with conventional powder substances of greater than submicrons in size.11 Thus, the bed packed with such ultrafine particles has a unique powdery structure with a small bulk density and a very large porosity. In evaluating the packing characteristics of particles, the tapping and compressive compaction methods were employed in the past.21 In each method, however, drawbacks exist, depending on the magnitude of load when applied. In the former, the arrangement of component particles is apt to become unhomogeneous due to their easy movement during tapping actions and in the latter, the bed porosity of the packed particles is locally distributed specifically on the pressurized surface of the piston and near the wall surface of the cylinder. Considering these, the authors newly developed a centrifugal compaction system which is capable of applying uniform compressive force as a centrifugal force at any height of the bed without causing any local disturbance. This system was found to yield highly reproducible data on the packing characteristics of ultrafine particles.

By this method, furthermore, the hysteresis of packing characteristics could be evaluated for each cycle composed of increasing and decreasing term of applied load to the packed bed of ultrafine particles. In contrast with the acceleration encountered in the conventional...
tapping method, which ranges from several tens to several hundreds G, the pressurizing force corresponding to several hundreds to several thousands G can be obtained by this centrifugal method. When compared with the range of the force attained by the compressive compaction method (exceeding several hundreds KPa), this method is deemed to be a testing method lying in between the tapping and compressive compaction methods. Moreover, this method allows us to observe the compaction process directly from the outside. It enables us observe the dispersed state of the tracer particles when the tracer particles are initially mixed in the form of a layer within the packed bed of ultrafine particles. In addition, the authors observed a group of ultrafine particles of ten kinds by means of an electron microscope and found that secondary particles, which are the agglomerate of the primary particles, could be largely classified into a chainlike structure and a lumplike one. In the present work, the elastic and plastic behavior which is characteristic of the agglomerate of ultrafine particles, was investigated from the compaction processes and discussed in connection with two types of the agglomerates mentioned above. Furthermore, to clarify the internal structure of the packed bed, the authors conducted a series of compaction tests by means of the tapping, compressive and centrifugal methods using tracer particles, and discussed the change in the porosity of the packed bed by comparing with each other.

2. Experimental

2.1 Specimen

The properties of six kinds of ultrafine particles of metals and metal oxides used in this experiment are shown in Table 1. Ultrafine particles of metals (hereafter called "UFMP") are prepared by the evaporation process in a gaseous state and ultrafine particles of metal oxides (hereafter called "UFP") are generated by hydrolysis in combustion with oxygen-hydrogen flame. The specimens used are three kinds of silica powders having the same components but different sizes, silica 300 and 380 which have the same particle size but different specific surface areas (BET specific surface areas 300 and 380 m²/g) and Al₂O₃ and TiO₂ powders which have the same particle size but different components. Fe and Co powders of UFMP are available only in the agglomerate state, which sizes approximately range from several mm and several tens mm even when they are kept in a dry and tightly enclosed state. Thus, these agglomerates were unfastened using a sieve with a 110 μm mesh opening and the particles which passed through the sieve, were used as the specimens.

2.2 Experimental apparatus and procedures

The schematic flow diagram of the experimental apparatus is shown in Fig. 1. While the centrifuge works, the cells (φ26 × 70 mm) become almost horizontal and the top of the cell is situated on the side of the rotating axis and its bottom on the circumference side. Enlarged photos of the boundary surface of the powder bed in the rotating cell of the centrifuge were taken by a VTR camera and the process of the centrifugal compaction was continuously observed. Simultaneously, the image was recorded on a VTR camera. Then,
### Table 1 Properties of specimen

| Specimen | Metal ultrafine particle | Metal oxide ultrafine particle |
|----------|--------------------------|-------------------------------|
|          | Fe | Co | Cu | Al | SiO₂ | SiO₂ | SiO₂ | SiO₂ | Al₂O₃ | TiO₂ |
| Mean size [nm] | 12 | 20 | 50 | 100 | 16 | 12 | 7 | 7 | 21 | 20 |
| Porosity [%] | 99.4 | 99.2 | 92.2 | 91.7 | 97.6 | 98.4 | 97.2 | 97.7 | 96.6 | 97.0 |
| True density (g/cm³) | 7.9 | 8.9 | 8.94 | 2.7 | 2.2 | 2.2 | 2.2 | 2.9 | 3.8 |
| Purity | UFMP | SiO₂ | Al₂O₃ | TiO₂ |
|          | >99.9% | >99.9% | >99.9% | >99.9% |

the average positions of the boundary surface were read on the reproduced still images using a mouse, and were numerically processed to obtain the average value of the bed height. The compressive strain of the powder bed under a centrifugal compressive force was calculated from the difference between the initial bed height and the average bed height when the compressive force was applied.

### 3. Experimental Results and Discussion

#### 3.1 Packing characteristics of ultrafine particles

The results of the observation of the ultrafine particles by means of an electron microscope of scanning-transmission type (STEM H-500, Hitachi) are illustrated in Fig. 2(a) through (e). From these images, UFMP of Fe and Co particles which takes the chainlike agglomerate structure as the secondary particles due to the magnetism, and UFMP which takes the lumplike structure with several primary particles assembled together, can be clearly distinguished.

#### 3.1.1 Metallic ultrafine particles with chainlike structure

The relationships between the centrifugal force F and compressive strain ε of the powder bed are indicated in the centrifugal compaction of ultrafine Fe and Co particles in Fig. 3. The relationship between these two factors is found to be linear on the logarithmic paper and accordingly, the compressive strain is approximately proportional to the centrifugal force to the power of m, from which the following empirical formula is obtained.

\[
\log \varepsilon = m \log F + A \quad (1)
\]

For the packed bed of TiO₂ particles which do not have a chainlike structure but a lumplike one, however, the linear relationship does not hold as depicted by the broken line.

Fig. 2 Transmission electron microscope photographs of ultrafines of Fe, Co, SiO₂ and Cu
curve in Fig. 3.

3.1.2 Metallic ultrafine particles with lumplike structure

The packing characteristics of ultrafine particles of Cu and Al and of oxides SiO₂, TiO₂ and Al₂O₃ are demonstrated in Fig. 4. From these diagrams, the following equation works well.

\[ \varepsilon = n \log F + B \]  

The values of the constants in Eqs. (1) and (2) for all of particles covered here were listed in Table 2. According to the data on SiO₂ 130 and SiO₂ 380, the variation of the strain with the centrifugal force deviates toward the higher side as compared with the data on other lumplike particles to which Eq. (2) is applicable, but for the sake of reference the average values determined by the method of least squares are indicated in parentheses. In the past, quite a number of empirical equations were proposed with regard to the compression issue, but none of them dealt with ultrafine particles and there could be found no equations which took an equivalent form to Eq. (1). In a certain way, however, the equation may resemble the empirical rule concerning the deformation during the triaxially isotropic compression of re-kneaded low-plasticity clay as well as the empirical equation proposed by Bal' shin.¹

![Fig. 3 Relationships between centrifugal force and compressive strain in the centrifugal compaction of ultrafine metal particles of Co and Fe](image)

![Fig. 4 Relationships between centrifugal force and compressive strain in the centrifugal compaction of ultrafine metal particles of Cu, Al, SiO₂, Al₂O₃ and TiO₂](image)

![Fig. 5 Relationships between porosity of packed bed and centrifugal acceleration in the packing of ultrafine particles](image)

3.2 Change in porosity of packed ultrafine particles

In Fig. 5, the relationship between the porosity and the centrifugal acceleration is presented. The porosity of UFP bed tends to increase as the size of the primary particles decreases. In this figure, however, the relationship is reversed. Such a reversion is
supposed to be caused by the fact that prior to the delivery, the powders would have received a compression treatment at the powder works. It is found in Fig. 5 and Table 1 that the porosity is independent of the true density of particle, and in case where the secondary particles exhibit the chainlike structure (Fe and Co particles as shown in Fig. 2 (a)and(b)), the porosity exceeds 99% and little change in the value of porosity with the centrifugal acceleration is recognized. In case of the lumplike structure, on one hand, the values of porosity for SiO$_2$ and Al$_2$O$_3$, particles slightly change in the beginning, but the change in the porosity becomes very small with a further increase in the acceleration. On the other hand, it is shown in Fig. 5 that with regard to TiO$_2$, Cu and Al, the change in the value of porosity with increasing acceleration is remarkable. This difference comes from the difference in the manner of the formation of the secondary particles between the chainlike and lumplike structures, and shows that it is caused by the adhesive and cohesive forces of particles. As mentioned above, in case of Fe and Co particles, the primary particles form secondary particles which take a rosary shape due to magnetism (with chainlike agglomerate structure) as illustrated in Fig. 2 (a)and(b). Fig. 2 (c) shows the agglomerate of a meshlike structure which is further agglomerated by these chainlike secondary particles. From Fig. 2 (d), it is found that the lumplike secondary particles are loose agglomerates of the primary particles. In other words, it may be said that the elements composing the meshlike structure are the chainlike secondary particles, whereas the elements composing the lumplike structure are the primary particles. In such agglomerate structures, the differences in adhesive and cohesive forces among the particles, retard their movement structurally, causing resistance to compaction by the centrifugal force. Thus, it is presumed that the porosity of the powder bed is kept high. Since Fe and Co particles often lumps of a few mm to several tens mm in size locally, even if they are kept in a desiccated container, the particles including such lumps are passed through a sieve of mesh opening 710 $\mu$m and those which pass through the sieve are used as the specimens. These lumpy particles, subdivided by this sieve, are here called “secondary agglomerated particles”. The surface of the secondary agglomerated particles that constitute the meshlike structure exhibits a network structure consisting of interwoven chainlike secondary particles as if a lot of bird nests were connected together (See Fig. 2 (c)). When these lumps of the agglomerate of the secondary particles classified by the sieve are accumulated and form layers, spaces are formed among the secondary particles. During the process in which these spaces are being filled by the compressive stress, a wide range of compressive strains is realized without any collapse accompanied.

### 3.3 Elastic and plastic behavior of powder beds

Loading and reloading followed by unloading are repeated to the agglomerate bodies which exhibit two sorts of elastoplasticity, i.e. chain and lumplike nature. Their elastic and plastic behavior is examined by measuring compressive strains of the
agglomerate bodies. The results are presented in Figs. 6 and 7. It can be seen from these figures that the agglomerate bodies with the chainlike structure are very elastic and do not hardly induce plastic deformation even after repeated cycles of loading and unloading are applied, while those of the lumplike structure induce considerable plastic deformation. Typical examples of the elastic and plastic hysteresis loops for these repetitions of loading and unloading, are indicated in Figs. 8 and 9. The operation mode of repeating loading and unloading to the chainlike structure and the similar mode for the lumplike structure are shown in Figs. 8 and 9, respectively. In these two operation modes, definite differences are recognized in the loop area and the time lag in the recovery of elasticity. Further, the theory of elastoplasticity based on Drucker's hypothesis that the yield surface does not conform to the
load surface, is not operative for the lumplike structure, and part of the strain is left every loop of the operation mode. Thus, the relationship between the elastic strain and the centrifugal force for the chainlike and lumplike structures is demonstrated in Fig. 10. From this figure, it can be seen that in the case of Fe and Co particles which are composed of meshlike agglomerates of secondary particles, the increasing rate of the compressive strain, \( \frac{dc}{dF} \), rises first and reaches a peak value in between 10 N and 100N, then decreases and rises again. On the contrary, in the case of lumplike particles of UFP, \( \frac{dc}{dF} \) shows a monotonously increasing trend with an increase in F.

3.4 Distinctive features of centrifugal compaction method and comparison with other methods

3.4.1 Relationship between the centrifugal force and the bed height

The difference in the centrifugal forces at the top and bottom of the powder bed due to the difference in the radii of rotation is less than 10%, when the radius of rotation at the bottom of the bed is 12.3cm and the bed height is equal to 2.7cm, and the centrifugal force depends mostly on the amount of particles remaining above the boundary surface of the bed. Therefore, to investigate the characteristics of the particles inside the bed, a tracer method was employed as follows: several portions of specimens with a prescribed equal weight were put into the cylinder while tracer particles of a different color were loaded among the portions, prior to the operation. After applying pressure, the cylindrical cake was cut vertically along a certain diameter and a photo of the section was taken. Then, similar procedures were repeated for the sections prepared by cutting the cake along the diameters at intervals of an equal central angle. The photos taken thus were numerically treated with a digigrammer. As a result, the process in which the saturated compaction layer develops from the bottom to the top of the bed with increasing centrifugal force, was confirmed. For instance, in the case of the cake in which five layers are initially marked with tracer particles and the lower three layers have reached a lower limit of porosity and the same height, the porosity of the top layer is higher by 2.7% and that of the second layer by 1.3% than the lower limit of porosity.

3.4.2 Comparison among the centrifugal compaction, tapping compaction and compressive compaction methods using tracer particles

(1) Compaction conditions and packing states

In the tapping method, the acceleration at the cell impact is apt to be unstable, ranging from several tens to several hundreds G, and in the case of UFP the limit of compaction is nearly reached after several tens tapping actions. In the compressive compaction method, rearrangement of particles and segregation in the particle concentration take place in the vicinity of the piston head and near the top of the cylinder wall, when the compressive stress is applied, causing inhomogeneity in the internal pressure of the bed. In contrast, in the centrifugal method, the compressive force remains the same irrespective of the bed height and the compaction condition is quasi-static, thus a homogeneously packed powder bed which enables one to evaluate the characteristics of the bed, is obtained with good reproducibility. Figure 11 presents the experimental results using a centrifugal method in which tracers are used in four layers at equal intervals and other two compaction methods, where the change in porosity with the height is shown. In the compression method, a distinctive feature is observed that the concentration of particles at the top and bottom of the bed becomes higher than that in the middle of the bed. In the tapping method, when TiO₂ particles were tested at a falling distance of 1cm, mixing of particles by 150% and 40% at the top of the bed and in the second layer, respectively, was observed. In addition, owing to the friction between the wall surface and the portion of the packed bed, the distribution of tracer particles takes an upward convex shape.
Fig. 11 Variation of bed porosity with bed height in the three types of compaction, viz. centrifugal, compressive and tapping: Height of bed 100% (cell top), 0% (cell bottom)

for the tapping method, whereas in the other two methods it tends to take a downward convex shape.

(2) Influence of the diameter and friction of the tube in each method

In the tapping method applied to TiO₂ particles where the falling distance is 10mm, the influence of the tube diameter is remarkable. When the influence of the wall friction on the bed height was compared for the tube diameters of 20, 30 and 50mm, differences in the values of strain to the initial bed height were estimated to be 20, 25 and 35%, respectively. In the cases for tube diameters of 40 and 50mm, such differences are hardly recognized. In the uniaxial compression test, powders stick around the piston head in a domelike shape and at the tube wall, slipped layers due to the shearing force were observed, starting from the top of the bed close to the piston and running downwards. Their influence diminishes with increasing distance from the piston. When a comparison is made among three methods with respect to the influence of the wall friction exerting when 30 and 50mm pistons are used, the extent of the influence is considerably large for the compressive compaction method, while for the centrifugal and tapping methods, the influence on the bed height for the same tube diameter is 3% or less, which is much smaller than that for the compressive compaction method.

4. Conclusion

A centrifugal compaction system was developed which has distinctive features of being capable of applying a uniform compressive force to any height of the bed and of determining the compressive strain by use of centrifugal force with good reproducibility without disturbing the packed bed. Thereby, the authors found that the relationship between the compressive strain and the centrifugal force for ten kinds of ultrafine particles can largely be divided into two categories. Namely, for Co and Fe particles, the logarithm of the compressive strain is linear to that of the centrifugal force, and for other particles of Cu, Al, SiO₂, TiO₂ and Al₂O₃, the compressive strain is in a good linear relation to the logarithm of the centrifugal force. In the former case, the agglomerate state of particles exhibits elastic and plastic behavior, which is supposed to reflect the meshlike structure composed of chainlike secondary particles. In the latter case, it is presumed that the agglomerate state of particles exhibits a three-dimensional lumplike structure.

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Nomenclature

A: constant appearing in Eq. (1) [-]
B: constant appearing in Eq. (2) [-]
F: centrifugal force [N]
m: constant appearing in Eq. (1) [-]
n: constant appearing in Eq. (2) [-]
ε: compressive strain [-]

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