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Quantitative analysis of de-aggregation behavior in alumina suspension by beads milling

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ABSTRACT

The de-aggregation behavior of alumina powders with milling process was analyzed by precisely measuring the aggregates in dried suspension. This analysis was conducted under the condition that primary particles constituting aggregates were unbroken by milling operations. The measured distribution for the number of particles in each aggregate was compared with the simulated distribution based on the de-aggregation theory modified for this study. The change in measured distribution with milling times agreed well to the simulated one for relatively short milling times. The fractions of single particles measured experimentally were less than those in simulated results after prolonged milling. This is caused by the presence of strongly bonded twin or triplet particles which were difficult to separate into single ones. The present study clarified that it was important to remove the strongly bonded aggregates for preparation of mono-dispersed suspension by a conventional milling technique.

1. Introduction

Aggregates play a very important role in processing of ceramics [1]. They consist of strongly bonded primary particles with the sizes ranging from a few microns to tens of micrometer and exist in virtually all ceramic powders. Their elimination before forming process is vital in production of ceramics. However, they often survive grinding [2] and classification process at least partially, and exert very detrimental effects on processing and properties of ceramics by introducing large non-uniformity in a green compact [3-8]. Understanding the behavior of aggregates during grinding is extremely important for controlling the uniformity of microstructure and properties of ceramics.

Although many theories have been reported on the grinding behavior of raw powders, they mainly concern with the breakage of primary particles [9–12]. A little attention has been paid specifically on the breaking of bonding between primary particles in aggregates. In the grinding process of aggregates, the breakage occurs at bonding region between primary particles by collision and/or shearing force among the media and particles. Particles are separated from the aggregates as a single or a small aggregate.

Traditional theory of grinding is the basis of the grinding of aggregates. The variation of particle size distribution with time has been treated as follows. The weight fraction of particles $y(x,t)$ with size x after milling time t is described by using selective function and breakage distribution function as the following equation, [13]

$$y(x,t) = y(x,0) + \int_0^t \left[\int_{x'=x}^{x'=x_{max}} s(x') B(x',x) \frac{\partial y(x',t)}{\partial x'} dx' \right] dt \quad (1)$$

where $y(x,0)$ is the weight fraction of particles with size x before milling. The selective function $S(x)$ means the probability of breakage in particles with size x in a unit time. The breakage distribution function $B(x',x)$ denotes the probability of breakage in particles with size x' into ones with smaller size less than x.

The de-aggregation process should be described in the similar way as grinding process; mean particle size in powder should be reduced with time in both processes. The significant difference between the traditional and the present treatments is in the process of separating particles. In the de-aggregation process, aggregates are separated into smaller aggregates which are formed with unbroken primary particles. Thus, the number of particles in an aggregate can be treated as a natural number. This number decreases with milling time and finally reaches unity (single particle). The analytical result should be useful to clarify the de-aggregation behavior of aggregates in powders.

The objective of this study is to investigate the de-aggregation behavior of aggregates in ceramic suspension during milling process. The numbers of particles constituting aggregates are counted directly with SEM micrographs. Based on ISO standard (ISO 14703), a great care is taken to avoid formation of agglomerate in the preparation of SEM samples. Dilute suspension after grinding is dried on a hydrophilic substrate for SEM observation. The obtained statistical data is

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compared with the simulated result based upon the de-aggregation theory to evaluate the grinding behavior in milling processes.

2. Theory of de-aggregation

The de-aggregation behavior can be described analytically under the concept of fracture kinetics. The variation in the distribution on the number of particles constituting an aggregates (aggregation number) is formulated by applying the variation in weight fraction such as Eq. (1). By introducing the selection function $S(n)$ and density function of de-aggregation $b(n',n)$ [14], mass balance equations are acquired for various aggregation numbers by a single batch operation. Here, the re-agglomeration of primary particles during the milling process is not assumed for making calculation simple. The differential in the fraction of aggregates with aggregation number n by a single milling process $\Delta w_i\,(n)$ is expressed from the following equation,

$$\Delta w_i(n) = -S(n)w_{i-1}(n) + \sum_{k=n+1}^{n'} S(k)b(k,n)w_{i-1}(k)(n' > n) \tag{2}$$

where i, n (n') and $w_i(n)$ are the milling times, aggregation number and the fraction of aggregates with aggregation number n after i times milling, respectively. The selective function $S(n)$ means the probability of de-aggregation in aggregates with aggregation number n by a single milling operation. The density function of de-aggregation $b(n',n)$ denotes the probability of aggregation in aggregates with number n' into ones with number n. The first term in the right hand of Eq. (2) corresponds to the fraction of aggregates with number n which fall out other sections (smaller aggregation numbers) by a single milling operation. The second term corresponds to the ones which fall into the section of number n from the sections of larger aggregation numbers. Note that the selection function $S(n)$ and density function $b(n', n)$ do not depend on the milling times.

The selection function $S(n)$ is assumed from the empirical rule as below,

$$S(n) = a \cdot n^{\alpha} \tag{3}$$

The density function $b(n', n)$ is defined as follows by differentiating the Gaudin- Schumann function [15],

$$b(n', n) = \frac{\beta}{n'}\left(\frac{n}{n'}\right)^{\beta-1} \tag{4}$$

where a, α and β are parameters in each equation. The forms of selection function and density function in the present study are based upon the assumption that bonding strength between initial particles is almost constant in an aggregate.

The differential $\Delta w_i\,(n)$ provides the fraction of aggregates with aggregation number n after $i+1$ times milling as bellow,

$$w_{i+1}(n) = w_i(n) + \Delta w_i(n) \tag{5}$$

By iterating the operation of recurrence Eq. (5) from $i=1$, the fraction of aggregates with number n after j times milling is determined from initial fraction of the aggregates $w_0(n)$ as follows,

$$w_j(n) = w_0(n) + \sum_{i=1}^{j} \Delta w_i(n) \tag{6}$$

For estimation of the variation in the fractions of each aggregation number, there is some problem in the form of $S(n)$ in Eq. (3). S(n = 1) has some positive value which should be zero ideally in the present study. As the result, the total weight of all aggregates is reduced. In order to solve the above problem, the fractions of aggregates for each aggregation number $w_i'\,(n)$ are redefined as the following equation,

$$w_i'(n) = w_i(n) \Big/ \sum_{k=1}^{n_{\max}} w_i(k) \tag{6}$$

where n_{max} is the maximum number of particles in an aggregate.

3. Experimental

3.1. Preparation of suspensions

5 vol.% of alumina suspension was prepared by adding the powders (AA15, Sumitomo Chemical CO. Ltd) to the distilled water with a hydrophilic dispersant (Ammonium polyacrylate; Seruna D305, Chukyoushi Japan). The alumina powders have spherical shapes with the mean diameter of 1.5 μm. The powders, distilled water and dispersant were mixed by a magnetic stirrer for three hours before milling process. The obtained suspension was milled by using a circulation-type grinding mill (SC-100/32; Nippon Coke & Engineering Co. Ltd (Formerly: Mitsui Mining company) Japan). Re-agglomeration of primary particles during the milling process was prevented by applying a wet process with limited rotary speed. 5 vol.% suspension is dilute enough to avoid the mechanochemical effect.

Fig. 1 shows the schematic illustration of the milling machine. The breakage of bonding regions between primary particles in aggregates

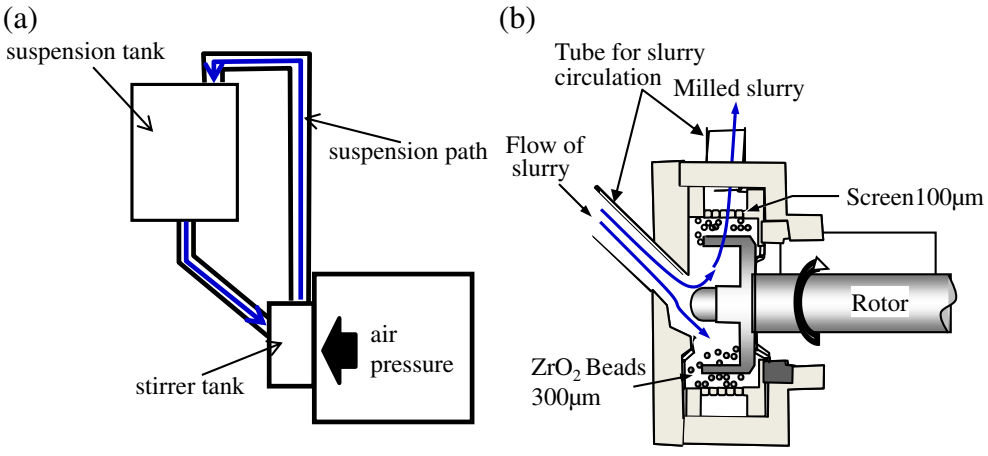

Fig. 1. Schematic illustration of the milling machine (a) overall machine structure and (b) internal structure of stirrer tank.