Journal of Thermal Analysis, Vol. 38 (1992) 1901-1910

FUNDAMENTAL PROPERTIES IN FRACTAL NATURE AND THERMAL ANALYSIS OF POWDERS

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Based on a formulation applied in the theory of stochastic processes, a master equation is introduced for the size distribution which describes a size reduction process. Using an absolute size constant and a scaling concept, we can get a generalized form of the Gaudin-Schuhmann equation and of the Rosin-Rammler equation for size-reduced products and show the intimate relationship between these two formulae.

From a newly developed fractal point of view, it is shown that the Gaudin-Schuhmann equation satisfies a self-similarity law of distribution in the fractal theory and plays an important role in determining the thermoanalytical properties of a powder. As an illustration, DTA curves for ground dolomites are shown to be greatly influenced by the difference in particle size distribution of the sample. The DTA curves as well as the TG curves reflect well the powder characteristics; the TG–DTA curves are therefore suggested as being useful for characterizing powder samples.

Keywords: fractal, TA of powders, theory of stochastic processes, size distribution

Introduction

It is well known that powders play an essential role in ceramic industry, and particle size distribution and specific surface area used as parameters to describe the powder characteristics. In general, the particle size distribution of a powder is often expressed by a function, and a variety of such functions have been proposed including a log-normal function, as well as empirical functions such as the Rosin–Rammler (R – R) distribution and the Gaudin–Schuhmann (G – S) distribution functions. The latter two functions, though they are widely used in practice, appear yet to be defined for the effective particle size range to which the functions apply. Furthermore, the terms ‘coarse grinding’, ‘medium grinding’, and ‘fine grinding’ also seem to be used without any definition; this is often confusing, and, in extreme cases, misleading. The problem is that a standard scale is still to be established.

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The first question that arises in this context is:

'Are the particle size distribution functions merely experimentally introduced?'

It is also known that industrially produced powders, i.e., those obtained by mechanical crushing and grinding, fit fairly well the R – R or the G – S distribution functions. The G – S distribution function, as is well known, is represented by a power law.

In this article, the phenomenologically obtained R – R and G – S distribution functions are derived theoretically by assuming that grinding follows a stochastic process. Then, by introducing an absolute size constant, x_e, to scale the particle size, we obtain a cumulative distribution function, $P(x, t)$, expressed by a power law as follows

$$P(x,t) \propto \left(\frac{x}{x_e}\right)^{\nu}.$$

This signifies that the particles obey a self-similarity law of distribution; i.e., it describes that the powder has a fractal particle size distribution.

The next question is, then:

'How is the powder, which is composed of a great number of particles and whose size distribution obeys a self-similarity law, characterized by a macroscopic method such as thermal analysis?'

To answer this question, pulverized dolomite samples differing in particle size distribution were taken as illustrative examples. It is shown that a decomposition reaction accompanying decarbonation is markedly influenced by the powder characteristics. This means that by detecting this decarbonation process using a pertinent method, the powder can be characterized by thermal analysis.

Framework of the theory and illustration

Model and an equation of motion for a size reduction process [1–4]

Here, the grinding process is assumed to follow a Markov process. By introducing the cumulative undersize distribution function, $P(x, t)$, the population of the particles in the range of particle size from x to $x + \mathrm{d}x$ at time t becomes proportional to $(\partial P(x,t)/\partial x)\,\mathrm{d}x$, and hence, the time evolution of the quantity $(\partial P(x,t)/\partial x)\,\mathrm{d}x$ within the time interval between t and $t + \mathrm{d}t$ by fracture, can be written as

$$\frac{\partial}{\partial t}\left\{\left(\frac{\partial P(x,t)}{\partial x}\right)\mathrm{d}x\right\}\mathrm{d}t, \tag{1}$$

It is assumed that in a grinding apparatus such as a mill, a crusher, etc., not all the particles are ground at one time, but only those chosen with a certain probability are size-reduced. A selection function, $S(x)$, is then introduced, where x is the particle size, which describes the probability to choose particles for size reduction per unit time. Thus, the loss of product in the range of size x and $x+\mathrm{d}x$ due to fractionation in time interval $\mathrm{d}t$ at time t can be written as

$$-S(x)\,\mathrm{d}t\left\{\left(\frac{\partial P(x,t)}{\partial x}\right)\mathrm{d}x\right\}, \tag{2}$$

The next step is to describe the supply for the particles in the range of size from x to $x+\mathrm{d}x$. Let us assume that a particle of a larger size, a, is ground and reduced to a size in the range from x to $x+\mathrm{d}x$. Then the partition function, $B(a,x)$, is introduced, which describes the cumulative undersize distribution function of the product generated by grinding a single particle of diameter a chosen at a probability defined by the selection function, $S(a)$. Thus, the number of the particles in the size range from x to $x+\mathrm{d}x$ which have been generated per unit time from a particle of size a can be expressed by

$$S(a)\,\mathrm{d}t\left\{\left(\frac{\partial P(a,t)}{\partial a}\right)\mathrm{d}a\right\}\left\{\left(\frac{\partial B(a,x)}{\partial x}\right)\mathrm{d}x\right\}. \tag{3}$$

Since the particle size a can take any value larger than x, we obtain from Eq. (3)

$$\int_x^{x_m}\left\{S(a)\,\mathrm{d}t\cdot\frac{\partial P(a,t)}{\partial a}\cdot\frac{\partial B(a,x)}{\partial x}\mathrm{d}x\right\}\mathrm{d}a. \tag{4}$$

where, x_m is the maximum particle diameter.

Now the master equation can be obtained as the sum of Eqs (2) and (4), which satisfies Eq. (1).

$$\frac{\partial}{\partial t}\left\{\left(\frac{\partial P(x,t)}{\partial x}\right)\mathrm{d}x\right\}=-S(x)\left\{\frac{\partial P(x,t)}{\partial x}\mathrm{d}x\right\}$$

$$+\int_x^{x_m}\left\{S(a)\cdot\frac{\partial P(a,t)}{\partial a}\cdot\frac{\partial B(a,x)}{\partial x}\mathrm{d}x\right\}\mathrm{d}a. \tag{5}$$

We can solve the equation analytically by explicitly giving actual forms to functions $S(x)$ and $B(a,x)$

Scaling and self-similarity law of distribution

We adopt $S(x) = kx^{\nu}$ from experimental data [5] and take $B(a, x) = (x/a)^{\lambda}$. By assuming $\nu = \lambda$ and that the functional form holds for all the particle sizes, we obtain from the master Eq. (5),

$$R(x,t) = R(x,0)\exp\left\{-kx^{\nu}t\right\} \tag{6}$$

where $R(x,t) = 1 - P(x,t)$, the oversize cumulative fraction.

Since the initial value, $R(x,0)$, may be assumed to be nearly 1 from experimental data shown in Fig. 1 [6], we obtain the well-known Rosin–Rammler distribution function

$$R(x,t) = \exp\left\{-kx^{\nu}t\right\}. \tag{7}$$

This can be rewritten as

$$P(x,t) = 1 - \exp\left\{-kx^{\nu}t\right\}, \tag{8}$$

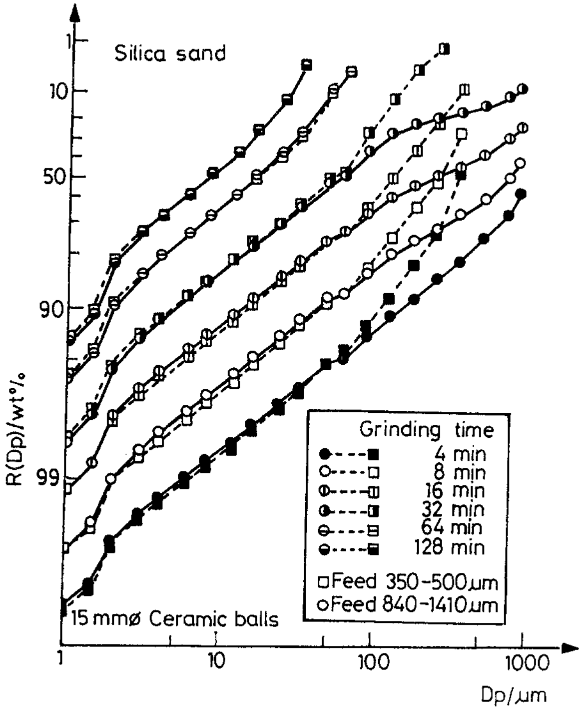

Fig. 1 Rosin–Rammler diagram for ball mill products. Quartz feeds differing in particle size were used

as the absolute size constant x_e, which is a function of time, can be defined as one satisfying the following relation:

$$kx^{v}t = \left(\frac{x}{x_e}\right)^{v}. \tag{9}$$

Substituting Eq. (9) into Eq. (8), we obtain

$$P(x,t) = 1 - \exp\left\{-\left(\frac{x}{x_e}\right)^{v}\right\}, \tag{10}$$

By expanding the right-hand side in case of $x \ll x_e$ and taking the first term, the power law distribution of the form is given as

$$P(x,t) \propto \left(\frac{x}{x_e}\right)^{v}, \tag{11}$$

which corresponds to the 'generalized' Gaudin-Schuhmann distribution function with arbitrary t as the parameter. The $P(x, t)$ suggests that the undersize distribution function obeys a self-similarity law with respect to (x/x_e); (x/x_e), which is the size of any particle scaled by the absolute size constant, x_e, is the scaling invariant in the fractal theory.

Particle size defined by fractal specific surface area [7, 8]

The fractal nature or self-similarity in the size distribution of the particles obtained by grinding suggests that the particles are also statistically self-similar with respect to their shape and morphology. Thus, the particle size, x which is defined by the mesh size of the sieve should be newly interpreted as the fractal particle size; then, the particle size x is defined using the fractal specific surface area s

$$s \propto x^{-D+3} \tag{12}$$

where, D is the fractal dimension which is in the range of

$$2 < D < 3.$$

Thermal analysis and fractal particle size distribution [2, 9]

The aforementioned fractal nature of the particle size distribution is reflected in the first step of a well-established two-step thermal decomposition reaction of dolomite [$CaMg(CO_3)_2$] in 100% CO_2 which is expressed by

$$CaMg(CO_3)_2 \Rightarrow CaCO_3 + MgO + CO_2\Uparrow$$

$$CaCO_3 \Leftrightarrow CaO + CO_2\Uparrow.$$

The reaction which is described by the first equation and shown up in the DTA curves as an endothermic peak, has been argued by many authors (see the review by Otsuka [10] and references cited therein). Many factors that affect the shape of DTA curves, including the particle size, have been pointed out. However, there are few studies concerned with the influence of the particle size *distribution* on thermoanalytical results (see, for example, Gallagher [11]), and even fewer on the decomposition of dolomite.

Experimental

A well-crystallized sample from Korea was crushed and ground by hand in an agate mortar with pestle. The powder thus obtained was passed through a 325-mesh Tyler sieve (having an opening of 44 μm), to give sample (1). Sample (2) was obtained in a similar manner, which consisted of particles passed through a 100-mesh Tyler sieve (opening: 149 μm). Samples (3) and (4), each having a narrower particle size range than the samples above, were prepared further by sieving sample (2) with 150- and 200-mesh Tyler sieves, respectively. This way, sample (3) consisting of particles 105–149 μm in size and sample (4) of 74–105 μm were obtained.

The particle size distribution measurement was carried out using a SALD-1100 laser diffraction particle size analyzer manufactured by Shimadzu Corp. The powder samples were dispersed in a 0.2 wt% aqueous solution of sodium metaphosphate glass by applying ultrasonic vibration.

The TG–DTA measurements were performed using 5 mg portions of the sample and reference (α–Al_2O_3), charged in a platinum pan mounted on a top-load type sample holder of a Rigaku Thermoflex simultaneous TG–DTA apparatus. The temperature was detected with a Pt–Pt 13%Rh thermocouple fixed in a position near the sample.

Thermoanalytical results and fractal particle size distribution

In Fig. 2 the particle size distribution is presented by plotting the Rosin–Rammler (R–R) diagram for samples (1) and (2). In the R–R diagram, the plots for both samples fall on parallel straight lines in the particle size range smaller than the absolute size constant x_e. The results indicate that the size distribution of the particles smaller than x_e are expressed by a power law function with $\nu = 0.95$; hence, from Eq. (11) in view of Eq. (8), the particle size distribution of those particles obeys the self-similarity law.

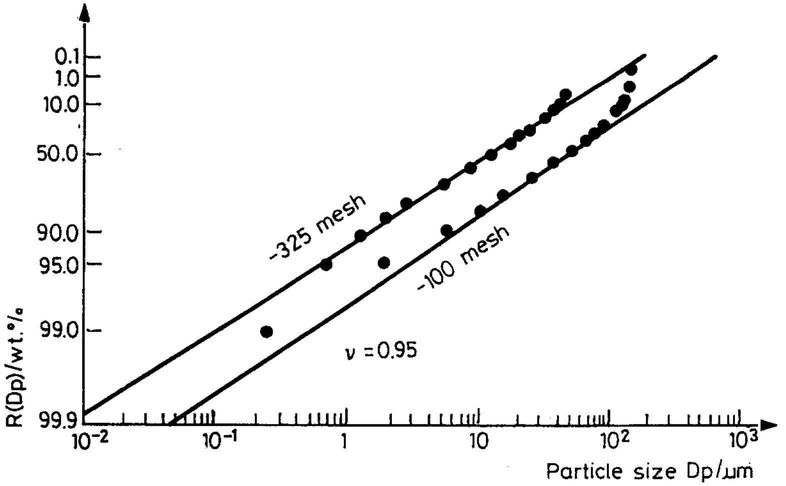

Fig. 2 Rosin–Rammler diagram of dolomite samples (1) (composed of particles 44 μm or less in size) and (2) (composed of particles 149 μm or less in size)

For samples (3) and (4), on the other hand, the particle size range is narrow. The self-similarity as set forth cannot be observed in these samples, because they each consist of particles in the size range over x_e.

In Fig. 3 are shown the DTA curves for all the samples in the temperature range from 700° to about 950°C. Samples (1) and (2), which have the self-similar particle size distribution, show a distinct peak indicating that the decomposition in both samples proceeds swiftly in a smooth manner ascribed to the self catalytic effect characteristic of powder samples having this self-similar particle size distribution [12]. The endothermic peak for sample (2) tails to a higher temperature range than in the case of sample (1), assumably due to the presence of coarser grains in which decomposition occurs in the bulk. However, the peak shape, particularly in the initial stage of decomposition, is quite similar to that of sample (1).

Samples (3) and (4), which are composed of particles having a narrow size range, yield a broader peak accompanied by small peaks or shoulders. This indicates that the decomposition proceeds over a wider temperature range; moreover, it seems as if several side reactions occurred during the main reaction. Since the DTA measurements are conducted in thermodynamic non-equilibrium states, it seems quite natural that the TG and DTA curves are influenced by the particle size distribution. This suggests that, though not strictly quantitatively, the DTA curves may describe the particle size distribution of powder samples.

The TG curves given in Fig. 4 more clearly show the difference between the two groups, i.e., the group of samples (1) and (2), and that of samples (3) and (4). In Fig. 4, the abscissa is the temperature and the ordinate is the weight loss

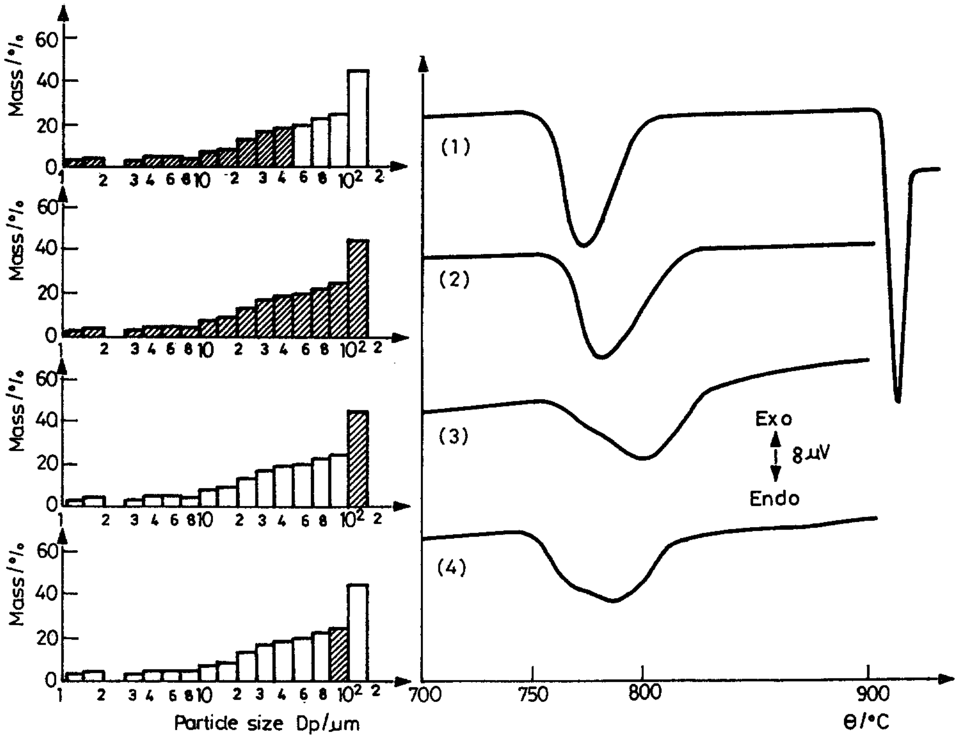

Fig. 3 DTA curves for dolomite samples each having a specified particle size distribution; samples for the DTA curves from the top to the bottom: (1) 44 μm or less in size, (2) 149 μm or less in size, (3) 105–149 μm in size, and (4) 74–105 μm in size. The shaded portion in the distribution diagram given on the left hand side of the curves indicates the particle size distribution of the corresponding samples

(downward). The main parts of the reaction for the former group are shown as parallel lines in the figure, indicating that the main reactions proceed at the same apparent rate of weight loss, i.e., at the same apparent rate of reaction. It seems as if the decomposition reaction for sample (1) shifted to the higher temperature side to give the reaction of sample (2). This similarity is evidently due to the self-similar particle size distribution. In other words, the decomposition reaction in samples (1) and (2) is more influenced by the powder characteristics. In contrast, the latter group yields TG curves with lower apparent reaction rate, and there is no similarity between the TG curves. This may suggest that the decomposition reaction occurs individually in each grain, in which the character as the bulk is more dominant. It can be seen, further, that a swift reaction in a smooth manner can be expected for a decomposition reaction dominated by powder characteristics, particularly for powder composed of particles characterized by the self-similar size distribution.

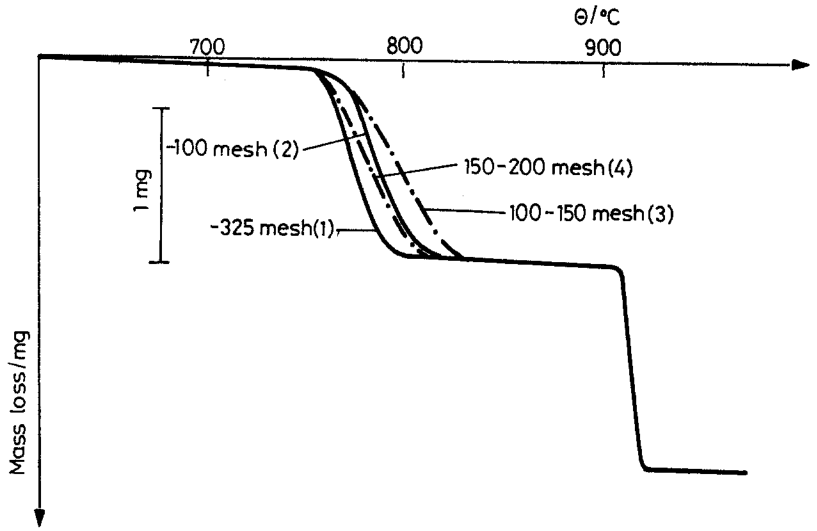

Fig. 4 TG curves for dolomite samples each having a specified particle size distribution, corresponding to the DTA curves in Fig. 3

Conclusion

The concept of self-similar particle size distribution was introduced to characterize a powder. This self-similarity or the fractal nature in the particle size distribution is naturally observed on powders obtained by size reduction using common methods such as milling, crushing, etc.

It has been also shown that a macroscopic feature of a powder sample, i.e., the particle size distribution, influences the thermal behaviour, such as the decomposition reaction of the sample. Hence, the results obtained by TG–DTA measurements, though not strictly quantitatively, effectively reflect the powder characteristics.

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Zusammenfassung — Basierend auf einer Aufstellung in der Theorie stochastischer Prozesse wurde eine Hauptgleichung für die Größeverteilung eingeführt, die einen Größenminderungsvorgang beschreibt. Unter Anwendung einer absoluten Größenkonstante und eines Skalenkonzeptes kann man zu einer verallgemeinerten Form der Gaudin-Schuhmann-Gleichung und der Rosin-Rammler-Gleichung gelangen und die enge Beziehung der beiden Formeln zeigen.

Von einem neuentwickelten Gesichtspunkt aus wird gezeigt, daß die Gaudin-Schuhmann-Gleichung das Gesetz der Selbstähnlichkeit der Verteilung in der Fractaltheorie erfüllt und bei der Bestimmung thermoanalytischer Eigenschaften von Pulvern eine bedeutende Rolle spielt. Als Beispiel wird gezeigt, daß DTA-Kurven gemahlener Dolomitproben durch Unterschiede in der Partikelgrößenverteilung der Probe entscheidend beeinflußt werden. Sowohl die DTA- als auch die TG-Kurven spiegeln die Pulvereigenschaften sehr gut wieder; beide werden deshalb zur Charakterisierung von Pulverproben vorgeschlagen.