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Thermal analysis and self-similarity law in particle size distribution of powder samples.
Part 1

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Abstract

Based on the self-similarity law (or fractal nature) in particle size distribution introduced recently by Ochiai et al. (Proc. Inst. Stat. Math., 38 (1990) 257) the DTA and TG curves for the decomposition reaction of dolomite are interpreted. The phenomenologically well-known Rosin–Rammler and Gaudin–Schuhmann functions are derived by a statistical approach, and the functions thus re-written (with a particle size scaled with the absolute size constant) obey a power law. The particles of a powder obtained by a mechanical size reduction can be seen therefore to be distributed in a self-similar manner. This also states that the majority of powders obtained by comminution have a distribution of a fractal nature.

Dolomite samples composed of particles whose size distributions obey the self-similarity law all undergo a similar decomposition reaction as observed in the TG–DTA curves. That is, they all appear to react smoothly and swiftly. Those having narrow particle size distibution, and to which the self-similar particle size distribution does not apply, appear to undergo a much delayed reaction; they yield irregular DTA peaks accompanied by small additional peaks or shoulders. This indicates that powder samples of dolomite having a fractal particle size distribution undergo an apparently regular and favorable reaction, and that the TG–DTA curves, though not strictly qualitative, provide speedy and useful information on the powder characteristics.

INTRODUCTION

Thermal analysis is widely applied nowadays in studying the thermal properties or thermal behavior of bulk inorganic materials such as minerals, rocks, sinterings, ceramics, etc. In performing the most common TG–DTA and DSC measurements, for example, it is customary to use powders passed through a 200 mesh sieve (see, for example, ref. 1). It

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should be noted, however, that when a bulk material is size reduced to a powder, it begins to exhibit particular properties in addition to the initial physicochemical properties attributed to its crystal structure, chemical composition, etc. The properties of the whole powder we observe in thermal analysis include the physicochemical properties of the bulk material and those properties definable as belonging to the powder, such as the particle size distribution and the morphology of individual particles.

The "powder" referred to herein is composed of particles about 2 μm or larger in diameter. This is a size well above the range of sizes at which the transition temperature is influenced by the particle size, as reported by, for example, van der Marel [2] and the Bayliss group [3,4]. It is also well known that 2 μm is the minimum limit attainable by a practical mechanical grinding process. Needless to say, quantum effects need not be considered for such a powder. Even in the range of grain sizes defined, it is still difficult to clearly distinguish the initial properties (which can be described by crystal structure, chemical composition, etc.) from the powder properties (which can be described by particle size distribution, etc.) by thermal analysis.

We present here an example of how the properties as a powder can be described by thermal analysis. We recently introduced the concept of a self-similarity law [5] in the particle size distribution, for interpreting the thermoanalytical results. First, the particle size distribution equations describing the powder characteristics are derived, not by the conventional phenomenological approach, but by defining a master equation describing the dynamics of a grinding system. Secondly, a scaling concept is introduced to obtain a "generalized" Gaudin–Schuhmann distribution function, which describes the self-similarity law in the undersized particle distribution. The results of TG–DTA measurements on classified dolomite powder samples are then related to the particle size distribution.

METHODS

Equations to describe particle size distribution

Here, the grinding process is assumed to follow a Markov process. That is, 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 diameter or size) which describes the probability of selection per unit time. By introducing the cumulative undersize distribution function $P(x, t)$, the population of the particles in the particle diameter range 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 this quantity

$(\partial P(x,t)/\partial x)\,\mathrm{d}x$, can be written as

$$\partial/\partial t\{(\partial P(x,t)/\partial x)\,\mathrm{d}x\}\,\mathrm{d}t \tag{1}$$

Thus, the manner in which the number of particles in the diameter range from x to $x+\mathrm{d}x$ reduces, in order to develop new particles of smaller diameter per unit time can be written as

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

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

$$S(\alpha)\,\mathrm{d}t\{(\partial P(\alpha,t)/\partial\alpha)\,\mathrm{d}\alpha\}\{(\partial B(x,t)/\partial x)\,\mathrm{d}x\} \tag{3}$$

The diameter α can take any value larger than x, so we obtain from eqn. (3)

$$\int_x^{x_\mathrm{m}}\left(S(\alpha)\,\mathrm{d}t\frac{\partial P(\alpha,t)}{\partial\alpha}\,\frac{\partial B(x,t)}{\partial x}\mathrm{d}x\right)\mathrm{d}\alpha \tag{4}$$

where x_m is the maximum particle diameter.

Now the master equation, eqn. (5), can be obtained from the sum of eqns. (2) and (4), which corresponds to eqn. (1).

$$\frac{\partial}{\partial t}\left(\frac{\partial P(x,t)}{\partial x}\mathrm{d}x\right) = -S(x)\left(\frac{\partial P(x,t)}{\partial x}\mathrm{d}x\right) + \int_x^{x_\mathrm{m}}\left(S(a)\frac{\partial P(a,t)}{\partial a}\,\frac{\partial B(a,x)}{\partial x}\mathrm{d}x\right)\mathrm{d}a \tag{5}$$

We can solve the equation analytically by explicitly stating functions $S(x)$ and $B(\alpha, x)$.

Rosin–Rammler (R–R) distribution function, Gaudin–Schuhmann distribution function, and self-similarity law of distribution

We adopt $S(x)=kx^{\nu}$ from experimental data [6] and take $B(\alpha,x)=(x/\alpha)^{\lambda}$. By assuming $\nu=\lambda$, and that the functional form holds for all particle sizes, we obtain from the master equation (5)

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

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

Because the initial value $R(x, 0)$ can be assumed to be approximately 1 from experimental data [7], we obtain the well-known Rosin–Rammler distribution function

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

This can be rewritten as

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

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

$$-kx^{\nu}t = (x/x_e)^{\nu} \tag{9}$$

Putting $X \equiv x_e/x$ and substituting eqn. (9) into eqn. (8), we obtain

$$P(x, t) \equiv 1 - \exp(-X^{-\nu}) \tag{10}$$

By expanding the right-hand side around $X^{-\nu}$ and taking the first term, a power law distribution is given of the form

$$P(x, t) \propto X^{-\nu} \equiv P(X), \tag{11}$$

which corresponds to the "generalized" Gaudin–Schuhmann distribution function with arbitrary t as the parameter. The function $P(X)$ suggests that the undersize distribution function obeys a self-similarity law [8–10] with respect to X; X, which is the size of any particle scaled by the absolute size constant x_e, is a measure of the deviation of the particle size from the characteristic size. This will be discussed in further detail elsewhere.

EXPERIMENTAL

A well-crystallized sample from Korea was used. The composition determined by wet chemical analysis is given in Table 1. The white massive sample consisting of 100–200 μm diameter subhedral dolomite grains in a

TABLE 1

Chemical composition of Korean dolomite

	% by weight [a]		% by mole [b]
SiO_2	0.198		
Fe_2O_3	0.324	$FeCO_3$	0.37
MnO	0.000	$MnCO_3$	0.00
CaO	30.54	$CaCO_3$	49.62
MgO	22.12	$MgCO_3$	50.01
Ig. loss	47.078		
H_2O (−)	0.056		
Total	100.316		100.00

[a] Wet analysis, by H. Nishido.

[b] As carbonates.

mosaic texture contains a trace amount of Fe but this is negligible for thermal analysis. The sample was crushed and ground by hand in an agate mortar and pestle. The powder thus obtained was passed through a 325-mesh Tyler sieve (having an opening of 44 μm), to give Sample (1). In a similar manner Sample (2) was obtained, consisting of particles passed through a 100-mesh Tyler sieve (opening of 149 μm). From Sample (2) were prepared Samples (3) and (4), each having a narrower particle size distribution, by classifying Sample (2) with 150- and 200-mesh Tyler sieves, respectively. Sample (3) consisted of particles 105–149 μm in size and Sample (4) of particles 74–105 μm in size.

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

The TG–DTA was 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 sampler 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.

RESULTS AND DISCUSSION

Table 2 and Fig. 1 show the particle size distribution and the Rosin–Rammler (R–R) diagram of Samples (1) and (2). The plots for both samples in the R–R diagram fall on straight parallel lines for particles smaller than the absolute size constant x_e (see Table 2: 17.9 μm for Sample (1); 74.8 μm for Sample (2)). The results indicate that the size distribution of particles smaller than x_e are expressed by the power law function with $\nu = 0.95$. Hence, from eqn. (10) and in the light of eqn. (6), the particle size distribution of those particles obeys the self-similarity law.

Samples (3) and (4), in contrast, both show narrow particle size distribution. In particular, because the samples are taken from the size range above x_e, the self-similarity as set forth above cannot be observed.

In Fig. 2 are shown the DTA patterns in the temperature range from 700°C to about 950°C for all samples. Samples (1) and (2), which have the self-similar particle size distribution, show a distinct peak and indicate 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 [11]. The endothermic peak for Sample (2) extends to a higher temperature than for Sample (1), presumably due to the coarser grains' showing some decomposition as a bulk material. However the peak's shape, particularly in the initial stages of decomposition, is quite similar to that of Sample (1).

TABLE 2

Particle size distribution for Korean dolomite samples

100-Mesh		325-Mesh	
Particle size Dp (μm)	Cumulative oversize distribution R(Dp) (wt.%)	Particle size Dp (μm)	Cumulative oversize distribution R(Dp) (wt.%)
147.96	1.0	44.09	1.0
140.05	5.0	40.63	5.0
130.75	10.0	36.68	10.0
122.06	15.0	33.11	15.0
113.96	20.0	29.38	20.0
90.04	30.0	21.72	30.0
74.79	36.8	17.87	36.8
68.40	40.0	16.30	40.0
50.82	50.0	11.26	50.0
36.28	60.0	7.51	60.0
25.20	70.0	4.93	70.0
15.05	80.0	2.55	80.0
9.95	85.0	1.74	85.0
5.44	90.0	1.14	90.0
1.87	95.0	0.61	95.0
0.00	–	0.24	99.0

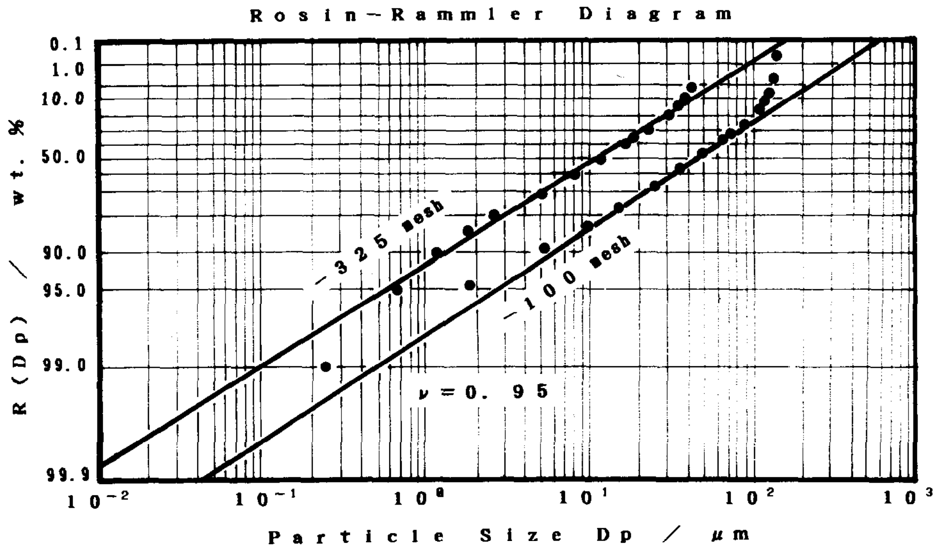

Fig. 1. Rosin–Rammler diagram for dolomite samples passed through a 325-mesh Tyler sieve (Sample (1); grains 44 μm or less in size), and for those passed through a 100-mesh Tyler sieve (Sample (2); grains 149 μm or less in size).

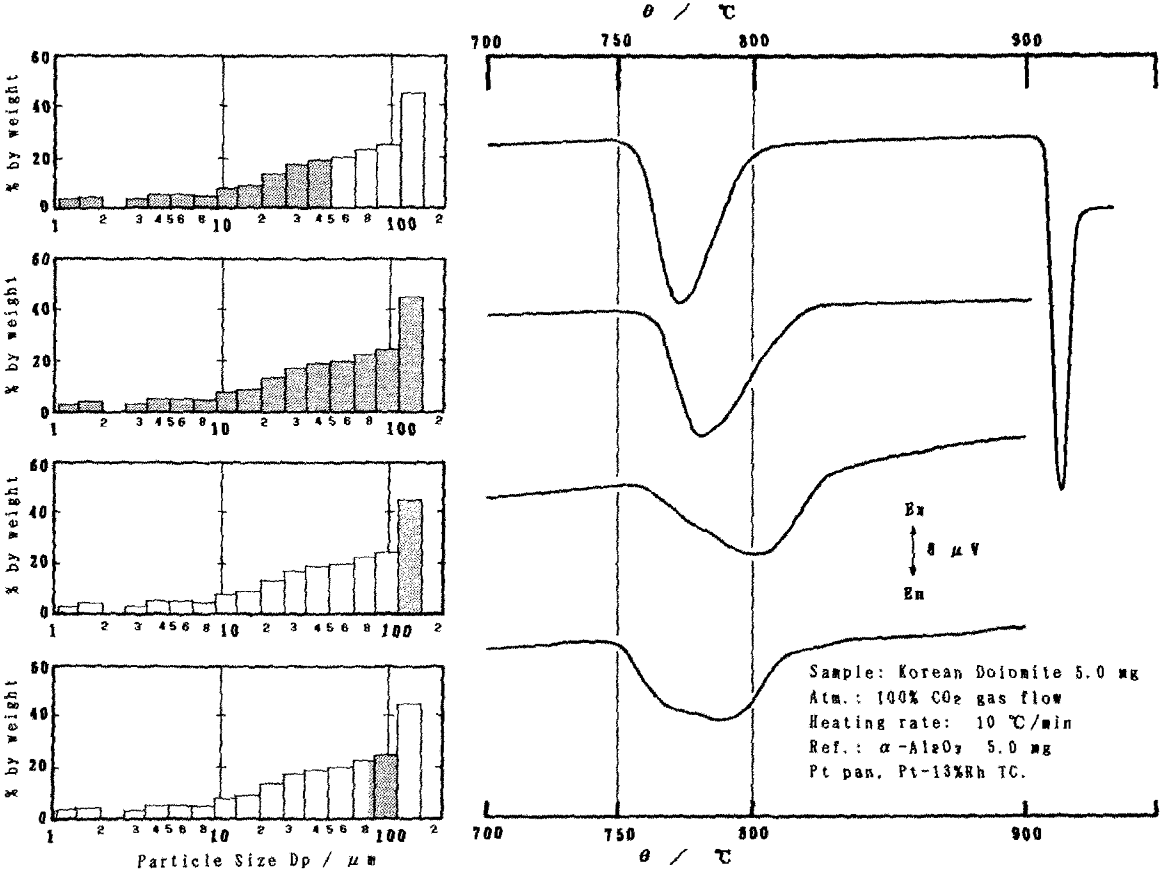

Fig. 2. DTA curves for dolomite samples, from top to bottom: 44 μm or less in size; 149 μm or less in size; 105–149 μm in size; 74–105 μm in size.

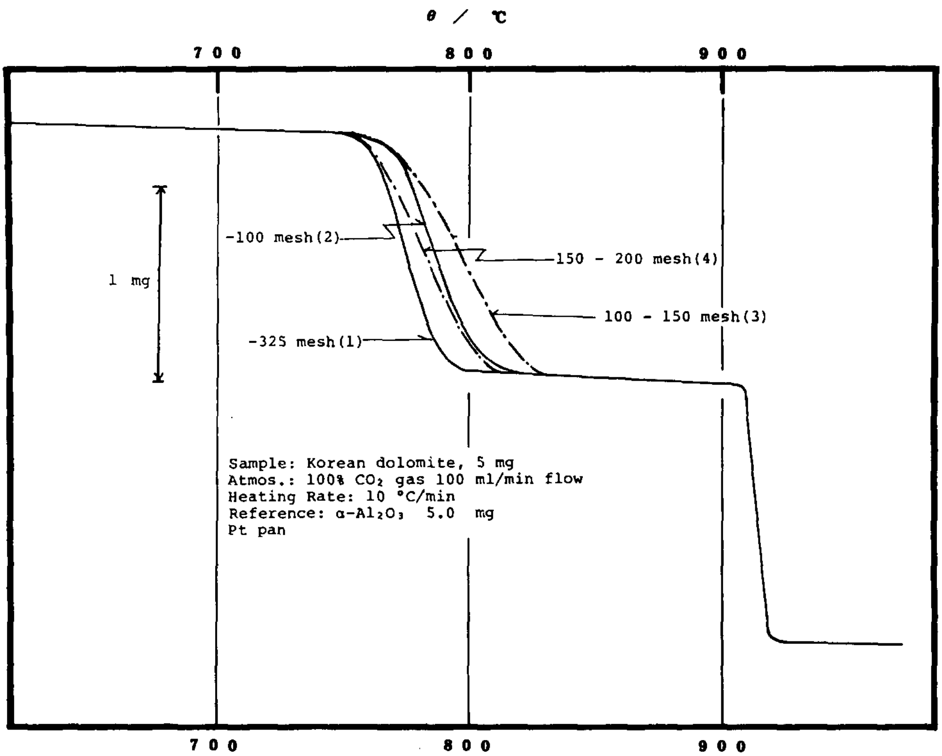

Fig. 3. TG curves for dolomite samples: (1) 44 μm or less in size; (2) 149 μm or less in size; (3) 105–149 μm in size; (4) 74–105 μm in size.

Samples (3) and (4), which are composed of particles having a narrow size distribution, yield a broader peak, accompanied by small peaks or shoulders. This indicates that the decomposition continues over a wider temperature range; it also seems that several side reactions occur. Gallagher [12] showed for gas–solid reactions of some oxides that the particle size distribution should be considered in describing the kinetics of the reactions. Although the DTA (and the TG) is conducted in thermal disequilibrium, it seems quite natural that the TG and DTA curves should be influenced by the particle size distribution. Though not strictly qualitative, the DTA and TG curves describe the particle size distribution of the powder sample.

The TG curves given in Fig. 3 show more clearly the difference between the two groups, i.e. the group of Samples (1) and (2), and the group of Samples (3) and (4). In Fig. 3, the abscissa is the temperature and the ordinate is the weight loss (downward). The main parts of the reactions for the former group are shown with parallel lines in Fig. 3, indicating that the main reactions proceed with the same apparent rate of weight loss, i.e. at the same apparent rate of reaction. It may seem that the decomposition reaction for Sample (1) is merely shifted to a higher temperature to give the reaction of Sample (2). This similarity is evidently due to the self-similar particle size distribution. In other words, the decomposition reactions of Samples (1) and (2) are more influenced by their powder characteristics. In contrast, the latter group yields TG curves with lower apparent reaction rates, and there is no similarity between the TG curves. This may suggest that the decomposition reaction occurs in each grain individually so that the character of the bulk is dominant. It can further be seen that a swift reaction in a smooth manner can be expected for a decomposition dominated by powder characteristics, particularly for powders composed of particles characterized by the self-similar manner in size distribution.

CONCLUSION

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

It has been proved that TG–DTA, though not strictly qualitative, effectively reflects the powder characteristics. Though the grinding effect on crystallinity is not considered in the present paper, the effect of the particle size distribution on the TG–DTA curves is shown to be valid in the papers.

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