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Thermal analysis and self-similarity law in particle size distribution of powder samples. Part 2

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Abstract

Based on the self-similarity law or the fractal nature of particle size distribution introduced in a previous paper, the role of the absolute size constant x_e in thermal analysis is discussed in further detail. In a powder obtained by a common size reduction process and not by applying a particular size control, a fractal nature (or self-similarity) in its particle size distribution can be safely assumed. In such a case, the thermal behavior of the whole sample is dominated by the portion consisting of particles below x_e in size. Thus, by taking this portion, the characteristic thermal behavior of the whole sample as a powder sample can be obtained.

It is further confirmed, by cutting off particles in the smaller size range, that the thermal characteristics (temperature and TG–DTA patterns) of a pulverized dolomite sample are little influenced by the crystallinity of the individual grains.

INTRODUCTION

In the most popular thermoanalytical methods, such as TG, DTA, and DSC, powder samples are often the subject of investigation. Thermal analyses are conducted, by definition, by the samples being brought into a thermal disequilibrium, so it can be readily accepted that the recorded temperature of transformation depends on the reaction rate, which is influenced by the particle size distribution. Although it is stated or implied that the particle size distribution of a sample has a great influence on the analytical results [1–3], and it is recommended to use the 200-mesh sieve (opening 74 μm) powder [4], no firm recommendation or theoretical basis for so doing can be given, as far as the present authors know.

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The effect of particle size (not the distribution) on TG–DTA curves (particularly DTA curves), in contrast, has frequently been considered in connection with the crystallinity of the grains comprising a powder. For example, Bayliss [5,6] explains that a decrease in the particle size in clay minerals is directly related to a loss of crystallinity, and that this decrease in crystallinity mainly accounts for the lowering of the recorded transition temperature. This, of course, does not hold true for all cases, and for size-reduced particles without internal crystal disruption, Bayliss [6] concludes that the recorded transformation temperature remains unaffected by any size greater than 1 μm.

In a previous paper [7], we reported that the particle size distribution greatly affects thermoanalytical results and introduced the concept of self-similarity in the distribution [8]. The undersize particle distribution function is given by the power law distribution of the form

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

which corresponds to the "generalized" Gaudin–Schuhmann distribution function with arbitrary t (duration of the grinding) as the parameter. The function $P(X)$ suggests that the undersize distribution function obeys a self-similarity law [7–10] with respect to the dimensionless X, i.e. the particle size scaled by the absolute size constant x_e.

This paper further discusses the role of x_e in powder samples, in relation to the method of obtaining consistent results by thermal analysis. Another object of the present paper is to show that the TG–DTA curves of pulverized dolomite samples are more influenced by the particle size distribution than by the decrease of crystallinity.

EXPERIMENTAL

The sample used and the method of its preparation are essentially the same as those reported in our previous paper [7]. By sieving Sample (2) (composed of particles 149 μm or smaller) of this previous paper [7] with 325-mesh and 200-mesh Tyler sieves, a sample portion consisting of particles in the range 44–74 μm was obtained. In other words, a sample partially maintaining a self-similar particle size distribution was prepared by cutting off particles smaller than 44 μm in size, i.e. those particles more susceptible to the decrease of crystallinity.

This sample was subjected to simultaneous TG–DTA under the same experimental conditions as described in ref. 7, and the results compared with the previous ones.

RESULTS AND DISCUSSION

Figures 1 and 2 show the DTA and TG curves, respectively, of the sample fraction composed of particles 44–74 μm, taken from the sample

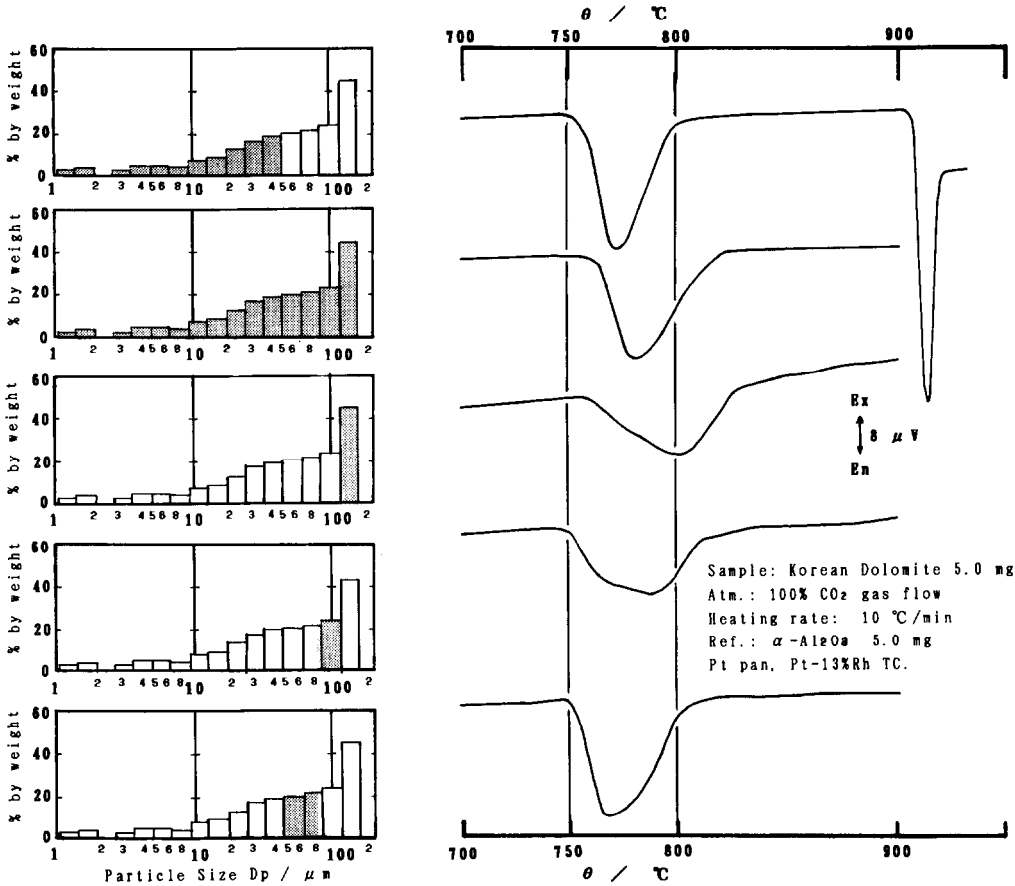

Fig. 1. DTA curves for dolomite samples. From top to bottom: 44 μm or less in size; 149 μm or less in size; 105–149 μm in size; 74–105 μm in size; 44–74 μm.

passed through a 100-mesh sieve. The curves of the other fractions of the original under-100 mesh sample and those of the samples having a self-similar particle size distribution are also given for comparison. It can be seen that the DTA curve, in addition to the TG curve, resembles that of the original sample, i.e. that of Samples (1) and (2) having the self-similar particle size distribution. It can also be seen that the initial temperature of decomposition, as observed clearly in the TG curves (Fig. 2), is the same for all the samples.

According to ref. 7, the samples having a narrow particle size distribution (i.e. 74–105 μm and 105–149 μm), and hence having no self-similarity in the particle size distribution, undergo decomposition in a manner quite different from that of the original sample. However, those fractions considered earlier both consisted of particles larger than the absolute size constant x_e and hence they retained the bulk properties of the initial sample. The value of x_e is a function of the grinding time and corresponds

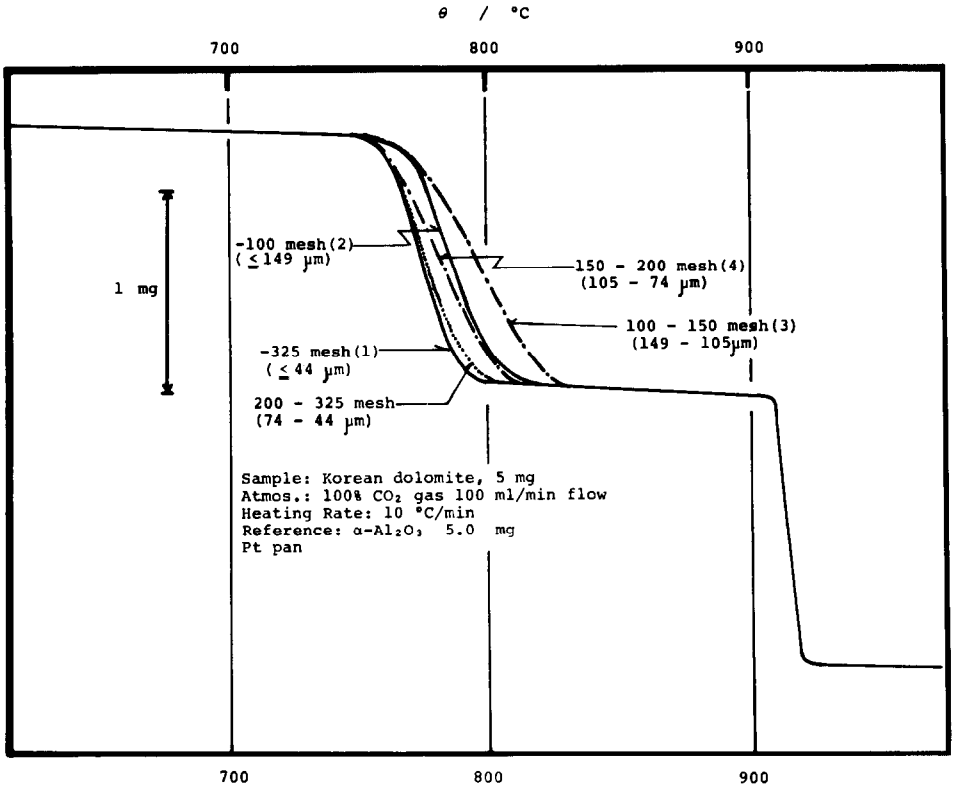

Fig. 2. TG curves for dolomite samples: (1) 44 μm or less in size; (2) 149 μm or less in size; (3) 105–149 μm in size; (4) 74–105 μm in size; (5) 44–74 μm.

to the size x that gives $R(x_e) = 36.8\%$. It can be seen that this absolute constant size may be considered as a critical value, or a threshold value, because the self-similarity in the particle size distribution holds only for particles smaller than x_e. That is, the power law function for the particle size distribution was derived by expanding the $P(x, t)$ function of the exponential form around $X^{-\nu}$; this requires the value of x/x_e to be around 0. The sample consisting of particles 44–74 μm in size maintains a so-called "partial" self-similarity in the distribution and is therefore clearly distinguished from the previous Samples (3) and (4). In other words, Samples (3) and (4) consist of particles not ground thoroughly enough to have self-similarity in the distribution, considering that x_e depends on the duration of grinding. This will be shown more clearly in the following discussion.

In the size reduction of a bulk feed, it is well established that a specific grinding machine or a crusher always yields a product having the same particle size distribution irrespective of the particle size of the initial feed, if the grinding is continued for a proper duration. Jimbo [11] reports on the grinding of feeds differing in particle size, using a ball mill. The first feed

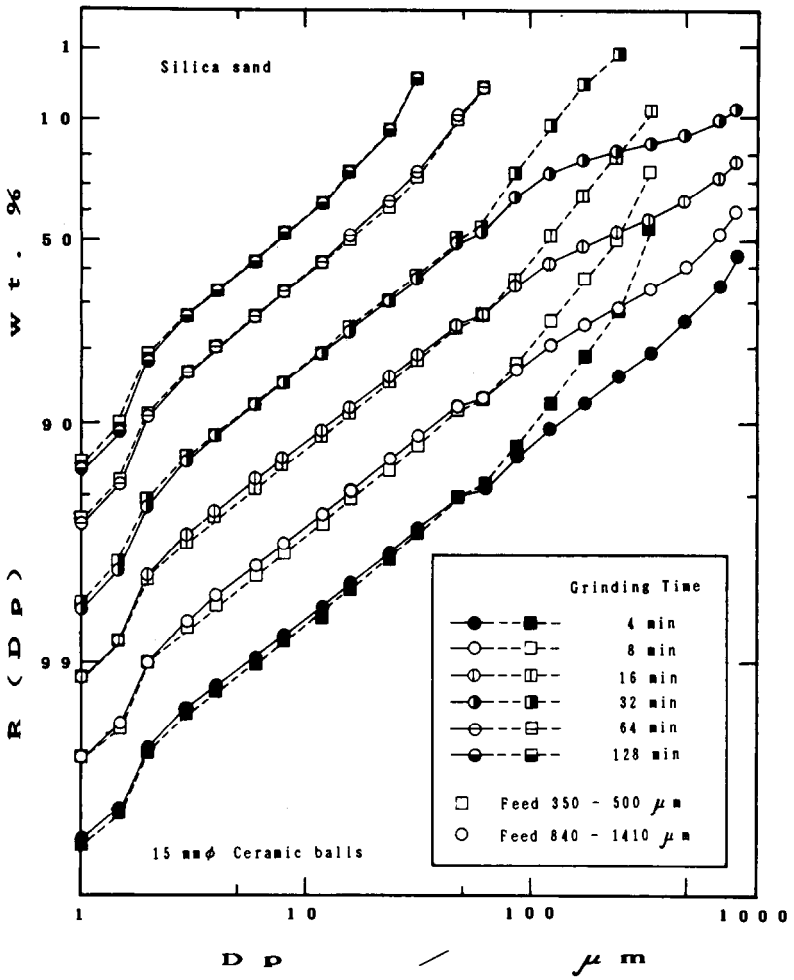

Fig. 3. Particle size distribution of ball mill products. Quartz feeds differing in particle size were used; squares indicate a feed consisting of particles 350–500 μm in size, and circles indicate a feed consisting of particles 840–1410 μm in size (reproduced with the permission of the Society of Chemical Engineers (Japan) from ref. 11).

consisted of particles 350–500 μm in size, and the second of coarser particles 840–1410 μm in size. The duration of grinding was also varied from 4–128 min. The particle size distribution of the products thus obtained is shown in Fig. 3. Those of the samples (differing in feed size) ground for only 4 min clearly disagree with each other in the size range larger than about 50 μm, whereas those of the samples ground for 64 min fall on a single curve and consist of particles about 70 μm or smaller. It can be clearly seen that x_e is a function of grinding time and that the samples composed of grains which fall on a straight line below x_e in the Rosin–Rammler (R–R) diagram obey the self-similarity law of distribution [8]. Those 2 μm or smaller are below the so-called grinding limit and greatly

deviate from the R–R distribution function. As mentioned in the Introduction, it is customary in thermal analyses to use powders of under-200 mesh. This convention seems reasonable from the viewpoint of powder technology as explained previously, if it is once confirmed that the powder sample is thoroughly ground and is not influenced by the initial characteristics of the bulk sample.

It can be seen from the previous discussion that the thermal analysis of a powder does not always yield the thermal characteristics of the bulk sample, nor those of the small sample portion. It clearly reflects the characteristic portion of the sample, e.g. those described by the powder characteristics of the particles not larger than the absolute size constant. It has also been seen that the thermal characteristics (temperature and the shape of the pattern) are less influenced by the crystallinity of the constituent grains. Thus, in a powder obtained by a common size reduction process and not by applying a particular size control, provided that the sample has no strong crystallographic anisotropy or orientation (as in acicular grains of magnetic materials), it can be safely assumed that it exhibits a fractal nature, or self-similarity, in its particle size distribution. Accordingly, if one desires to obtain a consistent result (i.e. characteristic thermal behavior of a powder sample which is not influenced by the individual bulk), the particles well below the absolute size constant x_e of a sample subjected to a common particle size reduction process for a duration long enough, should be chosen as the sample.

CONCLUSION

The use of under-200 mesh powder for the thermal analysis may give consistent and reproducible results provided the same grinding apparatus and method is used, and that the duration of the grinding has been long enough to give a consistent particle size distribution. By taking smaller sample portions consisting of particles smaller than the absolute size constant, and provided that this portion maintains the self-similar size distribution of the original sample, it is possible to predict the thermal behavior characteristics of the whole powder sample.

It has also been confirmed that the thermal characteristics (temperature range and the pattern of the TG–DTA curves), as observed on pulverized dolomite samples obtained by a normal grinding process, are less influenced by the crystallinity, but are dominated by the powder characteristics (particle size distribution, size range, etc.). Some results in thermal analyses related to particle size distribution will be presented in later papers.

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REFERENCES

1 P.D. Garn, Thermochim. Acta, 160 (1990) 135.
2 K.J. Gallagher, in G.M. Schwab (Ed.), Reactivity of Solids, Elsevier, 1965, p. 192.
3 K. Miyokawa and I. Masuda, Thermochim. Acta, 86 (1985) 113.
4 R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol. 1, Academic Press, London, 1970.
5 P. Bayliss, Nature, 201 (1964) 1019.
6 P. Bayliss, Nature, 207 (1965) 284.
7 M. Ochiai and R. Ozao, Thermochim. Acta, 198 (1992) 279.
8 M. Ochiai, R. Ozao, Y. Yamazaki, R. Otsuka and A. Holz, Proc. Inst. Stat. Math., 38 (1990) 257.
9 B. Mandelbrot, Fractals, Form, Chance and Dimension, Freeman, San Francisco, 1977; The Fractal Geometry of Nature, Freeman, San Francisco, 1983.
10 B.H. Lavenda, Sci. Am., 252 (1985) 2.
11 G. Jimbo, Chem. Eng. (Jpn.), 49 (1985) 124.