Fractal Reaction in Solids

—Reaction Functions Reconsidered—

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不均一系におけるフラクタル的反応

—反応機構式の再検討—

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Based on the fractal nature of pulverized solid particles described in previous reports by the authors, the reaction mechanism which defines the reaction rate of a heterogeneous system is reconsidered. The 9 functions given in a commonly used classification by Sharp et al. are shown collectively in 3 functions. The introduction of diffusion in a non-integer dimension results in functions deviating from the known ones, particularly in a diffusion-controlled reaction. Though the models referred here are too simple to be directly applied to a system consisting of many particles, this paper shows that it is meaningless to discuss a particular reaction by fitting it to a classical 1-, 2-, and 3-dimensional reaction mechanism.

Key-words : Fractal, Diffusion-controlled reaction, Reaction rate, Heterogeneous system, Solid reaction, Powder, Avrami equation, Ginstling-Brounshtein equation

1. Introduction

In the previous papers,¹⁾⁻⁵⁾ we have shown that the under sieve distribution function of a powder obtained after a sufficiently long grinding obeys a fractal power law function $P(x, t) \propto X^\beta$, where X is the particle size x scaled with a characteristic size constant, $x_e(t)$, and t is the duration of grinding. This was shown by describing the dynamics of size reduction based on a stochastic process. This in fact corresponds to a generalized Gaudin-Schuhmann (G-H) function. Thus, it is now well established that the phenomenologically derived Rosin-Rammler (R-R) and G-H functions can be each reduced to the power law described above. This fractal function is valid in the particle size range of from ca. $2 \mu\text{m}$ to x_e for all kinds of powders prepared by grinding, and the power β can be obtained as a parameter characteristic to the material to be ground. Also, it has been shown⁶⁾ that the known energy laws, e.g., Rittinger, Kick, Bond and Lewis, which each describe the size reduction process, can be derived collectively by assuming that a grinding process generates particles having a fractal surface. On the other hand, the fact that a pul-

verized product obeys a power law function signifies that the surface and the shape of the particles obtained by grinding are statistically self-similar. Hence, the particle size defined by the opening of a sieve can be said to be a fractal particle size. Then, the specific surface area S can be expressed with the fractal particle size x as $S \propto x^{D-3}$, where D is the surface fractal dimension.³⁾ This is in good agreement with the energy law explained above in Ref. 6. Moreover, this is essentially the same result as the one verified by the Avnir group.⁷⁾

The Avnir group has carried out numerous fractal analyses with an attempt to characterize a property of an object with a scale, or a yardstick, with a power-law scaling relation, *property* $\propto$ *scale* ^{D} . Despite many properties, such as physisorption monolayer, chemisorption capacity, and adsorbate surface reaction rate, were found to obey the power law function above with the particle size being the scale, the reaction rates at the solid interface could not be related to the surface roughness fractal dimension by a simple power law.⁷⁾

We have also reported previously that the apparent decomposition rate of a pulverized dolomite depends on the particle size, that is, to the surface fractal dimension which becomes fixed to a characteristic value in a sufficiently ground dolomite.^{4),5)} For example, in a powder composed of particles having a surface fractal dimension of about 2.32, the reaction rate remained unchanged even with an increase in surface area by about 30%.⁵⁾ This is a clear evidence that the reaction rate is dependent on the surface fractal dimension D , but not in a simple way as in a homogeneous system in which the reaction rate increases with increasing surface area.

Thus, the question is, how the reaction rate is related to the particle size, x , if a relation, *property* $\propto$ x^D , does not hold. As a step to consider this problem, we reconsider the known rate functions conventionally used for heterogeneous reactions. The functions were taken from the widely used classification by Sharp et al.⁸⁾

2. Framework of the theory

We describe a heterogeneous reaction in terms of a degree of conversion, α , as

$$\alpha = V/V_0 \quad (1.1)$$

where, the volume V of the reacted portion is selected as the changing property which can be monitored during the reaction, and V_0 is the initial volume of the system. Then, the reaction rate can be expressed as

$$\frac{d\alpha}{dt} = \frac{1}{V_0} \frac{dV}{dt} \quad (1.2)$$

If we assume that the rate can be described as in homogeneous reaction with Eq. (1.3)

$$\frac{d\alpha}{dt} = k(T) \cdot F(\alpha) \quad (1.3)$$

where

$$k(T) = Z \cdot \exp(-E/RT) \quad (1.4)$$

where Z : pre-exponential factor, E : activation energy, R : gas constant, and T : absolute temperature, and that the reaction occurs in a very narrow temperature range, we obtain

$$\frac{d\alpha}{dt} \propto F(\alpha) \quad (1.5)$$

The function $F(\alpha)$ depends on the physico-geometric relations at the boundary between the product and the initial material. Various types of $F(\alpha)$ have been proposed to the present mostly independently by many authors. In Table 1 are listed the most basic and commonly used ones, in accordance with the classification by Sharp et al.⁽⁸⁾

Here we reconsider the functions by assuming three simple processes:

- (1) Surface-controlled reaction: the chemical reaction is the rate-controlling process;
- (2) Diffusion-controlled reaction: the mass-transport of a material is the rate-controlling process; and
- (3) Nucleation-dependent process: the rate of nucleation formation and overlap of the formed and growing nuclei is considered.

2.1 Surface-controlled reaction

We assume that the reaction rate is proportional to the surface area A of the reacting boundary

$$\frac{dV}{dt} = k \cdot A \quad (2.1)$$

where, k is a constant, and with Eq. (1.2),

$$\frac{d\alpha}{dt} = \frac{k}{V_0} \cdot A \quad (2.2)$$

If the morphology of the reacting particle does not considerably change during the reaction, the initial volume V_0 and the unreacted or the remaining volume V' can be written as

$$V_0 = C \cdot r^D$$

$$V' = C \cdot r'^D$$

where, r' is the fractal size of the unreacted particle. Then, by adopting Mandelbrot's theory of co-dimension,⁽⁹⁾ the area A of the reaction boundary can be expressed by $A = C' \cdot r^{D-1}$. By simple substitution and $V = V_0 - V'$ and Eq. (1.1), we can rewrite Eq. (2.2) as

$$\frac{d\alpha}{dt} \propto (1-\alpha)^{\frac{D-1}{D}}$$

with D being fractal dimension of $2 \leq D \leq 3$. Hence we obtain the function forms in Table 1 as follows:

when $D=2$ (R_2), $F(\alpha) \propto (1-\alpha)^{1/2}$, and

when $D=3$ (R_3), $F(\alpha) \propto (1-\alpha)^{2/3}$.

2.2 Diffusion-controlled reaction

In this type of reaction, the rate of diffusion of a substance within a thin boundary layer between the unreacted material and the reacted product corresponds to the reaction rate. Here, the reacting volume is assumed to be proportional to the diffused amount, expressed by

$$\frac{dV}{dt} = K \cdot \frac{dN}{dt} \quad (3.1)$$

where, N is the quantity of the diffusing material, and K is a constant. By assuming a simple one-dimensional diffusion, we obtain $d^2N/dr^2 = 0$ according to Fick's second law; by further assuming the concentration gradient along the direction of the diffusion to be constant, we obtain $dN/dr = \text{constant}$ and

$$\frac{dV}{dt} = K \cdot \frac{dN}{dt} = -D' \cdot K \cdot A \cdot \frac{dN}{dr} \quad (3.2)$$

where, D' is diffusion constant and A is the cross section of the reaction system.

At an arbitrary position r in the product layer of a D -dimension particle, the diffusion flux per unit time becomes constant irrespective of r . Thus, by integration, Eq. (3.2) becomes

$$\frac{dN}{dt} \int_{r_0}^r -r^{-(D-1)} dr \propto \int_{N_0}^N dN \quad (3.3)$$

where, $1 \leq D \leq 3$.

Thus, from Eq. (3.3) and $\Delta N = N - N_0 > 0$, we obtain:

when $1 \leq D < 2$,

$$\frac{dN}{dt} \propto \Delta N [-r^{(2-D)} + r_0^{(2-D)}]^{-1} \quad (3.4)$$

when $D=2$,

$$\frac{dN}{dt} \propto \Delta N \left[-\ln \left(\frac{r}{r_0} \right) \right]^{-1} \quad (3.5)$$

when $2 < D \leq 3$,

Table 1. Commonly known reaction function forms.⁽⁸⁾

Symbol	Function Form $F(\alpha)$	Ref.
D_1	α^{-1}	
D_2	$[-\ln(1-\alpha)]^{-1}$	(8)
D_3	$(1-\alpha)^{1/3} [(1-\alpha)^{-1/3} - 1]^{-1}$	(10)
D_4	$[(1-\alpha)^{-1/3} - 1]^{-1}$	(11)
R_2	$(1-\alpha)^{1/2}$	(12)
R_3	$(1-\alpha)^{2/3}$	(12)
F_1	$1-\alpha$	
A_2	$(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	(13,14)
A_3	$(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	(13,14)

$$\frac{dN}{dt} \propto \Delta N [r^{(2-D)} - r_0^{(2-D)}]^{-1} \quad (3.6)$$

By substituting $r/r_0 = (1-\alpha)^{1/D}$, we obtain:

$$\begin{aligned} D_D (1 \leq D < 2) \quad d\alpha/dt &\propto [-(1-\alpha)^{(2-D)/D+1}]^{-1} \\ D_D (2 < D \leq 3) \quad d\alpha/dt &\propto [(1-\alpha)^{(2-D)/D-1}]^{-1} \\ D_D (D=2) \quad d\alpha/dt &\propto [-\ln(1-\alpha)]^{-1} \end{aligned}$$

Thus we obtain the three functional forms in Table 1 as follows:

when $D=1 (D_1)$, $F(\alpha) \propto 1/\alpha$,
when $D=2 (D_2)$, $F(\alpha) \propto 1/[-\ln(1-\alpha)]$, and
when $D=3 (D_4)$, $F(\alpha) \propto 1/[(1-\alpha)^{-1/3}-1]$.

2.3 Nucleation-dependent process

With respect to a process controlled by the nucleation growth mechanism, the basic concept follows that established by Avrami¹³⁾ and Yerofeyev,¹⁴⁾ which describe a process involving intergrowth of the nuclei during their rapid growth. Here it is assumed that the rate of forming the germ nuclei and that of the growth of the grains are each constant. Hence

$$\frac{dN}{dt} = k \cdot N_0 \quad (4.1)$$

and

$$V = K \cdot (k' \cdot t)^D \quad (4.2)$$

where, N is the number of grains; v , the volume of a grain or nucleus; D , the fractal dimension of the direction of growth; and k and k' are each rate constants of the formation of nuclei and of the growth of grains, respectively. N_0 is the number of sites suitable for nucleus formation, and K is a volume conversion factor.

The total volume, V , for the nuclei having formed in the initial stage can be obtained by

$$\begin{aligned} V &= K \cdot K' \int_0^t (t-\tau)^D \left(\frac{dN}{d\tau} \right) d\tau \\ &= \frac{1}{D+1} \cdot K \cdot N_0 \cdot k \cdot k'^D \cdot t^{(D+1)} \end{aligned} \quad (4.3)$$

By differentiation and substitution, we obtain

$$\frac{d\alpha}{dt} \propto \alpha^{\frac{D}{D+1}} \quad (4.4)$$

If the nucleation completes in the initial stage, the total volume V after time t becomes

$$V = K \cdot N \cdot k'^D \cdot t^D$$

thus

$$\frac{d\alpha}{dt} \propto \alpha^{\frac{D-1}{D}} \quad (4.5)$$

If the grains grow sufficiently large as to impinge upon one another, the actual amount reacted, α is related with the theoretical α' as

$$\alpha' = -\ln(1-\alpha).$$

Thus, we obtain

$$\frac{d\alpha}{dt} = (1-\alpha) \cdot \frac{d\alpha'}{dt} \quad (4.6)$$

If the nucleation proceeds at a constant rate, from Eqs. (4.4) and (4.6) we obtain

$$\frac{d\alpha}{dt} \propto (1-\alpha) \cdot [-\ln(1-\alpha)]^{\frac{D}{D+1}} \quad (4.7)$$

If nucleation completes at the initial stage of reaction, from Eqs. (4.5) and (4.6) we obtain

$$\frac{d\alpha}{dt} \propto (1-\alpha) \cdot [-\ln(1-\alpha)]^{\frac{D-1}{D}} \quad (4.8)$$

where $1 \leq D \leq 3$.

In Eq. (4.8), by putting $D=2$ and $D=3$, we obtain A_2 and A_3 functions in Table 1 as follows, respectively:

$$\begin{aligned} \text{when } D=2 (A_2), \\ F(\alpha) &\propto (1-\alpha) \cdot [-\ln(1-\alpha)]^{1/2}, \text{ and} \\ \text{when } D=3 (A_3), \\ F(\alpha) &\propto (1-\alpha) \cdot [-\ln(1-\alpha)]^{2/3} \end{aligned}$$

Then we can summarize reaction functions with non-integer D 's as in Table 2. By simple substitution of D with 1, 2, or 3, the function forms corresponding to those in Table 1 can be readily reproduced, except for $A_1=F_1$ (in Table 1) and $D_3=D_4$ (in Table 1), because D_3 in Table 1 is Janderian equation which holds only in the case where many simplifying assumptions are satisfied.

3. Discussion in comparison with the previous $F(\alpha)$'s

The generalized reaction functions with non-integer D 's listed in Table 2 are shown graphically in Figs. 2 to 4. In Fig. 1 are given the α - $\ln F(\alpha)$ plots corresponding to the $F(\alpha)$'s in Table 1.

Figure 2 shows the α - $\ln F(\alpha)$ plot curves for the surface-controlled reactions, i.e., those indicated with symbol R_D , where D is increased from 2 to 3 at a step of 0.1. Thus we can see that any sample which undergoes a reaction with its α - $\ln F(\alpha)$ plot falling within the area defined between the R_2 and R_3 curves possibly obeys a surface-controlled reaction.

The most distinguished features which are observed by introducing a fractal concept in the reaction of solids can be observed in Fig. 3, in which the α - $\ln F(\alpha)$ plots for diffusion-controlled reactions D_D are given. Those plots were made from $D=1.0$ to 1.9, and from $D=2.1$ to 3.0 at a step of 0.1. The curves with $D=2$ coincides with the D_2 curve in Fig. 1. It can be seen that the curves shift to the upper side of the graph with increasing D 's to 1.9. These

Table 2. Function forms with non-integer D 's.

Symbol	Function Form $F(\alpha)$
$D_D (D = 1 - 2; \neq 2)$	$[-(1-\alpha)^{(-D+2)/D} + 1]^{-1}$
$D_D (D = 2 - 3; \neq 2)$	$[(1-\alpha)^{(-D+2)/D} - 1]^{-1}$
D_2	$[-\ln(1-\alpha)]^{-1}$
$R_D (D = 2 - 3)$	$(1-\alpha)^{(D-1)/D}$
$A_D (D = 1 - 3)$	$(1-\alpha)[- \ln(1-\alpha)]^{(D-1)/D}$

Fig. 1. $\alpha\text{-}\ln F(\alpha)$ curves corresponding to the $F(\alpha)$'s in Table 1, according to the classification by Sharp et al.⁸⁾

Fig. 2. $\alpha\text{-}\ln F(\alpha)$ curves for the surface-controlled reactions, indicated with symbol R_D , where D is increased from 2 to 3 at a step of 0.1. Note that the $\alpha\text{-}\ln F(\alpha)$ plots fall within the area defined between the conventional R_2 and R_3 curves.

curves with D from 1.0 to 1.9 have never been discussed as being proper for describing reaction mechanisms before adopting the concept of a non-integer dimension. The D_D curves with $D=2.1$ to 3.0 cover an area defined between the conventional D_2 and D_4 curves.

In Fig. 4 are plotted the $\alpha\text{-}\ln F(\alpha)$ curves for $F(\alpha)$'s corresponding to A_D . The same discussion can be applied to those curves as in the discussion for the D_D and R_D curves above, except that A_1 corresponds to the conventional F_1 curve.

Quite many discussions have been made on the fittability of an actual data with the $\alpha\text{-}\ln F(\alpha)$ curves

Fig. 3. $\alpha\text{-}\ln F(\alpha)$ curves for diffusion-controlled reactions indicated with D_D , with $D=1.0$ to 1.9 and $D=2.1$ to 3.0 at a step of 0.1. The curves with $D=2$ coincides with the D_2 curve in Fig. 1. Note that the curves shift to the upper side of the graph with increasing D 's to 1.9, and then shift downward from $D=2.1$ to 3.0 to cover an area defined between the conventional D_2 and D_4 curves.

Fig. 4. $\alpha\text{-}\ln F(\alpha)$ curves for $F(\alpha)$'s corresponding to A_D . The curves fall between A_1 and A_3 curves in Table 1, except that A_1 corresponds to the F_1 curve in the conventional description.

to determine the pertinent reaction mechanism of a particular system, yet with many complaints failing to seek for the best fit. This has led Garn¹⁵⁾ to state that "...the material itself does not know any of our mathematics...". In general, reaction functions considering dimensions other than 1, 2, or 3 had been considered meaningless. In other words, the power in $F(\alpha)$ functions had been restricted to 0, 1/2, 2/3, -1, and 1. However, the present $F(\alpha)$ functions with non-integer D 's are based on a more physically

meaningful picture. It is more natural that experimentally obtained data deviate from the conventional $F(\alpha)$ functions. This may be particularly so for the D_D type reactions considering that the present reaction functions cover a wider area between that defined by the previous D_1 and D_3 functions (see Fig. 3). Of course, those reaction models are based on the geometry of a single reacting particle except for the nucleation-dependent processes, and hence the synergetic effects which may appear from a system consisting of a large number of particles, i.e., a powder, are not considered. Thus we should be well aware of the fact that the basic standpoint of this derivation is too simple, and yet more realistic reaction mechanisms, such as those involving catalytic reactions, parallel reactions, reversible reactions, etc., must also be taken into consideration in future studies.

4. Conclusions

The conventional reaction functions for describing the reaction mechanisms in heterogeneous system were reconsidered from a fractal point of view. The 9 reaction function forms which were mostly independently derived were shown collectively in 3 types.

It seems meaningless to discuss a particular reaction as being 1-, 2-, or 3-dimensional. Since it is well-established at present that an industrial powder obtained by a mechanical size-reduction process is composed of particles having a surface defined by fractal dimension, it is more natural to assume reactions involving a non-integer dimension.

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References

- 1) M. Ochiai, R. Ozao, Y. Yamazaki, R. Otsuka and A. Holz, *Proc. Inst. Stat. Math.*, **38**, 257–63 (1990).
- 2) M. Ochiai and R. Ozao, *Thermochimica Acta*, **198**, 279–87 (1992).
- 3) M. Ochiai and R. Ozao, *Seramikkusu*, **26**, 1181–85 (1991); M. Ochiai and R. Ozao, *J. Therm. Anal.*, **38**, 1901–10 (1992).
- 4) R. Ozao and M. Ochiai, *Thermochimica Acta*, **198**, 289–95 (1992); R. Ozao and M. Ochiai, *Gypsum & Lime*, **233**, 524–30 (1991).
- 5) R. Ozao and M. Ochiai, *Thermochimica Acta*, **208**, 161–67 (1992).
- 6) M. Ochiai and R. Ozao, Y. Yamazaki and A. Holz, *Physica A*, to be published.
- 7) See, for example, the summary given by D. Farin and D. Avnir, in K. K. Unger et al. (Eds.), “Characterization of Porous Solids”, Elsevier Science Publishers B. V., Amsterdam (1988) pp. 421–33, and references cited therein.
- 8) J. H. Sharp, G. W. Brindley and B. N. N. Achar, *J. Am. Ceram. Soc.*, **49**, 379–82 (1966).
- 9) B. B. Mandelbrot, “The Fractal Geometry of Nature”, W. H. Freeman, New York (1983) p. 365.
- 10) J. B. Holt, I. B. Cutler and M. E. Wadsworth, *J. Am. Ceram. Soc.*, **45**, 133–36 (1962).
- 11) A. M. Ginstling and B. I. Brounshtein, *J. Appl. Chem. USSR* (in Eng.), **23**, 1327–38 (1950).
- 12) J. Sestak, V. Satava and W. W. Wendlandt, *Thermochimica Acta*, **7**, 333–556 (1973).
- 13) M. Avrami, *J. Chem. Phys.*, **7**, 1103–12 (1939); *ibid.*, **8**, 212–24 (1940); *ibid.*, **9**, 177–84 (1941).
- 14) B. V. Yerofeyev, *Compt. Rend. Acad. Sci. URSS* (in Eng.), **52**, 511–14 (1946).
- 15) P. D. Garn, *J. Therm. Anal.*, **13**, 581–93 (1978).