EFFECT OF PARTICLE SIZE ON ABSORPTION OF X-RAYS REFLECTED FROM MIXED POWDER (II) EXTRA ABSORPTION COEFFICIENT

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ABSTRACT

In the previous paper (Part I), the 'self-absorption factor, τ_1 ,' and the 'extra absorption coefficient, $\Delta\mu$,' were derived and introduced to the formula of reflected X-ray intensity. In this paper, the coefficient $\Delta\mu$ is proved to be non-negative in a mixed powder of multiple components and to be zero in a powder of single component. The relation of magnitudes between $\Delta\mu/\mu$ and μD is estimated on the assumption of $\mu > (\mu_i \sim \mu_j)$.

Discussion is made on the magnitude of particle size D to make the particle effects on reflected X-ray intensity negligible.

Introduction

When particle sizes of a homogeneously mixed powder are sufficiently small and the powder is densely packed, the X-ray intensity reflected from the powder block having a flat surface can be given by a simple formula as (9) in this paper. In the case of coarser particles, however, the formula must be corrected by some factors.

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In Part I of this paper, two factors, the self-absorption factor τ_1 and the extra absorption coefficient $\Delta\mu$, were theoretically derived. The former is due to the absorption by the particles causing X-ray reflection and the latter is due to the absorption in case a powder has multiple components. It was there assumed that the variation of a true absorbing path length is negligible among many X-ray beams reflected from layer elements of a specimen at a level of the same depth, and that so-called 'extinction effects' are out of scope in the course of study, though those are not always negligible.

The reflected X-ray intensity, I_1 , of the first component in a mixed powder composed of n kinds of components was thus given by

$$\begin{aligned} I_1 &= K_1 \cdot \tau_1 \cdot \frac{1}{1 - (\Delta\mu/\mu)} \frac{f_1}{\mu} \\ &= K_1 \cdot \tau_1 \cdot \frac{1}{1 - (\Delta\mu/\mu)} \frac{x_1/\rho_1}{x_1(\mu_1^* - \mu_M^*) + \mu_M^*}, \end{aligned} \quad (1)$$

where

$$\frac{f_1}{\mu} = \frac{\rho(x_1/\rho_1)}{\mu} = \frac{x_1/\rho_1}{\mu^*}, \quad (2)$$

$$\Delta\mu = \frac{1}{2} H \left(\sum_{i=1}^n f_i \mu_i^2 - \mu^2 \right),$$

or

$$\frac{\Delta\mu}{\mu} = \frac{1}{2} (\rho'/\rho)^{1/3} \mu D \frac{\sum_{i=1}^n f_i \mu_i^2 - \mu^2}{\mu^2}, \quad (3)$$

$$H = (\rho'/\rho)^{1/3} D, \quad (4)$$

$$= 0.9047 D, \quad (5)$$

$$f_i = \frac{x_i/\rho_i}{\sum_{i=1}^n (x_i/\rho_i)}, \quad x_i = \frac{f_i \rho_i}{\sum_{i=1}^n f_i \rho_i}, \quad (6)$$

and

$$\tau_1 = \frac{1}{V_0} \int_0^{V_0} \exp(-\mu_1 z) \cdot dV_0. \quad (7)$$

The value of $0.9047D$ was derived assuming that the particles are spherical with an equal diameter D (*i.e.*, mean particle size of the powder) and packed in the way of closest packing. A weight fraction x_i is interchangeable with the volume fraction f_i by (6). The physical meaning of the above formulae and the definition of symbols were described in Part I, and the symbols will be used in common in this paper.

In (1), the correction terms correspond to

$$\tau_1 \cdot \frac{1}{1 - (\Delta\mu/\mu)} \quad (8)$$

If $1 - \tau_1$ and $\Delta\mu/\mu$ are sufficiently small, the magnitude of (8) approaches to unity, and then the reflected intensity can be given by

$$I_1' = K_1(f_1/\mu) \quad (9)$$

Both $1 - \tau_1$ and $\Delta\mu/\mu$ are negligible, if the magnitude of $\mu_1 D_1$ and μD makes the reflected intensity fall in the range of an allowable error. This relation will be discussed in the following chapters.

The sign of $\Delta\mu$

An elementary proof of non-negativity of $\Delta\mu$ is as follows:

$$\begin{aligned} Y &\equiv \sum_{i=1}^n f_i \mu_i^2 - \mu^2 = \sum_{i=1}^n f_i \mu_i^2 - \left(\sum_{i=1}^n f_i \mu_i \right)^2 \\ &= \sum_{i=1}^n f_i \mu_i^2 - \sum_{i=1}^n f_i^2 \mu_i^2 - 2 \sum_{\substack{i=1 \\ i < j}}^n f_i f_j \mu_i \mu_j \\ &= \sum_{i=1}^n f_i (1 - f_i) \mu_i^2 - 2 \sum_{\substack{i=1 \\ i < j}}^n f_i f_j \mu_i \mu_j \\ &= \sum_{i=1}^n f_i \left(\sum_{i=1}^n f_i - f_i \right) \mu_i^2 - 2 \sum_{\substack{i=1 \\ i < j}}^n f_i f_j \mu_i \mu_j \\ &= \sum_{\substack{i=1 \\ i < j}}^n f_i f_j (\mu_i - \mu_j)^2 \geq 0, \end{aligned} \quad (10)$$

because of $f_i > 0$, and $f_j > 0$. On the other hand, $H > 0$. Therefore

$$\Delta\mu \equiv \frac{1}{2}HY = \frac{1}{2}H \left(\sum_{i=1}^n f_i \mu_i^2 - \mu^2 \right) \geq 0, \quad (11)$$

where the equality is satisfied in the trivial case of single component. Apart from that case, it is valid only when all μ_i 's are the same, though it does not seem likely to occur.

It seems worthwhile to mention that the above non-negativity relation is included in a more general theorem on the inequality. According to this theorem, the average value, $\overline{\varphi(\mu)}$, of any continuous convex function, $\varphi(\mu)$, is not smaller than $\varphi(\overline{\mu})$ where $\overline{\mu}$ is the average value of μ . The present case corresponds to a special case when $\varphi(\mu) = \mu^2$.

Relation between $\Delta\mu/\mu$ and μD

The object of this chapter is to estimate the magnitude of μD to make $\Delta\mu/\mu$ negligible, accordingly, to make $1/[1 - (\Delta\mu/\mu)]$ approach unity. When the volume fractions f_i 's (or weight fractions x_i 's) and the linear absorption coefficients μ_i 's are known, the magnitude of $\Delta\mu/\mu$ can be determined by the formula

$$\frac{\Delta\mu}{\mu} = 0.4524 \mu D \frac{\sum_{i=1}^n f_i \mu_i^2 - \mu^2}{\mu^2}, \quad (12)$$

which is obtained from (3) and (5). However, if the magnitudes of f_i 's and μ_i 's are known, the quantitative X-ray analysis to which the subject of this paper is related is no longer necessary.

Thus, we must here consider a general case. We must treat this problem with making some assumptions, because the upper and the lower limits are unknown for the values of μ_i 's in (12).

It is necessary that another expression without including f_i 's and μ_i 's should be substituted for the term $\left(\sum_{i=1}^n f_i \mu_i^2 - \mu^2 \right) / \mu^2$, in order to obtain the relation between $\Delta\mu/\mu$ and μD .

Now, assume that the difference $\mu_i \sim \mu_j$ is not larger than μ . Then, the relation

$$\mu^2 \sum_{\substack{i=1 \\ i < j}}^n f_i f_j > \sum_{\substack{i=1 \\ i < j}}^n f_i f_j (\mu_i - \mu_j)^2 \quad (13)$$

clearly holds. Here, let the arithmetic mean value of f_i 's be $f_0 (= 1/n)$, and the deviation of f_i from f_0 be ε_i , namely,

$$f_i - f_0 \equiv f_i - \frac{1}{n} = \varepsilon_i, \quad (14)$$

where $\sum_{i=1}^n f_i = 1$ and n is an integer ($n \geq 2$) which is the number of kinds of components. Then, the following equation can be derived:

$$1 = \left(\sum_{i=1}^n f_i \right)^2 = \sum_{i=1}^n f_i^2 + 2 \sum_{\substack{i=1 \\ i < j}}^n f_i f_j,$$

namely,

$$\begin{aligned} 2 \sum_{\substack{i=1 \\ i < j}}^n f_i f_j &= 1 - \sum_{i=1}^n f_i^2 = 1 - \sum_{i=1}^n \left(\frac{1}{n} + \varepsilon_i \right)^2 \\ &= 1 - \frac{1}{n} - \sum_{i=1}^n \varepsilon_i^2, \end{aligned} \quad (15)$$

because $\sum_{i=1}^n \varepsilon_i = 0$. Therefore, the relation

$$\frac{1}{2} \left(1 - \frac{1}{n} \right) > \sum_{\substack{i=1 \\ i < j}}^n f_i f_j \quad (16)$$

holds, and, from (10), (13) and (16), the relation

$$\frac{1}{2} \left(1 - \frac{1}{n} \right) \mu^2 > \sum_{i=1}^n f_i \mu_i^2 - \mu^2 \quad (17)$$

also holds.

Consequently, from (12) and (17), we obtain the relation

$$0.2262 \mu D \left(1 - \frac{1}{n} \right) > \frac{\Delta \mu}{\mu}, \quad (18)$$

Besides, we have the relation

$$1 > \frac{\Delta\mu}{\mu} \geq 0, \quad (19)$$

because $\Delta\mu \geq 0$ as shown in (11), and because $\mu > \Delta\mu$ (i. e., $\mu = \beta + \Delta\mu$) where $\mu > 0$ and $\beta > 0$ as mentioned in p. 188 of Part I (β corresponds to the linear absorption coefficient of the residual path which excludes the 'reflecting-particle').

The value of $0.2262\mu D (1-1/n)$ is an upper limit of the magnitude of $\Delta\mu/\mu$ under consideration, and it must be less than 1. Under the assumption of $\mu > (\mu_i \sim \mu_j)$, the magnitude of $\Delta\mu/\mu$ in practice is sufficiently smaller than $0.2262\mu D (1-1/n)$. In other words, in order to expect that the magnitude of $\Delta\mu/\mu$ is less than a definite value $(\Delta\mu/\mu)_a$, the value less than $(\Delta\mu/\mu)_a/0.2262 (1-1/n)$ is safe enough for the condition of μD . This is represented by a formula

$$\mu D \leq 4.42 \frac{n}{n-1} \left(\frac{\Delta\mu}{\mu} \right)_a. \quad (20)$$

Formula (20) is not a necessary condition but a sufficient one, because the left side of (18) shows an upper limit of $\Delta\mu/\mu$. According to (20), the magnitude of μD decreases as the number n of the kinds of components increases, when a certain magnitude $(\Delta\mu/\mu)_a$ is appointed. However, whether this tendency is valid or not in practice is unknown.

The treatment by means of the assumption of $\mu > (\mu_i \sim \mu_j)$ is applicable to many examples, for instance, to many of the mixtures of rock-forming minerals, or many of the ceramic materials in which $\mu_i \sim \mu_j$ are not so large. However, in practical cases, whether μ is larger than the difference $\mu_i \sim \mu_j$ or not is unknown before carrying out quantitative analysis, because $\mu (= \sum_{i=1}^n f_i \mu_i)$ and the values of f_i 's are unknown.

Thus, we cannot but use the largest μ_i instead of μ in (20). Then, the magnitude derived from this modified formula may give a

much severer condition for μD or for the particle size D so that it gives a sufficiently safe condition.

Relation between the relative error of reflected X-ray intensity and the particle size of a mixed powder.

Let us derive the mean particle size D in a mixed powder small enough to make the relative error $\Delta I_1'/I_1'$ of reflected intensity negligible, when formula (9) is used instead of (1). The relative error $\Delta I_1'/I_1'$ is given by

$$\begin{aligned}\frac{\Delta I_1'}{I_1'} &= \frac{K_1(f_1/\mu) - K_1(f_1/\mu)\tau_1[1/(1-\Delta\mu/\mu)]}{K_1(f_1/\mu)} \\ &= 1 - \tau_1 \frac{1}{1-(\Delta\mu/\mu)}.\end{aligned}\quad (21)$$

Formula (21) can be re-written as (22) with the parameters b and c as follows:

$$\begin{aligned}\frac{\Delta I_1'}{I_1'} &= 1 - (1-b)(1+c) \\ &= b - c + bc,\end{aligned}\quad (22)$$

where

$$b = 1 - \tau_1, \quad (23)$$

$$1 > b > 0, \quad (24)$$

because τ_1 is the function with the range of $1 > \tau_1 > 0$ as already mentioned in p. 190 of Part I, and

$$c = \frac{1}{1-(\Delta\mu/\mu)} - 1, \quad (25)$$

$$c \geq 0, \quad (26)$$

because of (19).

If the values b and c are as small as negligible, (9) can be used

instead of (1). The values b and $-c$ have opposite signs and both are so small that bc may be negligible in comparison with b and c , and therefore, the smaller D among two upper limits of D values which are derived in order to suppress the values b and c under certain value should be chosen as the value of D .

Before considering the relation between particle size D and the values of b and c , the brief review of τ_1 and $\Delta\mu/\mu$ may be necessary. τ_1 is a monotonically decreasing function as $\mu_1 D_1$ (or D_1) increases as already mentioned in p. 190 of Part I. On the other hand, $\Delta\mu/\mu$ is a monotonically increasing function as D increases, as known from (3). Here, μ and μ_1 are the linear absorption coefficient of a mixture and the linear absorption coefficient of the first component (which causes X-ray reflection) respectively. D and D_1 are the mean particle size of the mixture and the mean particle size of the first component respectively.

The effect of τ_1 causes attenuation of the reflected intensity I_1 ($=I_1' - \Delta I_1'$) as particle size D_1 increases (see Part I); in other words, the value b increases as D_1 increases (also see (23)). On the other hand, the effect of $\Delta\mu$ causes augmentation (recovery) of I_1 as particle size D increases; in other words, the value $-c$ decreases as D increases (see (3) & (25)). Thus the effects on reflected intensity I_1 by τ_1 and $\Delta\mu$ have a tendency to counterbalance each other, in other words, the values b and $-c$ have this tendency on relative error $\Delta I_1'/I_1'$ as the particle size increases.

Now, let us consider the particle size to make $\Delta I_1'/I_1'$ negligible. This should be obtained from the relation between τ_1 and $\mu_1 D_1$ and from the relation between $\Delta\mu/\mu$ and μD . The relation τ_1 and $\mu_1 D_1$ can be obtained by direct reference to the numerical tables by Evans and Ekstein (1952). Accordingly, the relation between b and $\mu_1 D_1$ can also be derived from their tables and (23). On the other hand, though $\mu > (\mu_i \sim \mu_j)$ should be assumed, the relation between $\Delta\mu/\mu$ and μD , accordingly, the relation between c and μD can be calculated from

(20) and (25) as follows:

$$\mu D \leq 4.42 \frac{n}{n-1} \frac{\gamma}{1+\gamma}, \quad (27)$$

where γ is a certain value of c . In other words, in order to expect that the magnitude of c is less than a definite value γ , the value of the right-hand side of (27) is safe enough for the condition of μD . In (27), the relation $n/(n-1) < 1$ holds, because $\lim_{n \rightarrow \infty} n/(n-1) = 1$. Formula (27) as well as (20) is not a necessary condition but a sufficient one for the value of μD .

As far as the practical example of a mixed powder is concerned, D_1 may be unable to be measured though D can be measured, and therefore D must be substituted approximately for D_1 ; μ_1 can be calculated from the ideal chemical formula and ideal density of the first component, while μ cannot be calculated before carrying out quantitative analysis. Therefore, $\mu_1 D$ should be substituted for $\mu_1 D_1$ when Evans and Ekstein's table is applied, and $\mu_i D$ (where μ_i is the largest μ_i) should be substituted for μD when (27) is used. Thus, the smaller D should be chosen as the value of D , in which the smaller D can be derived from two upper limits of D in order to suppress the values of b and c under a certain value.

When $\Delta I_1'/I_1' \leq 0.1$ is required, for example, it is safe enough that both b and c are less than 0.1. According to Evans and Ekstein's table, the condition $\mu_1 D \leq 0.1$ is necessary, while according to (27), $\mu_i D \leq 0.4 < 0.4n/(n-1)$ is necessary. Thus, in this case, formula (9) can be used instead of (1) provided $\mu_1 D \leq 0.1$ and $\mu_i D \leq 0.4$ are satisfied. The smaller D , which is deduced from these two upper limits, should be chosen as the value of D .

Summary and conclusion

The intensity of X-rays reflected from a mixed powder can be given by (1), in which the self-absorption factor τ_1 and the extra

absorption coefficient $\Delta\mu$ are involved as the correction terms for the particle effects of absorption.

The self-absorption factor is always positive, less than unity in both powders of single and multiple components, and the factor is a monotonically decreasing function with the increase of particle size (see p. 190 of Part I).

The extra absorption coefficient is non-negative in the case of multiple components and it is zero in the case of single component (see (11)). The $\Delta\mu/\mu$ is less than unity and it is an increasing function with the increase of particle size, as shown in (3) and (19).

The effect of the self-absorption factor causes the attenuation of reflected X-ray intensity (see Part I), while the effect of the extra absorption coefficient causes the augmentation (see (1), (11) & (19)). Therefore, both effects have a tendency to counterbalance each other.

If (9) is used instead of (1), the relative error of reflected intensity is given by (21) or (22). The smaller D , which can be derived from two upper limits of D values in order to suppress the values b and c under a certain value, should be chosen as the required value of D .

One of two upper limits of D can be obtained by (7) (see Part I) and (23), and the other is obtained as an order of magnitude by (27) in which the largest μ_i should be used instead of μ in (27), and formula (27) has been derived under the assumption of $\mu > (\mu_i \sim \mu_j)$.

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