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Determination of Plutonium Dioxide Surface Areas from X-Ray Crystallite Sizes

INTRODUCTION

Plutonium dioxide is used as a reactor fuel and can be prepared by several different methods. Once the dioxide is formed, characterization becomes important in order to evaluate both the product and its reactivity as well as the methods of preparation. The plutonium oxide properties which can be used for characterization include chemical composition, solubility, crystallite size, surface area, particle size, lattice constant, and density (*1, 2*). Evaluation of these properties can be accomplished with varying degrees of difficulty. For example, accurate measurement of powder surface areas requires specialized apparatus and can be time consuming. Therefore, if two properties can be measured at the same time with the same sample it should be done. This paper describes an empirical relationship between plutonium dioxide surface areas and the X-ray crystallite sizes. Use of this relationship permits the oxide surface area to be determined from the easily measured X-ray crystallite size.

EXPERIMENTAL

Seven batches of plutonium dioxide were prepared by the calcination of plutonium peroxide at 400°C. Part of each batch was then ground and screened through a 48 mesh sieve. Fourteen samples of the ground and calcined oxide were then used for the surface area and crystallize size analyses. Prior to measuring the surface areas, each sample was outgassed under a vacuum of 10^{-4} Pa at 400°C. In order to increase the data base for exploring the relationship between surface area and crystallite size, data from earlier investigations (*1–4*) were also included. The criteria for selecting the additional data were a minimum calcining temperature of 400°C and, in the case of multiple types of samples, the highest calcining temperature reported. Methods of preparation for these samples included peroxide, oxalate, nitrate, and hydroxide calcination(*1*) and oxidation of the metal (*2–4*).

Surface areas were measured by this author using the BET technique (*5*) with nitrogen as the adsorbate. In all cases the samples were outgassed under vacuum prior to measuring the nitrogen adsorption. The precise methods used for the other data (*1, 2*) are either unknown or poorly described. The surface areas were measured with a Perkin-Elmer adsorbtometer but the pretreatment of the samples is unknown.

Crystallite sizes were determined from the powder X-ray diffraction patterns obtained from the oxide. Average crystallite sizes were calculated using the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta_{1/2} \cos \theta} \tag{1}$$

where λ is the wave length of the incident radiation, $\beta_{1/2}$ the width at half-maximum of the *hkl* (220) peak, and θ is the Bragg angle of diffraction. The computer program used to make the calculation also took into account instrument broadening.

RESULTS AND DISCUSSION

Surface areas and crystallite sizes obtained in the present investigation as well as those measured earlier are summarized in

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TABLE 1

Surface Areas and Crystallite Sizes for Plutonium Dioxide

Sample	Oxide source	Calcining temp. (°C)	Surface area (m^2/g)	Crystallite size (Å)
1	Peroxide	400	14.3	125
2	Peroxide	400	16.7	109
3	Peroxide	400	19.9	103
4	Peroxide	400	16.6	133
5	Peroxide	400	19.4	112
6	Peroxide	400	18.9	117
7	Peroxide	400	20.9	107
8	Peroxide	400	17.5	126
9	Peroxide	400	19.0	104
10	Peroxide	400	19.2	109
11	Peroxide	400	19.0	104
12	Peroxide	400	17.7	101
13	Peroxide	400	19.7	117
14	Peroxide	400	21.4	86
15	Metal (*2*)	300	13.6	122
16	Metal (*2*)	500	11.3	167
17	Metal (*2*)	700	7.6	269
18	Metal (*2*)	900	5.4	442
19	Metal (*3*)	100	16.9	97
20	Metal (*3*)	800	6.5	260
21	Metal (*4*)	800	3.5	682
22	Peroxide (*1*)	600	8.9	277
23	Nitrate (*1*)	400	11.5	130
24	Oxalate (*1*)	400	41.4	57
25	Hydroxide (*1*)	600	22.3	100

Table 1. A superficial examination shows that as the crystallite size decreases the surface area increases. The following discussion will show that this change is systematic and predictable.

The term "surface area" can be defined as the sum of the surface area of nonporous particles, the external surface area, or the surface area of particles having porosity or fine structure, the internal surface area. Microscopic measurement of particles determines only the external surface areas. Measurement of surface areas by adsorption methods determines the internal or total surface area of a particle. The difference between these two methods is more a question of degree of resolution or penetration and there is no sharp boundary between the two.

The specific surface area of a sphere or cube is related to its projected diameter or edge length by the equation

$$S = \frac{6}{\rho D} \tag{2}$$

where S is the area, ρ the density, and D the particle diameter or edge length. For nonstandard particles the factor 6 must be replaced by the ratio, α_s/α_v, of the shape and volume factors (*6*, *7*). Therefore, the equation describing the total surface area per unit weight becomes

$$S_w = \frac{\alpha_s \Sigma D_i^2 n_i}{\alpha_v \rho \Sigma D_i^3 n_i}. \tag{3}$$

By performing a statistical analysis of the particle diameters using a log normal distribution, the surface area of a powder may be calculated using the equation (*8*)

$$\log S_w = \log \frac{\alpha_s}{\alpha_v} \rho - \log D_g - 5.757 \log^2 \sigma_g. \tag{4}$$

In this case, D_g is the geometric mean particle size and σ_g the geometric standard deviation. The practical use of this equation requires that the particle sizes obey a log normal distribution. Particles analyzed in this investigation did not satisfactorily follow a log normal distribution. Therefore, alternative methods for determining total surface areas needed to be investigated.

One problem with using particle sizes when calculating a total surface area is that most particles have some "internal area." Even well-crystallized materials may contain crystallites which produce an internal area greatly exceeding the external area determined from the particle diameter. For example, if particles 0.1 μm in diameter are composed of crystallites 0.01 μm long the external area would be on the order of 100 times smaller than the internal surface areas.

Allred *et al.* (*9*) have seemingly eliminated the problem of external versus internal surface area when they substituted the crystallite size for the particle diameter in Eq. (2). Evaluation of surface area and X-ray crystallite size data for thorium oxide showed the data fit an equation of the form

$$S = \frac{6}{\rho D}\frac{1}{F} \quad (5)$$

where F is a packing factor indicative of the relative crystallite surface unavailable for nitrogen adsorption. For S in m²/g and D in Angstroms the average value for the SD product for all thorium oxides was 3600. Results obtained by Brey and Davis (*10*) on thorium oxide also confirm the relationship between surface area and crystallite size found by Allred. However, they also found that the surface area–crystallite size relationship could be affected by preparation techniques and calcination temperature.

Crystallite size and surface area data obtained during this investigation have little variation (Table 1). Therefore, data from earlier investigations (*3*, *4*) and other workers (*1*, *2*) were combined for this analysis. Figure 1 shows the theoretical relationship between surface area and crystallite size which was obtained using Eq. (2). Also shown in Fig. 1 is the actual relationship obtained for a wide variety of plutonium dioxide samples. These data fit Eq. (5) where ρ was taken as 11.46 g/cm³. The packing factor (F) was calculated to be 3.22. From Eq. (5) it follows that the SD product becomes

$$SD = 1625. \quad (6)$$

Upon further examination of the data it was determined that an exponential function would empirically fit the data. The equation used was

$$S = A(1)e^{-\ln D/N} + A(2) \quad (7)$$

where $A(1)$ and $A(2)$ are constants and N is

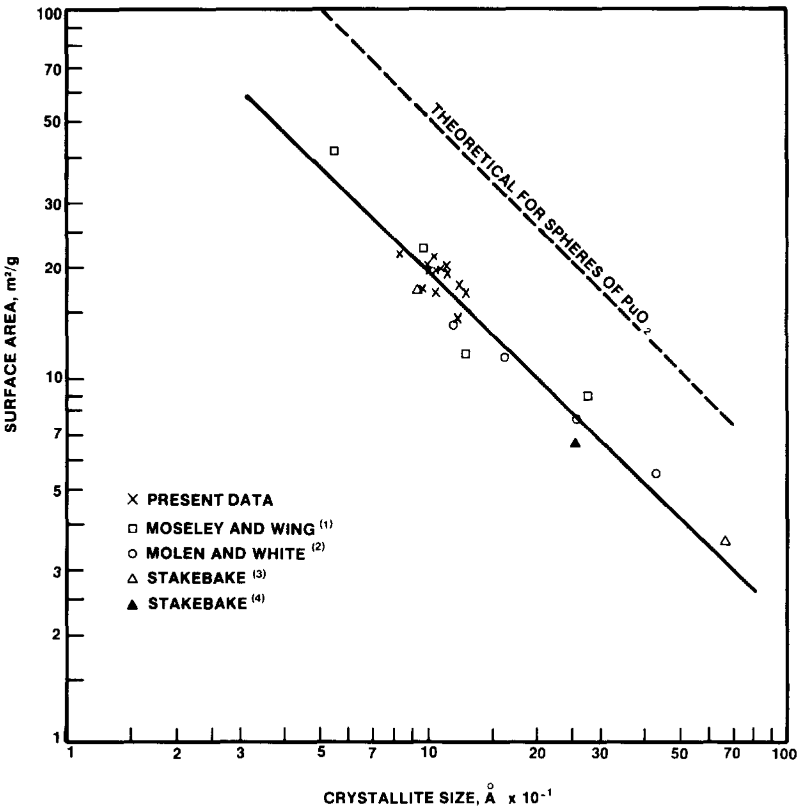

FIG. 1. Relationship between surface area and the average X-ray crystallite size for plutonium dioxide.

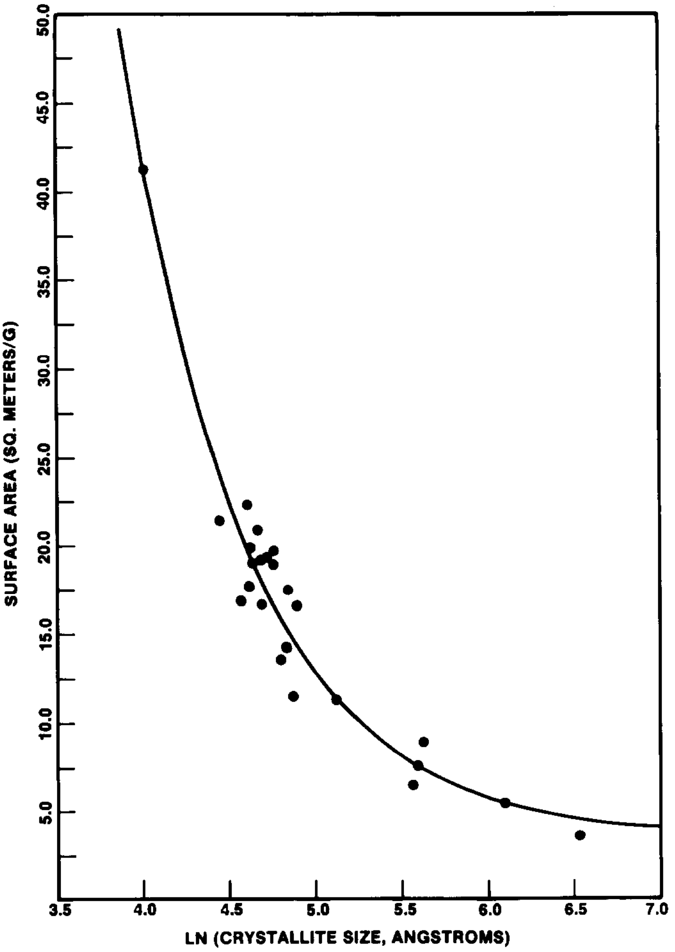

FIG. 2. Empirical relationship between surface area and average X-ray crystallite size for plutonium dioxide.

the nonlinear parameter determined by the regression analysis. Following the regression analysis this equation was reduced to

$$S = 1.12 \times 10^4 e^{-1.41 \ln D} + 3.33. \quad (8)$$

Figure 2 shows a plot of the experimental values and the predicted fit. The error in the surface areas calculated using Eq. (8) and measured crystallite sizes was ±2 m^2/g at the 68% confidence level. This empirical model is not valid for surface areas less than 3 m^2/g or crystallite sizes greater than 1000 Å.

Data shown in Figs. 1 and 2 were obtained using plutonium dioxide formed by peroxide, oxalate, nitrate, and hydroxide calcination, and metal oxidation. The relationship between surface area and crystallite size appeared to be independent of the method of preparation. It should be noted, however, that not all of the data available in the literature were used in this analysis. The reason for this was that some of the measured values were thought to be in error. Recently it has been found that adsorbed water decreased the measured surface area of plutonium dioxide (*11*). This same phenomenon appeared to be occurring with the sample outgassed at 100°C in Ref. (*2*). Most of the experimental details of the earlier investigations are unknown. Therefore, the extent of the problem of water and other factors affecting surface area values was uncertain. Because of the potential sources of error, samples which were outgassed at temperatures less than 300°C were excluded from this analysis. The exception to this was the sample prepared by metal oxidation at 100°C. Since the oxidation was done in dry air the oxide was assumed free of adsorbed water.

Although it was not observed in this investigation, there are other factors which may affect the relationship described by Eqs. (6) and (8). One such factor is a process which would increase the porosity of the oxide without changing the crystallite size (*10*). Another factor is the level of impurities in the oxide or an oxide sample with a range of stoichiometries.

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