

DETERMINATION OF CRYSTALLITE SIZE IN UO_{2+x} POWDER BY X-RAY DIFFRACTION

H.G. RIELLA, L.G. MARTINEZ and K. IMAKUMA

Diretoria de Materiais Nucleares, Instituto de Pesquisas Energéticas e Nucleares, CNEN/SP, Sao Paulo, Brazil

An X-ray diffraction method was applied to measure the mean crystallite size (MCS) of the UO_{2+x} powder, where x varied from 0.10 to 0.20. The MCS determination of UO_{2+x} powder plays an important role in the process control of UO_2 pellets productions. The method is based on the Fourier analysis of X-ray diffraction profiles corrected for instrumental line broadening. The MCS was derived after performing appropriate correction of the diffraction profile to minimize the effect due to the presence of very low amount of the U_4O_9 phase in UO_{2+x} powders.

1. Introduction

Uranium 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 uranium dioxide properties which can be used for characterization include chemical composition, crystallite size, surface area, O/U ratio, flowability and bulk density. 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.

An important measure for the sinterability of powder is its surface area [1]. However, the specific surface area does not provide an absolute standard but only gives a relative comparison of powders which came from the same production line but have undergone different thermal treatments [2]. Several powders of equal surface areas, which, however, were prepared by different processes, have been found to exhibit strong differences in sintering behavior.

The crystallite sizes determined by X-ray diffraction are said to allow a general statement concerning the sintering behavior. The X-ray powder diffraction method is a non-destructive technique and it averages a reasonable volume. From the analysis of X-ray diffraction line profiles measures for deviations from the perfect crystal structure can be obtained. Principal imperfections are crystallite size and lattice distortions. For the analysis of the peak shape several methods have been proposed. Much work has been done using the integral breadth and full width at half maximum [3]. For a more detailed analysis a variance method [4] and a Fourier series method [5] are avail-

able. In this paper, we will confine our attention to crystallite size analysis using Fourier series representations of the measured line profiles.

2. X-ray method

A line profile h measured on a specimen containing structural imperfections is determined by [5]:

- the structural imperfections to be investigated which cause line broadening effects contained in the structurally broadened profile,
- the non-ideal geometry of the diffractometer, and
- the wave length distribution.

Usually (a) and (b) are taken together into a function g called the standard line profile. The line profile h can be described by a convolution [6]

$$h(x) = \int_{-\infty}^{+\infty} f(y) \cdot g(x-y) dy. \quad (1)$$

Since convolution of functions is equivalent to multiplication of the complex Fourier coefficients of these functions, deconvolution can be accomplished using

$$F(n) = H(n)/G(n), \quad (2)$$

where $F(n)$, $G(n)$ and $H(n)$ are the Fourier coefficients of the profiles f , g and h respectively, normalized such that $F(0) = G(0) = H(0) = 1$, and n is the harmonic number.

X-ray diffraction peaks are represented in the Warren-Averbach analysis [7] by a Fourier series, and the coefficients of the sample and standard peaks are used to compute the coefficients for the broadening function by the method of Stokes [8]. All forms of instrumental broadening are eliminated from the broadening function by this technique. The intensity of an X-ray diffraction peak expressed as a Fourier series is given by

$$I(h_3) = K(\theta) \sum_{-1/2}^{+1/2} A(n) \cos(2\pi h_3) + B(n) \sin(2\pi h_3), \quad (3)$$

where θ is the Bragg angle and h_3 is a continuous variable characterizing a position in reciprocal space in a direction perpendicular to the diffracting planes. If $A(n)$ and $B(n)$ are coefficients derived for the broadening function, they can be defined by the expression

$$F(n) = A(n) + iB(n), \quad (4)$$

with

$$A(n) = \exp(-n/\bar{N}_3) \cos(2\pi nH\bar{e}_n) \quad (5)$$

and

$$B(n) = \exp(-n/\bar{N}_3) \sin(2\pi nH\bar{e}_n), \quad (6)$$

where \bar{e}_n is the strain average in a column of n cells, \bar{N}_3 the average number of cells of a column normal to the diffracting planes and H is the order of the reflection.

The mean crystallite size in nanometer (nm) units is then given by [5]

$$\bar{D} = 0.1 \bar{N}_3 a_3. \quad (7)$$

The pseudo lattice parameter a_3 is computed from the expression

$$a_3 = \lambda/4(\sin\theta_2 - \sin\theta_0), \quad (8)$$

where λ is the X-ray wavelength in angström units, $2\theta_0$ is the position of the peak of the line radians; and $(2\theta_2 - 2\theta_0)$ is one-half the total interval $(2\theta_1 - 2\theta_2)$ of the Fourier expansion of the line profile.

3. Experimental procedure

The diffraction profile measured on a UO_{2+x} , where x ranges from 0.10 to 0.20, consists of an equipment broadening function and the physical profile whose broadening is caused by the limited size of the coherently scattering domains, the lattice distortion, O/U distribution inside each powder particle and presence of U_4O_9 phase.

The line profile due to the instrumental conditions was obtained from measured line profile of the silicon standard. Fig. 1a shows the measured (111) profile of the standard silicon specimen. The elimination of instrumental effect is the first step of the calculation to achieve the pure diffraction profile from the observed profile.

The elimination of the effects, caused by O/U distribution and the presence of the U_4O_9 phase, was carried out by performing an additional heat treatment of the UO_{2+x} specimen at 500°C for 3 h under hydrogen atmo-

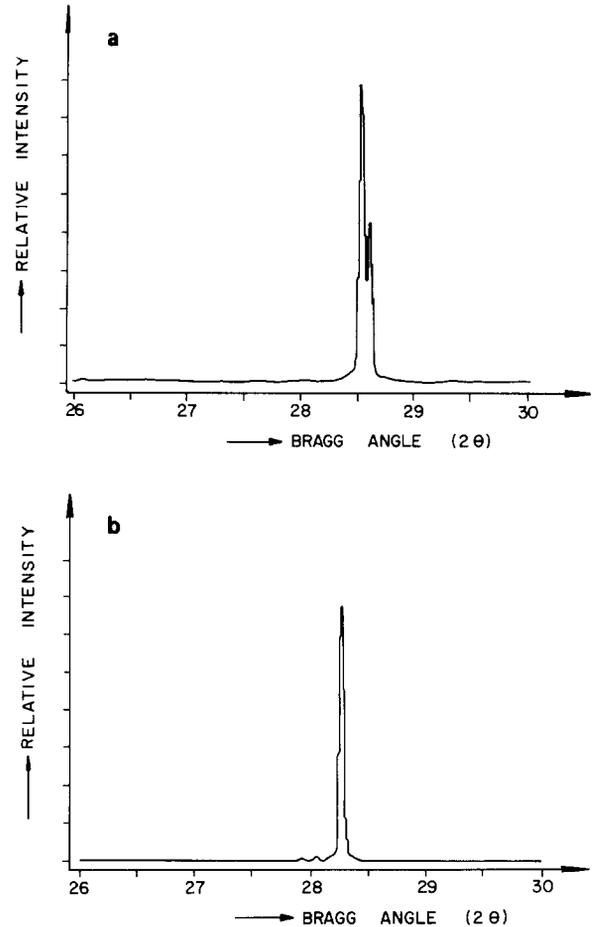


Fig. 1. (a) Measured X-ray diffraction profile of the silicon standard sample. (b) Profile of the silicon standard after correction for the contribution of the K_{α_2} line.

sphere; the reduced UO_2 specimen was encapsulated, as to avoid reoxidation, and a new X-ray diffraction profile was measured. Figs. 2a and 2b show the measured profile of specimen I before and after reduction treatment. In fig. 2b a decrease of the profile shape after reduction is observed. The mathematical procedure for correcting the effects due to O/U distribution and to the presence of U_4O_9 will be described later.

The effects of strain distribution and crystallite size can be distinguished using eqs. (5) and (6), which gives [5]

$$\bar{e}_n = \frac{\arctan B(n)/A(n)}{2\pi nH}. \quad (8)$$

From eq. (8), \bar{N}_3 can be derived with the help of eq. (5) and consequently the D value is obtained.

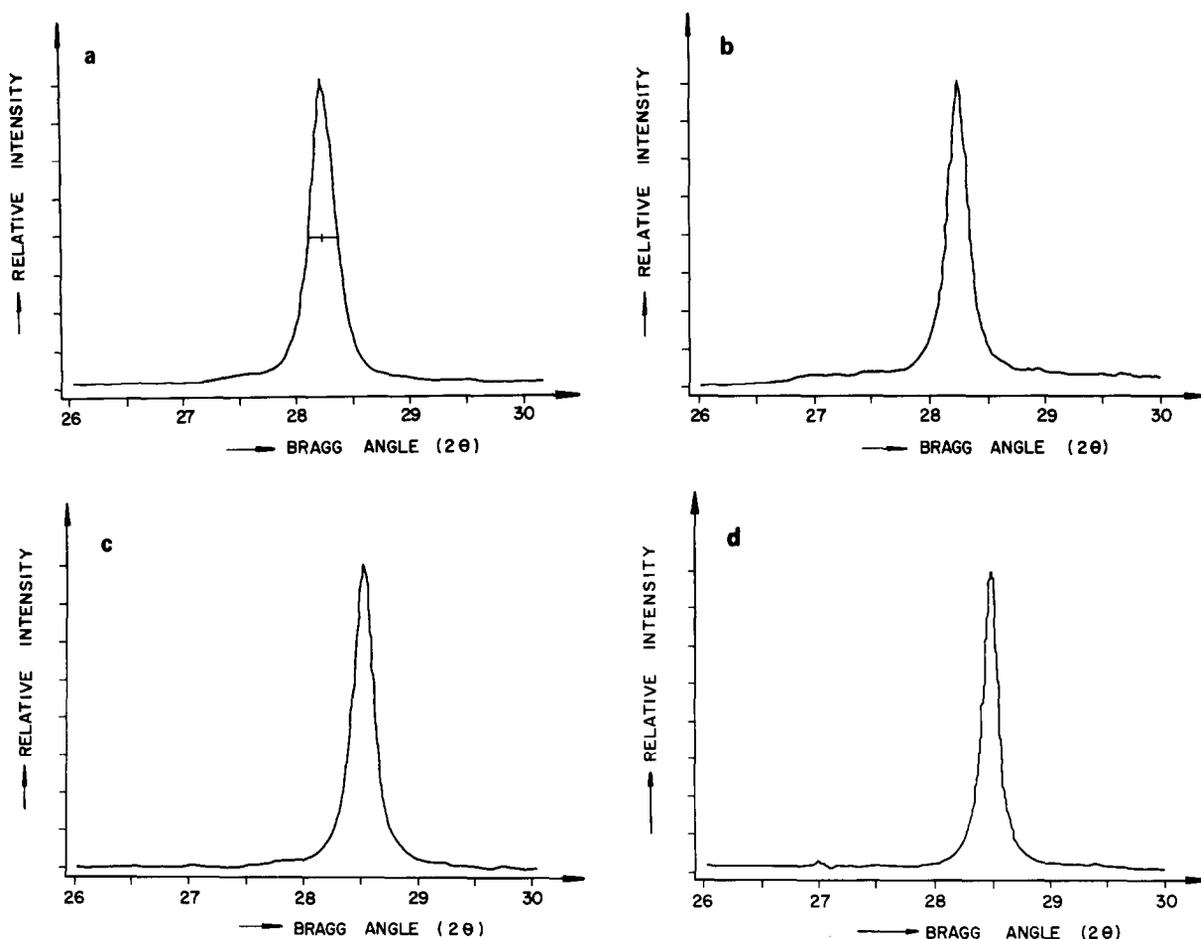


Fig. 2. (a) Measured X-ray diffraction profile of UO_{2+x} (sample I). (b) Measured profile of sample I, after heat treatment (500°C, H_2 , 3 h). (c) Measured X-ray diffraction profile after instrumental effects separation. (d) X-ray profile of heat treated sample I corrected for the contribution of the $K_{\alpha 2}$ line and instrumental effects.

The profiles were step-scanned according to the preset time method on a Rigaku SG-8 diffractometer equipped with an X-ray tube (cooper) operated at 40 kV and 20 mA. The line profiles of the (111)-reflections from a standard silicon powder and UO_{2+x} powder were recorded applying the CuK_{α} doublet. The $Cu-K_{\alpha 2}$ component was separated from the composite doublet by Gangulee's procedure, fig. 1b [7].

The line profiles were corrected for the background by linear interpolations. Choosing much too low background can cause oscillations of the Fourier coefficients at low harmonic values. On the other hand, taking the background too high produces a large "hook effect" [9].

4. Results and discussion

Various UO_{2+x} powder samples, obtained from reduction of AUC powder, were examined by X-ray diffraction. The brief understanding of the variation of Fourier coefficients due to effects of O/U distribution and U_4O_9 phase was considered to be important before starting the analysis of these effects on the determination of the mean crystallite size.

Figs. 2c and 2d describe the intensity distribution after deconvolution by means of a silicon standard (fig. 1b). It is observed a lower peak area (fig. 2d) than the peak area of profile shown in fig. 2c. This means that the O/U distribution and U_4O_9 phase produces a significant broadening of the X-ray diffraction profile. The domain size function produces a symmetrical enlargement of diffrac-

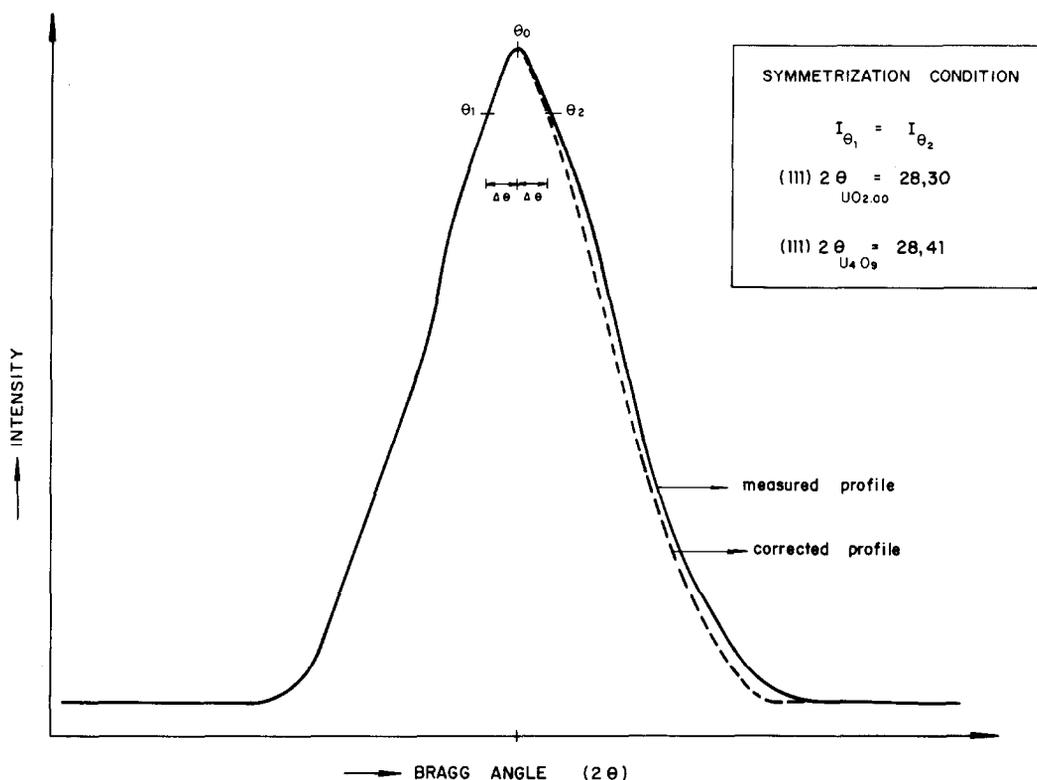


Fig. 3. Schematical representation of an X-ray profile. The dotted line represents the profile corrected by a symmetrization method.

tion profile [5]. Neglecting the influence of O/U distribution on the broadening of the diffraction profile, the effect of the presence of U_4O_9 can be corrected by a symmetrization of the measured profile after performing the deconvolution (fig. 3).

Fig. 4. shows the variation of the Fourier coefficients with the harmonic number for a profile corrected by deconvolution. A strong decrease of the coefficients with the harmonic number for the non symmetric Fourier function suggests that the U_4O_9 phase stimulates a significant broadening of the diffraction profile. Fig. 5 shows another effect of peak broadening produced by O/U distribution, which prevails even after the correction of U_4O_9 enlargement effect. This remaining effect is eliminated when the UO_{2+x} powder is heat-treated at $500^\circ C$ for 3 h under hydrogen atmosphere.

Table 1 summarizes the mean crystallite dimensions of several UO_{2+x} powder samples derived by different approaches of calculation. It can be concluded, from table 1, that the determination of the mean crystallite size performed on the as-produced powder is affected by considerable error sources.

A possible relationship between the surface areas and

X-ray mean crystallite sizes of uranium dioxides is discussed. This kind of dependence could be associated to the X-ray mean crystallite size value and to the oxide surface area. The surface areas and the crystallite sizes investigated in this work are summarized in table 2.

A rough examination shows that mean crystallite size decreases while the surface area increases. Nevertheless, an empirical relationship between surface area and mean crystallite size in this work was not possible to be established since the surface area is dependent of the preparation route. The establishment of a relationship between crystallite sizes and the sinterabilities of the powder oxides seems to be more significant and this is the subject of our future investigation.

Acknowledgements

The authors express their thanks to B. Sc. Newton Itiro Morimoto for assistance with the micro-computer calculations. One of the authors, L.G. Martinez, wishes to thank FAPESP, Fundação de Amparo à Pesquisa do Estado de São Paulo for the financial support given under contract

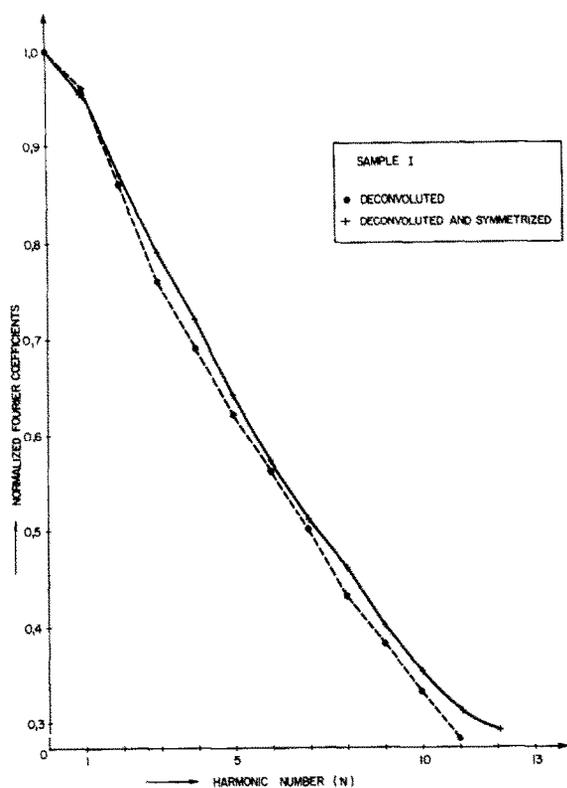


Fig. 4. Normalized Fourier coefficients of deconvoluted and deconvoluted-symmetrized profiles.

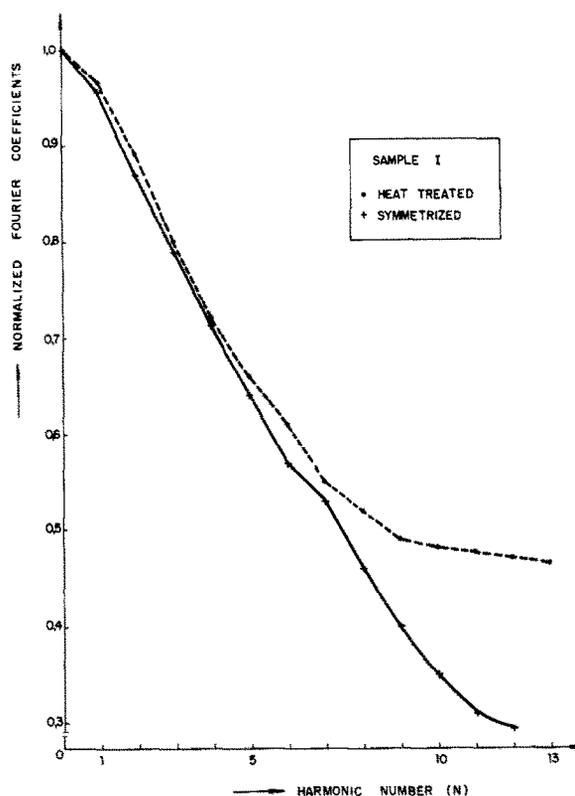


Fig. 5. Normalized Fourier coefficients of heat treated samples after deconvolution and symmetrization.

Table 1

The mean crystallite size (nm) of several UO_{2+x} powder samples by different approaches of calculation

Sample	Production UO_{2+x}	After symmetrization UO_{2+x}	After heat-treatment $UO_{2.0}$
I	44	46	65
II	50	55	70
III	60	69	75

Table 2

The variation of the mean crystallite size with the surface area of uranium dioxide powders

Sample	Surface area (m^2/g)	Mean crystallite size (nm)	O/U ratio
I	7.0	65	2.17
II	6.2	70	2.12
III	5.1	75	2.09

No. 85/2518-5 that enabled part of the work mentioned in the paper to be carried out.

References

- [1] E.J. Ramm and C.E. Webb, AAEC -E- 250 (1972).
- [2] D. Vollath, in: Gmelin Handbook of Inorganic Chemistry, supplement volume C4 (Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1984) p. 76.
- [3] H.D. Klug and L.E. Alexander, X-ray Diffraction Procedures (John Wiley & Sons, New York, 1958).
- [4] A.J.C. Wilson, Elements of X-ray Crystallography (Addison Wesley, Reading, MA, 1970).
- [5] H.G. Riella, KFK-Bericht 3619 (1983).
- [6] R. Delhez, Th. H. de Keijser and E.J. Mittemeijer, in: National Bureau of Standard Special Publication 567 (1980) p. 213.
- [7] B.E. Warren and B.L. Averbach, J. Appl. Phys. 21 (1950) 595.
- [8] A.R. Stokes, Proc. Phys. Soc. 61 (1948) 382.
- [9] H.G. Riella and D. Vollath, J. Nucl. Mater. 106 (1982) 93.