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The use of X-ray diffraction peak-broadening analysis to characterize ground Al_2O_3 powders

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X-ray peak broadening has been used to study the milling behaviour of a number of commercial alumina powders. It is shown that the milling behaviour is dependent upon the original particle size, internal defects in particles and the milling liquid used. Peak-broadening studies allow the effects of milling upon reduction of crystallite size and increase in stored energy to be separated. The effect of these two parameters was separated using the Cauchy correction method. Measurement of the particle size of the unmilled alumina powders in the transmission electron microscope was used to determine that the Cauchy method gave the most correct estimation of crystallite size. Both alumina crystallite size and stored energy are expected to enhance sintering of the powder to a high density. Attempts are made to predict the sintering ability of the materials studied in terms of the above parameters.

1. Introduction

In the production of sintered aluminium oxide based ceramic bodies, milling of the raw materials is one of the most important steps. The aim is not only to obtain a suitable grain size, but also to "mechanically activate the materials" [1]. Crystal lattice distortions and defects as well as micro-strains are important sources of stored energy. This energy will be of significant importance in the activation of the sintering process during which the material is heated to elevated temperatures.

There is a need for a method to characterize the properties of a ground starting material, such as aluminium oxide. Grain or particle size can be measured by a number of methods. In a recent review by Allen [2], a series of different physical techniques were listed that could measure the particle size. However, methods to measure the more diffuse term of stored energy are rare.

In fact, practical sintering experiments have, in the past, been mainly used to study the sintering ability of a ground powder. Undoubtedly this is the best way as it gives a true picture of the sintering ability. On the other hand, it has two drawbacks. It is quite time consuming and it is a rather expensive method. Thus, there is a need for a characterization method that is more rapid and cheaper.

This is a suitable task for X-ray diffraction. Both crystallite size and micro-strains in the crystals will cause broadening of the X-ray diffraction peaks. The use of peak-broadening analysis for this concept is a well-known technique and the main features have been reviewed in the textbook of Klug and Alexander [3]. The method will give an integrated picture of a great number of crystallites and it has its optimal sensitivity for materials with a mean crystal size smaller than about 0.3 μm, which is the area of interest concerning milled alumina powders. Ziegler has used an advanced X-ray diffraction technique to measure the structural changes of ground aluminium oxide powders [4–6]. He found that the X-ray peak-broadening analysis gave a good measure of the

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TABLE I Diffraction peaks and measurement parameters used

Peak no.	alpha-Al_2O_3			Measurement parameters		
	hkl	*d* (nm)	$2\theta^\circ_{Cu}$	Angle interval, $2\theta^\circ$	Step length ($2\theta^\circ$)	Time (sec/step)
1	012	0.348	25.5	25.0–26.5	0.01	2
2	113	0.209	43.3	42.8–44.5	0.01	2
3	116	0.160	57.5	57.0–58.5	0.01	2
4	030	0.138	68.2	67.7–69.5	0.01	2
5	226	0.104	95.2	94.7–96.5	0.01	10

enhanced activity of the powders caused by milling.

As a part of an extensive study of the mechanical activation of ceramic powders and their influence upon the subsequent properties of sintered ceramic bodies, X-ray diffraction measurements was one of the techniques used to characterize the starting materials. In this publication is reported the change in peak broadening of aluminium oxide ground in water or acetone for up to 10 days and from these data the changes in crystallite size and lattice distortions ("stored energy") are calculated. The particle size of the unground powder has also been directly determined by transmission electron microscopy. This information indicates which of the X-ray methods yields the best estimate of alumina grain size.

This report demonstrates the usefulness of the X-ray diffraction method for the determination of crystallite size. The method can be used for any crystalline ceramic powder.

2. Materials studied

The aluminium oxide starting materials were four commercially available and often used alumina powders for technically advanced ceramics. These will be denoted by the numbers 1 to 4 in the following text. All powders have been ground in water for times up to 9 days and in acetone for times up to 10 days. In total about 60 samples have been carefully measured.

3. The X-ray method used

Grinding of Al_2O_3 powder will cause the measured X-ray diffraction peaks to broaden. However, the effects are quite small, which means that accurate measurements are a necessity. The instrumental conditions have, therefore, been optimized to give good measuring statistics with a reasonable measuring time. Several peaks have been measured for each sample to allow the effects of crystallite size and lattice distortions to be separated. A summary of the parameters used to measure each of the five alpha-Al_2O_3 peaks selected for this study is given in Table I.

All samples have been measured using a Rigaku X-ray powder diffractometer equipped with a graphite monochromator and a rotating anode that has been operated at 50 kV and 190 mA, i.e. 9500 W. All data have been collected using Cu$K\alpha$ radiation and by operating the equipment in a step scan mode with 0.01° in 2θ per step. The recorded data was plotted on an X-ray diagram with an extended scale so that 1° in 2θ corresponds to 10 cm. Using this scale the peak widths could be measured with the accuracy of a step size, i.e. ±0.01° in 2θ.

The peak widths have been measured at one third of the peak heights. Such widths can be accurately measured, but are composed of both the alpha$_1$- and alpha$_2$-components from each peak. The alpha$_2$-contribution has been eliminated and the peak width of only the alpha$_1$-peak at half its height has been calculated by a graphical correction method [7]. In the correction method the alpha$_1$- and alpha$_2$-peaks have been assumed to be identical in shape and with a peak shape being described by a simple exponential function. The separation of the two peak positions in 2θ degrees is obtained from the Bragg equation for every pair of peaks and the known alpha$_1$- and alpha$_2$-wavelengths. This method can give rise to a systematic error in the calculated values, as the peak shapes have been assumed to be described by the same simple function. However, as a relative comparison is attempted using the same correction routines, the results will not be biased.

4. Results of the peak-broadening analysis

The measured and uncorrected peak widths obtained for the various grinding times are summarized in Figs. 1 to 3. The relative change of the

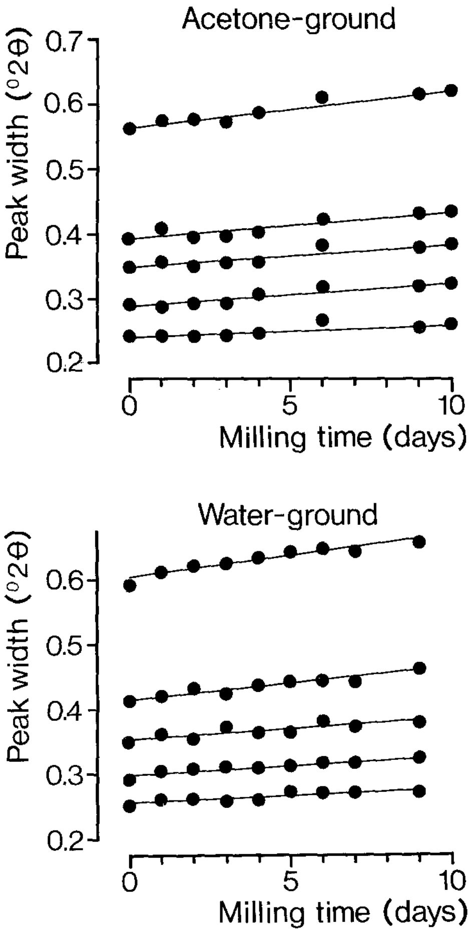

Figure 1 The uncorrected measured X-ray diffraction peak widths of material 1 as obtained after different milling times.

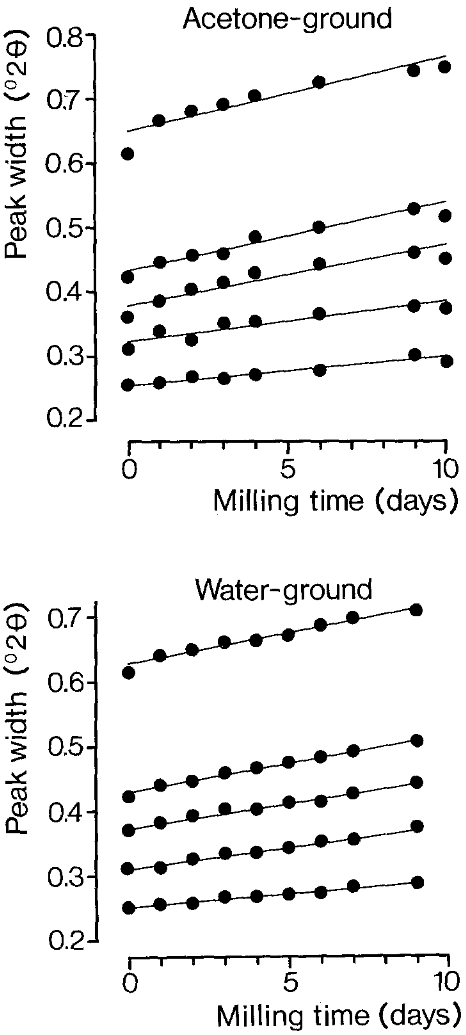

Figure 2 The uncorrected measured X-ray diffraction peak widths of powder 3 ground in water or acetone.

peak widths for a particular unground starting material is easily visualized, especially for the peaks at high 2θ-angles. In this form, the measured data can already be used as quick guide to the state of "mechanical activation". This requires, however, previous experience to relate this information to its effect upon sintering properties. In all these diagrams it can be seen that grinding of the aluminium oxide causes the diffraction peaks to broaden. The broadening of the peaks is approximated as a linear function of grinding time.

It is of interest to obtain more detailed information on the milling process of a material, both regarding the reduction of crystallite size as well as the increase of its stored energy in the form of lattice distortions. To obtain this information the widths of only the alpha$_1$-component peak at half of the peak maximum, called beta, have been calculated. For each sample, all the five alpha-Al_2O_3 diffraction peaks selected for measurement have been plotted as (beta $\cos\theta$) against $\sin\theta$. Example of one such diagram for alumina powder no. 3 ground in water is shown in Fig. 4. When plotted in this way all data should fall upon a straight line, the slope of which is a relative measure of the average lattice distortions. The reciprocal of the intercept on the (beta $\cos\theta$)-axis gives a relative measure of the mean crystallite size. From such a plot it can thus be seen that the peak broadening has two sources. First of all, grinding changes the intercept on the ordinate, i.e. a decrease in crystallite size occurs. Secondly, an increase in the slope of the plot indicates a significant increase in lattice distortion with grinding time. It is now evident why it is important to plot (beta $\cos\theta$)

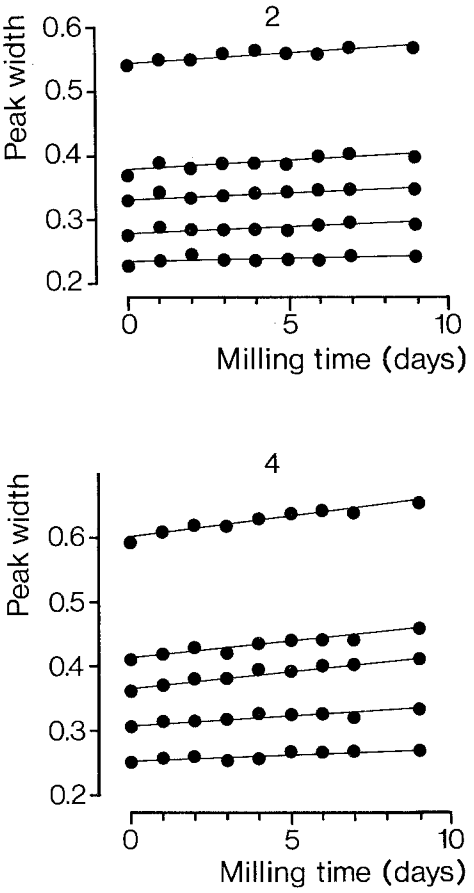

Figure 3 The uncorrected measured X-ray diffraction peak widths of materials 2 and 4 ground in water for different times.

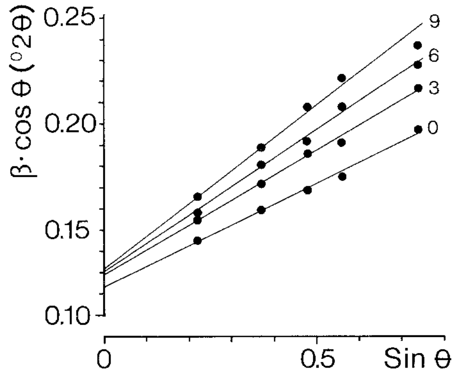

Figure 4 The calculated peak widths at half of the peak height plotted against $\sin\theta$ for material 3 ground in water. The figures denote the unground and the 3, 6 and 9 days ground samples.

against $\sin\theta$. The increase in the stored energy of the crystals due to lattice distortions and microstrains is as important as a reduction in crystallite size in this material. These findings strongly support Naeser's [1] contention that the so-called "mechanical activation" of solids is very important. Also, two different materials can behave quite differently upon grinding, as will be seen below.

Finally, the "absolute values" for crystallite sizes and lattice distortions, will be calculated. First of all, however, it must be stressed that a number of factors can influence the magnitude of "absolute values" obtained and they have to be used with some care. Besides the influence of statistical errors upon the measured parameters, the calculation method used is also of great importance. For instance, the method to measure peak widths, as well as that used to strip away the alpha$_2$-component, will give slightly different results. Also the reduction functions used (i.e. "Cauchy", "Gauss" or "Kochendörfer") will give clearly different results for the crystallite size and lattice distortions [4]. Thus, the "absolute values" obtained from peak-broadening measurements are always to a great extent relative values and depend upon the analytical method applied. However, if the same method is used, the relative changes in the properties of a series of ground aluminium oxide materials may well be discussed.

To calculate the absolute values mentioned the peak broadening caused by the instrument setup itself has first to be separated. Therefore, the unground sample of alumina no. 1 was heated at 1500° C for 4 h. Very sharp and well-defined X-ray diffraction peaks were obtained for this sample. The peak widths were measured in the same way as for all the other samples and these values, representative of the "instrument broadening", will be called b in the formula given below. In addition, X represents the true width of the X-ray diffraction peak, (a measure of its physical state) and β is, as before, the measured peak width). Three different ways are discussed by Ziegler [4] to separate the instrument broadening:

$$X = \beta^2 - b^2 \quad \text{(Gauss)}$$

$$X = \beta - b \quad \text{(Cauchy)}$$

$$X = \beta - \frac{b^2}{\beta} \quad \text{(empirical)}$$

Ziegler came to the conclusion that the empirical

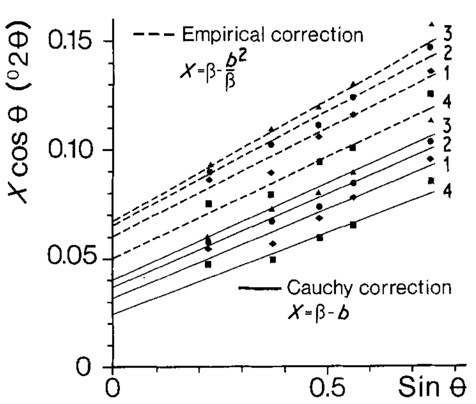

Figure 5 A comparison of the obtained values for the unground starting materials after using two different methods for the correction of instrumental broadening, cf. text. The dashed line denotes empirical correction, the full line Cauchy correction and numerals 1 to 4 denote the four alumina powders investigated.

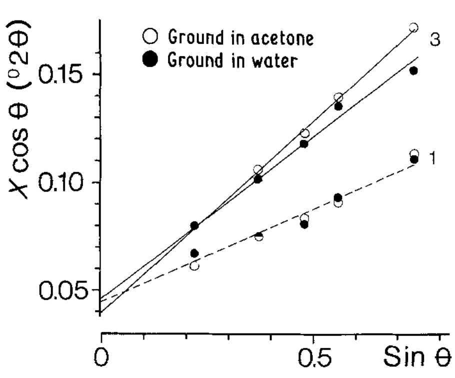

Figure 6 The two alumina materials 1 and 3 ground in water or acetone for 9 or 10 days, respectively. The values are corrected for instrumental broadening according to Cauchy.

method represented a very good approximation, with values that fall between the values obtained by the other two methods [8, 9]. However, lattice distortions are best approximated by the Gauss distribution and crystallite size best by the Cauchy distribution.

The use of one or other of the correction methods gives significantly different levels for the X-values, as illustrated in Fig. 5. In addition, several expressions exist to describe how the X-values are comprised of the two components X_C and X_D where X_C describes crystallite size broadening and X_D lattice distortion broadening. For instance:

$$X = X_C + X_D \quad \text{(Cauchy)}$$

$$X = X_C^2 + X_D^2 \quad \text{(Gauss)}.$$

Calculations made by us for different correction methods, as well as evaluation of X_C and X_D by different formulae, gave significantly different values for crystallite size and stored energy. The use of the different correction methods did not alter the relationship of the individual values to one another. A relative comparison is therefore always possible. On the other hand, results from the transmission electron microscopy study reported below showed that the best fit was obtained for the Cauchy correction and a Cauchy function to describe the broadening. Thus

$$X = X_C + X_D.$$

From the Scherrer equation we know that

$$X_c = \frac{K\lambda}{D\cos\theta}$$

where K is the shape factor, λ the X-ray wavelength, θ the Bragg diffraction angle and D the mean crystallite size.

In addition, by differentiating the Bragg equation with respect to the Bragg angle, θ, we obtain:

$$X_D = 2\Delta\theta = 4\frac{\Delta d}{d}\tan\theta.$$

Substituting these expressions in the Cauchy function gives

$$X = X_C + X_D = \frac{K\lambda}{D\cos\theta} + 4\frac{\Delta d}{d}\tan\theta.$$

This formula can be rewritten as

$$X\cos\theta = \frac{K\lambda}{D} + 4\frac{\Delta d}{d}\sin\theta,$$

which means that a straight line relationship should be obtained upon plotting ($X\cos\theta$) against $\sin\theta$. The intercept on the ($X\cos\theta$) axis will allow calculation of the "absolute value" of the mean crystallite size. Similarly from the slope of the line the average lattice distortions $\Delta d/d$ can be obtained.

Fig. 6 illustrates typical plots and that different materials exhibit significantly different behaviour upon being milled. The behaviour also depends upon the milling liquid used. The plot in Fig. 6 has to be compared with the plot of the Cauchy corrected values of the corresponding unground materials shown in Fig. 5.

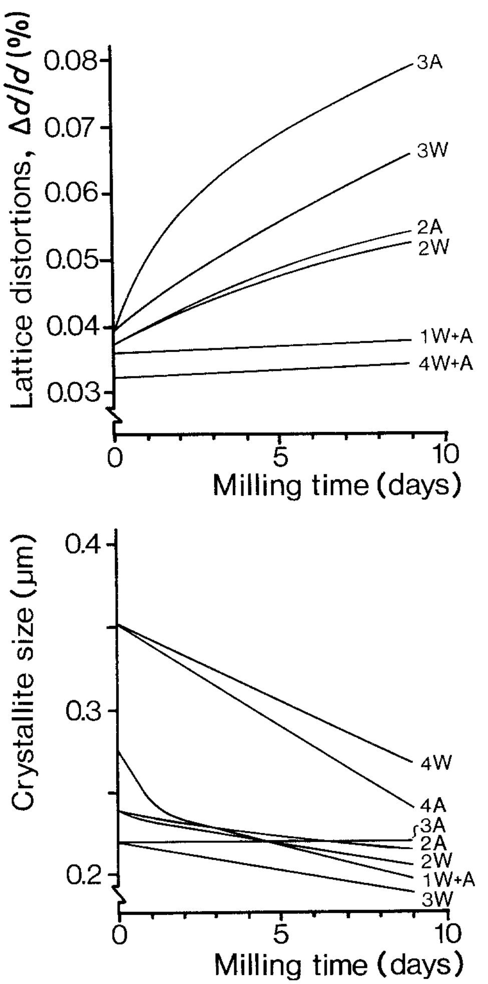

Figure 7 A summary of the calculated changes in crystallite size and lattice distortions upon milling of different alumina powders in water or acetone. Numerals 1 to 4 denote the different powders and the letters A and W are prefix for milling in acetone or water, respectively.

The calculated values of crystallite size and lattice distortions are summarized in Fig. 7. This figure also shows the milling behaviour as a function of time. Thus it can be seen that upon being milled material no. 1 mainly changes its particle size. This behaviour is also independent of the milling liquid used. The milling behaviour of material no. 3 is quite different. A large amount of stored energy is milled into this powder. However, upon milling the powder 3 in acetone, no change in particle size appears to occur. Hence peak broadening is entirely due to lattice distortions.

The fine-grained starting powders 2 and 3, can be seen to behave in a different manner to the coarse grained. Their particle size is only slightly reduced, if at all, during grinding, but large amounts of energy are stored in the particles.

5. Transmission electron microscopy study of powders

Two of the unground alumina powders, nos. 1 and 3, were studied in the TEM to obtain a direct measure of the alpha-alumina particle size.

The powders were dispersed in alcohol by shaking in an ultrasonic cleaner for 10 min. Using disposable pipettes a drop of the liquid was dropped on to a carbon film supported on a 3 mm microscope grid. The alcohol was allowed to evaporate before mounting the grid into the microscope's specimen holder.

The powders were examined in a Jeol 100C STEM instrument operating at 100 kV. A number of micrographs were obtained of each powder at x 298 000. The microscope magnification was calibrated using a replica of a 2160 lines mm^{-1} cross-grating.

Mean particle size and particle size distribution were measured on enlargements. The particle size measured was the largest projected particle diameter for each particle. If the particles are assumed to be spheres then the mean particle size obtained is a true mean particle size. For non-spherical particles this need not be true.

Representative micrographs of both powders are illustrated in Figs. 8 and 9. As seen it was not possible to completely disperse the alumina particles. They exist as agglomerates. Consequently, considerable particle overlap occurs which makes measurement of particle size more difficult. However, as particles are being examined in transmission, differences in thickness and diffraction contrast between the individual particles

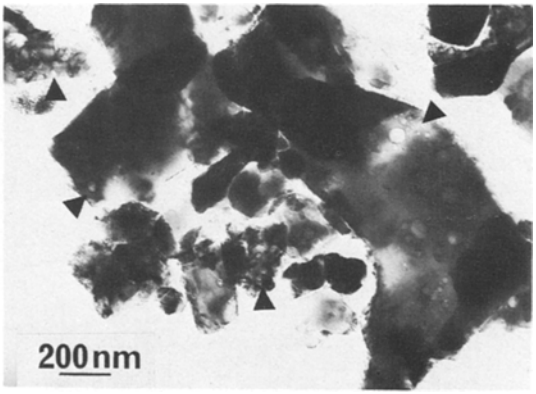

Figure 8 Electron micrograph of the unground material 1.

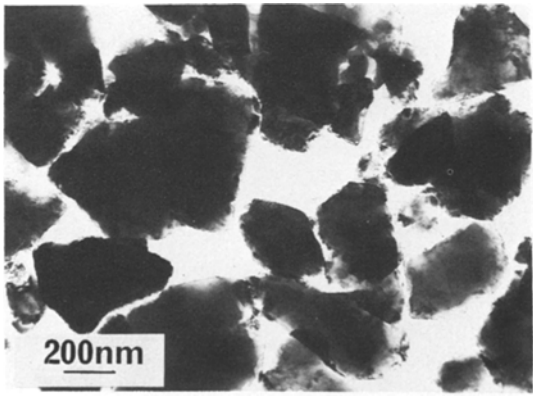

Figure 9 Electron micrograph of the unground material 3.

allows the majority of particle boundaries to be identified and particle size to be measured. Note that the smallest particles usually lie on the surfaces of the large ones.

Alpha-alumina particles in both powders contain facetted internal voids, arrowed in Fig. 8. These are a result of the decomposition of the aluminium hydroxide starting material to alpha-alumina [10]. There are a much larger number of voided particles in powder no. 1. The majority of the no. 3 powder particles are void-free. Both powders contained small amounts of discrete particles of non alpha $\bar{H}$ alumina phases (gamma $\bar{H}$, theta $\bar{H}$, delta $\bar{H}$ alumina) as identified by electron diffraction patterns. Their particle size was generally smaller than that of the alpha alumina particles but occasional large particles could be found. It is difficult to quantify the amount of foreign phases in the two powders, but it is felt that powder no. 1 contained more.

No attempt has been made to see if any differences in particle shape occurs between the two powders. Electron transmission through material no. 1 was easier suggesting that the particles are thinner than those in powder no. 3. The powders were also examined in the SEM mode. A tilting experiment indicated that the larger particles have a plate-like morphology. This conclusion is supported by Wilson's [10] observation that upon reduction of aluminium hydroxide to alpha-Al_2O_3 the plate-like morphology of the alumina hydroxide crystals is maintained. Crushing of the powder after reduction will merely break up the large flake-like crystals.

The mean particle sizes obtained for materials 1 and 3 were virtually identical, being 0.22 and 0.23 μm, respectively. It is noted that BET measurements for these two powders were also identical, giving a calculated value of 0.4 μm. The particle-size distribution in the two powders is shown in Fig. 10. They are almost identical, the main difference being that powder 3 contains more very large particles which shifts the median of the grain-size distribution to a slightly higher value.

6. Discussion

6.1. Particle-size measurements errors

In this article we have used the mean particle size as measured by transmission electron microscopy to determine which of the various correction terms (Cauchy, Gauss or empirical) used to obtain an X-ray crystallite size is the most correct. There are errors associated with this approach, the major being that the TEM particle size need not be the same as the X-ray crystallite size, as the crystals can contain domains that cause broadening of the X-ray reflections, but are not observed in the TEM. For example, Snell and Larsson [11] found that the peak broadening of ground TiC powders was due to the formation of slightly disoriented sub-grains in the TiC particles as a result of the extensive deformation they were subjected to. However, this is not felt to be the case for the alumina powders studied here. The TEM study

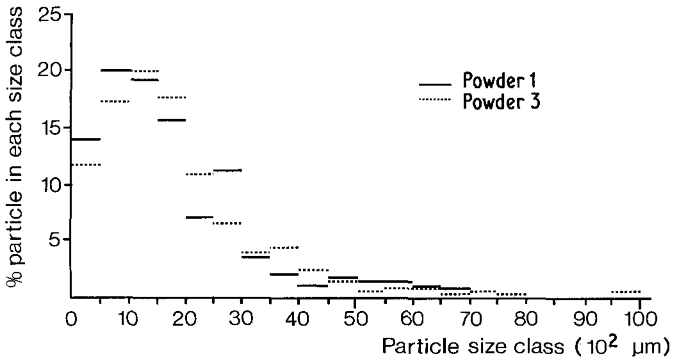

Figure 10 Alumina particle size distribution for the two unground materials 1 and 3.

shows that they generally have a low dislocation density with no sub-boundary formation.

Other techniques for measuring particle size can also give very different answers. For instance the BET values, while indicating the same particle size for both materials 1 and 3, greatly over emphasize it. This must be due to the assumptions made in converting the powder surface area, which is what BET measures, to an equivalent particle size. Radford [12] has also measured the particle size of powders 1 and 3 using an optical particle-size analyser and obtains mean particle sizes of 1 and 0.67 μm, respectively. Once again, with such an instrument, the particle size obtained depends upon certain assumptions such as grain shape, lack of agglomerates and so on. As seen from our TEM pictures there is a great tendency for the Al_2O_3 particles to agglomerate. The tendency to agglomerate is reflected in Radford's [12] much larger mean particle size. Quite clearly the TEM and X-ray methods are superior to optical instruments for particle-size measurement of Al_2O_3 powders.

6.2. Milling behaviour and its possible effect upon sintering

This study has shown how the milling behaviour of different powders varies greatly and depends upon the milling fluid. It has been assumed that to achieve a fully dense body after sintering that the particle size should be small and that the grains should contain a large amount of stored energy. However, we see from Fig. 7 that milling for a very long time only causes a moderate (10 to 25%) decrease in crystallite size. It is thus concluded that if a fine-grained alumina is desired then it is more economical to purchase such a powder from the manufacturers than attempt to grind a coarse powder down.

We relate the difference in the particle-size reduction that occurs upon grinding to the different internal structures of the powders. We expect powders that contain a large number of internal voids to grind down much better than void-free powders, the internal voids acting as fracture-initiating sources. This implies that the method the individual manufacturers use to obtain alumina powders, which controls the occurrence of internal defects, determines their grinding properties.

The occurrence of the voids will also affect the other parameter that is important for good sintering behaviour, the stored energy. Quite clearly void-free particles will deform more and thus contain more stored energy than voided-particles.

Milling fluids can alter grinding behaviour in various ways. They might act as lubricants and possibly reduce both increase in stored energy and reduction in particle size. They might also act by altering the fracture surface energy of the alumina by absorbing to greater or lesser extent upon the crack surfaces, the Rehbinder effect [13]. This effect might explain the pronounced difference in behaviour for number 3 when milled in water and acetone. Number 1 material, however, is unaffected by changes in milling liquid because internal defects act as crack initiating sources to which the fluid cannot penetrate. For the latter powder cracking occurs at the particle surface and water reduces surface energy and thus aids the reduction in particle size by mechanical processing. In such a situation the internal energy of the powder not being mechanically reduced should be expected to be greater, as is indeed so, Fig. 7.

Without performing practical sintering experiments it is difficult to predict the sintering behaviour of ceramic powders. However, as we suspect that both a fine particle size and a large stored energy should give a powder that sinters rapidly to a high final density then we can rank the powders studied:

$$\text{no. } 3 > \text{no. } 2 > \text{no. } 1 > \text{no. } 4.$$

Sintering experiments are at present in progress to confirm this and the results of these will be reported elsewhere [14].

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