X-ray diffraction analysis of kaolin M1 and M2 via the Williamson–Hall and Warren–Averbach methods

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Abstract
Kaolin M1 and M2 studied by X-ray diffraction focus on the mullite phase, which is the main phase present in both products. The Williamson–Hall and Warren–Averbach methods for determining the crystallite size and microstrains of integral breadth $\beta$ are calculated by the FullProf program. The integral breadth ($\beta$) is a mixture resulting from the microstrains and size effect, so this should be taken into account during the calculation. The Williamson–Hall chart determines whether the sample is affected by grain size or microstrain. It appears very clearly that the principal phase of the various sintered kaolins, mullite, is free from internal microstrains. It is the case of the mixtures fritted at low temperature (1200 °C) during 1 h and also the case of the mixtures of the type chamotte cooks with 1350 °C during very long times (several weeks). This result is very significant as it gives an element of explanation to a very significant quality of mullite: its mechanical resistance during uses at high temperature remains.

Keywords
distribution of sizes, kaolin M1, kaolin M2, microstrains, method of stokes

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Introduction
When recording a diffraction pattern using powders, it is common to observe that the shape or width of the lines do not correspond to the instrumental resolution function that would be measured, for example, using a reference sample. This additional intrinsic enlargement is due to the microstructure of the sample and comes mainly from two effects size and microstrain.

To find the true profile of the sample $f(x)$, a deconvolution operation is used. Deconvolution is an operation that corrects the observed line patterns of instrumental broadening provides the function $f(2\theta)$.

In addition to the analytical methods that use rigorous deconvolution, simple methods are often used to separate the widths of the convoluted functions. The intrinsic error of these methods has been treated in particular by several methods, as related by authors.1–3 To be reliable, the quality of the recording, with sufficiently long times, is required. This makes it difficult to study low symmetry compounds where the overlap of the lines is greater. Moreover, using these methods, the deconvolution is always carried out based on the hypotheses of the profiles of the components involved. The microstructural results can differ significantly from one hypothesis to another.1–15

Methods of microstructural analysis
The intrinsic diffraction line pattern is mainly caused by the size and internal stresses of the sample. The methods used for the evaluation of these two phenomena are as below.

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The Scherrer method is used when the integral breadth ($\beta$) results only from the crystallite size effect (when the matter does not contain microstrains). The grain size is given by the well-known Scherrer relation (equation (1))\(^{16}\)

$$D_f = \frac{C\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

For widths specified in $2\theta$, $C$ is a coefficient which depends on the shape of the crystallites and can assume values between 0.8 and 1.39.\(^{17}\)

For spherical particles, it is generally given as (equation (2))

$$\frac{1}{D_f} = \frac{1}{\beta^*}$$  \hspace{1cm} (2)

For widths in units where reciprocal $\theta$ is the Bragg angle, $D_f$ is the average grain size, $\lambda$ is the wavelength, and $\beta^*$ is the integral width characterizing enlargement, expressed as the reciprocal lattice.

The Warren–Averbach method. If the sample does not contain a microstrain, then $A^0(l,n) = 1$, therefore $A_{(l,n)}^0 = A^0(l)$. The initial slope of the curve giving $A_{(l,n)}^0$, according to the length of the columns $L$ is inversely proportional to the apparent size of the crystallites in a direction perpendicular to the plane $(hkl)$, considered in Figure 1. This apparent size is given by the following equation (equation (3))\(^{8,10}\)

$$\Delta s = \frac{1}{D_f} = \frac{dA_{(l,n)}}{dL}$$  \hspace{1cm} (3)

$\Delta s = \lambda/2 (\sin \theta_2 \sin \theta_1)$ and $\theta_1$ and $\theta_2$ are the values of the limit angles that define the profile.

In Figure 2, the point of intersection of the initial slope of the curve with the $x$-axis (L) provides the size $D_f$.

The Williamson–Hall method. This method applies to Voightian or pseudo-Voightian profile types. It uses the commonly called Williamson–Hall plot.\(^{20}\) This graph, as a straight line, gives valuable indications on the presence or absence of microstresses in the sample. The slope of the line shows the presence of the latter (Figure 2).

Results and discussion

Since the data is obtained from point-by-point survey, they do not correspond to that obtained by the Stokes method, which works on constant steps. For this reason, we have written a program that performs this adaptation of the data. The profile parameters obtained for the different kaolins are recorded in Tables 1 and 2.

Moreover, from the hypothesis of a pseudo-Voightian shape of quartz peaks, we automated obtaining the standard corresponding to each peak of the studied sample. This makes it much easier to use the standard in analyses of different samples. It is therefore interesting to use this second method for microstructural analysis.

If the profiles are purely Gaussian or purely Voightian, this method provides a very simple and quick way to evaluate the effects of stress and size. For the other pseudo-Voightian profiles, approximations are necessary for the separation of these two effects.\(^{21,22}\)
show the true profile and the experimental profile for a peak chosen from the diffractogram of each kaolin DD studied. As can be seen in these figures, the calculated and experimental profiles are sufficiently superposed. From the results obtained, the microstructural parameters are deduced.

The application of the Stokes method provides the profile of the true function. Figures 5 and 6 show two profiles corresponding to the peaks, respectively, at $2\theta = 16.36^\circ$ and $2\theta = 31^\circ$. In these latter figures and taking into account the difference introduced by the intrinsic effect of the sample, it is easy to see that the calculated and experimental profiles are sufficiently superimposed.

**Williamson–Hall plot**

The Williamson–Hall diagram of each sample of kaolin DD is given in Figure 7. Note that the curve is a straight line with an almost zero slope. The negative value of this slope is probably due to the accuracy of the data obtained from the diffraction and fitting data. It can be deduced that the sample has no microstrains.

**Table 2. Parameters of the X-ray diffraction profiles for KT2 kaolin at 1350 °C.**

| Pic | $2\theta_0$ | $a$ | $b$ | $2\omega$ ($^\circ/2\theta$) | $\beta$ ($^\circ/2\theta$) | $\phi$ |
|-----|-------------|-----|-----|---------------------------|---------------------------|------|
| 110 | 16.36       | 51.30 | 17.42 | 0.34                      | 0.354                     | 0.96 |
| 021 | 19.50       | 18.52 | 20.48 | 0.26                      | 0.273                     | 0.96 |
| 200 | 23.68       | 22.58 | 24.78 | 0.38                      | 0.41                      | 0.92 |
| 120 | 26.28       | 24.62 | 27.38 | 0.38                      | 0.41                      | 0.92 |
| 210 | 26.28       | 25.08 | 27.48 | 0.3                      | 0.33                      | 0.91 |
| 001 | 31.30       | 30.08 | 31.98 | 0.22                      | 0.25                      | 0.88 |
| 220 | 33.2        | 32    | 34.4  | 0.42                      | 0.43                      | 0.97 |
| 111 | 35.28       | 34.02 | 36.54 | 0.34                      | 0.37                      | 0.92 |
| 130 | 36.86       | 35.78 | 37.94 | 0.42                      | 0.42                      | 0.95 |
| 230 | 40.8        | 39.62 | 41.98 | 0.34                      | 0.36                      | 0.94 |
| 311 | 49.48       | 48.50 | 50.46 | 0.32                      | 0.36                      | 0.88 |
| 041 | 57.58       | 56.66 | 58.48 | 0.38                      | 0.40                      | 0.95 |
| 331 | 60.62       | 59.50 | 61.74 | 0.32                      | 0.33                      | 0.96 |
| 002 | 64.48       | 65.00 | 63.04 | 0.38                      | 0.40                      | 0.95 |

Figure 3. Profile of the peak (001) of kaolin DD at 1200 °C.

Figure 4. Profile of the peak (210) of kaolin DD at 1200 °C.

Figure 5. Profile of the KT2 kaolin peak (100).

Figure 6. Profile of the KT2 kaolin peak (110).

Figure 7. Williamson–Hall plot of kaolin DD at 1200 °C.
Figure 8 shows the Williamson–Hall diagram of kaolin KT2. It was observed that the curve is a straight line with a negligible and negative slope.

**Evaluation of kaolin’s DD crystallite size**

Since the sample does not have any microstrains, the Warren–Averbach method was applied to a non-distorted case. Figures 9 and 10 show the variation of the Fourier coefficients as a function of $L$ (harmonic number) for two peaks of kaolin obtained at 1200 °C (peaks (100) and (001)). The slope originally obtained by extrapolation provides an average value for the crystallite size in the direction perpendicular to the diffractive plane. So (equation (4))

$$
\left. \frac{dA}{dL} \right|_{L \to \infty} = \frac{1}{D_f}
$$

where $L$ harmonic number is

$$
L = nt
$$

with

$$
t = \frac{\lambda}{2} \left( \sin \theta_2 - \sin \theta_1 \right)
$$

$2\theta_1$ and $2\theta_2$ are the values of the limit angles that define the profile.

The values obtained for the size of the crystallites of the different kaolin DD studied are reported in Table 3. As can be seen, the crystallites are of quasi-nanometric dimensions. This result is consistent with observations on other DD kaolin. The values found can be somewhat confirmed by the Williamson–Hall plot. Indeed the average size can be evaluated as (equation (5))

$$
\varepsilon = \frac{1}{\beta^*}
$$

where $\beta^*$ is the integral width in reciprocal coordinates. For kaolin at 1200 °C, the average value found from the Williamson–Hall plot is about 190 Å (compared with 114 Å found by the Warren–Averbach method.

Figures 11 and 12 show the variation of the Fourier coefficients as a function of $L$ (harmonic number).

The average value of the size of the crystallites in the direction perpendicular to the diffracting plane is provided by the slope at the origin.

The values obtained for the average crystallite size are reported in Table 4.

As can be seen in Table 4, the dimensions of the crystallites are of nanometric order.

To confirm, to some extent, the values found, the average crystallite size from the Williamson–Hall diagram was
evaluated. The value found is 230 Å, which is close with the average size determined using the Warren–Averbach method (245 Å).

Table 4. Average size of KT2 crystallites from different diffraction peaks.

| Pic   | ε(Å) |
|-------|------|
| (110) | 130  |
| (021) | 143  |
| (200) | 109  |
| (120) | 106  |
| (210) | 143  |
| (001) | 217  |
| (220) | 132  |
| (111) | 150  |
| (130) | 127  |
| (230) | 148  |
| (311) | 173  |
| (041) | 226  |
| (331) | 241  |
| (002) | 205  |

Table 5. Dominant size of mullite in kaolin DD (1200 °C).

| Pic   | Dominant size (Å) |
|-------|-------------------|
| (110) | 150               |
| (210) | 71                |
| (001) | 131               |
| (220) | 64                |
| (111) | 111               |
| (201) | 98                |
| (230) | 193               |
| (311) | 91                |
| (420) | 150               |

Table 6. Dominant size of the main phase of kaolin KT2.

| Pic   | Dominant size (Å) |
|-------|-------------------|
| (110) | 82                |
| (210) | 120               |
| (001) | 73                |
| (220) | 64                |
| (111) | 60                |
| (230) | 52                |
| (320) | 72                |
| (240) | 40                |
| (041) | 51                |

Size distribution in the main phase of kaolin DD and KT2

A study of the size distribution within the main phase of kaolin DD was performed. This distribution was calculated using a parabolic approach. The values of the dominant size for each peak are given in Table 5.

The values of the dominant size evaluated from the relation of the second derivative of the different peaks of the principal phase of kaolin KT2 are given in Table 6.

According to Table 6, the average arithmetic size of the crystallites is 164 Å. From the Wielliamson–Hall diagram, we can estimate this average size (this time in the least squares sense) as 229 Å. The relative difference between the two values is less than 40%, which, in our opinion, is acceptable because the size of a monocrystallite can vary greatly depending on the direction of the diffracting planes and, moreover, there are several crystallites of varying size diffracting in the same direction.

Conclusion

By studying the contours of the lines, it seems very clear that the main phase of many sintered kaolin and mullite is devoid of internal microstrains. This is the case where the mixtures are whipped not only at low temperature (1200 °C) for 1 h, but also at a temperature of 1350 °C for very long periods (several weeks).

The Williamson–Hall plot was constructed and used to determine whether a sample is affected by deformation and to determine the size of the crystals. Since the specimen had no small folds, we applied the Scherrer relation. The Warren–Averbach method was also used in an undistorted condition.
This result is very important because it gives an element of explanation for a very important quality of mullite: its mechanical resistance during repeated use at high temperatures.

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