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X-ray diffraction line broadening in dry grinding of kaolinite

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Abstract. The influence of dry milling on the crystalline microstructure of two kaolinites of different origins is studied by X-ray diffraction (XRD) and by analysing field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) images. Two methods of XRD microstructural analysis are used: the Voigt function and the Warren-Averbach methods; good linear correlation between average apparent crystallite size estimated by both methods is found.

Introduction and aim

Kaolinite has a wide range of uses, based on brightness, whiteness, opacity, gloss, among others, of kaolinite bearing materials, and these properties are influenced by the degree of “crystallinity” of kaolinite [1].

Kaolinite is a sheet silicate with marked exfoliation providing platelets of the {001} form. A method for FESEM measurement of thickness of these kaolinite platelets at crystallite level has been shown [2] and a very good correlation has been found between these values and those of the apparent crystallite size obtained from XRD Voigt function method [3,4].

The aim of the present paper is to compare the average apparent crystallite size obtained with the Warren-Averbach method [5] and with the Voigt function method for a set of ground samples of two kaolinites showing very different apparent crystallite size.

Materials

The materials used are a well crystallised kaolinite from Georgia (the reference sample KG-A1 provided by the Clay Minerals Repository, Clay Minerals Society, USA) and a poorly crystallised kaolinite from North Queensland, Australia [6].

The mechanical dry milling was performed in a Fritsch Pulverisette 9 vibrating cup mill (equipped with tungsten-coated steel cup, ring and cylinder) on 10 g samples, at different milling times: 3, 6, 12, 24 and 36 s. From this experiment two sets of samples were generated, set W (of Georgia kaolinite): W0 (not milled), W3, W6, W12, W24, W36, and set Q (of Qeensland kaolinite): Q0 (not milled), Q3, Q6, Q12, Q24, Q36.

Methods

Field emission electron microscopy and atomic force microscopy

Oriented aggregates for FESEM observation were prepared as shown in [2]; a gold-palladium coating was made by using a Biorad RC500. A Hitachi 4100 FESEM operating at 30 kV accelerating voltage was used for observation. The image collection was made by the EMIP program (supplied by Hitachi).

Powder X-ray diffraction analysis

The equipment used for XRD characterization was a Bruker D5000 diffractometer, running under the Bruker Diffract-Plus system (for diffractometer control, data collection and preliminary evaluation of data), working at 40 kV, 30 mA, with Ni filter, 1º divergence slit, 1º antiscatter slit, graphite diffracted beam monochromator and scintillation detector. General identification was performed using the range 5º - 65º 2θ, with 0.04º 2θ step size and 8s counting time for each sample. Microstructural analysis of 001 direction of diffraction in kaolinites was developed from scans 11º - 13.5º 2θ (for 001) and 24º - 26º 2θ (for 002) with a step size of 0.01º 2θ and counting times of 12s and 18s respectively for 001 and 002 profiles. Background subtraction was performed using the enhanced method of the Eva program of the Diffract-Plus system on the whole range including both 001 and 002 reflections.

The studied direction of diffraction corresponds to planes of greater morphological expression for which the thickness of crystallites can be measured by FESEM.

The instrumental profiles were produced from the X ray powder diffraction pattern of the LaB_6 standard (NIST SRM660a) obtained in the same experimental conditions. The pure line profile for each reflection was obtained by deconvolution of the instrumental profile from the experimental one. With the data obtained at the fitting stage two different methods of microstructural analysis were applied, using the Profile program (Bruker, Socabim). For the Voigt function method [3,4], the profiles of XRD patterns were fitted to Voigt functions and calculations were performed as shown in [7,8]. The Warren-Averbach method [5] was applied using the WinCrySize program (from the Bruker Diffrac-Plus suite).

The 002 pure line profiles were calculated after deconvolution by separating them from overlapping peaks on the right of them (see figures 2 and 3), corresponding to anatase.

Results

Clear difference of “crystallinity” [9] between both source kaolinites were found as difference in particle size and in values of thickness of kaolinite flakes perpendicularly to (001) faces by means of high-magnification FESEM and AFM images. Average flake thickness in direction perpendicular to (001) from that images for W0 and Q0 samples were 789Å and 200Å respectively, and were close to the volume-weighted average crystallite sizes <Dv> estimated by the Voigt function method rather than to the surface-weighted sizes L provided by the Warren- Averbach method. Table 1 includes the characteristics of the XRD line profiles and the microstructural parameters obtained by the Voigt function method. Continuous decrease of <Dv> with milling time can be observed in both sample series (with anomalies in Q sample from 0 to 3 seconds for 001 and from 3 to 6 seconds for 002). Greater e (strain) values were found in W sample, and no clear tendency was recognised; such ambiguity of strain values (as well as size anomalies) could be attributed to the instability that frequently appears when the Voigt function method is used.

Table 1. Characteristics of peaks and microstructural parameters from the Voigt function method. Pos. - is the peak position, Nor. Area - is the normalised area, Max. - is the peak maximum, FWHM - is the full width at half maximum of a pure line profile, β_{int} - is the integral breadth of a pure line profile, ϕ - is the Voigt line profile aspect ratio, <Dv> - is the volume-weighted apparent crystallite size, e - is the strain; data for standard profiles (STD) are given for comparison.

Sample	Pos. (°2θ)	Nor. Area cps·°2θ	Max. cps	FWHM °2θ	β_{int} °2θ	ϕ	<Dv> (Å)	e
001								
STD	12,364	2636	40030	0,055	0,066	0,835		
W0	12,294	294	1598	0,133	0,184	0,723	795	0,0027
W3	12,302	279	1460	0,136	0,191	0,712	718	0,0025
W6	12,286	215	925	0,154	0,233	0,661	465	0,0008
W12	12,267	139	549	0,170	0,253	0,671	438	0,0019
W24	12,262	88	209	0,269	0,422	0,637	225	-
W36	12,259	66	129	0,323	0,508	0,636	184	-
Q0	12,253	123	249	0,314	0,493	0,636	190	-
Q3	12,232	143	292	0,326	0,491	0,664	208	0,0043
Q6	12,241	126	246	0,335	0,511	0,656	194	0,0036
Q12	12,242	128	211	0,385	0,604	0,637	154	-
Q24	12,201	104	139	0,476	0,748	0,637	123	-
Q36	12,215	77	99	0,497	0,780	0,637	118	-
002								
STD	24,866	3364	47796	0,059	0,064	0,920		
W0	24,811	236	1248	0,137	0,189	0,726	672	0,0012
W3	24,818	205	1062	0,143	0,193	0,741	705	0,0015
W6	24,795	188	783	0,158	0,241	0,656	407	-
W12	24,292	136	430	0,201	0,316	0,636	291	-
W24	24,781	71	164	0,277	0,435	0,636	211	-
W36	24,777	62	109	0,362	0,569	0,637	161	-
Q0	24,777	117	215	0,347	0,546	0,636	167	-
Q3	24,756	159	256	0,396	0,621	0,637	148	-
Q6	24,773	129	228	0,359	0,564	0,637	163	-
Q12	24,779	110	186	0,377	0,593	0,636	154	-
Q24	24,748	93	119	0,495	0,781	0,634	116	-
Q36	24,748	85	90	0,601	0,944	0,637	97	-

Table 2 includes results of the Warren-Averbach method that were produced from 001 and 002 peaks. Continuous decrease of the average crystallite size value as well as of the width of the relative frequency distribution with milling time is observed in samples of both series. A quite clear increase of strain at the average L of the apparent surface-weighted crystallite size distribution (SACF) can be observed from 3 to 36 seconds of milling in samples of both series, with greater values for the Q samples. There is also a continuous increase of the strain at the maximum of relative frequency (SMRF) from 6 seconds of milling time in both sample sets.

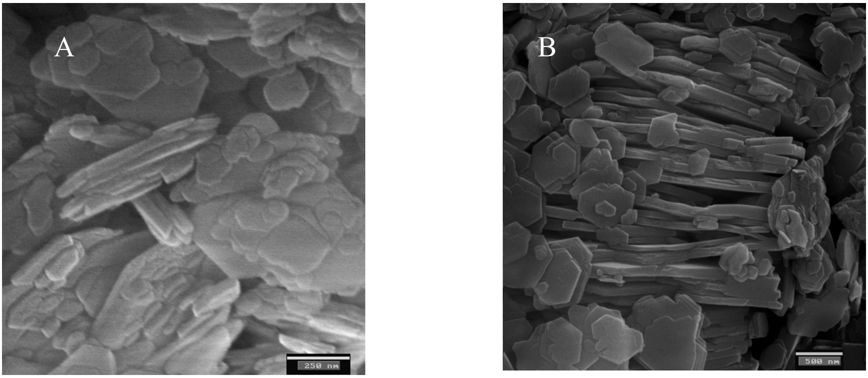

Figure 1. FESEM images of samples Q0 (A) and W0 (B); scale bar = 250 nm.

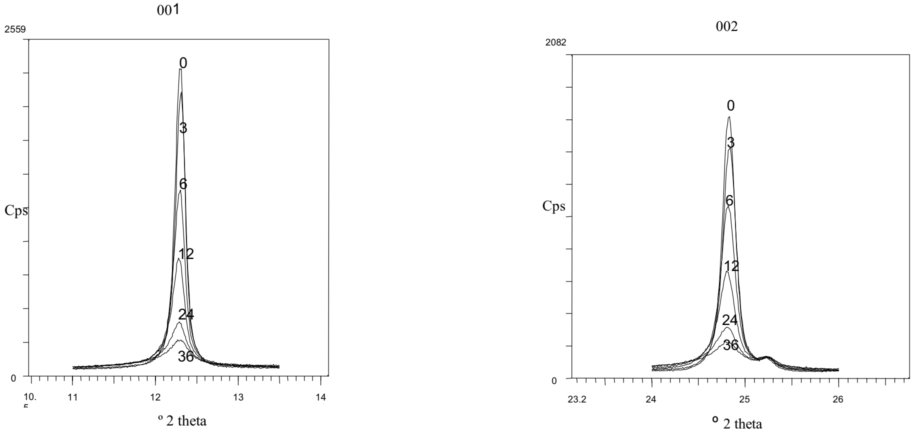

Figure 2. X-ray diffraction patterns of 001 and 002 reflections for samples W.

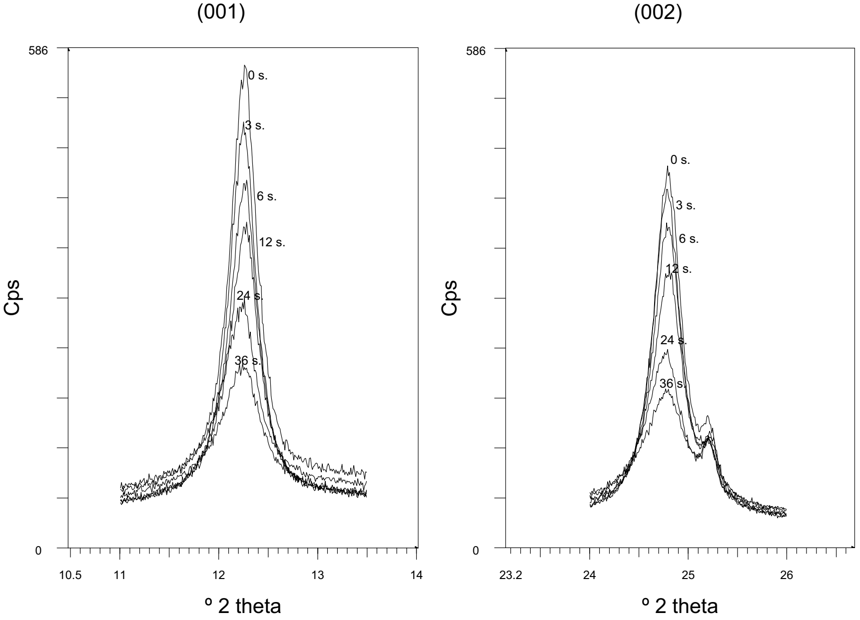

Figure 3. X ray diffraction patterns of 001 and 002 reflections for samples Q

Table 2. Microstructural parameters from the Warren-Averbach method; L - is the average surface-weighted apparent crystallite size, FWHM-L - is the full width at half maximum of a size distribution, SACF is the strain at average value L of a size distribution, SMRF - is the strain at maximum of a size distribution.

Sample	W0	W3	W6	W12	W24	W36	Q0	Q3	Q6	Q12	Q24	Q36
L (Å)	399	370	269	207	120	85	120	118	107	97	75	61
FWHM-L (Å)	654	569	318	221	140	100	158	151	127	113	87	71
SACF $\cdot 10^3$	0.262	0.600	0.578	1.231	1.598	3.947	-	2.032	1.773	3.121	4.321	5.600
SMRF $\cdot 10^3$	0.292	1.046	1.009	1.837	2.122	4.725	0.123	3.257	2.902	4.501	5.289	7.340

Conclusions

The vibrating-cup dry grinding of kaolinite had as a result a quick change of the microstructure with milling time, with decrease in average crystallite size and in the width of distribution of sizes. These decreases were found to be greater for the well crystallised kaolinite (reference sample KG-A1). Good linear correlation has been found between the surface-weighted average apparent crystallite size (L [Å]) provided by the Warren-Averbach method and the volume-weighted average apparent crystallite sizes (<Dv> [Å]) provided by the Voigt function method, in the wide range of crystallite size studied: <Dv> = 1,9935L - 19,228 with R^2 = 0,9868 for 001 and <Dv> = 1,7875L- 27,75 with R^2 = 0, 0,9714 for 002. Characteristic flakes of kaolinite (with base faces in (001) planes) were identified as crystalline grains formed probably as monolayers of crystallites, with approximately the same mean volume-weighted size of both flakes and crystallites in direction perpendicular to (001) planes.

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