Review

Effect of Grinding on The Structure, Particle Size and Shape of Pyrophyllite and Talc

by

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ABSTRACT

Pyrophyllite and talc structural alterations, induced after dry grinding, were studied by nitrogen adsorption, thermal analysis and by X-ray diffraction methods. Structural degradation after grinding for a short time was followed by particle breakdown. After prolonged grinding, particle breakdown resulted in about 0.04 μm for pyrophyllite and about 0.02 μm (lateral diameter) for talc and about 0.02 μm and 0.01 μm in thickness, respectively.

Key Words: Pyrophyllite, Talc, Polytypism, Dry Grinding effect

1. INTRODUCTION

The mechanical effects acting on solid materials during a prolonged static or repeated dynamic load, e. g. grinding, can result in the decrease of crystallite size and increase of crystal lattice deformation and amorphism of the material. In consequence the increase in surface area and intensification of the chemical reactivity of materials are observed. The latter is of major interest from the point of view of industrial processes.

In the previous paper [1] the effect of mild grinding on the polytypic structure of triclinic pyrophyllite has been studied in detail using 02l and 11l series of reflections. The effect of prolonged grinding has been approached from the point of view of changes in particles sizes and shape estimated from BET, SEM and Scherrer broadening. This paper provides a comparison of the behaviour of pyrophyllite and talc on grinding up to 30 min.

2. EXPERIMENTAL

Raw pyrophyllite from Zalamea (Badajoz) and talc from Puebla de Lillo (Leon), both in Spain, were used for this study. The samples were subjected to dry grinding by ball milling, for periods rang-
The infrared (IR) spectra were recorded for samples in KBr pellet form (2 mg of sample and 300 mg of KBr) using FTIR apparatus (Nicolet, model 510P).

The differential thermal analysis (DTA) curves were obtained in static air with a thermal analyser (model PTC-10A Thermoflex, Rigaku) at a heating rate of 12°C/min. Calcined alumina was used as a reference material. Samples of 33 mg were gently packed in a platinium holder and heated up to a maximum temperature of 1050°C.

The surface area analysis was carried out using an automatic system (Micromeritics, 2200A model) with nitrogen gas as the adsorbate at liquid nitrogen temperature. Samples were degassed over two hours at 150°C prior to analysis, and the BET (Brauner-Emmett-Teller) method was used to calculate the nitrogen surface area. Average particle sizes (D) in µm were estimated using the equation: $D = \sqrt[6]{\frac{S}{\rho}}$, where $\rho$ is the density of pyrophyllite (2.8 g/cm³) and S is the measured surface area (m²/g).

XRD transmission patterns were recorded with CoKα and CuKα radiation using a Sigma 2070 focusing diffractometer, a stepscan of a 0.04° 2θ, and DRX software. Quasi-randomly oriented samples were prepared by sieving the samples onto a Myllar foil. Another Myllar foil was used to lock them in the transmission window of the diffractometer.

The structural refinement data of Lee and Guggenheim [3] for pyrophyllite, and of Gruner [4] and Perdikatsis and Burzlaff [5] for talc were used as input data for modelling the diffraction powder patterns. The DIFK program [6, 7, 8] was used to perform the calculations.

3. POLYTYPIC STRUCTURES

The structure of minerals which are classified in the talc-pyrophyllite group is built up of 2:1 layers, characterised by three octahedral positions per four tetrahedral positions and no charge on the layer.

Theoretically possible 2:1 structures were derived by Đurović and Weiss [9]. These authors showed 22 nonequivalent polytypic meso-octahedral MDO (maximum degree of order) structures of pyrophyllite and 10 homo-octahedral structures of talc. Each of the two assemblages splits into A and B subfamilies. Structures belonging to subfamily B have never been encountered in nature (and probably never will be), thus the number of possible homo-octahedral structures characteristic of pyrophyllite is limited to 11 and homo-octahedral structures characteristic of talc to only 5. Among these, both, one-layer triclinic and two-layer monoclinic modifications of talc and pyrophyllite were identified, by means of oblique-texture electron diffraction [10]. They are 1Aα-II, 2Mα-IV talcs and 1Aα-II, 1, 2Mα-IV, 1 and 2Mα-V, 1 pyrophyllites [6]. 0 layer charge and a lack of any interlayer matter are responsible for the weakness of the interlayer bonding, limited to Van der Waals attraction. Interlayer repulsion is minimized by translations b/3 of the adjacent layers, due to this tetrahedral cations are never superimposed in the neighbouring layers. The bonding forces are most frequently too weak to keep layers together in periodic position. Therefore, the structure of naturally occurring minerals is disordered to varying degrees by random layer translations. This explains difficulties in finding sufficiently well crystallised material for structural analysis [11]. Perhaps it also explains why the earlier structural refinements were carried out in a monoclinic system for both pyrophyllite...
Fig. 1 Experimental transmission diffractograms of purified pyrophyllite from Zalamea, using CoKα radiation: (a) randomly oriented powder sample, (b) preferentially oriented powder sample in a symmetrical setting (γ =90°), (c) preferentially oriented powder sample in an oblique setting (γ =55°). R = rutile, Q = quartz. Notice the highest intensities of the polytypic diffractions (02l and 11l) at incidence angle γ = 55° [1].
and talc [4]. The subsequent structural refinements proved only triclinic structures 1A, II for talc [12, 13, 5], and 1A, II, 1 for pyrophyllite [14, 3].

Identification of talc and pyrophyllite polytypes in natural samples encounters several difficulties. By powder methods, not only are some polytypes indistinguishable [6], but frequently polytypic diffractions can not be determined because they are completely or severely blurred due to random translations of structural layers. In such cases the oblique-texture transmission diffractometry [15], appears very helpful. It permits enhancement of any chosen series of diffractions (in this case 02l, 11l or 20l, 13l) in a textured sample (Fig. 1) and comparison of the experimental patterns with those

![Fig. 2 Oblique texture transmission diffractograms of talc for $\nu = 58^\circ$ and CuKα radiation:](image)

- a - smoothed experimental curve of a sample from Egypt,
- b - calculated curve using structural data of Perdikatsis and Burzlaff [5], and a texture coefficient $g = 2.5$. Important diffractions are indexed, dashed lines identify polytypic (MDO group) diffractions in the sample from Egypt.
calculated for a given oblique-texture axis and coefficient of texture, \( g \) (Fig. 2). The comparison enables the determination of \( 1\overline{A}_\alpha - \overline{I}_I \) triclinic structure of talc from Egypt. This task could not be fulfilled by the powder method on random samples. But even using oblique-texture technique we have never been able to demonstrate the existence of ordered monoclinic forms of pyrophyllite. It seems that formation of the less stable monoclinic varieties must be the product of certain crystallisation conditions, e. g. low temperature \([16]\) or varying chemical composition (cases of ferripyrophyllite \([17]\)). Less varied conditions may lead to the co-existence of single layers and of pairs of layers in the same domain, as proved by HREM images \([18]\). Such mixed structures would show disordered X-ray powder diffraction patterns due to statistical averaging of the diffraction effects.

4. EFFECT OF A SHORT GRINDING TIME ON STRUCTURE ORDERING

Diffractograms presented in Fig. 1 clearly showed a \( 1\overline{A}_\alpha - \overline{I}_I \) structure of pyrophyllite from Zalamea (Spain). By comparison to those in simulated diffractograms, the diminished intensity of \( 11l \) and \( 02l \) reflections is recognised to be due to random translations along the \( b \) axis. A short grinding time caused further degradation of the \( 11l \) and \( 02l \) diffractions \([1]\). This leads to disordered forms and not to the formation of a monoclinic polytype as has been sometimes previously claimed. Talc from Puebla de Lillo, Spain shows no \( 11l \) and \( 02l \) reflections, thus full determination of its polytypic structure is not possible.

5. MODIFICATIONS OF SURFACE AREA, PARTICLE SIZE AND SHAPE ON GRINDING

Thermal behaviour on grinding of pyrophyllite, as studied by Hayashi et al. \([19]\), Wiewióra et al. \([1]\) and of talc by Aglietti and Porto Lopez \([20]\), showed a temperature shift in the main endothermic peak after grinding. For pyrophyllite this shift was greatest during the first few minutes of grinding. In addition, DTA peak areas decreased with increasing grinding time and with increasing surface area of the ground silicate. These changes are related to a progressive delamination and structural breakdown during grinding. Prolonged grinding, up to 30 min, created a turbostratic-type structure. Reduction in particle size and changes in shape on grinding of pyrophyllite and talc are estimated according to a method developed by Wiewióra et al. \([1]\) and are presented in table 1 and in fig. 3.

Let us first compare unground pyrophyllite and talc. Equivalent spherical diameter from BET measurement shows evidently bigger particles of pyrophyllite (1.83 µm) than of talc (0.73 µm). At the same time the domain thickness from Scherrer broadening is bigger for talc than for pyrophyllite. As seen from aspect ratio (160 for pyrophyllite compared to 56 for talc) together with domain thickness and average particle diameter in (001) plane, the particles of talc are smaller but thicker than those of pyrophyllite. A five minute grinding time resulted in the breakdown and drastic size reduction of relatively thin particles (as indicated by high values of aspect ratio). With further grinding, the rate of size reduction decreases with time, but reduction continues up to about 30 min. At this stage particle size was reduced to 0.04 µm for pyrophyllite and 0.02 µm for talc, lateral diameter. A similar aspect ratio for both pyrophyllite (2.4) and talc (2.6) indicates similar particle shape. After 30 minutes of grinding the mechanochemical reduction of the original particles appears to have reached a limit. After a longer time there is an increasing degree of amorphism and a decrease in the surface area by reaggregation of the ground powder. Thus, the thermal behaviour is strongly dependent on the structural state of the material.
Fig. 3  Relationship between average particle size from surface data (e. s. d.) and average domain thickness from Scherrer broadening. Particle diameter (a) and aspect ratio (A. r.) are also shown (table 1): (a) - pyrophyllite, (b) - talc.
Table 1. Surface area and particle sizes for ground pyrophyllite and talc.

<table>
<thead>
<tr>
<th>Grinding time (min)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>e.s.d. (D) (µm)</th>
<th>$\epsilon_{Sperme}$ (µm)</th>
<th>$a^1$ (µm)</th>
<th>Aspect ratio A.r. = $a/\epsilon$</th>
</tr>
</thead>
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<tr>
<td>Pyrophyllite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0</td>
<td>1.17</td>
<td>1.83</td>
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<td>5</td>
<td>14.01</td>
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<td>0.044</td>
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<td>4.6</td>
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<tr>
<td>10</td>
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<td>240</td>
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<td></td>
<td></td>
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<td>Talc</td>
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<tr>
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<td>20</td>
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<td>0.009</td>
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$^1 a^2 = [4/3\pi(D/2)^3]/\epsilon$

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6. REFERENCES


