JOURNAL OF MATERIALS SCIENCE 26 (1991) 5297–5300

X-ray diffraction study of ground talc $Mg_3Si_4O_{10}(OH)_2$

K. SUGIYAMA, P. F. JAMES*, F. SAITO, Y. WASEDA
Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Sendai Aoba-ku 980, Japan

A structural analysis of talc ground under dry atmospheric conditions for different grinding times has been made by X-ray diffraction. The SiO_4 tetrahedra are found to remain unchanged in the ground talc samples by analysing the radial distribution function. On the other hand, with an increase of the grinding time a change in oxygen coordination number around magnesium has been quantitatively confirmed. This variation is attributed to the change of a hydroxyl induced by the prolonged grinding.

1. Introduction

Recently the structural changes of various inorganic substances induced by the usual grinding technique has received much attention, from the viewpoint not only of a better understanding of the mechanochemical effects but also of the relatively new method for producing several interesting materials. In these regards, clay minerals, which are often used as raw material for various ceramic products, are known to display strong mechanochemical effects with characteristic structural changes on applying prolonged grinding (see e.g. [1]). This has led to an increasing demand for characterizing the structure of ground clay minerals. However, clay minerals are inclined to adopt a so-called amorphous structure by grinding, due to their lack of internal structural order. Therefore, the structural changes in clay minerals induced by prolonged grinding have not been fully revealed yet, although a few structural investigations have been carried out (see e.g. [2]).

Among many clay minerals, talc [$Mg_3Si_4O_{10}(OH)_2$] is relatively simple in its chemical composition and is reported to show distinct mechanochemical effects [3]. Thus, in order to understand the structural changes of talc induced by prolonged grinding, a structural investigation of ground samples with different grinding times was performed in this work by applying radial distribution function analysis to measured X-ray scattering intensities, as commonly used for structural study of disordered systems such as liquids and glasses. The results are described below.

2. Experimental procedure

The talc sample used in this study was prepared from a compact mineral of white colour from Kaijo in China. The dry grinding experiments were carried out by a planetary mill, with a mill pot made of stainless steel. Stainless steel balls of 16 mm diameter were employed as grinding media. The bulk talc sample was first ground in an agate mortar for about 30 min to obtain the starting powdered samples. It is worth mentioning from the preliminary X-ray diffraction analysis that the diffraction pattern of the original powdered talc agreed well with previous results [3] and JCPDS card No. 19-770, and no significant structural change was detected in this stage of sample preparation. 3.5 g powdered talc samples and stainless balls were charged in the mill pot and then ground under dry atmospheric conditions for the desired duration of time: for 60, 120 and 240 min. The soapy feel of the starting powdered samples changed into a rough feel with increased grinding time. This change suggests a structural breakdown of the original talc samples. Additionally the colour of the ground talc samples, on the whole, changed slightly to black, indicating contamination by a small amount of stainless steel fragments. Such changes of the ground material, of course, depend on several factors, for example grinding speed, grinding media and sample volume and quality. The details of the effects of these operational parameters, including the grindability of talc samples, on the structural breakdown by using various grinding mills are given in a separate paper [4] and are therefore not duplicated here.

X-ray diffraction profiles for the ground talc samples were measured using MoK_α radiation with a singly-bent pyrolytic graphite monochromator with a diffracted beam in the wave vector range of $Q = 5$ to $153\ nm^{-1}$. Here $Q = 4\pi \sin\theta/\lambda$ where θ is half of the angle between incident and diffracted beams and λ the wavelength of the incident beam. After applying corrections for absorption, polarization and Compton scattering [5, 6] to the measured intensity data in the

---

* *Permanent address*: Industrial Technology Development Institute (MSD), Department of Science and Technology, Bicutan, Tagig, Metro Manila, Philippines.

0022–2461/91 $03.00 + .12

usual manner [7], the X-ray scattering intensities were converted into electron units by the generalized Krogh–Moe–Norman method [8] with the densities measured by the Archimedes method with toluene, and then the reduced interference function $i(Q)$ was obtained. In this work, the observed intensity data at Q less than $5\,\mathrm{nm}^{-1}$ were smoothly extrapolated to zero at $Q = 0\,\mathrm{nm}^{-1}$. The effect of this extrapolation or of truncation up to $Q = 153\,\mathrm{nm}^{-1}$ for the broad peaks observed in a disordered system is known to make no critical contribution to the radial distribution function (RDF) calculated from the interference function by Fourier transformation, if only the Q value exceeds about $70\,\mathrm{nm}^{-1}$ [9].

3. Data processing

The method for analysing the X-ray diffraction patterns of disordered systems is very common and has already been described in detail [5–7]. Consequently, only the essential features are given below.

The electron RDF can be readily estimated by applying Fourier transformation to the reduced interference function in electron units, $i(Q)$, which is directly obtained from experiments. These are defined by

$$i(Q) = \left[\frac{I_{\mathrm{eu}}(Q)}{N} - \sum_{\mathrm{uc}} f_j^2\right] \Big/ f_e^2 \qquad (1)$$

$$RDF_{\mathrm{exp.}} = 2\pi^2 r \rho_e \sum_{\mathrm{uc}} Z_j + \int_0^{Q_{\max}} Q\,i(Q)\,\mathrm{e}^{-\alpha^2 Q^2} \sin(Qr)\,\mathrm{d}Q \qquad (2)$$

where I_{eu}/N is the intensity of unmodified scattering in electron units per unit of composition and f_j, f_e are the atomic scattering factor and the average scattering factor per electron, respectively. ρ_e is the average number density of electrons and Z_j is the atomic number of element j. In the present case, the unit of composition is composed of five major elements of Si, Mg, O and H and the structural unit is considered to be $(1/21)[\mathrm{Mg_3Si_4O_{10}(OH)_2}]$. The contribution of absorbed water and the impurity originating from stainless steel fragments induced by dry grinding are not taken into account in the present structural analysis, because the total weight corresponding to both absorbed water and stainless steel impurity is of the order of 3.0–4.0 wt % at most and thus their contribution to the scattering intensity is negligibly small. The term $\exp[-\alpha^2 Q^2]$ is a convergence factor, usually introduced to minimize the truncation error and weigh down the uncertainties in the higher wave vector region. However, a zero value of α is assumed in the present calculation of the experimental RDF, although this artificial parameter is known not to be critically selected. The calculated radial distribution function ($\mathrm{RDF_{exp.}}$) in the low r region below the nearest-neighbour peak should be zero, because the atoms do not approach one another inside the atomic diameter. Therefore, the interference functions described in this work include corrections so as to remove such spurious oscillations in the low r region in the usual manner [6].

On the other hand, the electron RDF can also be calculated for particular distances r_{ij} and coordination numbers N_{ij} of i–j pairs by using the equation

$$\mathrm{RDF_{cal.}} = \sum_{\mathrm{uc}} \sum_{i} \frac{N_{ij}}{r_{ij}} \int_0^{Q_{\max}} \times \left[\frac{f_i f_j}{f_e^2} \mathrm{e}^{-\alpha^2 Q^2} \sin(Qr_{ij}) \sin(Qr)\right] \mathrm{d}Q \qquad (3)$$

This equation, using the concept of pair functions, was originally employed by Mozzi and Warren [10] under the name of Pair Function Distribution (PDF). The correlation distance is readily determined from the position of the corresponding peak in the experimental RDF data. In addition, the so-called coordination numbers can be estimated by finding the quantity of N_{ij} which will bring the calculated RDF using Equation 3 to the best fit with the experimental RDF. In this process, the value of $\alpha = 0.07$–0.08 is employed on the basis of previous studies on various oxide glasses [11]. It should, however, be noted that the present approach by applying Equation 3 is effective for only a few near-neighbour correlations such as Si–O, Mg–O and O–O.

4. Results and discussion

Fig. 1 shows the X-ray scattering intensity patterns of the ground talc samples as a function of grinding time. The basic profiles of the intensity patterns of these three samples appear to be no closer to that of the original talc structure than that of a common disordered structure like a glass. However, a few small spikes are detected at $Q = 7$, 14, 19, 24, 41 and $47\,\mathrm{nm}^{-1}$ in a sample ground for 60 min, and this implies that a small amount of the original talc structure still remains in that sample, although such incidental observation vanishes on further grinding.

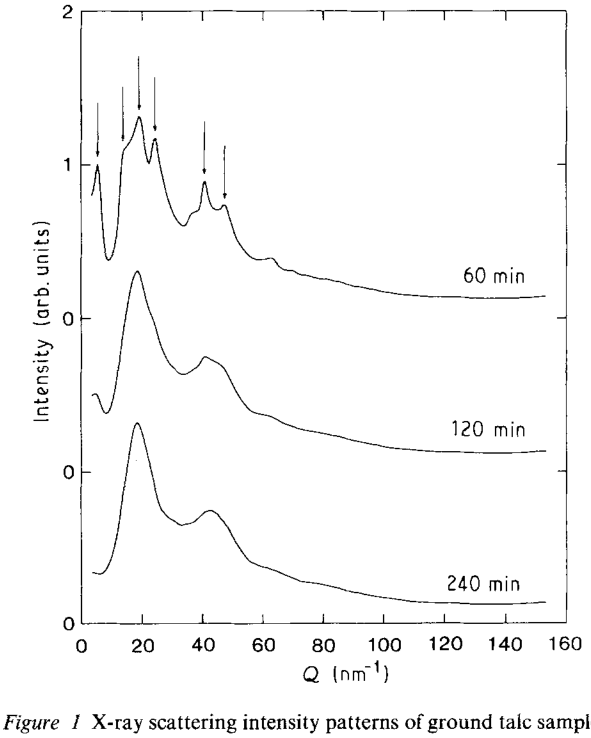

Figure 1 X-ray scattering intensity patterns of ground talc samples as a function of the grinding time, obtained by MoK_α radiation.

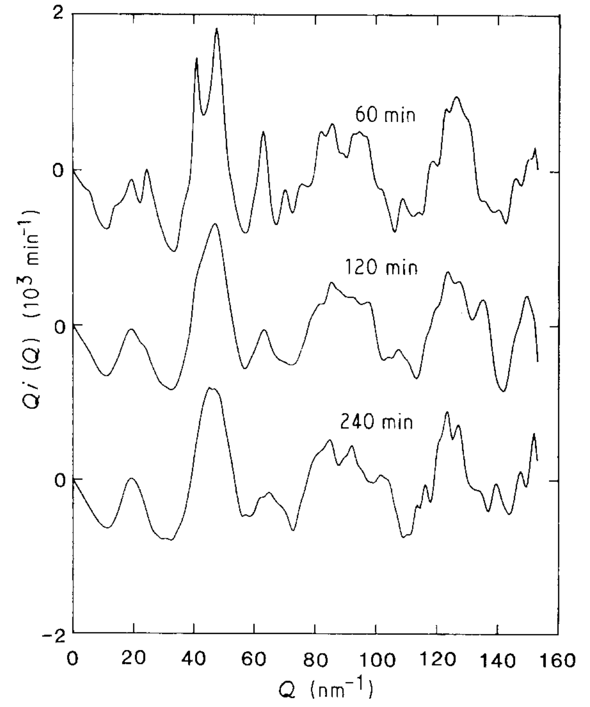

Figure 2 Reduced interference function, $Qi(Q)$, of ground talc samples as a function of grinding time.

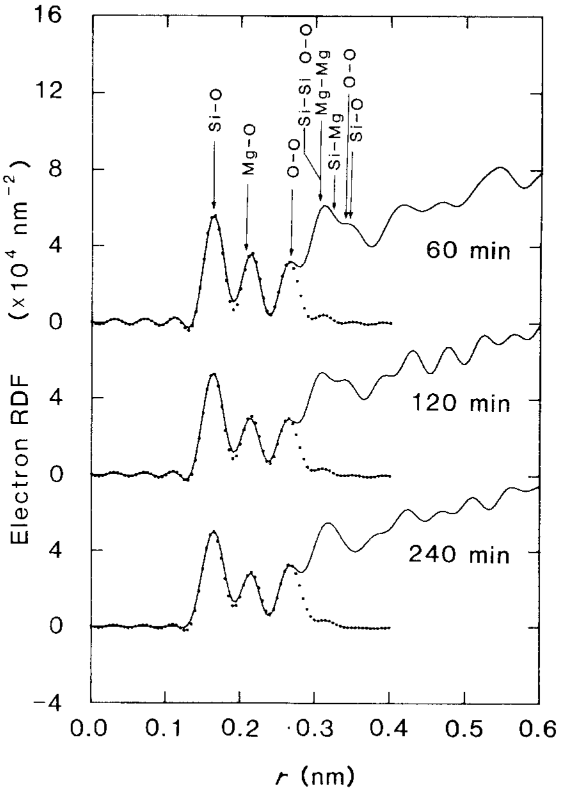

Figure 3 Electron radial distribution functions (RDFs) for ground talc samples as a function of grinding time. The solid line is the experimental data and the dotted line is the calculated sum of a few pair functions. The arrows indicate positions of some pairs observed in crystalline talc [12].

Fig. 2 shows the reduced interference function $Qi(Q)$ of the ground talc samples with variation of the grinding time. The reason for the introduction of the factor Q is to complement the resolution of the small oscillating behaviour observed in the high Q region. The general features of the reduced interference function $Qi(Q)$ for three ground talc samples are almost identical, and very close to those of oxide melts and glasses [6]. These basic profiles observed in the present three samples imply that a considerable fraction of the local ordering unit structures, such as SiO_4 tetrahedra, remains although its distribution appears to vary with grinding time. It may also be noted that their oscillating behaviour slightly differs from the metallic melt and glass cases where the damping behaviour of the function $Qi(Q)$ is rapid and monotonic [6].

The RDFs of the ground talc samples are shown in Fig. 3, which correspond to the Fourier transform of the $Qi(Q)$ functions in Fig. 2. The general features of the RDFs are again found to be almost independent of the grinding time, although the damping behaviour of RDFs at the larger values of r has some relevance to the increment of grinding time. The first two peaks in the RDFs of all ground samples appear almost completely resolved and the subsequent oscillations are reduced so as to converge to the average number density value at larger values of r. This behaviour of RDFs is consistent with the contrast between the narrow distribution of local ordering unit structures and a loss of positional correlation at a few near-neighbour distances away from any starting point. Information of such local ordering unit structures could be obtained by fitting the respective peaks by the pair function method.

Original crystalline talc is known to have a three-layered structure, in which a sheet of octahedrally coordinated magnesium is sandwiched between two sheets of linked tetrahedrally coordinated silicon. For convenience of discussing the structural features of ground talc, several interatomic distances in crystalline talc are calculated and their averaged values are shown in Fig. 3 [12]. Taking into account these atomic pairs in crystalline talc structure, it is probably reasonable to identify the first peak at around 0.16 nm with Si–O pairs, the second one around 0.21 nm with Mg–O pairs, and the third one around 0.27 nm with O–O pairs. The peak around 0.32 nm corresponds to the mixed correlation of several atomic pairs such as Si–Si, Si–Mg and Mg–Mg pairs. Therefore the interatomic distances and coordination numbers of the first three correlations were estimated by means of the pair function method. The results are summarized in Table I with the measured densities of the ground talc samples. The dotted lines in Fig. 3 denote the calculated RDF with the structural parameters listed in Table I.

The most striking results are as follows. The number of oxygens around silicon in the present ground talc samples is well-confirmed to be four. Thus, the SiO_4 tetrahedra remain unchanged as the local ordering unit structures in the present samples. On the other hand, the coordination number of Mg–O pairs estimated here decreases with an increase of the grinding time. It is also worth mentioning that the estimated distance (0.212 nm) of Mg–O pairs is slightly longer than that observed in the crystalline talc structure (0.207 nm), although the coordination number is smaller than six in the crystalline case. Taking into

TABLE I Comparison of distance (r) and coordination number (N) for ground talc samples determined in this work together with the density values measured by the Archimedes method; variations of r and N are of the order of ± 0.002 and ± 0.2, respectively

Grinding time (min)	Si–O		Mg–O		O–O		Density
	r (nm)	N (atom)	r (nm)	N (atom)	r (nm)	N (atom)	(Mg m^{-3})
60	0.163	4.0	0.212	4.6	0.265	4.9	2.48
120	0.163	4.0	0.212	4.1	0.265	4.9	2.38
240	0.163	4.0	0.212	3.9	0.268	5.8	2.31

account the suggestion that the distance of Mg–O pairs in crystalline talc is compressed by the effects of the neighbouring tetrahedral silicon sheet [12], it is feasible to consider that the breakdown of such sheets of coordination polyhedra forms a looser environmental structure around magnesium. The present Mg–O distances in the ground talc samples are also comparable to the Mg–O distance (0.212 nm) found in magnesium orthosilicate melt [13].

The present RDF analysis for the ground talc samples suggests that the crystalline talc structure is collapsed by dry grinding and changes its structure towards that of disordered atomic arrangements like glasses and liquids. This includes the characteristic variation of the environmental structure around magnesium, where magnesium of the $MgO_4(OH)_2$ octahedra in the crystalline talc changes its oxygen coordination number towards reduction. Therefore, the change in the role of a hydroxyl induced by prolonged grinding [3] may be attributed to the variation of the environmental structure around magnesium. The structural information on the ground talc samples obtained in this work is insufficient to build up a full structural model of the ground talc. Nevertheless, the present authors maintain the view that the prolonged dry grinding of crystalline talc readily induces its structural breakdown, accompanying the change in role of a hydroxyl towards the reduction of the oxygen coordination number around magnesium. It would be useful to carry out some further structural studies of various ground clay minerals, in order to get a definite view on the role of hydroxyl and to test the present concluding remarks on a wider base.

Acknowledgements

The authors wish to express their thanks to T. Kihara of Kihara Kasei Co. Ltd for their supply of talc samples. One of the authors (P.F.J.) also wishes to thank Japan International Cooperation Agency for financial support.

References

1. R. C. MacKENZIE and A. A. MILNE, *Mineral. Mag.* **30** (1953) 178.
2. H. KODAMA, L. S. KOTLYAR and J. A. RIPMEESTER, *Clays & Clay Miner.* **37** (1989) 364.
3. H. TAKAHASHI, *Bull. Chem. Soc. Jpn* **32** (1959) 374.
4. F. SAITO, P. F. JAMES, K. SUGIYAMA and Y. WASEDA, to be submitted.
5. C. N. J. WAGNER, *J. Non-Cryst. Solids* **31** (1978) 1.
6. Y. WASEDA, "The Structure of Non-Crystalline Materials" (McGraw-Hill, New York, 1980).
7. B. E. WARREN, "X-ray Diffraction" (Addison-Wesley, Reading, Massachusetts, 1969).
8. C. N. J. WAGNER, H. OCKEN and M. L. JOSHI, *Z. Naturforsch.* **20a** (1965) 325.
9. K. FURUKAWA, *Rep. Progr. Phys.* (1962) 25.
10. R. L. MOZZI and B. E. WARREN, *J. Appl. Crystallogr.* **2** (1969) 164.
11. A. C. WRIGHT and A. J. LEADBETTER, *Phys. Chem. Glasses* **17** (1976) 122.
12. J. H. RAYNER and G. BROWN, *Clays & Clay Miner.* **21** (1973) 103.
13. K. SUGIYAMA, E. MATSUBARA, I. K. SUH, Y. WASEDA and J. M. TOGURI, *Sci. Rep. Res. Inst. Tohoku Univ.* **A34** (1988) 143.

Received 17 September
and accepted 20 December 1990