THE EFFECT OF MECHANICAL TREATMENT ON THE CRYSTAL STRUCTURE AND THERMAL BEHAVIOR OF KAOLINITE

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Abstract—The destruction of the crystal structure of kaolinite caused by mechanical forces was investigated by X-ray diffraction, thermal analysis, infrared spectroscopy, and specific surface area determination. Attention was also directed to the change of thermal reactions of milled kaolinite. Grinding experiments for 5 min, 10 min, and 1, 2, 4, 6, and 10 h were carried out in an AGO I planetary mill. After 1 h of grinding, the crystalline order of kaolin is destroyed; but the amorphization continues in the course of prolonged grinding. Grinding for 1 h produces a favorable state for forming mullite-type crystals after heating even at 1000°C.

Key Words—Amorphization, Crystal structure, Grinding, Kaolinite, Mechanochemistry, Thermal behavior.

INTRODUCTION

The mechanochemical amorphization of kaolinite and the mechanism are widely discussed (e.g., Kelley and Jenney, 1936; Laws and Page, 1946; Wiegmann, 1957; Köhler *et al.*, 1960). Schrader (1970) observed that the crystal structure was deformed mainly along the c-axis during mechanical treatment. Juhász (1974), Hlavay *et al.* (1977), Aglietti *et al.* (1986), and Juhász and Opoczky (1990) suggested that the OH groups are displaced irreversibly during mechanical treatment. The rupture of the O–H, Al–OH, Al–O–Si and Si–O bonds during grinding was reported by Miller and Oulton (1970), Hlavay *et al.* (1977), Juhász (1980), and Aglietti *et al.* (1986). Juhász and Wojnárovits (1984) compared the character of metakaolin and the so-called kaolin-xerogel produced by mechanical treatments of kaolin. Hlavay *et al.* (1977), Juhász (1980), and Aglietti *et al.* (1986) observed that the specific surface value of kaolin reaches a maximum at various grinding times.

The thermal decomposition of kaolinite has been the subject of numerous studies (e.g., Brindley and Nakahira, 1959; Grofcsik, 1961; McConnel, 1970; Cameron, 1977). Brindley and Nakahira (1959) documented completely the alterations caused by heat treatment. The appearance of well-crystalized mullite was observed only above 1200°C (Grofcsik, 1961; Kotsis, 1980).

Most researchers study the amorphization of kaolinite until the appearance of a disordered kaolinite structure and do not investigate the kaolinite-mullite transformation in the ground kaolin. However, the series of reactions producing mullite are perhaps the most important in the various fields of ceramic technology. The present work studies the mechanically induced crystal-structural distortion of kaolinite to the quasi-amorphous state and the results of mechanical handling and subsequent heating on the formation of mullite.

EXPERIMENTAL METHODS

Materials

All grinding experiments were performed using high-grade, natural kaolin from Sedlec (Zettlitz) in Czechoslovakia. Its chemical composition in oxide wt. % is: MgO, 0.66; CaO, 0.25; SiO_2, 44.26; Fe_2O_3, 0.73; K_2O, 0.99; Al_2O_3, 39.72; TiO_2, 0.05; Na_2O, <0.1; loss on ignition, 13.22. The major mineral impurities are 5 wt. % illite and 3 wt. % quartz. The crystallinity index calculated by the Hinckley (1963) method is 0.67. The specific surface of the starting material was 17.7 m²/g.

Milling procedure

An AGO I planetary mill was used for mechanical treatment of solids. Samples were ground for 5 min, 10 min, and 1, 2, 4, 6, and 10 h. Each milling was carried out with a 20 g air-dry sample in a 150 cm³ capacity steel pot with 121.1 g, 7 mm diameter steel balls. The pots were rotated at 1820 rpm. The intensive cooling of pots with cold running water increased the efficiency of mechanical treatment (Juhász and Opoczky, 1990).

Heat-treatment procedures

The original and mechanically treated samples of Zettlitz kaolin were fired at various temperatures (at 900°C, 1000°C, 1200°C, and 1400°C) in a super cantal kiln (type KLO II) for 1 h. The material was placed in a corundum sample holder and heated and cooled in air.
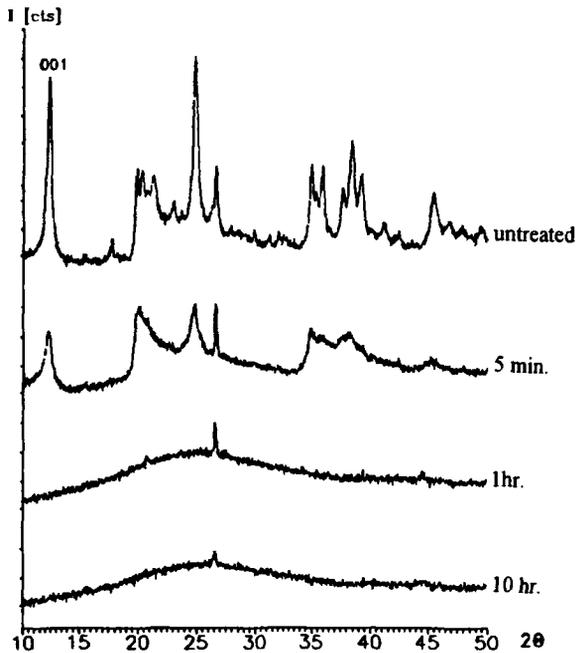
Figure 1. X-ray diffractograms of the original kaolin and after grinding for times indicated. (CuK$_\alpha$ radiation.)
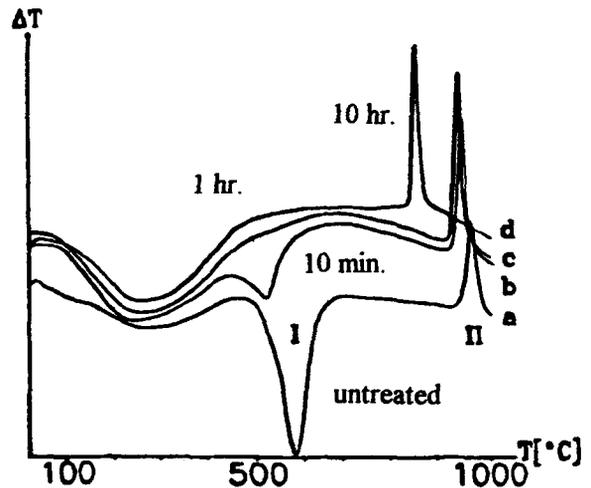

Figure 2. Evolution of DTA diagrams of the kaolin after grinding. a) untreated; b) 10 min; c) 1 h; d) 10 h. I = Major endothermic peak. II = Major exothermic peak.

mined by the BET method from the adsorption of Ar at 77.3 K on an ATLASMAT Betograph.

Examination of materials

X-ray diffractograms were obtained on a Phillips PW 1825/00 diffractometer at a scanning speed 0.035° 2Θ per sec using Cu K$_\alpha$ radiation (at 40 kV, 40 mA). Data collection and evaluation were performed with an APD 1700 software system. Line profile analysis (LPA) and an estimation method for lattice parameters (ELP) were applied to extract information on the microstructure and the structural imperfections of the kaolinite and alteration product (Klug and Alexander, 1972; Delhez et al., 1982). For LPA, a deconvolution method was used to determine structural broadening after K$_{\alpha2}$ peak stripping, linear background elimination, and correction for the Lorentz polarization factor. The corrected intensities were used to calculate the mean lattice distortion where e = β/4/tgΘ, and β is the integral breadth of the strain-broadened profile taken on a 2Θ scale. Lattice parameters were estimated from nonoverlapping K$_{\alpha1}$ peaks by an iteration technique using a set of standards (from 15-776 ASTM data) to correct for instrumental parameters (Klug and Alexander, 1972).

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed with a MOM Derivatograph. The runs were made at a constant heating rate of 10°C per min in a corundum sample holder applying high-grade corundum as a reference material.

Infrared spectra were obtained with a Fourier Transform Spectrometer (model BIORAD FTS 45) from pressed disc utilizing 1.0 mg of material with 800 mg of KBr.

The specific surface area of the samples was deter-

RESULTS

The diffractograms of the original sample and those from mechanically treated ones at various times show a rapid deterioration of the kaolinite structure during grinding (Figure 1). All reflections of kaolinite have disappeared after 1 h of grinding, reflecting the complete destruction of the crystal structure. The rapid production of an amorphous material by grinding is reflected also in the mean lattice strain calculated by LPA for the (001) reflection. It is 2.188% after 5 min and 3.719% after 10 min of grinding.

The considerable structural deformation caused by milling is confirmed by DTA (Figure 2), TG, and IR analyses (Figure 3). The endothermic (peak I) due to dehydroxylation (Figure 2) is moved to the same interval as adsorbed water. The decrease of bonding energy of OH groups is essentially finished after 1 h of grinding (Aglietti et al., 1986). The temperature of the exothermic peak (II) decreases, because of the deformation of the Si–O–Al bonds produced by mechanical forces. It continues with increased length of milling, and there is an almost linear relationship between temperature and grinding time.

Within 1 h, the IR spectra show (Figure 3, as per the literature); the absorption bands due to OH stretching (3698, 3654, 3620 cm^{-1}) are rapidly reduced; and the broad absorption band (3400 cm^{-1}) corresponding to the randomly attached OH ions and absorbed water increased. After 1 h of grinding, the disappearance of the 912 cm^{-1} and 936 cm^{-1} bands indicates the breakage of Al–OH linkage. The alteration of Si–O stretching and the disappearance of the Al–O–Si band indicate the distortion of tetrahedral and octahedral layer.
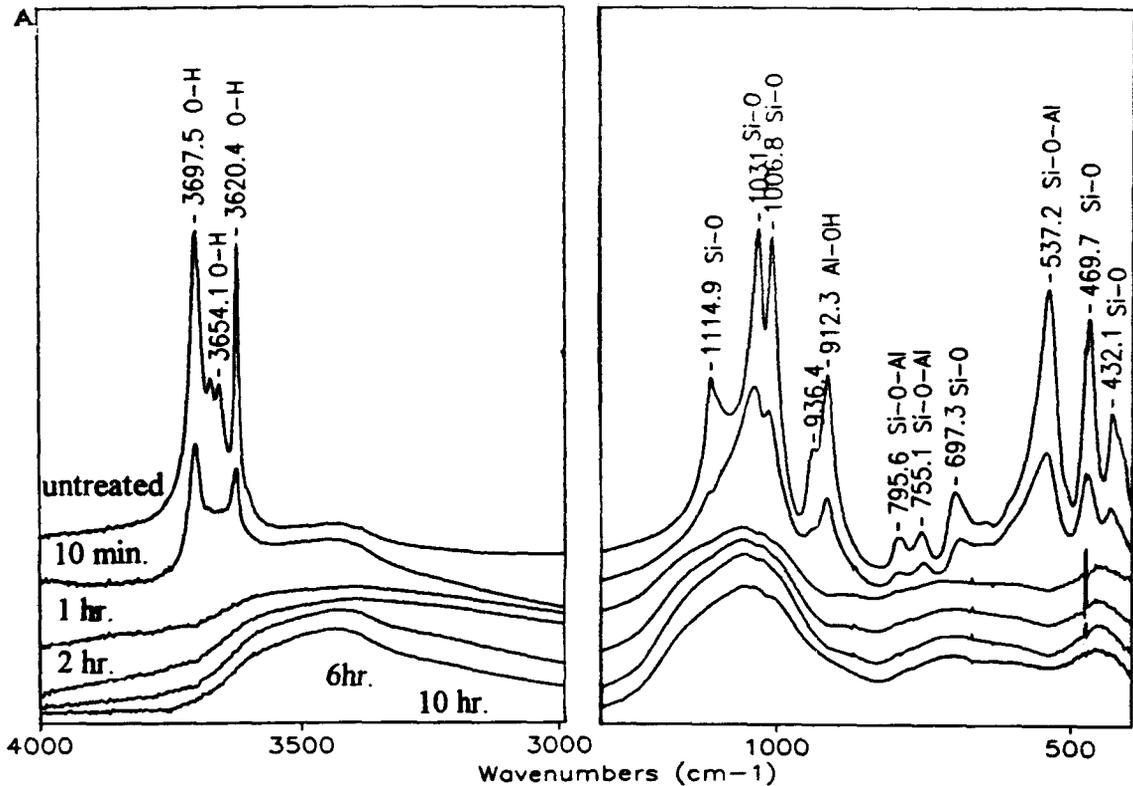
Figure 3.   Evolution of IR spectra of the kaolin after grinding for times indicated.

The curve relating the specific surface of kaolin *vs* grinding time passes through a narrow maximum (63 m²/g) at 5 min and declines even below the initial value (17.8 m²/g) for the unground sample. After 1 h, it is practically constant (9 m²/g; See Figure 4). The specific
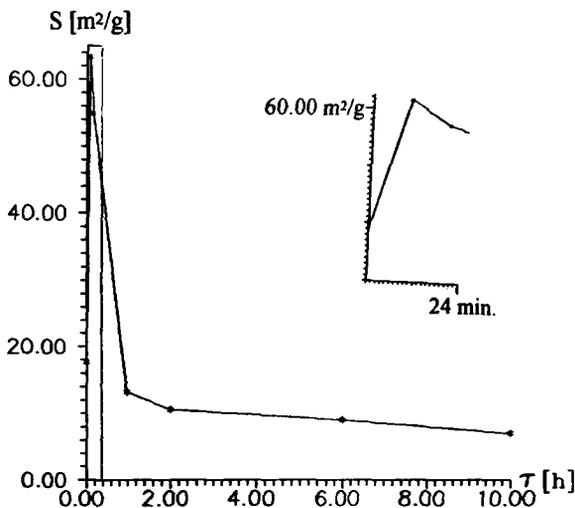

Figure 4.   The 'total' specific surface area of the kaolin as a function of grinding time, τ[h]. Inset provides enlarged view of changes occurring with less than 24 min of grinding.

surface area determination was carried out also for the samples after heating at 1000°C. The decrease of specific surface resulting from heating for 1 h at 1000°C is 6.1 m²/g, 8.4 m²/g, 5.8 m²/g in the samples milled for 0 h, 1 h, and 4 h, respectively.

The diffractograms on Figure 5 show that the products of heat-treatment at 900°C lack of full three-dimensional regularity. For the 6 h and 10 h ground and heated samples, the broad band in the range of 15° to 35° 2Θ slightly decreases with grinding time, and two smaller bands appear in the range of 35° to 50° 2Θ. (These may indicate a quasicrystalline product described as metakaolin or spinel phase in Brindley and Nakahira, 1959, and Grofcsik, 1961.)

In the diffractogram of the kaolinite sample milled for 1 h and heated at 1000°C for 1 h, mullite reflections were apparent (Figure 6). Milling more than 1 h reduces the intensity of these mullite reflections and after 4 h they almost disappear. This seems to prove that the samples milled for periods of time greater than 1 h are substantially different in structure because the formation of mullite at 1000°C is influenced mainly by the structural state.

Figure 7 shows the diffractograms of samples ground for various times and heat-treated for 1 h at 1400°C. No detectable changes in the reflections of the mullite present were found, but a reduction in the area of cris-
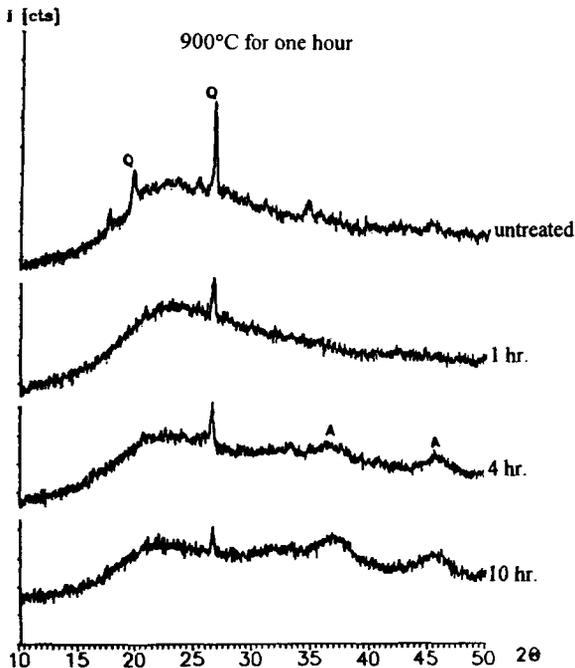
Figure 5.   X-ray diffractograms (CuK$_\alpha$) of the kaolin ground for various times, and heated at 900°C for 1 h. Q = β quartz, A = spinel phase.

tobalite peaks was observed as a function of grinding time. The explanation of this phenomenon is probably that at high temperature the Fe impurity reacts with cristobalite.
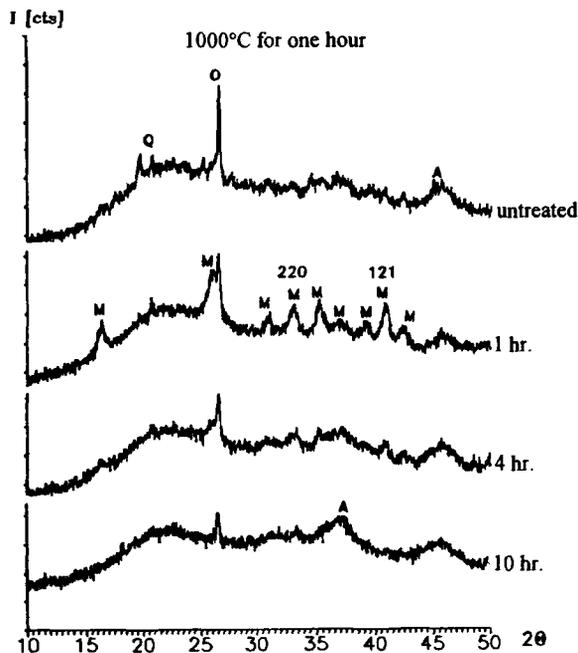

Figure 6.   X-ray diffractograms (CuK$_\alpha$) of the kaolin ground for various times and heated at 1000°C for 1 h. M = mullite, Q = β quartz, A = spinel phase.
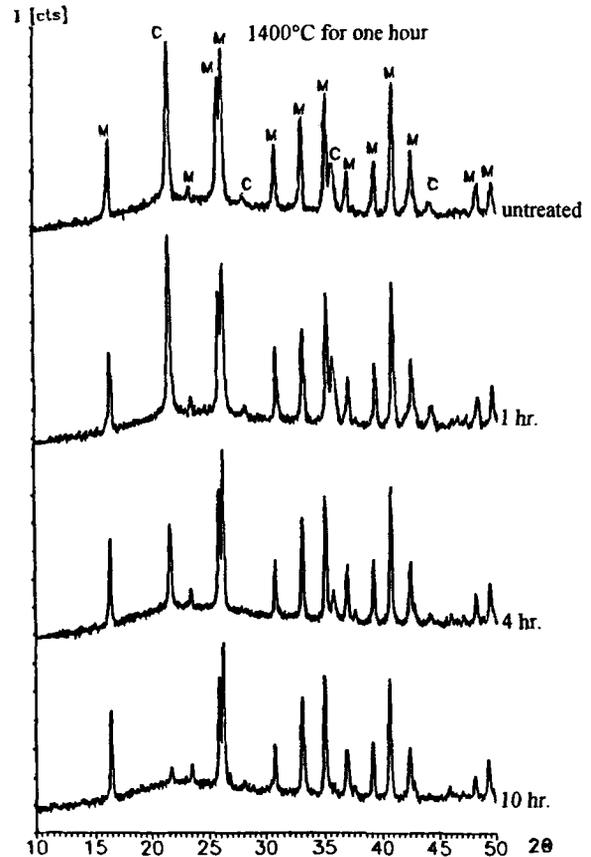

Figure 7.   X-ray diffractograms (CuK$_\alpha$) of the kaolin ground for various times and heated at 1400°C for 1 h. M = mullite, C = cristobalite.

The crystal structure of mullite present in specimens ground and heat-treated for 1 h at 1000°C, 1200°C, and 1400°C were examined applying the ELP. (The data of ASTM card No. 15-776 were used as reference.) There was no considerable difference between the cell parameters of analyzed mullites formed from samples ground and heated at 1000°C and that formed from unground, heat-treated kaolinite at 1200°C and 1400°C. These results demonstrate also (corresponding to Cameron (1977)) that Fe from the grinding procedure does not enter the mullite crystals.

DISCUSSION

The XRD and IR data illustrate, that the 1 h-milled kaolinite has a completely different structure from the original; all the reflections of kaolinite disappear, the structural OH groups are removed irreversibly from their position, and the tetrahedral and octahedral layer are distorted. After 1 h, the alteration of this quasi-amorphous structure is accompanied by further destruction of the Si-O-Al network (considering the DTA and IR curves).

The exothermic reaction about 950°C during the heat-

treatment of kaolinite can be regarded as the beginning of mullite crystallization. Grofcsik (1961) supposes that the nuclei of mullite crystals appear after this reaction, while other authors (Brindley and Nakahira, 1959; McConnel, 1970) postulate the formation of well-oriented spinel-type phase as a transitional structure to mullite. The shifting of the exothermic peak of DTA and the XRD pattern of the 900°C heat-treated samples suggest that grinding and mechanical distortion of kaolinite speed up the formation of this transitional (spinel) phase at lower temperature. At about 950°–1100°C, the development of mullite crystals is prevented since the thermal energy is not sufficient for formation of high quality mullite (Brindley and Nakahira, 1959; Kotsis, 1980). After 1 h of grinding of kaolinite, there is probably a favorable structure (considering the results of XRD, DTA, IR, and XRD of heat-treated samples), so the heat energy is sufficient to connect the building elements of mullite crystals at 1000°C. After 1 h of grinding, the mechanical forces destroy this active transitional state; thus the mullite crystallization requires more energy. (Before 1 h and after 4 h of grinding, the appearance of mullite peaks in the samples heat-treated at 1000°C was not observed.) While the formation of mullite during the heat-treatment at 1000°C is favored by the presence of a transitional structural state, the heat energy at 1400°C is sufficient for mullite crystallization regardless of the structural state of the sample.

CONCLUSION

When ground mechanically, kaolinite suffers significant and rapid crystal structural alteration due to the distortion or breakage of the crystalline network. After 1 h of grinding, small groups of atoms corresponding to the original kaolinite crystals are probably present, but their connections do not fit in the regularity of a crystalline state. Further mechanical deformation destroys these regular groups and produces a more irregular crystalline state.

The investigation with heat-treatment illustrates that the quasicrystalline state created by destruction of the kaolinite structure is favorable for forming mullite below the temperature necessary for the diffusion processes of this solid-state reaction in the original kaolinite. Nevertheless, the mullite crystals formed at 1000°C are not the same size and regularity as those present in samples heated at higher temperatures (e.g., 1200°C and 1400°C). The results confirmed the fact that the so-called crystalline and amorphous materials do not represent two well-separated states, but intermediate states in which various regularities of the building elements of crystals exist.

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