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The effect of mechanical treatment on the crystal structure and thermal decomposition of dolomite

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Abstract

The crystal structural deformation of dolomite caused by intensive grinding was investigated by X-ray diffraction (XRD), thermal analysis. Applying high temperature XRD, attention was mainly directed to the change of the thermal decomposition of mechanically treated dolomite. Grinding experiments for 1, 5 and 7 h were carried out in FRITSCH *pulverisette*5/2 planetary mill. Structurally deformed dolomite crystallites developed due to the mechanical treatment decomposes in two steps at higher and lower CO_2 partial pressure as well. Deformed dolomite decomposes directly to calcite and periclase accompanied by the formation of CO_2 between 500°C and 600°C. The proportion of structurally distorted dolomite increases with the grinding time. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal; Decomposition; Dolomite; Grinding; X-ray diffraction

1. Introduction

Changes in the structure and in the physicochemical properties of solids due to the mechanical treatment (e.g. grinding) are widely discussed [1–11].

The mechanically induced crystal-structural distortion of dolomite was studied mainly by thermoanalytical methods [7–11]: a decrease of the peak temperature of the first DTA endotherm (in the two-step decomposition) was observed in the case of ground dolomite samples. This phenomenon is attached by most of the researchers [7,9–11] to the deformation of the dolomite crystalline network without any phase disintegration that was found by Molchanov [8].

The thermal decomposition of dolomite in air or in CO_2 has been extensively studied [12–16]. Dolomite decomposes in two separate stages, if the partial pressure of CO_2 is high enough [12,13]:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \quad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

The two decomposition process can merge owing to the low partial pressure of CO_2 [12,13]:

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2\,CO_2 \quad (3)$$

Some of the thermoanalytical researches are expanded to investigate the high temperature phases in situ using high temperature X-ray diffraction (XRD) [14,16]. Engler et al. [14] found that dolomite decomposes directly to calcite and periclase in CO_2 between 550°C and 765°C. In air, simultaneous for-

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mation of calcite, lime and periclase accompanied by dolomite decomposition was observed between 700°C and 750°C.

Although the thermal analysis of ground dolomite is perhaps one of the most important method for its mechanochemical study, most of the researches are not expanded to investigate the high temperature formed phases in situ. Recently, in the case of milled dolomite, the formation of calcite and periclase was observed in air at 580°C [17]. Since the investigation of high temperature formed phases of ground dolomite seemed to be important in respect to clarify the mechanochemical alteration of dolomite, we have performed more detailed thermoanalytical and high temperature XRD measurements.

2. Experimental

2.1. Materials

A well-crystallized natural dolomite from Pilisvörösvár (Hungary) was investigated. Its chemical composition in oxide wt% is: MgO, 21.43; CaO, 29.82; SiO_2, 1.87; Fe_2O_3, 0.07; loss on ignition, 46.81.

2.2. Milling procedure

Mechanical treatment of solids was performed by a FRITSCH *pulverisette* 5/2 laboratory planetary mill. 10 g air-dry sample of dolomite was intensively ground in a 80 cm^3 capacity stainless steel acidproof (18% Cr + 8% Ni) pot with 64.1 g, 10 mm diameter stainless steel acidproof (18% Cr + 8% Ni) balls for periods of 1, 5 and 7 h.

The 'total' specific surface of the starting powder was 0.58 m^2/g. The specific surface areas of the milled dolomite samples were 10.69, 7.73 and 6.17 m^2/g for 1, 5 and 7 h grinding time, respectively. The variation of the specific surface area with the grinding time is suitable to characterize the changes of degree of dispersion. Corresponding to the literature [5,9,11] three regions of this grinding process can be distinguished: first, the degree of dispersion of dolomite increases (the Rittinger stage of grinding); second, it tends to a maximum value (aggregation stage); and third, it decreases in the final period of grinding because of the particle interaction (agglomeration stage). The obtained values support that the transformations in solids induced by grinding are complex, and the intensive grinding is not equivalent to the particle size reduction.

2.3. Examination of materials

The specific surface area of the samples was determined by the BET method from the adsorption of N_2 at 77.3 K on a Micrometrics ASAP 2000 equipment.

The thermal analyses (DTA and TG) were performed on a Derivatograph, MOM (Hungary) [18]. The thermoanalytical curves were recorded at two different mass of each ground sample (1000 and 130 mg). The runs were made at a constant heating rate of 10°C min^{-1} under static air atmosphere. The samples were packed in the alumina crucibles applying high grade alumina as reference. Additional measurements were carried out by a Derivatograph PC, MOM (Hungary) for the exact determination of mass loss (mass of sample: approximately 55 mg; heating rate: 5°C min^{-1}; atmosphere: air, static; crucible: alumina).

The normal room temperature and high temperature XRD measurements were carried out on a Philips PW3710 based diffractometer equipped with two goniometers (PW1820, PW3020) using CuKα radiation (40 kV, 40 mA). Curved graphite crystal monochromators were used to obtain monochromatic radiation. Data collection and evaluation were performed with PC-APD 3.6 and PC-IDENTIFY 1.0 softwares. The normal, room temperature diffractograms were recorded at a scanning speed 0.02° 2θ per second. The high temperature scans was made by an Anton Paar HTK 16 high-temperature camera fitted on the PW 1820 goniometer. Approximately 100 mg of dolomite samples grounded at different time were packed on the prestressed platinum heating filament of the high temperature attachment. Fig. 1a shows the temperature profile applied for the high temperature measurements which was controlled by PC-APD 3.6 software as well. These studies require that samples be brought to a specific temperature in a specific time and held for the duration of the XRD measurement. The samples were scanned from 27.5° 2θ to 45° 2θ at a scanning speed 0.025° 2θ per second. The heating and cooling rate was 100°C min^{-1} between 25°C and 400°C,

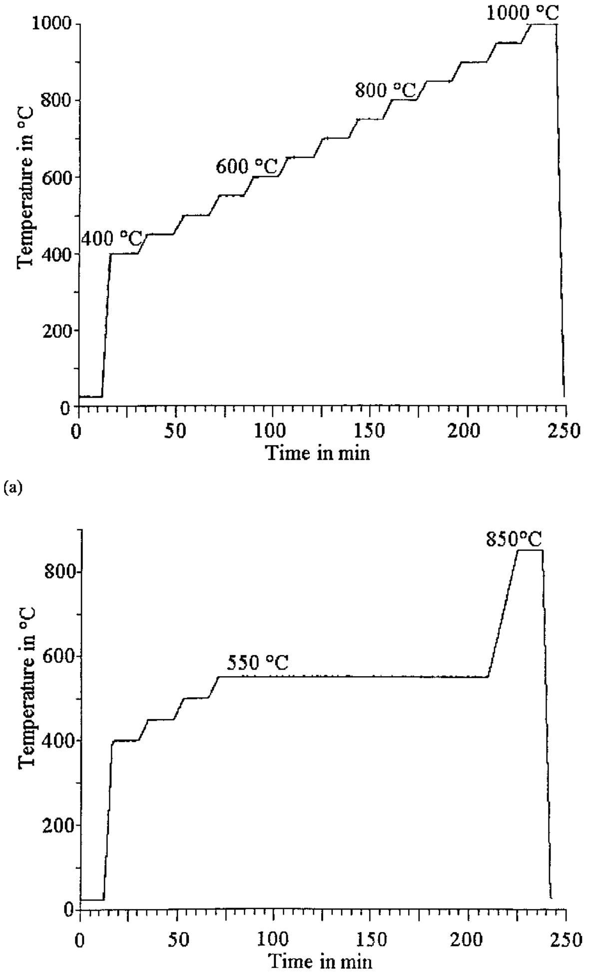


Fig. 1. The temperature profiles of high temperature XRD measurements: (a) quasi-dynamic profile; (b) a ‘static’ profile with keeping the sample at 550°C for 2 h.

10°C min^{-1} between 400°C and 1000°C and −195°C min^{-1} between 1000°C and 25°C (Fig. 1a). Additional high temperature measurements were carried out to study the changes of phases formed at different temperature. In this case results are obtained by holding the sample for 2 h at one specified constant temperature (500°C, 550°C, 600°C, 650°C, 700°C or 750°C; see, as an example, Fig. 1b). As shown in Fig. 1b, the same temperature profile was used up to the given temperature. The diffractograms were also recorded from 27.5° 2θ to 45° 2θ at a scanning speed 0.025° 2θ per second every 0.5 h.

3. Results and discussion

The thermoanalytical curves recorded at two different mass of samples show remarkable alteration in the thermal decomposition of dolomite ($CaMg(CO_3)_2$) in the function of grinding time. As can be seen in Fig. 2a, for 1000 mg sample mass, the untreated dolomite shows two DTA endotherms (MgI, 770°C; CaI, 900°C) due to a two-step decomposition reaction according to Eqs. (1) and (2). Fig. 2a shows the DTA curves of large amount (1000 mg) of samples grounded for different time. As a result of grinding, the first endothermic peak (MgI) — indicating CO_2 loss during the formation of calcite ($CaCO_3$) and periclase (MgO) (Eq. (1)) — separates into two parts (MgI, MgII). Both MgI (690°C) and MgII (580°C) peaks can be observed after grinding for 1 h but only MgII (580°C) peak appears after grinding for 5 and 7 h. In the post-5 h period, the maximum temperature of the first endotherm representing Eq. (1) is found to be approximately 200°C lower, while the maximum temperature of the second endotherm, which indicates CO_2 loss during the formation of lime (CaO) (Eq. (2)), is almost constant [11].

When the sample mass is 130 mg, practically one peak (DI, 810°C) with a small shoulder (700°C) appears in the DTA curve of untreated dolomite (Fig. 2b). As the CO_2 partial pressure is lower here, this curve represents the mergence of the two-step decomposition of dolomite. As can be seen, a second endotherm (DII, 540°C) appears at lower temperature after grinding for 1, 5 and 7 h. The proportion of CO_2 released at the lower temperature (DII) increases with the grinding time (Fig. 3).

The diffractograms of the original and the mechanically treated samples indicate that dolomite suffers significant structural degradation (Fig. 4). The distortion of structure induced by grinding is reflected in the line broadening and reflection shifting, as well as the reduction of peak intensities (areas). Recently, it was shown that this X-ray line broadening is mainly due to lattice microstrains, rather than microcrystalline size [9,11].

High temperature XRD was used to elucidate the effect of structural deformation caused by grinding on the thermal decomposition process of dolomite. Fig. 5 shows the high temperature diffractograms of the dolomite samples in the temperature range

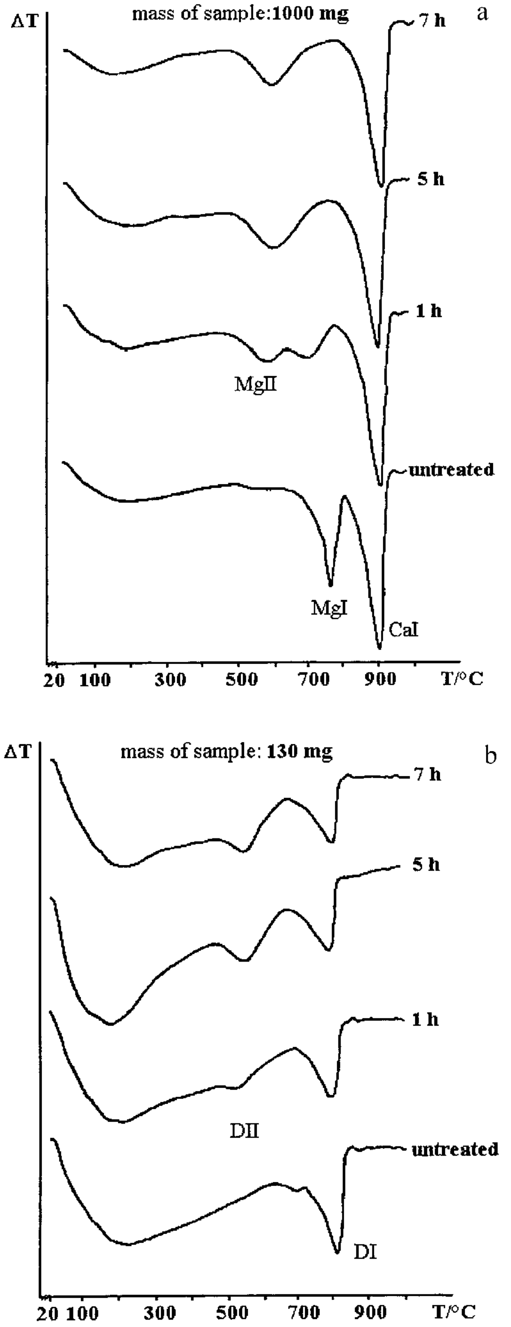


Fig. 2. DTA curves of the dolomite samples grounded for times indicated (mass of sample: (a) 1000 mg; (b) 130 mg).

(400–850°C) where the phase transformations are detected. The high temperature XRD scans of untreated sample shown in Fig. 5a practically correspond to a one-step decomposition. As can be seen, between 550°C and 600°C, a small $CaCO_3$ (C (104)) peak appears, while the main dolomite peak (D(104)) slightly reduces. The presence of MgO (P(200)) is detected at 600°C. The MgO and $CaCO_3$ peaks continues to grow between 600°C and 750°C, while CaO peaks appears at 700°C. Finally, the rapid increase of MgO and CaO peaks and the rapid decrease of dolomite peaks occur at 750°C. The decomposition seemed to be complete by 800°C, where only CaO and MgO are present. These results practically suit to the thermoanalytical measurements (DTA, TG) made by small amount (130 mg) of untreated dolomite samples. In that case, the partial pressure of CO_2 is low enough that undistorted dolomite could dissociate into CaO and MgO between 600°C and 800°C while some $CaCO_3$ forms and decomposes.

Considering the high temperature diffractograms of mechanically treated samples Fig. 5b–d, the formation of growing amounts of $CaCO_3$ and MgO are found between 550°C and 700°C, when increasing the applied grinding time. Simultaneously, the dolomite peaks reduce. After that, the formed $CaCO_3$ and the remained dolomite disintegrate into CaO and MgO at 750°C. Comparing the high temperature diffractograms and the DTA curves recorded at the lower sample mass (130 mg) of the ground samples with that of the unground sample, it can be established that the dolomite peaks obtained at 600°C represent the structurally undistorted part of the samples. It can be seen furthermore that, in spite of the low CO_2 partial pressure, structurally deformed dolomite decomposes in two steps (Eqs. (1) and (2)).

The relative peak areas of the phases detected at different temperatures were determined in the case of the samples grounded for various time (Fig. 6) to estimate the concentration of this phases. Analyzing the decomposition of the untreated dolomite sample (Fig. 6a) between 550°C and 600°C, a formation of a small and fairly constant amount of $CaCO_3$ ($\sim$0.06) and a reduction of the dolomite content (to $\sim$0.80) was found. In this temperature region, the dolomite content of samples grounded for 1, 5 and 7 h rapidly reduces to 0.60, 0.35 and 0.40 of the initial value, respectively. Both $CaCO_3$ and MgO peaks of mechanically treated samples grow at similar and rapid rates between 500°C and 600°C. The values for the relative peak area of $CaCO_3$ of the untreated dolomite sample show a max-

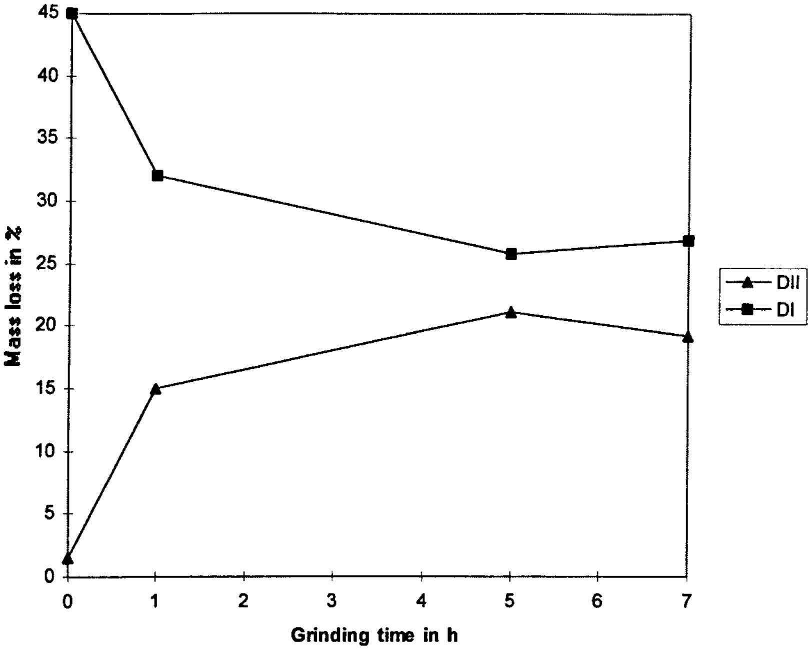


Fig. 3. Changes in mass loss of the dolomite samples as a function of grinding time (mass of sample: approximately 55 mg; heating rate: 5°C min^{-1}; atmosphere: air, static; crucible: alumina).

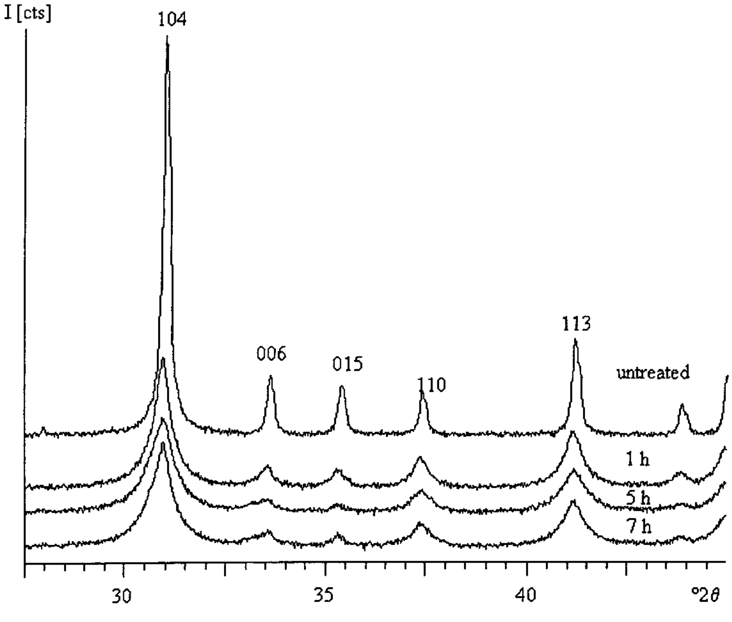


Fig. 4. X-ray diffractograms of the dolomite samples grounded for times indicated.

imum (0.29) at 750°C while those of CaO (0.30) and MgO (0.60) rapidly increase here. As shown in Fig. 6a, a significant amount of dolomite (0.46) is still present at 750°C, but above this temperature dolomite peaks decrease and disappear at 800°C. Between 750°C and 800°C, the MgO content of the untreated dolomite sample grows with approximately half rate than the CaO content. Fig. 6b shows that the relative peak area of $CaCO_3$ of 1 h grounded dolomite sample reaches the maximum value (0.51) at 650°C and it is almost double of that of the untreated sample. Simultaneously, its dolomite content lowers down to almost half of its initial amount. At 700°C, the maximum relative peak area of $CaCO_3$ of the dolomite sample grounded for 5 and 7 h is 0.69 and 0.70, respectively. Namely, the maximum amount of $CaCO_3$ formed from these samples is by almost 50% greater than that of 1 h grounded dolomite sample. Comparing Fig. 6b with Fig. 6c and d between

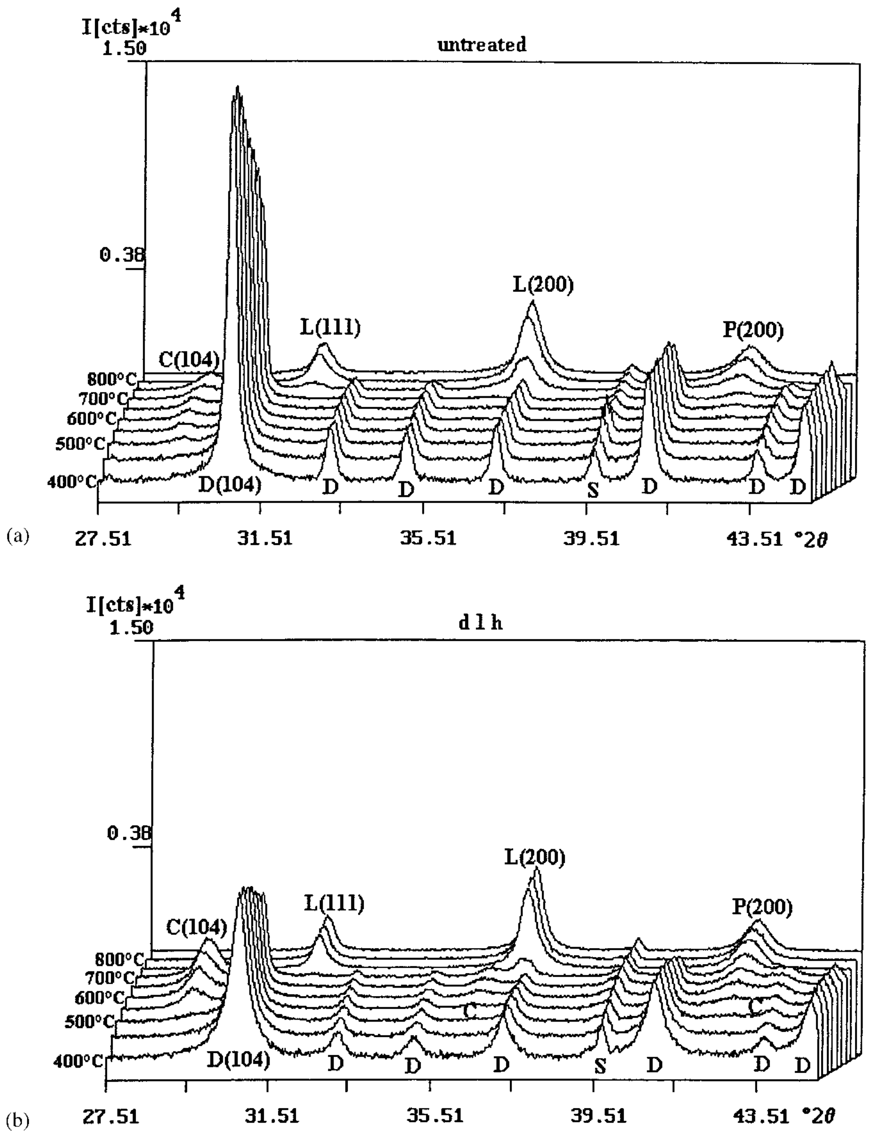
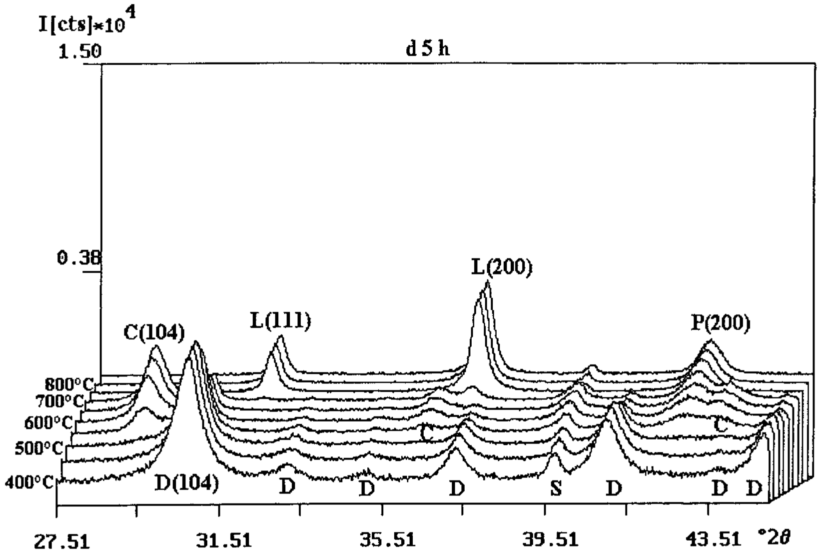
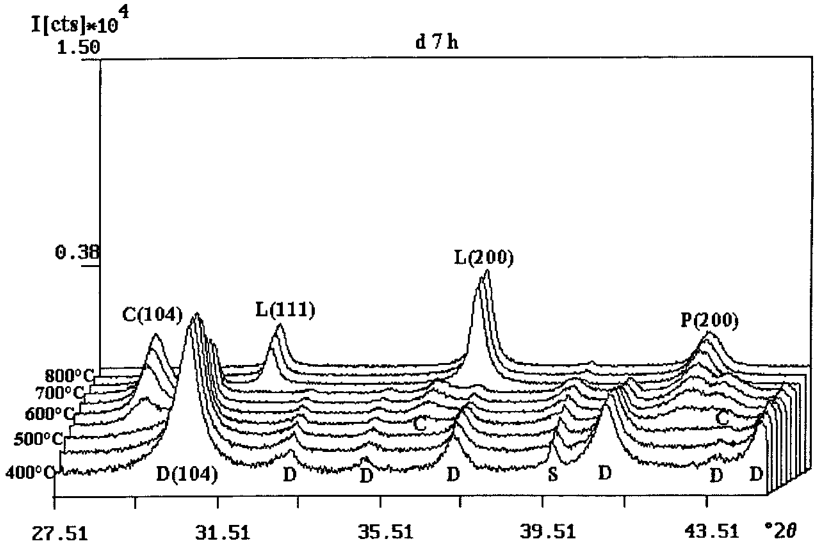


Fig. 5. High temperature X-ray diffractograms of the dolomite samples measured at 400°C, 450°C, 500°C,. . .,850°C after grinding: (a) 0 h; (b) 1 h; (c) 5 h; (d) 7 h (C, calcite ($CaCO_3$); D, dolomite ($CaMg(CO_3)_2$); L, lime (CaO); P, periclase (MgO); S, sample holder).



(c)



(d)

Fig. 5. (*Continued*).

600°C and 750°C, the dolomite content of the samples grounded for 5 and 7 h is much less than that of samples grounded for 1 h. These results coincide with the observation of the thermoanalytical measurements recorded at the lower sample mass (130 mg). The increase of $CaCO_3$ and MgO content of sample grounded for 1, 5 and 7 h between 550°C and 600°C corresponds to the rising amount of CO_2 (proportional to the grinding time) released at the lower temperature (DII).

Finally, the rapid decrease of $CaCO_3$ content (starting from 700°C) parallel with the further decrease of dolomite content and the rapid increase of CaO and MgO content indicates the complete disintegration of dolomite.

The changes of phases formed at different temperatures were followed by X-ray scans keeping the sample at a given constant temperature (500°C,. . ., or 750°C) for 2 h. The previously detected high tem-

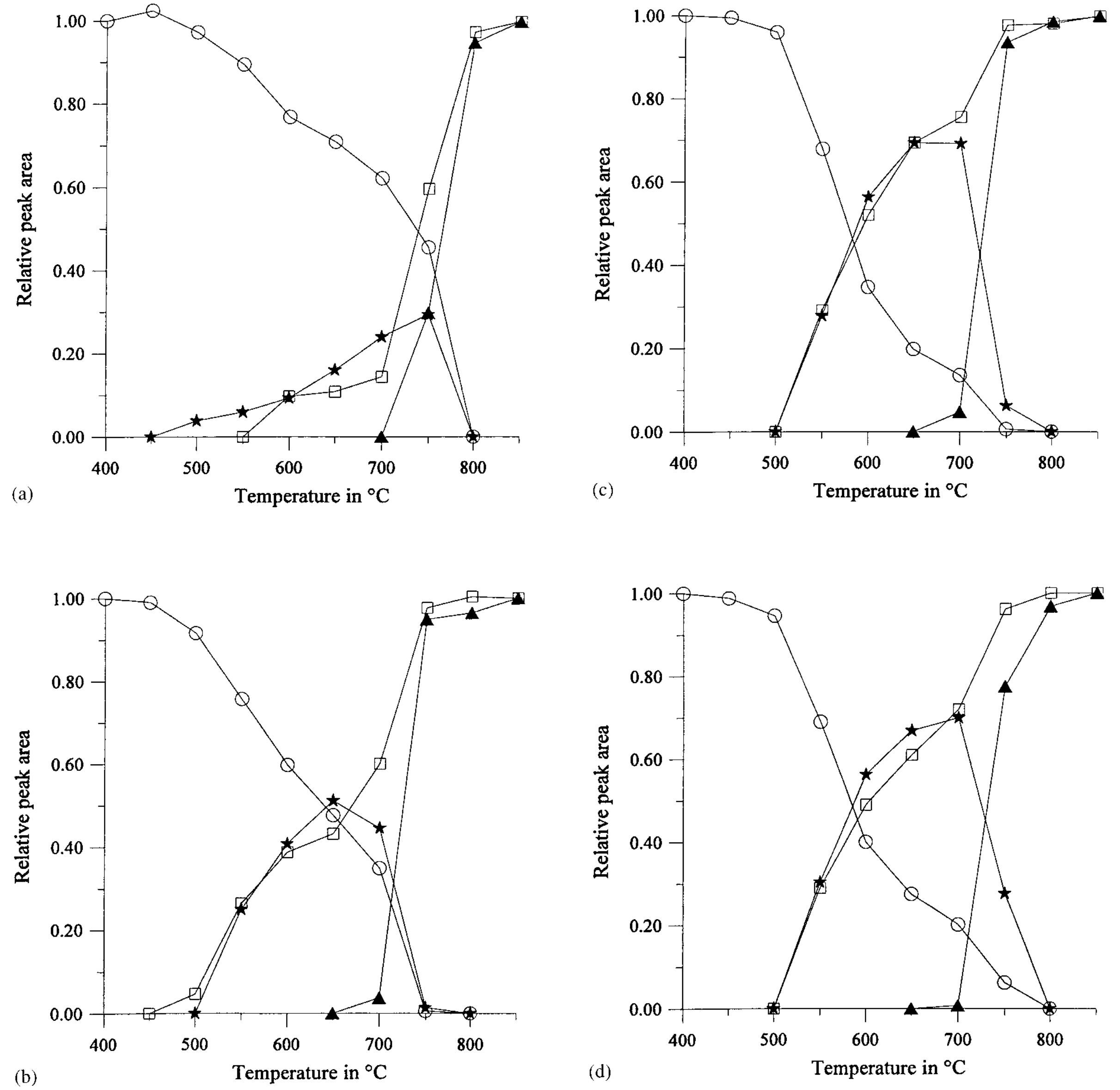


Fig. 6. Changes of the relative peak area for different phases during the thermal decomposition of the dolomite samples between 400°C and 850°C after grinding: (a) 0 h; (b) 1 h; (c) 5 h; (d) 7 h. (○), D(104) peak area divided by D(104) peak area at 400°C; (★), C(104) peak area divided by L(200) peak area at 850°C; (□), P(200) peak area divided by P(200) peak area at 850°C; (▲), L(111) peak area divided by L(111) peak area at 850°C. Because the C (104) peak areas do not yield a well characterized maximum, an arbitrary peak possessing sufficiently large peak area was chosen for normalization.

perature phases of untreated sample (dolomite, $CaCO_3$ and MgO) were proved to be stable for 2 h at 500°C, 550°C, 600°C as well as 650°C. At 650°C, a large constant amount of dolomite is still present but a small constant amount of $CaCO_3$ and MgO are detected. At 700°C, the dolomite content lowers continuously in the 2 h period but some dolomite (relative peak area: 0.15) still remains after 2 h. At the same time, the relative peak area of MgO increases up to 0.73, CaO appears and its relative peak area increases up to 0.62

and the relative peak area of $CaCO_3$ slightly increases then decreases. Keeping the temperature 750°C to be constant, the phase transformation is characterized by a rapid disappearance of dolomite and $CaCO_3$ peaks and a rapid growth of MgO and CaO peaks. Practically, only MgO and CaO peaks remain after 0.5 h. These results also support that, at low CO_2 partial pressure, the decomposition of ungrounded dolomite is a one-step process between 600°C and 800°C.

Remarkable changes were observed in the transformation of high temperature formed phases of mechanically treated dolomite at various fixed temperature. The relative peak area of MgO slightly increases as well as $CaCO_3$ appears; then their relative peak area values tend to a maximum after holding for 1 h at 500°C. At the same time, the dolomite content slightly decreases and remains constant after 1 h. Keeping the temperature 550°C to be constant, these processes are more intense. After 0.5 h, the $CaCO_3$ and MgO contents of the grounded dolomite samples become about twice as much and the dolomite content reduces to the half of the initial value. Then the relative peak areas of these phases become stable. At 600°C, there are almost no changes in the relative peak areas of these phases during the 2 h observation. At 650°C, some CaO appears after 2 h holding. The phase transformations of mechanically treated samples at 700°C and 750°C are characterized by the rapid disappearance of dolomite and $CaCO_3$ peaks as well as the rapid growth of MgO and CaO peaks. Practically, the MgO and CaO content do not change after 1 h at 700°C and after 0.5 h at 750°C.

These results indicate that the thermal decomposition of grounded samples separates into two parts. Between 500°C and 600°C, a given part of dolomite, proportional to the grinding time, decomposes directly to $CaCO_3$ and MgO. Between 650°C and 750°C, the remaining part of dolomite and the formed $CaCO_3$ decompose to CaO and MgO. The presence of $CaCO_3$ and MgO peaks between 500°C and 600°C can be attributed to the decomposition of the structurally deformed part of dolomite phase and the remained dolomite peaks represent the structurally undeformed part of dolomite phase. Comparing the DTA curves and high temperature diffractograms of the ground and unground samples, the relative peak areas of the dolomite peaks remained after keeping the temperature 550°C for 2 h were found to be suitable to represent the structurally undistorted part of the samples. Thus, the undistorted parts of the dolomite samples are 92%, 60%, 23% and 28% for 0, 1, 5, 7 h grinding time, respectively. This indicates that the starting dolomite sample (see Section 2) contains some structurally deformed dolomite crystals. It practically suits to the fact that the dislocation density of a real crystal is usually high [5]. (One has to keep in mind that the starting dolomite sample is a pre-milled powder.) As a result of intensive grinding, the proportion of structurally undistorted dolomite reduces to 23%. Milling for periods of time additional to 5 h, the re-arrangement of crystal structure (as a typical secondary mechanochemical process) causes some increase in the portion of structurally undistorted dolomite.

4. Conclusion

Under the condition studied, dolomite suffers significant crystal structural alteration due to the rising over the critical amount of the point defects and lattice microstrain. In the post 1 h period, the mechanical treatment results in the development of a structurally deformed form of dolomite. The nuclei of this structure exists already in the untreated sample as it consist of real crystals. The applied mechanical forces give rise to an increase in the proportion of structurally distorted dolomite up to 77%. The thermal decomposition of structurally deformed dolomite, in spite of the low CO_2 partial pressure, separates into two parts. Between 500°C and 600°C, deformed dolomite, proportional to the grinding time, decomposes directly to $CaCO_3$ and MgO. Between 650°C and 750°C, the formed $CaCO_3$ decomposes to CaO and MgO. At the same conditions, the thermal decomposition of undistorted dolomite is a one-step process. Between 600°C and 800°C, the undistorted dolomite disintegrate into CaO and MgO while some $CaCO_3$ also forms and decomposes.

Acknowledgements

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