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The effect of quartz content on the mechanical activation of dolomite

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Abstract

Dolomite surface and structure was modified by mechanical activation in a planetary mill. The attention was mainly directed to the role of quartz content (<1, 49, and 72 wt.%) in the modification of dolomite. The mechanically activated samples were studied by X-ray diffraction, thermal analysis, scanning electron microscopy and determination of the quadratic square mean diameter. The increased quartz content accelerated the mechanochemical deformation and amorphization of dolomite phase. While the amorphization reduced primarily the relative peak area of the (0 1 5) reflection, the deformation mostly increased the lattice strain in the (1 0 4) lattice plane. After grinding the dolomite/quartz mixtures, the thermal decomposition of dolomite showed a four- or three-step weight loss, instead of the original two- or one-step one. The mechanical activation of the mixtures produced a favourable state for the formation of calcium magnesium silicates at temperature even as low as 880 °C.

Keywords: Dolomite/quartz mixture; Milling; Defects; X-ray methods; Thermal properties

1. Introduction

Dolomite finds widespread application in the ceramic, glass, chemical, pharmaceutical industry, etc.[1] The industrial application of dolomite depends on its physical, chemical, structural and thermal properties. These properties can be significantly modified by mechanical activation (dry grinding).[2–10] It has been found that the grinding of dolomite causes a crystal structural degradation due to the rising over the critical amount of point defects and lattice microstrains, rather than the reduction of crystallite size.[2,6–8] Recent study[7] has shown that the "magnesite-type" lattice plane can be deformed to the greatest extent. Numerous authors[2–5,7–10] reported that the mechanically induced crystal-structural distortion of dolomite is accompanied by a progressive lowering of the first endotherm reaction temperature in a two-step thermal decomposition.[11] This phenomenon was assigned by most of the researchers[2,3,5–10] to the deformation of the dolomite crystalline network without any phase disintegration that was found by Molchanov et al.[4] Recently, in the case of mechanically deformed dolomite, the formation of calcite and periclase was observed between 500 and 600 °C at higher and lower CO_2 partial pressures as well.[8]

Structural changes and amorphization of quartz as a consequence of mechanical activation has been reported in several papers.[3,12–18] It has been established by several authors, mainly on the basis of dissolution experiments, that an amorphous surface-layer develops on finely ground quartz particles.[12–18] It was found that the density of the quartz particles decreases as a function of the grinding time (or particle size) apparently due to the creation of deep amorphous layers on the particles.[14]

Manufacturing processes often require ground products of mixtures of raw materials. One of the possible ways to produce ground mixtures is common grinding.[19] In common grinding, the ground components exercise an effect on each other, which can help or hinder the comminution of the other. At the same time, common grinding supplies a more homogeneous product,[19] and promotes the aggregation of reaction partners.[18]

There have been many studies on the dry grinding of dolomite[2–10] as well as quartz.[3,12–18] However, to the best of our knowledge, there have been no studies of the behaviour of dolomite/quartz mixtures during intensive dry grinding and of the nature of their ground products. In view of the industrial importance of common grinding, this work focuses on the influence of the quartz content in the surface and structural modification of dolomite caused by mechanical activation.

2. Experimental

The high-grade natural dolomite from Pilisvörösvár in Hungary was used in the experiments. Its chemical composition in weight % (wt.%) is MgO, 21.34; CaO, 30.58; SiO_2, 0.49; Fe_2O_3,

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0.05; Al_2O_3, 1.19; K_2O, 0.01; Na_2O, 0.05; TiO_2, 0.01; loss on ignition, 46.20. The major mineral constituent is dolomite (99 wt.%). Some minor amount of quartz is also present. The quadratic square mean diameter is 5.37 μm.

The natural sand from Fehérvárcsurgó in Hungary was used to produce samples with different quartz contents. Its chemical composition in wt.% is CaO, 0.28; SiO_2, 96.99; Fe_2O_3, 0.07; Al_2O_3, 1.86; K_2O, 0.29; Na_2O, 0.04; TiO_2, 0.01; loss on ignition, 0.23. This natural sand consists mainly of quartz (97 wt.%) with some impurities of feldspars (3 wt.%). The quadratic square mean diameter is 15.14 μm.

The samples with different quartz contents were made by homogenizing the dolomite with 50 and 75 wt.% of sand. (The symbols of the samples containing 100, 50, 25 wt.% of dolomite and 100 wt.% of sand are D, D50, D25 and Q, respectively.) The SiO_2 content of the D50 and D25 sample is 48.95 and 71.92 wt.%, respectively.

Samples were ground (mechanically activated) for 0, 2, 4, 6 and 10 h using a Fritsch pulverisette 5/2 type laboratory planetary mill. Each milling was carried out with a 10 g air-dried sample in an 80 cm^3 capacity stainless steel (18% Cr + 8% Ni) pot using 8 (29.51 g) stainless steel balls (10 mm diameter). The applied rotation speed was 374 rpm. (The symbols of samples ground for 0, 2, 4, 6 and 10 h are “0 h”, “2 h”, “4 h”, “6 h” and “10 h”, respectively.)

The X-ray diffraction (XRD) analyses were carried out on a Philips PW 3710 based diffractometer. The radiation applied was Cu Kα from a broad focus Cu tube, operating at 50 kV and 40 mA. The samples were measured in step scan mode with steps of 0.02° 2θ and a counting time of 1 s. Data collection and evaluation were performed with PC-APD 3.6 software. Profile fitting was applied to extract information on the microstructure and structural defects of dolomite, quartz and its alteration products. The fitted profile was suitable for the calculation of the mean lattice distortion (lattice strain)[20] with PC-APD 3.6 software.

Thermal analyses (DTA, TG) were performed on a Derivatograph, MOM (Hungary) under dynamic heating conditions (10 °C/min heating rate) in static air atmosphere applying high-grade corundum as reference. A ceramic crucible was used for the experiments filled with 700 mg sample in each case.

The quadratic square mean diameter (QSMD) was determined from the Fraunhofer diffraction pattern by Fritsch Laser Particle-Sizer “Analysette 22” type equipment. The diffraction pattern was generated using a convergent laser beam with 632.8 nm wavelength. A stainless steel ultrasonic bath was used for dispersing approximately 0.5 g sample in 250 cm^3 distilled water.

The microstructure of the samples was analyzed with a scanning electron microscope (ESEM, Philips XL31) in the secondary electron mode. The instrument was equipped with an energy dispersive X-ray microanalyzer (EDX). An accelerating voltage of 20 kV was used.

3. Results and discussion

The preliminary examination of the XRD patterns of the original and mechanically treated mixtures shows that the grinding causes a rapid broadening and decrease of the dolomite reflections while quartz peaks is almost not altered. Comparing the XRD patterns of samples with different quartz contents, it can be established that the increase in the quartz content caused an accelerated diminution of the dolomite peaks.

For a more exact representation of the amorphization and the structural deformation process through diffraction data, the mean lattice distortions and the relative peak areas were determined for the (1 0 4), (0 0 6), (0 1 5), (1 1 0), (1 1 3) dolomite and (1 0 0), (1 0 1) quartz reflection. Comparing changes in the relative peak areas and the lattice strains of the dolomite reflections, the area of the (0 1 5) reflection decreases and the lattice strain of the (1 0 4) reflection increases to the greatest extent. The relative peak areas and the lattice strains of the (1 0 0) and (1 0 1) quartz reflections are close to each other. Therefore the variations in the relative peak areas and the lattice strains of the (1 0 4) and (0 1 5) dolomite and the (1 0 0) quartz reflections (Figs. 1 and 2) was used to compare the different dolomite/quartz mixtures. The main loss of the peak areas is observed up to 4 h of grinding (Fig. 1, the standard deviation of the relative peak areas is approximately ±0.01). Afterwards, there is an apparent decrease in the reduction rate of the original crystalline phase. After 10 h of grinding the (1 0 4) peak area for the D, D50, and D25 samples decreases to 58, 42, and 29%, respectively. This means that amorphization of dolomite caused by grinding accelerates with the increase of the quartz content. At the same time, the area of the (1 0 0) quartz reflection of the D50, D25, and Q samples reduces to 80, 78, and 73%, respectively. These results indicate that the presence of dolomite retards the amorphization of quartz. Fig. 1 illustrates that the peak area reduction with respect to the individual lattice planes of dolomite shows different behaviours with the grinding time. Calculations show that the relative peak area reductions of the dolomite reflections are in the following order: (0 1 5) > (0 0 6) > (1 0 4) > (1 1 3) and (1 1 0), i.e., the localized degradation of the dolomite crystal structure occurs primarily in the (0 1 5) and (0 0 6) lattice planes. Fig. 2 indicates that the main increase of the lattice strain belongs to the first 4 h of grinding and after that no considerable changes occur. (The standard deviation of the calculated lattice strains is ±0.03%.) Fig. 2a and b clearly show that the increase in the quartz content resulted in a slight increase in the mean lattice distortion of dolomite. These figures also illustrate that the deformation of the (1 0 4) lattice plane is the most intense; after 4 h of grinding the lattice strain of this reflection is twice as much as that of the (0 1 5) reflection. Interestingly, the (1 0 4) reflection, the mean lattice distortion of which is the highest, exhibits one of the lowest peak area reduction during the grinding process.

Rate of mass loss (DTG) curves of the original and ground D, D50, and D25 samples are shown in Fig. 3, which also displays the characteristic temperatures of the mass loss steps and the associated mass losses. The DTG curves show a two-step mass loss for the ungrounded D and D50 samples due to the reactions[21,22]:

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

$$CaCO_3 \rightarrow CaO + CO_2. \qquad (2)$$

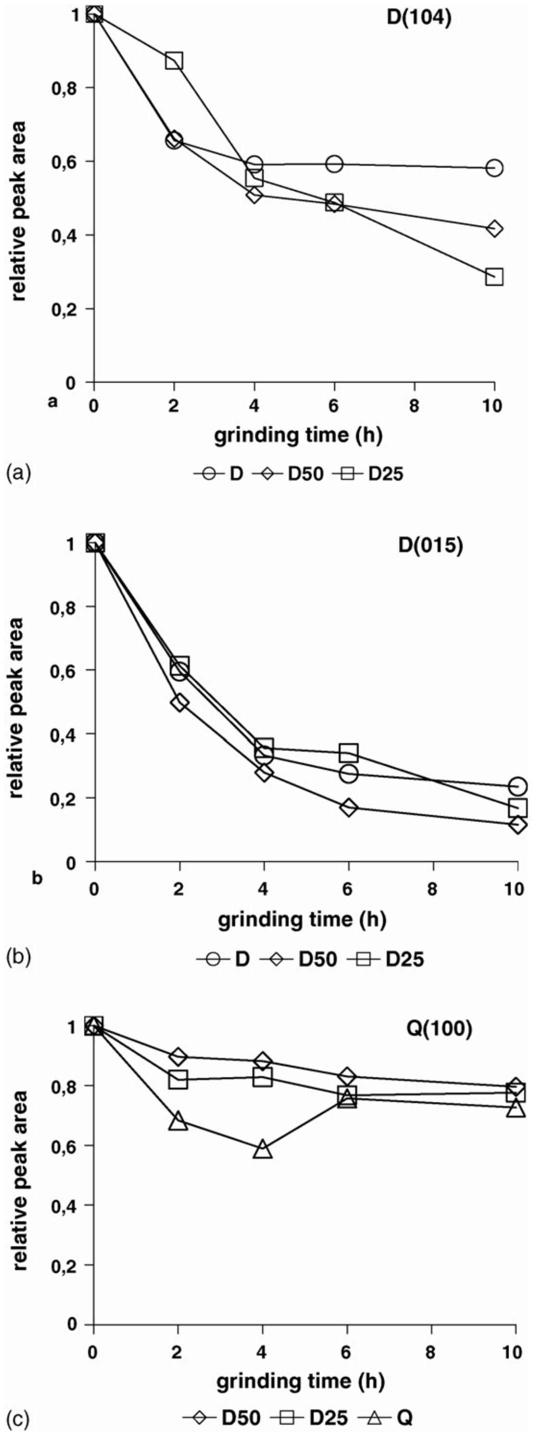

Fig. 1. Changes of the relative peak areas of the dolomite (1 0 4) (a), (0 1 5) (b) reflections and the quartz (1 0 0) (c) reflection of the samples as a function of grinding time.

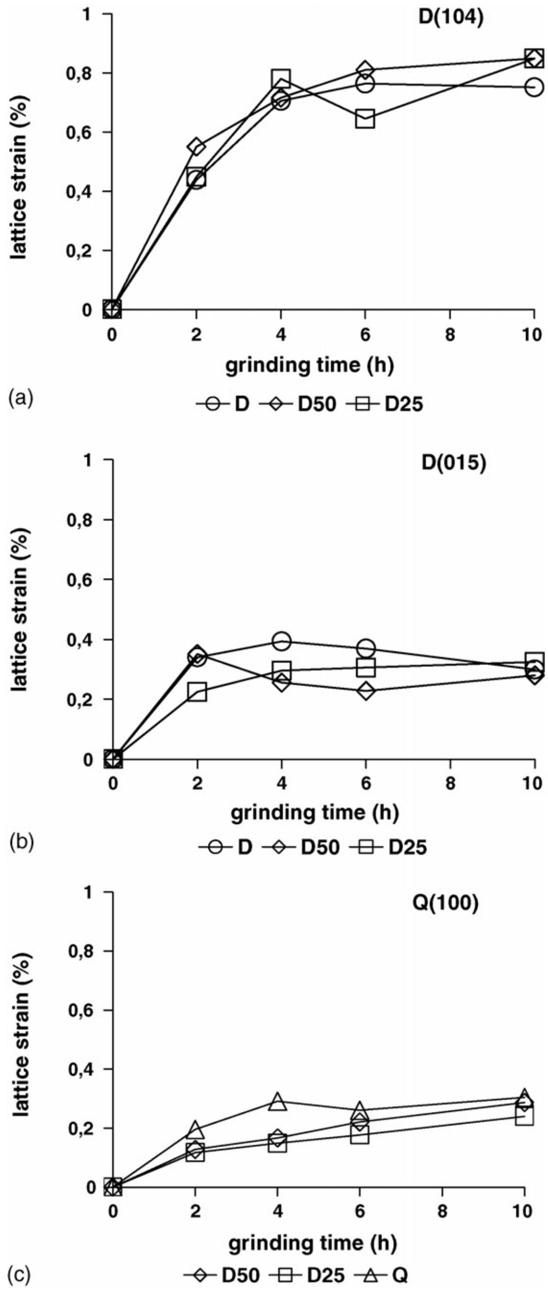

Fig. 2. Variation in the lattice strain of the dolomite (1 0 4) (a), (0 1 5) (b) reflections and the quartz (1 0 0) (c) reflection of the samples with grinding time.

At the same time, the thermal decomposition of the untreated D25 sample proceeds in only one step owing to the low partial pressure of CO_2[21,22]:

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

As a result of grinding, the first step (775 °C) of decomposition (Eq. (1)) in the D sample separates into two parts (585, 725 °C). Both DTG peaks can be observed up to 6 h of grinding but only the peak at 570 °C appears after 10 h of grinding. This figure gives some indication that no considerable changes in the decomposition of $CaCO_3$ (at around 880 °C) occur during the applied grinding. This observation fits well with our previous findings,[7,8] where it was established that mechanically deformed dolomite decomposes directly to calcite and periclase between 500 and 600 °C. In contrast, the thermoanalytical curves of the mechanically treated D50 and D25 mixtures show remarkable alteration in the complete thermal decomposition of dolomite. After 2 h of grinding, the DTG curves (Fig. 3) of the mechanically treated D50 and D25 mixtures indicate a four- or three-step mass loss of dolomite, instead of the original two- or one-step

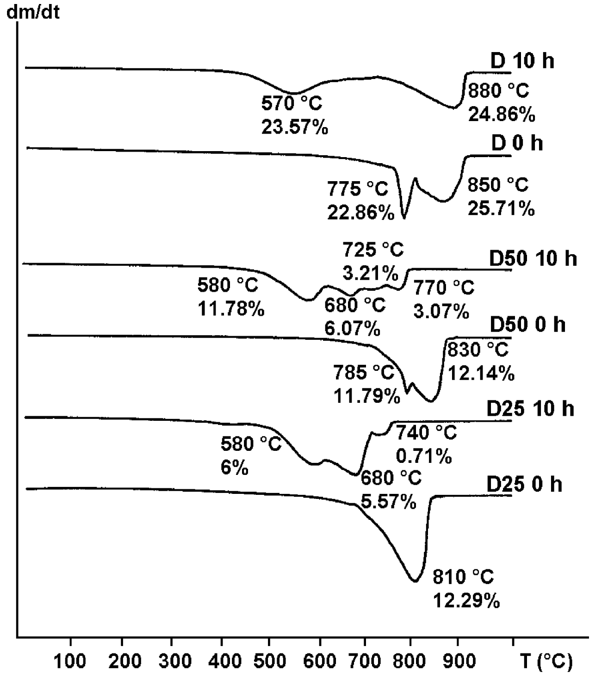

Fig. 3. Derivative thermogravimetric analysis of the D, D50 and D25 samples ground for 0 and 10 h.

ones. Simultaneously, a new DTA exotherm appears (the corresponding figure is not presented here) with no changes of mass at 880 and 860 °C for the D50 and D25 samples, respectively. This exothermic peak is presumable due to a solid-state reaction, which will be discussed below. It can be observed furthermore that the total mass loss shifts to a lower temperature range with increasing grinding time. Instead of the original temperature range between 540 and 880 °C, the D50 sample mechanically activated for 10 h release its CO_2 between 440 and 800 °C. Even after 4 h of grinding the decomposition of dolomite in the D25 sample finished below 800 °C. In both cases, the proportion of CO_2 released below 700 °C increases with the grinding time.

To identify the exothermic reaction of the mechanically treated D50 and D25 mixtures, extra XRD measurements were performed after the thermoanalytical investigation of these mixtures. As an illustrative example, Fig. 4 shows the XRD patterns of the thermally treated mechanochemically activated D25 mixture after heating to 1000 °C, then quenching to room temperature and collecting the data. At 0 h of grinding the heat treated mixtures mainly consist of quartz and decomposition products of dolomite (L, P). Some minor amount of portlandite is also present in the thermally treated D50 mixture, which is probably formed by the reaction of lime and adsorbed water during the cooling process. Heating to 1000 °C also results in the appearance of traces of calcium magnesium silicates. The diffractograms of mechanically and thermally treated mixtures show the formation of growing amounts of calcium magnesium silicates (d, M, m) with increasing grinding time. The diffractograms of the 4 and 10 h treated and heated D25 mixtures (Fig. 4) suggest that their phase compositions are similar. In both cases, the major constituent is diopside beside quartz and periclase. A slight increase in the quantity of diopside occurs with the duration of grinding. More pronounced changes can be observed in the XRD patterns of the mechanically and thermally treated D50 mixtures with the grinding time. At 4 h, merwinite is predominantly formed as calcium magnesium silicate during heating, while additional grinding mainly resulted in the formation of monticellite and diopside in the heat-treated sample. These results suggest that the exothermic peak of the ground and heated dolomite/quartz mixtures at around 880 °C can be attributed to the formation of calcium magnesium silicates. The amount and the type of these calcium magnesium silicates likely depend on the dolomite/quartz ratio and of the duration of grinding.

Fig. 5 displays the variation of QSMD values of samples during the grinding process. The investigation of particle sizes shows that grinding consists of three steps in the case of the Q sample. The degree of dispersion is characterized by the significant decrease of particle size up to 2 h (the Rittinger section).[18] After 6 h of grinding, the rate of particle size reduction decreases with the grinding time (the aggregation section).[18] After 10 h of grinding the agglomeration causes an increase in the QSMD value (the agglomeration section).[18] The QSMD value versus grinding time data of the D and D50 sample series can be separated into the Rittinger and the agglomeration section. The Rittinger section belongs to the first 2 h of grinding and, after 6 h of grinding, the agglomeration section appears. The curve of the D25 sample shows a monotonous decrease of the particle size.

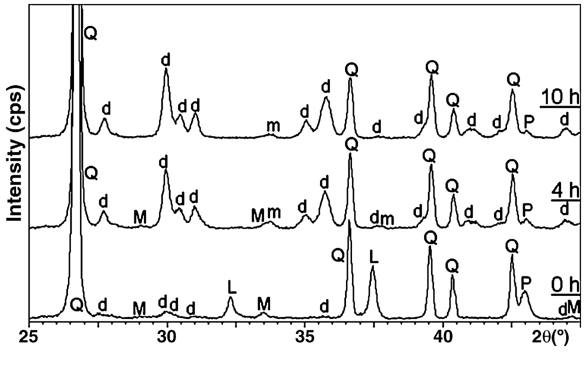

Fig. 4. XRD spectra of the D25 mixture ground for 0, 4, 10 h after heating at 1000 °C (Q, quartz (SiO_2); L, lime (CaO); P, periclase (MgO); d, diopside ($CaMg(SiO_3)_2$); M, merwinite ($Ca_3Mg(SiO_4)_2$); m, monticellite ($CaMgSiO_4$)).

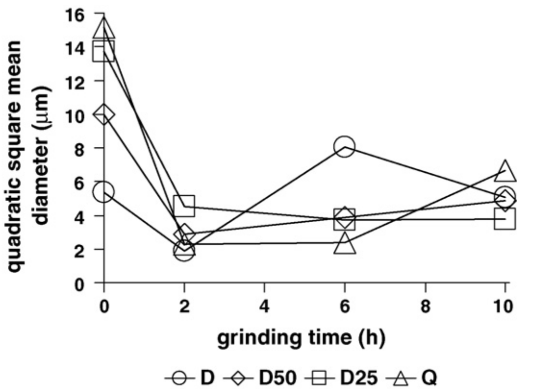

Fig. 5. Quadratic square mean diameter of the D, D50, D25 and Q samples as a function of grinding time.

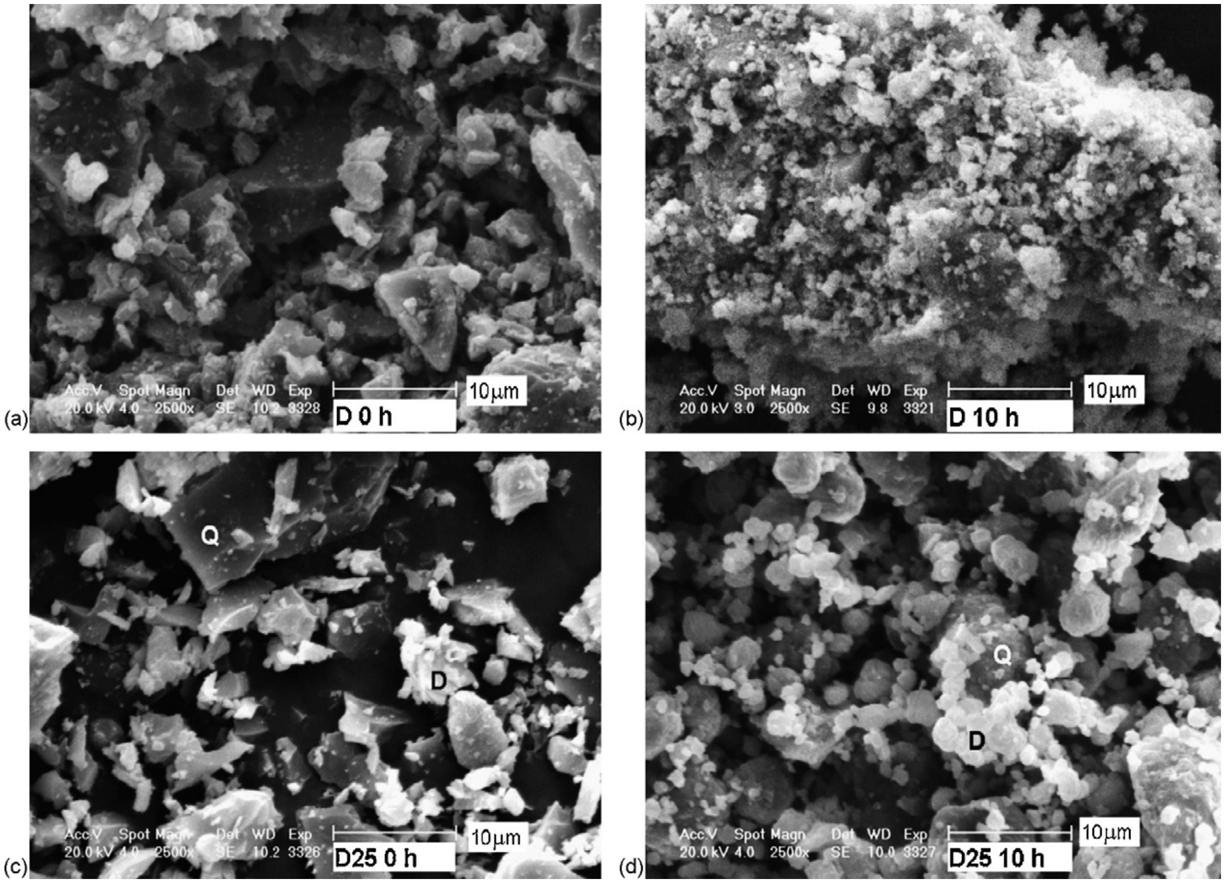

Fig. 6. Microstructure of the samples ground for 0 and 10 h: (a) D sample ground for 0 h, (b) D sample ground for 10 h, (c) D25 sample ground for 0 h, (d) D25 sample ground for 10 h. D, dolomite; Q, quartz.

These results also seem to prove that the change of the measured and calculated properties of the dolomite/quartz mixtures is mainly due to their crystal-structural alteration, rather than the particle size reduction.

Scanning electron micrographs of ground D (Fig. 6a and b) and Q samples show that the original particle shape of dolomite and quartz is destroyed by the mechanical activation forming agglomerates of small spherical particles with diameters below 1 μm. The fragmentation of the particles and the formation of spherical shape by grinding are also easily discerned on the SEM images of the D50 and D25 (Fig. 6c and d) mixtures. These images illustrate that the particle size reduction of dolomite grains is higher than that of the quartz ones. The agglomerates formed by common grinding were found to be quartz grains covered by smaller dolomite grains. The agglomerates created in this way ensure a close contact between the dolomite and quartz particles, which can be favourable for solid-state reactions leading to the formation of calcium magnesium silicates at lower temperatures.

4. Conclusion

Different dolomite/quartz mixtures were mechanically activated by common dry grinding. On increasing the quartz content the dolomite phase showed accelerated mechanochemical deformation and amorphization. At the same time the presence of dolomite retards the crystal structural alteration of quartz. The localized deformation of the dolomite structure occurred primarily in the (1 0 4) lattice plane, while substantially higher breakage of the crystalline network was found in the (0 1 5) lattice plane. Common dry grinding of dolomite and quartz yielded a separation of the thermal decomposition of dolomite into three or four steps and its shift to a lower temperature range. The mechanochemically induced defects of crystal structure as well as the agglomeration of dolomite particles with quartz ones promoted the solid-state reaction between dolomite and quartz phases. Based on these experimental results, the mechanical activation of dolomite/quartz mixtures might be suitable for synthesizing calcium magnesium silicates at around 880 °C. However, further investigations are still required for its practical utilization.

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