Influence of the mechanical treatment on the structure and the thermal stability of alkaline-earth carbonates

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The change of specific surface during the grinding of alkaline-earth carbonates is depending on the lattice energy of these compounds. The maximum value reached by the specific surface area, before the particle aggregation begins, is higher the higher is the lattice energy of the salt. A mechanism has been proposed for explaining this behaviour that implies to assume that when the lattice energy increases, slipping of the lattice planes becomes more difficult and the fracture of the particles would be favoured with regards to the plastic deformation of the crystal. This model account for the changes observed for the activation energy and the enthalpy of the thermal decomposition of alkaline-earth carbonates as a function of grinding. © *2004 Kluwer Academic Publishers*

1. Introduction

The number of papers devoted to mechanical alloying has increased dramatically during the last decade [1], although lacks of agreement among the results obtained by different authors for the same process have been very often reported. This is because the particular set of events observed by anyone researcher would vary according to the particular mill and its operating conditions due to the different stress operating in the individual mills [2, 3]. Thus, in order to withdrawn fundamental conclusions on the factors governing the mechanochemical reactivity it would be very interesting to study the influence of the grinding, under the same experimental conditions, on the reactivity of a family of compounds with related structures but varying in thermodynamical stability and mechanical properties.

The alkaline-earth carbonates belongs to a family of compounds $M^{n+}(XO_3)^{n-}$ with a planar anion XO_3^{-n}, that together with the alkaline nitrates and the rare earth borates, can adopt either calcite structure, with a coordination number of the cation equal to 6 or aragonite structure with coordination number of the cation equal to 9. Geometrical rather than chemical considerations are the primary factors dictating the adopted structure. Thus, the calcite structure, with lower coordination number, is preferred for cationic radius lower than 0.98 Å and aragonite structure is stabilized for larger radii. The radius of Ca^{++} ($r = 0.99$ Å) is very close to the frontier between the two structures and both calcite and aragonite structures have been reported for $CaCO_3$. This feature, together with the fact that anhydrous alkaline-earth carbonates are quite stables (while the isostructural nitrates and borates tend to form hygroscopic hydrates) become to alkaline-earth carbonates into a ideal set of starting materials for a systematic study of the influence of grinding on both their kinetic and thermodynamic stability as a function of their lattice energies.

A perusal of the literature shows that the publications concerning to the influence of grinding on the texture, structure and thermal stability of alkaline-earth carbonates are exclusively focused on the double magnesium and calcium carbonate (dolomite) [3–7] and calcium carbonate. In the case of $CaCO_3$ most of the works refer to the influence of grinding on the aragonite → calcite or calcite → aragonite polymorphic transformation. It is noteworthy to point out that the results reported for this polymorphic transition are contradictory. Some authors [8–12] have reported that both the calcite into aragonite and the aragonite into calcite transitions take place during grinding, while others have exclusively observed either the calcite into aragonite transition [13], the aragonite into calcite [14–16] or even no polymorphic transition at all [17]. The study of the influence of grinding on the textural and structural changes of calcium carbonate together with the results obtained for the other members of the alkaline-earth single carbonates family would allow a better inside on the mechanism of the polymorphic transition.

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2. Experimental

Magnesite from Navarra (Spain) was used. The composition of this carbonate is the following: SiO_2 1.76%; Fe_2O_3 1.12%; Al_2O_3 0.32%; CaO 0.98%; MgO 45.35%; loss of ignition 50.50%. Calcium, strontium and carbonates D'Hemio a.r. were also used.

The ground samples were prepared in a Colerecord 20A centrifuge mill with a speed of 400 r.p.m. and a spinning radius of 20 mm. The mill is equipped with a steatite jar (capacity 300 cm^3) containing 20 balls with 20 mm in diameter. Samples of above 3 g were ground for different periods of time.

TG curves were obtained with a Chan Electrobalance, model RG, at a vacuum of 10^{-6} mbar.

The specific area of the sample was determined from the absorption isotherm of nitrogen at a temperature of 77 K by using the B.E.T. method.

X-ray diffraction diagrams were obtained with a Phillips PW 1060 instruments using Ni-filtered Cu K$_\alpha$ radiation and a scanning speed of $1°$/min. The composition of the $CaCO_3$ samples was determined using a calibration curve prepared from known mixtures of calcite and aragonite. The (104) and (111) lines of calcite and aragonite, respectively, were used.

3. Results

Fig. 1 shows that the specific area of $MgCO_3$, $SrCO_3$ and $BaCO_3$ does not rise continuously as a function of grinding time. The specific surface reaches a max-
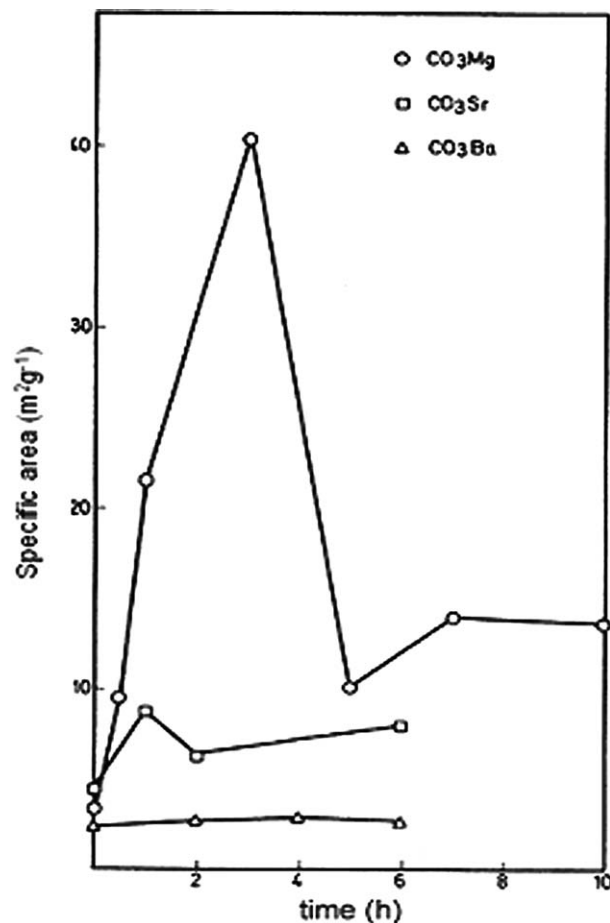

Figure 1 Specific area of alkaline-earth carbonates as a function of the grinding time.

imum with continued grinding and thereafter starts to decrease. The maximum value of specific surface reached during the grinding of alkaline-earth carbonates decreases when we move from $MgCO_3$ to $BaCO_3$ where almost no influence of grinding is observed on $BaCO_3$. It must be pointed out that that in spite that the particle size must follow the same trend that the specific surface, the broadening of the XRD lines does not follow this trend, but they are continuously increasing by increasing the grinding time. This means that the crystal size and/or the level of microstrains are continuously increasing by increasing the grinding time. Unfortunately, the anisotropic distribution of crystal size and/or microstrains has not allowed separating the contribution of both factors to the broadening.

In the case of $CaCO_3$ [10] successive calcite → aragonite and aragonite → calcite phase transformation take place at the time that the surface pass through successive maxima an minima as shown in Fig. 2. It must be also emphasized that the broadening of the XRD peaks of calcite and aragonite are continuously increasing as a function of the grinding time. The analysis carried out with the peaks (111), (012) and (221) of aragonite in the ground samples of calcium carbonate by means of the Wagner and Aqua method has shown an isotropic distribution of microstrains, $\langle \varepsilon \rangle$, and crystal size, D, in this phase [11]. The crystal size is decreasing from 74 nm in the sample ground for two hours down to 33 nm in the sample ground for 24 h, while the level of microstrains remains approximately constant at a value $\langle \varepsilon \rangle \approx 3 \times 10^{-3}$. An anisotropic distribution was found in the case of calcite and it was not possible to determine the values of D and $\langle \varepsilon \rangle$.

A kinetic study of the thermal decomposition of the alkaline-earth carbonates was carried out from the TG curves recorded for the as received and ground samples at heating rates ranging from 2 K/min to 10 K/min using sample weight ranging from 30 to 50 mg. The kinetic results obtained were independent of the experimental conditions (i.e., starting sample size and heating rate), what means that the influence of heat and mass transfer phenomena has been minimized and the results obtained are representative of the forward reaction [18]. The values obtained for the activation energy are included in Table I. The samples ground for more than

TABLE I Influence of grinding on the activation energy (E) and the enthalpy (ΔH) obtained for the thermal decomposition of alkaline-earth carbonates

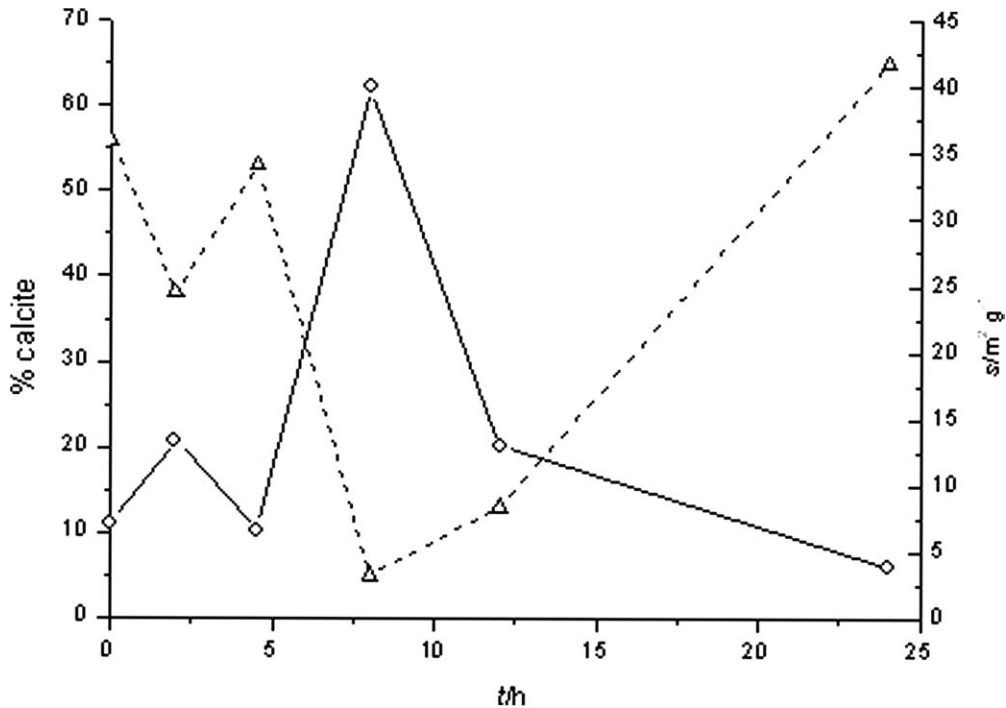| Compound	Grinding time (h)	E (kJ/mol)	ΔH (kJ/mol)
$MgCO_3$	0	108 ± 3	
	0.5	100 ± 3	
	3	100 ± 3	
$CaCO_3$	0	163 ± 5	171 ± 5
	4.5	163 ± 5	171 ± 5
	8	154 ± 4	171 ± 5
$SrCO_3$	0	251 ± 8	263 ± 7
	2	205 ± 7	238 ± 7
	6	171 ± 5	214 ± 6
$BaCO_3$	0	260 ± 8	
	2	188 ± 6	
	4	176 ± 5	
	6	177 ± 5	

Figure 2 Surface area ($\triangle$) and percentage of calcite ($\bigcirc$) as a function of the grinding time of calcium carbonate.

12 h were not studied because in such a case the contamination with ensteatite coming from the grinding media was significant and its reaction with the carbonates during heating would be considered.

On the other hand, the enthalpy of decomposition of the ground carbonates was also measured by a method that has been extensively described in a previous paper [19] that is based on the overlapping of the reaction of formation and decomposition of the salts at different constant pressure of CO_2. The temperature at which the overlapping occurs could be the temperature at which the equilibrium pressure is the CO_2 pressure used in the experiment. Fig. 3 shows, by way of example, the TG diagrams of CaO-CaCO$_3$ recorded for the as received sample of calcium carbonate at different pressures of CO_2. From the diagrams of Fig. 3, equilibrium dissociation temperatures have been determined at different CO_2 pressures and have been represented in Fig. 4 by means of the Clausius-Clapeyron equation. Our results for the dissociation pressure of CO_2 are compared with those tabulated by Stern *et al.* [20]. The excellent agreement of both sets of data supports the validity of this method. The values of ΔH_0 determined for the thermal decomposition of ground samples of calcium and strontium carbonates are shown in Table I. Unfortunately, it was not possible to extend this study to $MgCO_3$ and $BaCO_3$ due to the difficulties of the MgO recarbonation and the high stability of $BaCO_3$. In this salt the temperature required for the equilibrium constant measurements was higher than that allowed by our experimental system.

The results reported in Table I show that grinding of alkaline-earth carbonates leads to a diminution of both the activation energy and the enthalpy of the thermal decomposition reaction, with the only exception of the thermal decomposition of $CaCO_3$, whose activation energy and enthalpy remain near unchanged. It is
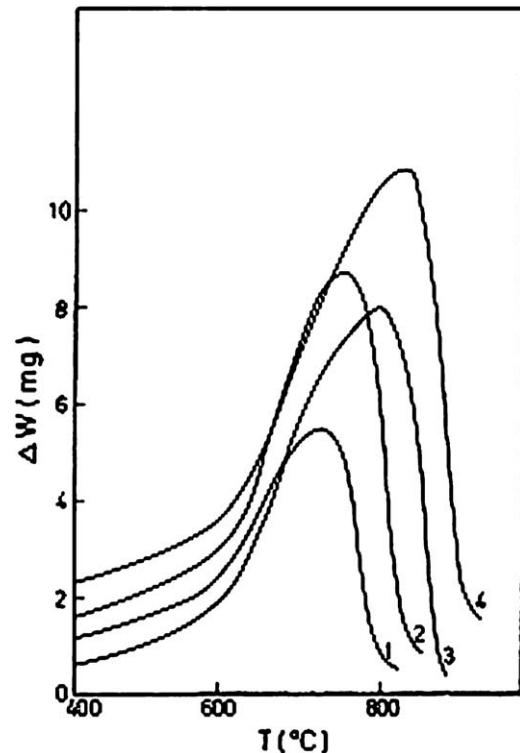

Figure 3 TG diagrams of a CaO-CaCO$_3$ sample obtained at different CO_2 pressures: (1) 30 mbar; (2) 61 mbar; (3) 134 mbar, and (4) 184 mbar.

noteworthy to point out that the diminution observed for the above parameters in the case of $MgCO_3$, $SrCO_3$ and $BaCO_3$ becomes greater as the cation radius decreases. This finding will be discussed later.

4. Discussion

Specific area changes induced by grinding on $MgCO_3$, $SrCO_3$ and $BaCO_3$ (Fig. 1) show the maximum value
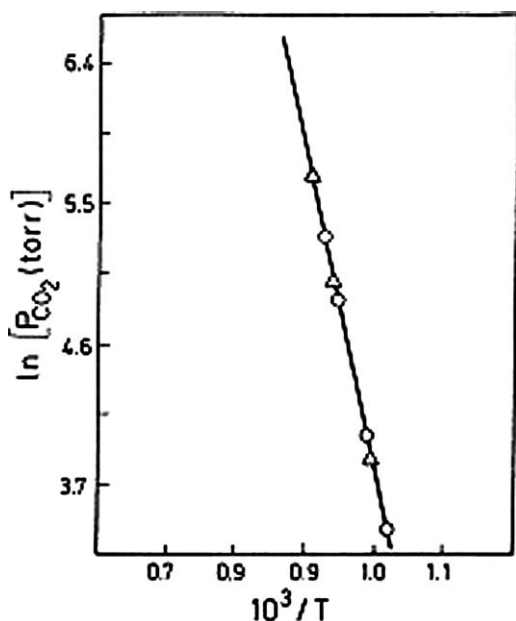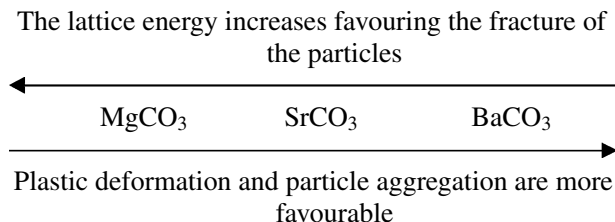
Figure 4 Clausius-Clapeyron of CO_2 equilibrium pressures of $CaCO_3 \Leftrightarrow CaO + CO_2$. (○) this work; (△) Ref. 20.

reached, before the aggregation of particles begins, is greater the higher the lattice energy of the salt. It would be expected that when the lattice energy increases, slipping of the lattice planes becomes more difficult and, therefore, the fracture of particles should become easier than the plastic deformation of the crystal. It has been reported that the microstrains induced by plastic deformation promote the cold-welding of the particles [20]. Thus, the particle aggregation would be favoured with regards to their fracture according to the following scheme:

The lattice energy increases favouring the fracture of the particles

⬅

$MgCO_3$ $SrCO_3$ $BaCO_3$

➡

Plastic deformation and particle aggregation are more favourable

This scheme explains not only the results reported in Fig. 1 but also the results reported in Fig. 2 for the textural and structural transformations undergone by calcium carbonate because of grinding if we take into account that the lattice energy of aragonite would be higher than the lattice energy of calcite provided that the coordination number of Ca^{++} in aragonite (9) is higher than its coordination number in calcite (6). In fact, aragonite has a hardness of 4.5 in the Mohrs's scale that is considerably higher than the hardness of calcite (3 in the Mohrs's scale). As a consequence, it would be expected that calcite was more ductile than aragonite and the plastic deformation of calcite was easier than in aragonite. Fig. 2 shows that the higher is the percentage of aragonite in the sample, the higher is the specific surface, what means that aragonite of high surface area is transformed into low area calcite. This calcite is further deformed, leading to a more unstable high energy calcite. The free energy stored in calcite microstrains might be enough to favour its phase tran-

sition in aragonite. The grinding of this newly formed aragonite, more brittle than calcite, would lead to a fracture of the particles giving a high surface area. In summary, the energy stored in microstrains would be the driving force of the transformation of calcite into aragonite, while the stored surface energy would be the driving force for the transformation of aragonite in calcite. The results reported above show that the grinding of aragonite leads to a decrease of the crystal size, while the level of microstrains remains constant, what supports the assumption that aragonite mainly increases its surface energy by grinding. The storing of energy during the grinding of aragonite has been clearly demonstrated in other works [11, 15] from DSC measurements.

According with the proposed mechanism explaining the textural and structural changes observed during the grinding of alkaline-hearth carbonates, it would be expected that the stored deformation energy induced by grinding increases across the series $MgCO_3$, $SrCO_3$ and $BaCO_3$. Thus, it would be expected larger decrease in the activation energy and the enthalpy for the thermal decomposition of these carbonates as far as the lattice energy decreases, what is in good agreement with the results reported in Table I. The fact that the activation energy of the ground samples of $CaCO_3$ does not undergo significant alterations during grinding is in an accordance with the elimination of the extra energy as a consequence of the successive phase transformations undergone by this salt.

In summary, the mechanism here proposed account for both, textural, structural modifications and changes in the kinetic and thermodynamic stability of alkaline-earth carbonates induced by grinding.

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