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Solid products and rate-limiting step in the thermal half decomposition of natural dolomite in a CO₂ (g) atmosphere

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Abstract

Natural dolomite powders obtained from caves which give unusual high resistance building materials, have been decomposed in a Knudsen cell at high CO₂ pressures in the temperature range of 913–973 K. XRD traces for the final solid products, after the first half thermal decomposition, have shown, that beside the XRD patterns for the calcite and MgO, the existence of a new structure with major peaks at 2θ equal to 38.5 and 65°. This finding has been ascribed to a solid solution of MgO in calcite. The kinetic analysis of the TG curves yield a total apparent enthalpy (ΔH^*) for the decomposition equal to $440 \pm 10 \text{ kJ mol}^{-1}$ for a range of fraction decomposed (α) varying between 0.2 and 0.7. This value is much closer to the theoretical expected at 950 K value $\Delta H = 486 \text{ kJ mol}^{-1}$ for the dolomite decomposition in CO₂ environment, where CaO, MgO and oxides of solid solution can be the solid reaction products. The rate determining step is the transport of CO₂ across the reacting interface through an high activated thermal process due to solid state diffusion of CO₃²⁻ in the bulk and/or the grain boundaries phases of CaCO₃ and/or of the solid solution. The microstructure evolution of the solid products follows a shear-transformation mechanism. At temperatures below 943 K, porous product particles are characterized by a monomodal narrow pore size distribution around 0.05 μm . At higher temperatures, a critical level of tensions inside the particles is reached and a bimodal pore size distribution around 1 and 0.05 μm is formed.

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Keywords: Dolomite; Solid solution; Kinetic analysis and CO₂ desorption from MgO surface; Microstructure and shear-transformation mechanism

1. Introduction

Researchers [1,2] engaged in the preservation of cultural heritage have shown, rather surprisingly, that ancient building materials, formed with the products of the thermal decomposition of Ligurian natural dolomite stones, were able to resist deterioration from natural agents even for some centuries. In order to understand this interesting behavior, the nature and

the microstructure of the calcium and magnesium oxides produced in the pioneering ovens used to decompose that dolomite, are very important issues. It is well known [3] that the thermal decomposition of dolomite, starts at the external surface of each grain forming a reactant–product interface through which the carbon dioxide diffuses outside, while the interface moves towards the core of the grain. It is also known [4] that the microstructure and the nature of the solid products are strongly dependent upon the CO₂ partial pressure near the reacting interface and upon the decomposition temperature. Very reasonably

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the mineral stones decomposed in ancient ovens were decomposing under high CO_2 pressure and low temperature. Taking into account these conditions, the thermal decomposition of the large dolomite samples was a very slow process, probably near to equilibrium conditions. Furthermore, since wood was used as the combustible, water vapor was part of the gaseous environment. It can be calculated [5] that at the total pressure of about 1 atm, a volumetric fraction of CO_2 equal to 0.1–0.11 and of H_2O (v) equal to 0.075 can be produced by the combustion of wood. On this basis we have designed an investigation into the thermal decomposition of Ligurian natural dolomite under experimental conditions that may give information on the calcination process in those ancient ovens. This paper will study the high CO_2 pressure regime using Knudsen cells [6,7] where a back CO_2 flux was applied in a TG oven at 1 atm of CO_2 in the temperature range between 913 and 973 K. The effect of water vapor on the dolomite thermal decomposition will be the topic of future work [8].

Studies [9–13] performed on the formation of oxide solid solutions have been carried out using carbonate solid solutions as precursors. In the conversion of dolomite, at CO_2 pressure higher than 3.2 kPa, there is a first stage of cation demixing, with the formation of MgO and CaCO_3 [4]. It is not clear [14] whether the value of the threshold pressure to obtain the demixing process is a thermodynamic or a kinetic parameter or whether it is a temperature dependent parameter. Similar demixing processes in microcrystalline Mn–Ca and Sr–Ca carbonate solid solutions occur in inert gas without any CO_2 [10]. The evidence that dolomite decomposition requires a significant ambient pressure of CO_2 could be due to the texture of the dolomite which is somewhat different from that of the Mn–Ca and Sr–Ca systems [10]. Accordingly, with the well established accepted view of dolomite decomposition in CO_2 [15–18], the crystallization of MgO proceeds with the formation of CaCO_3 . Therefore the final solid products after the first half decomposition are only those two phases. However, as has been suggested previously [19], it is possible that the calcite dissolves some amount of MgO forming a solid solution whose stability could be influenced by the CO_2 pressure. In the most recent papers [20,21] on dolomite decomposition in CO_2 , this solid solution has not been found. This is

probably due to the decomposition temperature being too high. In this paper, in order to get information for the ancient oven decompositions, we are more interested in the lower decomposition temperature regime. It might be possible that under such a conditions a solid solution between calcite and MgO will be formed.

Another question which will be addressed is the one concerning the nature of the rate-limiting step for this endothermic decomposition reaction. Quite often the inferences about this step are based on models and data that are difficult to be experimental tested. In seeking to overcome this difficulty in this paper we will compare the kinetics of the dolomite decomposition with the high temperature desorption of CO_2 from the surface of one of the decomposition solid products. If the temperature dependence for these two independent phenomena are equal, then there may be strong experimental evidences to state that the desorption of the CO_2 from the interface reaction is the rate-limiting step, since it has already been proposed [22,23]. As the final item, this paper will also investigate the mechanism by which the microstructure of the solid products are changing. Whether or not shear-transformation mechanisms [13,24,25] are enhanced over the long-range diffusion ones in producing the product porous phases, will be clarified through detailed microstructure analysis.

2. Experimental

2.1. Materials

The natural dolomite stones used throughout this work came from ancient Ligurian caves near to Genoa, which is well known for producing high purity dolomite (about 98%) with some impurity of CaCO_3 . The stones were taken at three different cave sites taking care to rid the surface of extraneous materials. The stones were manually broken into small grains of about 1 cm in diameter and then mixed. The mixture was divided in order to obtain grains of uniform composition [5] and finally the sample batches were ground for 30 min in an agate mill. The powders were dry-sieved, and as starting materials only the ones with particle dimensions in the range of 30–40 μm were used.

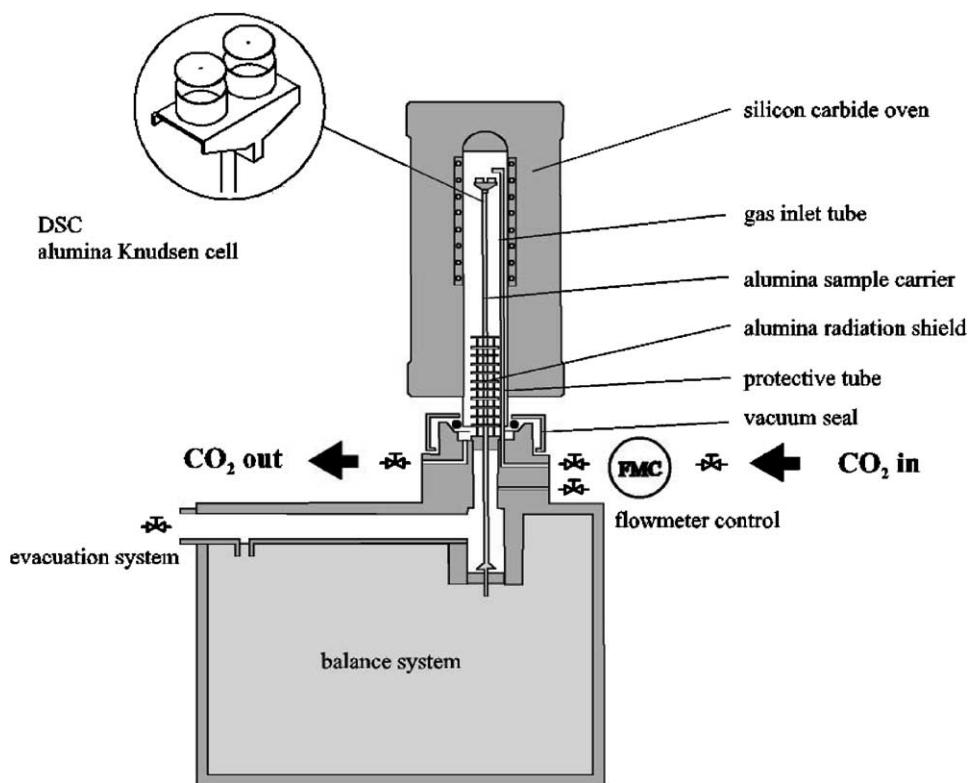


Fig. 1. TG-DSC apparatus used to decompose the dolomite natural powders in CO₂ atmosphere.

2.2. Techniques

Fig. 1 illustrates the experimental oven coupled with the TG-DSC Netzsch Gerätebau STA 409 (Germany) where the decomposition experiments were carried out. A 55 ± 2 mg sample of dolomite natural powder was introduced using an alumina Knudsen crucible with a lid having an orifice with a diameter equal to 0.1 mm (see enlarged view in Fig. 1). Calcinated kaolin powders were used as the reference material. The crucibles were placed inside the TG-oven. A CO₂ (g) flux was introduced at the top of the crucible with a constant rate of 35.10 ± 0.05 ml min⁻¹ at room temperature. It has been calculated that the CO₂ flux fills the entire volume of the oven in a period of time equal to 3 min [5]. As soon as the CO₂ pressure inside the oven reached the value of 1 atm, the samples were pre-heated to 823 K for 30 min still under CO₂ flow. No weight loss was observed during this

period of time. The temperature was raised rapidly, at a speed of $50^\circ\text{C min}^{-1}$ to the selected isothermal decomposition temperatures (913–973 K). No weight loss was recorded during this rapid heating treatment, but it has been proved that the sample lost weight during the heating at a temperature higher and or equal to 993 K. The isothermal decompositions were all carried out under the CO₂ (g) flux. At the end of the dolomite half decomposition a flux of N₂ was introduced at the rate of 52.91 ± 0.05 ml min⁻¹ to get rid of the CO₂. The cooling step to room temperature was done in these inert gaseous environment conditions to avoid any back reactions. Each dolomite decomposition test was repeated three times and the reproducibility of each run was evaluated to be equal to the 98% level.

XRD powders patterns for dolomite and products obtained after thermal treatments were taken using a Philips (Hannover, Germany) PW 1710 X-ray

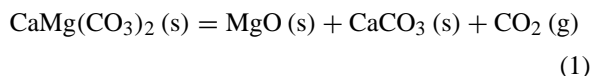
diffractometer with a Cu K α radiation and a Ni-filter. A source of 40 kV and 40 mA was used, the 2θ angles ranged between 10 and 100° at a rate of 0.02° min⁻¹ with a counting time (τ) equal to 0.5 s per step.

Scanning electron microscopy (SEM) was used to investigate the microstructure of both the starting and reaction products. Before any examination, the samples were covered with a thin film layer of gold with thickness of 20 nm using a sputter coater. The SEM accelerating voltage was set at 10 kV and pictures with a magnification of up to 20,000 \times were taken.

Mercury porosimeter intrusion–extrusion technique was used in the range up to 180 MPa. The starting pressure for the intrusion curves was 0.01 MPa, while the final pressure for the extrusion experiments was 0.1 MPa. The experimental results on the solid decomposition products gave data from which both the internal particle and inter-granular porosity can be derived. To evaluate the inter-granular porosity fraction, Hg-blank runs were done on non-porous dolomite samples having particle dimensions equal to the porous ones obtained from the decomposition reaction.

3. Results and discussion

Typical TG traces illustrating the fraction of dolomite decomposed (α) versus time (t) are reported in Fig. 2 at different isothermal decomposition temperatures (913–973 K). The fraction (α) accounts for the total theoretical CO₂ loss (47.7%) in stoichiometric dolomite. The natural stones have a maximum CO₂ content of 46%, thus the natural dolomite stones are of high purity with impurities amounting to less than 2%. Since it is possible to observe all the isotherms, they show that the decomposition rates become negligible when the fraction decomposed (α) is equal to 45%. This is in agreement with previous researchers [4] where the TG reported in Fig. 2 can be considered as the first half thermal decomposition of dolomite in CO₂ partial pressure regime greater than 3.2 kPa. Accordingly, the general reaction:



might be considered as the one which describes the decomposition process under our experimental conditions. However, before accepting this model, further

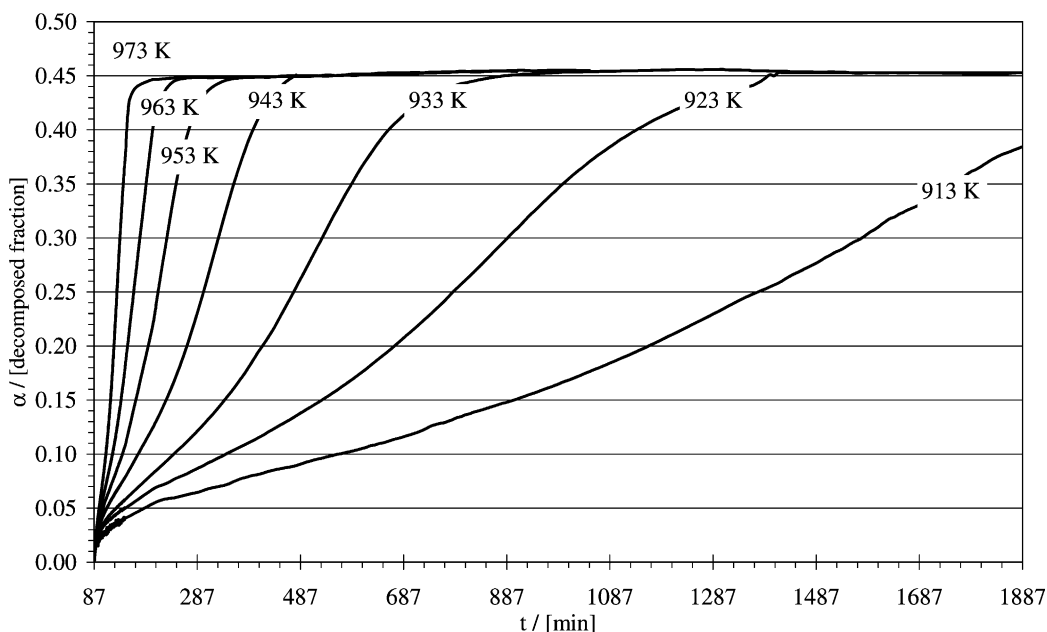


Fig. 2. Decomposed fraction of dolomite vs. time at various temperatures.

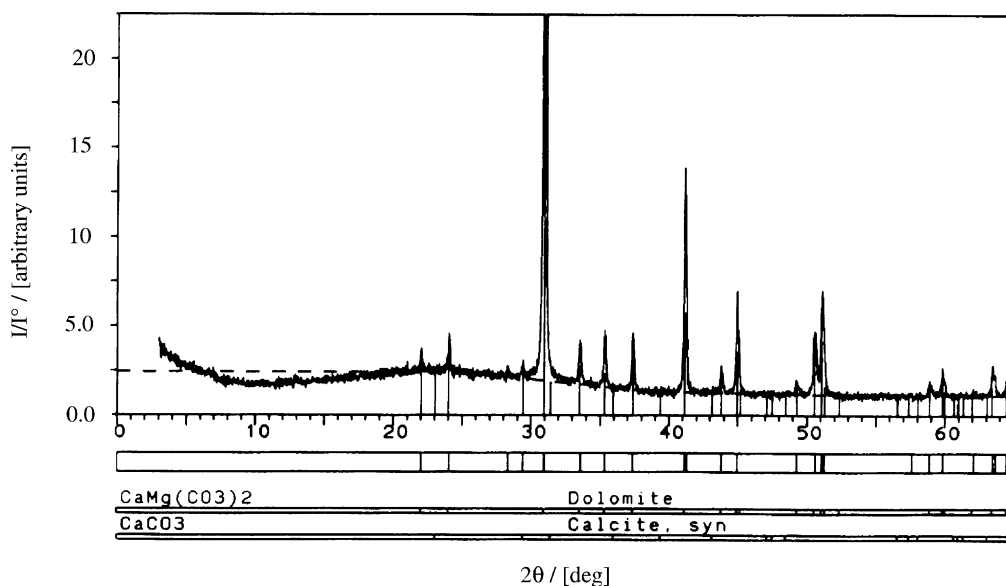


Fig. 3. XRD pattern for natural dolomite. The vertical bars show the expected position of the XRD peaks of dolomite and calcite.

data are required. Fig. 3 shows the XRD patterns concerning the starting dolomite powders. All experimental peaks can be described by the dolomite structure [26], but the line at $2\theta = 29.2^\circ$ belongs to the major calcite diffraction peak. No other lines for the calcite structure can be observed. However, the one reported makes it reasonable to assume that in our dolomite samples the impurities are mainly due to calcium carbonate. Fig. 4 shows three XRD traces for the solid products obtained from the decomposition at 913 K (pattern I), at 943 K (pattern II) and at 973 K (pattern III). Comparison between these patterns show that the products are the same despite the different decomposition temperatures. This evidence strongly suggests that just one decomposition reaction path is occurring under our experimental conditions. The analysis of the above reported XRD patterns is given in Fig. 5 and it is based on tabulated structure references [26]. The square symbol, in Fig. 5, is ascribed to the calcite phase, while the round one is relevant to the MgO. Beyond any doubt these two phases are present in the solid products obtained from the first half dolomite thermal decomposition in CO_2 . However, as can be observed, the group of lines (star symbols in Fig. 5) with the most significant diffraction intensities at 38.5° and 65° and two minor peaks between 43.5° and 45° ,

cannot be ascribed either to calcite or to magnesium oxide. Further attempts to reconcile the unknown peaks with those of the calcium oxide, undecomposed dolomite and magnesium carbonate did not prove fruitful. When dolomite is heated in CO_2 , there is general agreement that the first half decomposition reaction yields MgO and CaCO_3 [15,20], although the mechanism of formation has been debated for a long time [27]. Spinolo and Beruto [14], have demonstrated that $\text{CaCO}_3\text{--MgCO}_3$ solid solutions can be intermediate compounds for the formation of MgO and calcite. Hashimoto et al. [28] provided experimental evidence in favor of direct CaCO_3 formation through magnesium calcite solutions. The experimental fact that we found new peak lines in the final product at CO_2 pressure equal to about 1 atm, it is plausible to infer that the formed calcite can dissolve the magnesium oxide to form a solid solution which is stable in the temperature range between 913 and 973 K and at a high CO_2 concentrating. Since the Mg^{2+} cations and the O^{2-} anions have dimensions smaller than those of the Ca^{2+} and the CO_3^{2-} ions, the solid solution lattice spacing are expected to be less than those of calcite. It is interesting to observe that the main peaks of the phase, that we claim to be the solid solution, are shifted toward diffraction angles higher than the

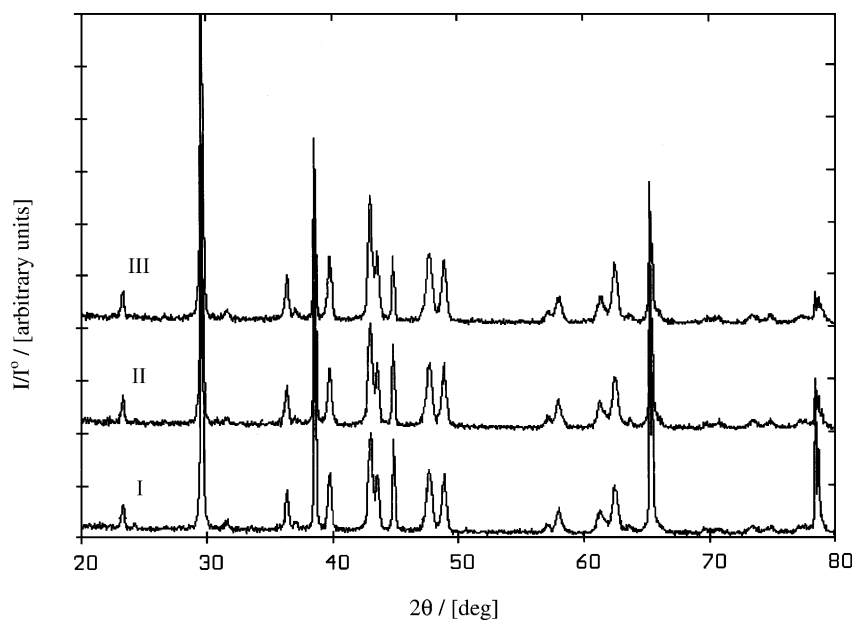


Fig. 4. XRD patterns for the solid product obtained from dolomite half decomposed in CO_2 atmosphere at 913 K (pattern I), 943 K (pattern II) and 973 K (pattern III).

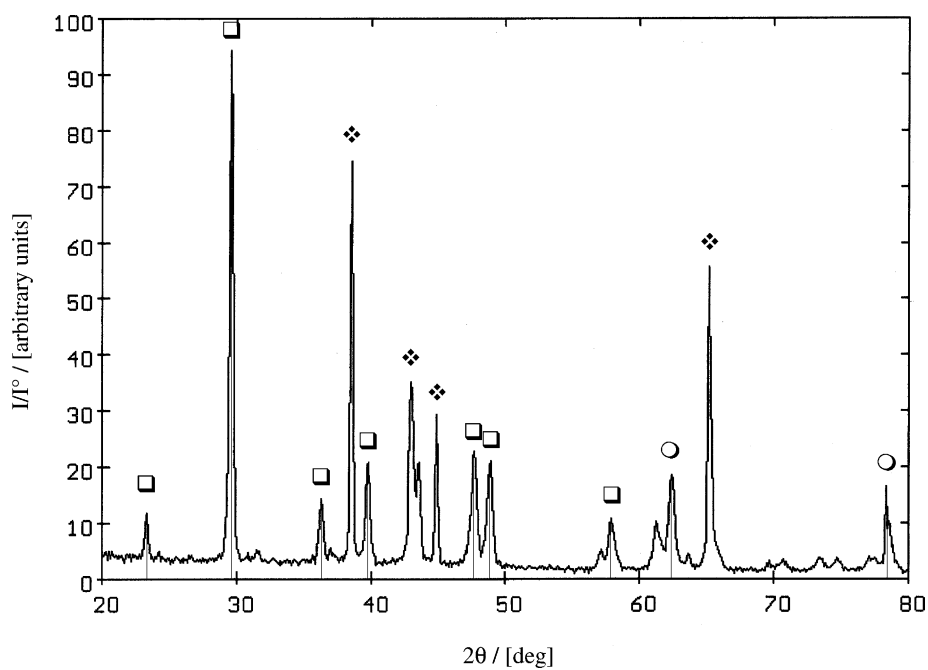
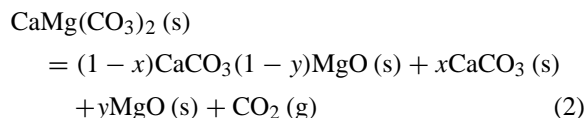


Fig. 5. XRD pattern for the solid product obtained from dolomite half decomposed in CO_2 atmosphere at 943 K (the vertical bars showing the expected position of the XRD peaks of calcite (\square), periclase (\circ) and solid solution $\text{CaCO}_3\text{-MgO}$ (\diamond)).

main peaks of the calcite (i.e. the lattice spacing is lower). On this basis, the reaction that accounts for all experimental evidences could be depicted as:



This model predicts that the amount of MgO that can be extracted from dolomite is less than the theoretical one, as it has been previously observed [19]. To obtain a deeper insight into the possibility of forming calcite–magnesium oxide solid solutions thermodynamic models that give molar free energy versus composition in the MgO–CaCO₃ section of the ternary system CaO–MgO–CO₂ [14] are requested. As far as we know, the information on this topic is scanty. In any event, it should be kept in mind that at constant temperature the composition of the solid solution must be fixed if its equilibrium with dolomite, periclase, calcite and carbon dioxide phases are assumed. If calcite solid solutions occur at different compositions then it might be formed only through non-equilibrium processes. In order to make a kinetic analysis of the reaction (2), one must observe that the CO₂ molecules will escape from the small Knudsen orifice into the large

volume of the thermo-balance when the CO₂ pressure inside the cell is greater than 1 atm. The net CO₂ escaping flux (J_n) per unit of orifice area, will be dependent upon the CO₂ pressure gradient between the inside and the outside of the Knudsen cell, and upon the CO₂ diffusion coefficient through the orifice. The change of (J_n) with time at constant temperature can be derived from the slope of the thermogravimetric traces (see Fig. 2) at different fraction decomposed (α). Thus, the temperature dependence of (J_n) can be obtained at constant (α). Fig. 6 shows these results. As can be observed for any (α) ranging between 0.2 and 0.7, the (J_n) versus ($1/T$) functions are fairly linear and parallel. The slope of these straight lines yields a total apparent enthalpy (ΔH^*) for the decomposition reaction equal to $440 \pm 10 \text{ kJ mol}^{-1}$. Powell and Searcy [29] reported a value of 219 kJ mol^{-1} in the temperature range of 1023–1173 K, where they decomposed the (1 0 0 $\bar{1}$) face of a dolomite single crystal in high vacuum, with torsion effusion and with Langmuir technique. The value here obtained is close to the theoretically expected at $T = 950 \text{ K}$ value $\text{DH} = 486 \text{ kJ mol}^{-1}$ for the dolomite decomposition in the presence of CO₂ [30]. As far as the nature of the rate determining step for these processes is concerned, according to Searcy and Beruto [22,23], surface steps

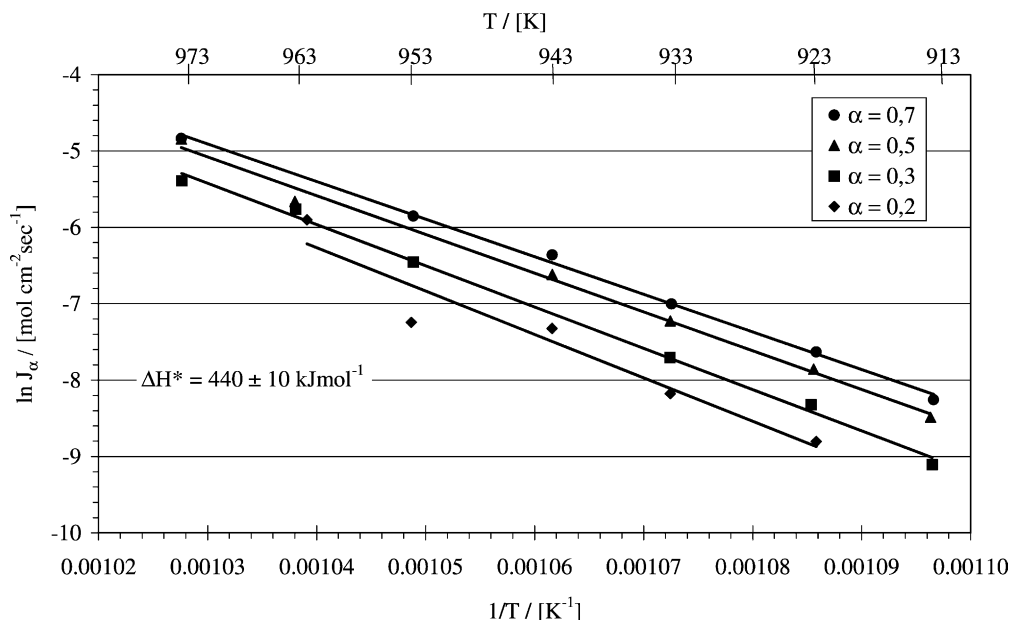


Fig. 6. Arrhenius plot relating to dolomite half decomposition.

such as the diffusion of solid or gaseous reaction products from the reactant–product interfaces into the new formed layers, might be important both in vacuum and in CO_2 . In vacuum the interfacial solid products are formed by CaO and MgO [29], while in the first half dolomite decomposition in CO_2 , MgO , CaCO_3 and the carbonates solid solutions are the solid components (this work [31]). In both cases the reaction proceeds by transport of CO_2 from the decomposing interface into the product layers. This step implies the desorption of the CO_2 from the reactant–product surfaces. The enthalpies and the entropies of adsorption of the CO_2 presents as CO_3^{2-} ions at the oxides surface are usually higher than the ones corresponding to the same species in the carbonate bulk [32]. Thus the desorption of the CO_2 strongly bonded to the reactant–product interfaces is a step involving a significant amount of work. If this amount is close to the apparent enthalpy of the decomposition reaction then there are reasons to believe that the rate determining step is the transport of the CO_2 across the interface reaction. Unfortunately there are not many experimental data for adsorption–desorption phenomena of gas on solid oxides surfaces at high temperature. However, as far as the systems CaO–CO_2 [32] and MgO–CO_2 are concerned [33], one of the authors investigated the gas–solid chemiadsorption process in the same temperature range where this dolomite decomposition study has been carried out. From those studies we learned that the enthalpy of desorption of the CO_2 from the CaO is $199 \pm 8 \text{ kJ mol}^{-1}$ in the temperature range 923–1013 K [32] and $207 \pm 2 \text{ kJ mol}^{-1}$ in the temperature range 880–950 K when the CO_2 desorbs from a low covered surface of MgO [33]. These thermodynamic values are very close to the apparent total enthalpy of activation of the dolomite decomposition obtained in vacuum by Powell and Searcy [29], thus in vacuum it is highly plausible that the desorption of the CO_2 from the surface of the oxides into the reaction interface layer be the rate determining step. The presence of the CO_2 during the dolomite decomposition reaction increases the value of the apparent enthalpy of activation by about 220 kJ mol^{-1} . This change clearly indicates a change in the rate determining step that is controlling the vacuum experiments. The composition of the solid phases forming the interface reaction under CO_2 is changing, thus some new solid step concerning the nucleation and the transport

of the product solid phase might become important. But also some important change in the CO_2 transport across the reacting interface might occur when in the crucible there is an high pressure of CO_2 . Indeed under these conditions the CO_2 might be released not only by the solid product surfaces of MgO , CaCO_3 and of the solid solution, but also from the bulk and/or the grain boundaries phases of the CaCO_3 and/or the solid solution where the CO_3^{2-} can be trapped [34]. If so the transport of the CO_2 across the reacting interface should be a very high thermal activate step that can easily reach an apparent activation enthalpy of $440 \pm 10 \text{ kJ mol}^{-1}$. For instance in the case of the chemisorption of CO_2 on CaO [32] carried out at high temperature (923–1013 K), the apparent activation enthalpy for adsorption was $61 \pm 10 \text{ kJ mol}^{-1}$, but this value raised to $303 \pm 15 \text{ kJ mol}^{-1}$ when a slow dissolution process of CO_2 into CaO starts, perhaps as CO_3^{2-} , at grain boundaries. In this framework the rate determining step of the dolomite decomposition in CO_2 is still the transport of the CO_2 across the boundary reaction interface as in vacuum, but this time, the transport process will be dominated by slow dissolution process of CO_2 as CO_3^{2-} .

Fig. 7(a) and (b) shows that during the first half decomposition process of dolomite powders, the particles kept substantially their external shape—compare the block-like shape of a starting dolomite particle (Fig. 7(a)) with the block shape of a half decomposed dolomite particle (Fig. 7(b)). On this basis the divalent cations and anions do not undergo long-range diffusion steps. They only have local rearrangements to sites of the new phases coupled with local shrinkage that account for the difference in molar volume between the reactants and the products. These are distinguished features of shear-transformation mechanisms [13,24,25], that can occur in calcite structures in carbonate decomposition. In recent investigations, Samtani et al. [20,21] decomposed dolomite in an atmosphere of CO_2 (g) in the temperature range between 998 and 1193 K. They did not find any solid solution, neither the conservation of the initial dolomite particles shape. Evidently the temperature of decomposition does have an effect on the de-mixing of the MgO–CaCO_3 solid solution and on the shear-transformation mechanism.

Fig. 8 shows the Hg intrusion–extrusion curves for two samples obtained from the dolomite half

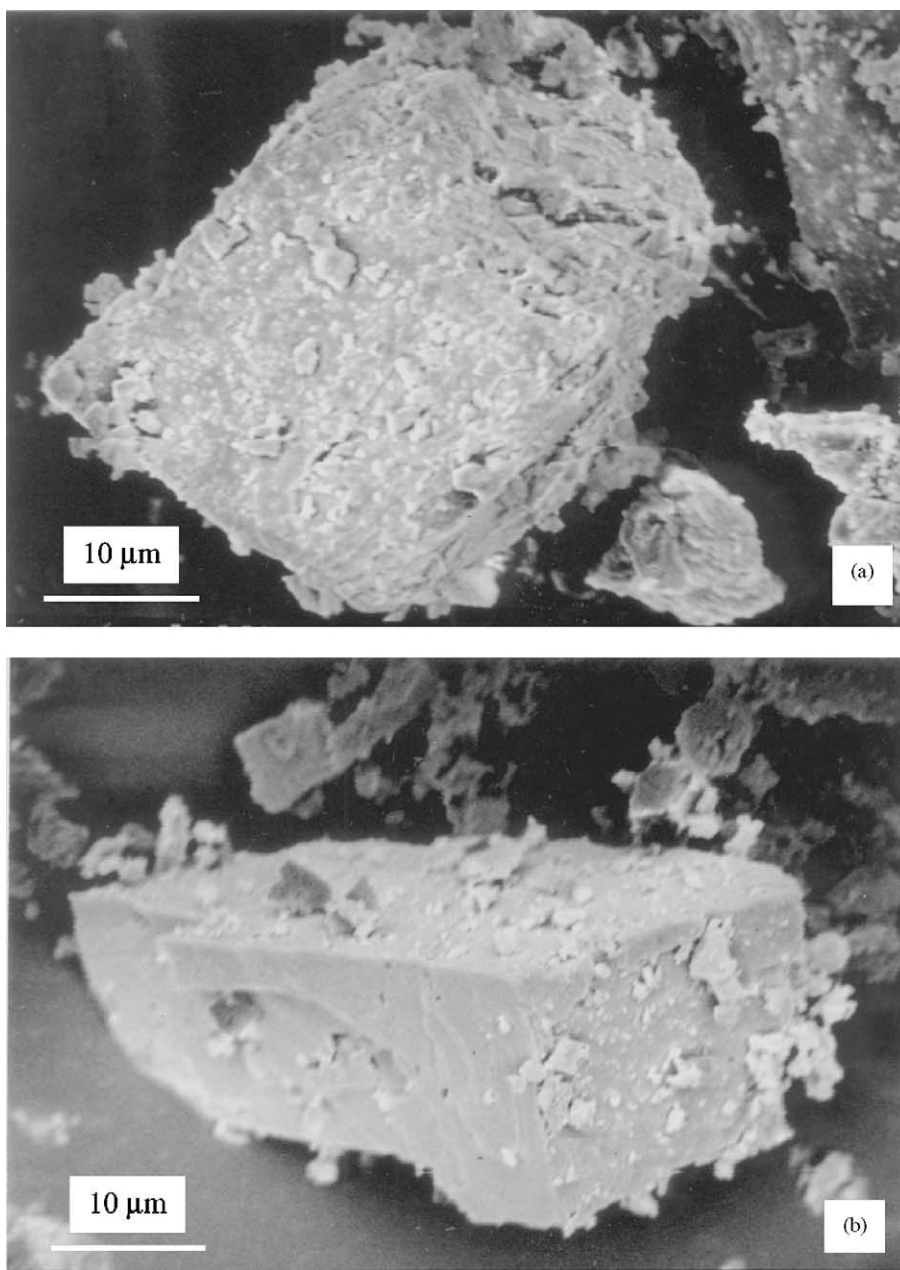


Fig. 7. SEM micrographs of: (a) undecomposed; and (b) half decomposed in CO_2 atmosphere at 943 K dolomite particles.

decomposition at 943 and 973 K. The curves account only for the porosity due to the cavities inside the decomposed grains because the contribution of the inter-granular voids have been subtracted from the experimental curves. The expected theoretical total

porosity from the dolomite half decomposition is equal to $0.12 \text{ cm}^3 \text{ g}^{-1}$, if the reactant forms only MgO and CaCO_3 phases. The experimental porosity value is about $0.10 \text{ cm}^3 \text{ g}^{-1}$ for the samples decomposed at 973 K and about $0.11 \text{ cm}^3 \text{ g}^{-1}$ for the specimen

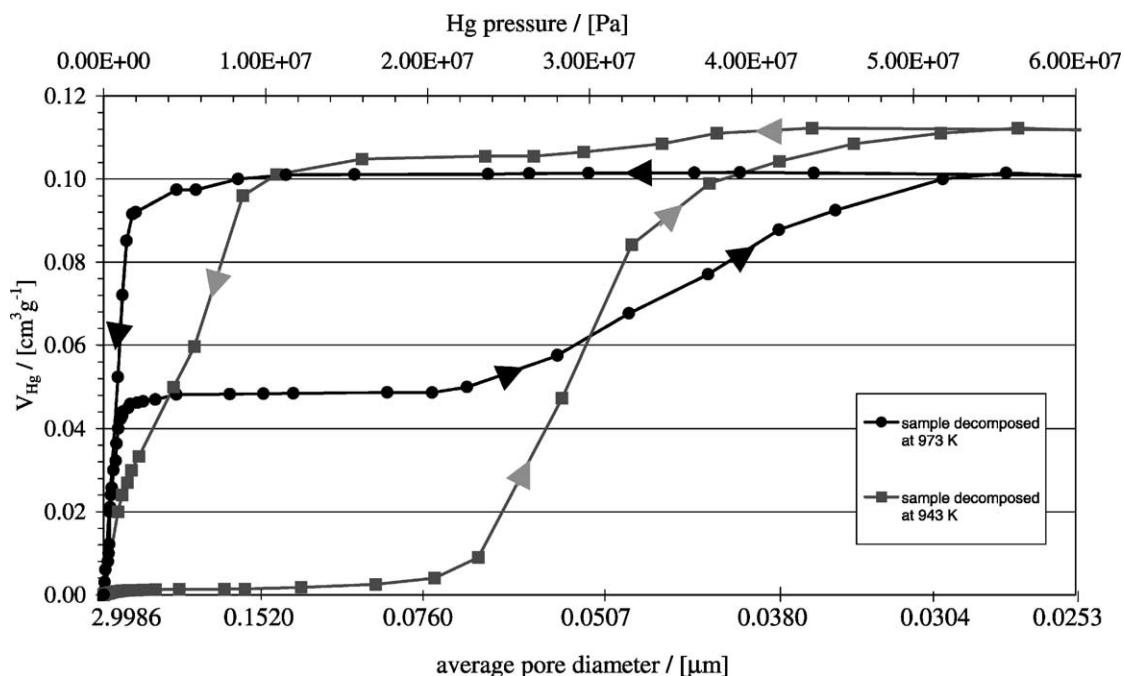


Fig. 8. Comparison of cumulative pore volume curves (intrusion and extrusion) vs. pressure for the solid product obtained from dolomite half decomposed in CO_2 atmosphere at 943 K (■) and 973 K (●).

obtained at 943 K. From the shape of the intrusion curves it is possible to argue that the average diameter dimension at which the Hg enters into the porous structure, changes as the decomposition temperature does too. For the samples decomposed at low temperature a narrow monomodal pore size distribution exists around the average dimension of $0.05 \mu\text{m}$. In the specimen obtained at high temperature a bimodal pores size distribution has been formed. The small pores are still gathered around $0.05 \mu\text{m}$ in a broader distribution, but a new set of cavities have been formed with an average dimension of about $1 \mu\text{m}$. As a consequence of these changes also the shape of the intrusion–extrusion Hg loop is also changing. The amount of Hg that is intruded into the smaller cavities at the pressure range between 20 and 50 MPa is extruded at a pressure lower than 10 MPa. This behavior is accounted for by the ink-bottle model, while an open long cylindrical symmetry is more suitable for the large pores [35]. Detailed SEM microstructures of block-like decomposed particles (see Fig. 7) are in agreement with the results obtained by the Hg porosimeter technique. The most interesting obser-

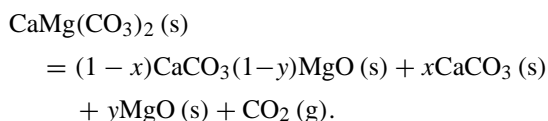
vation about the evidence described above, is, in our opinion, the formation of a bimodal pore structure of almost constant particle shape as the decomposition temperature is increased. Since the cooling period was kept constant for all decomposition tests, there are reasons to believe that the formation of the large cavities occur at the high temperature process. These cavities are like cracks that are propagating inside the particles because a level of mechanical tensions are built up inside them.

The source of these tensions should be the driving force for the shear-transformation mechanism. It is well known [4] that mechanical tensions can be formed at the reactant–product interface due to the difference in molar volume between reactant and parents, to the number of new nuclei, to their dimension, and to pre-existing tensions in the dolomite stone texture. The subsequent formation of the solid solution between CaCO_3 and the MgO , and any grain growth step due to temperature will increase this level. At higher decomposition temperature the level of these tensions inside the particles might exceed a critical cohesion value among the decomposed grains. If so, a type of

collapse and or rearrangement might occur inside the particles. These particles might eventually lose their initial shape if the level of tension becomes too high, as it might happen when the decomposition temperature is increased [21], or when the starting particles have been ground for a long time [36]. The transformation from the monomodal pore size distribution to the bimodal one at almost constant particle shape is, according to our opinion, a particular stage of this diffusion-less process.

4. Conclusions

1. The general reaction path for the first half thermal decomposition of a natural dolomite in CO₂ is:



2. The apparent total enthalpy of activation (ΔH^*) for the dolomite decomposition in CO₂ is $440 \pm 10 \text{ kJ mol}^{-1}$.
3. In vacuum the rate-limiting step for the dolomite decomposition is the transport of CO₂ across the reacting interface controlled by the desorption of CO₂ from the solid interfacial surfaces. In CO₂ environment the rate determining step is still due to the transport of CO₂ across the reacting interface, but this time this process is controlled by an high activated step such as the solid state diffusion of CO₃²⁻ through the bulk and/or the grain boundaries phases of CaCO₃ and/or of the solid solution.
4. The microstructure evolution of the decomposing dolomite particles obeys a shear-transformation mechanism in the temperature range 913–973 K and at 1 atm of CO₂.

Monomodal–bimodal pore size transformation accounts for the level of tension reached inside the particles and increases with the decomposition temperature.

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