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Effect of mixtures of H_2O (g) and CO_2 (g) on the thermal half decomposition of dolomite natural stone in high CO_2 pressure regime

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Abstract

Natural dolomite powders have been decomposed in high CO_2 partial pressure regime with H_2O (g) flowing and in the temperature range 913–973 K. All kinetics and microstructure data concerning the first half decomposition step have been compared with equivalent data obtained from the *same* dolomite powders decomposed under the *same conditions* with no H_2O fluxing. The water vapor reduced the value of the total apparent enthalpy of the reaction from 440 ± 10 to $345 \pm 10\,\mathrm{kJ\,mol^{-1}}$, but the rate-limiting step of the half decomposition process is not changed, consisting in each case in the transport of the CO_2 from the reacting interface. It has been showed that this possibility is plausible because H_2O (g) can enhance the sintering of the formed MgO crystallites with subsequent changes of the CO_2 mode of adsorption on the MgO surfaces from a strong bonded regime to a weaker one. In presence of H_2O (g) and high CO_2 (g) pressure, the rate-limiting step of the first half decomposition of dolomite is still the transport of CO_2 across the reacting interface, as it has been proved for the decompositions in CO_2 environment. In the temperature range explored, H_2O (g) does not change the nature of the solid products which are formed by MgO, $CaCO_3$ and a solid solution of MgO into $CaCO_3$. The microstructure of the solid products is still formed through a shear-transformation mechanism, but H_2O (g) enhances the rate at which this step is occurring. Critical analysis of the microstructure data, allow to conclude that the stress level inside the decomposing particles is increasing and enhancing the cracking rate because H_2O (g) can increase the MgO grain growth rate. These findings might explain the technical procedure used to decompose the dolomite stone in the ancient ovens.

Keywords: Dolomite; Water vapor sintering of MgO; Change in CO_2 adsorption mode on MgO; Microstructure and shear-transformation mechanism

1. Introduction

In our recent paper [1] we carried out an investigation on the half decomposition of a Ligurian dolomite stone in high CO_2 pressure regime to obtain information on the nature and on the mechanism of formation of products, that, according to cultural heritage studies [2], gave unusual and resistant building materials when they were obtained from thermal heating process carried out in ancient ovens. To complete that study [1] it must be kept in mind that wood was used as combustible in the pioneering ovens; thus a considerable amount of H_2O (g) and CO_2 (g) was present in the gaseous atmosphere of the furnace [3]. Further cultural heritage studies [4] provide information from

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which it is possible to learn that extra-sources of water vapor were placed inside the ancient ovens. Summing up all this information there is no doubt that to obtain insight on the phenomena that were occurring in the ancient ovens the effect of H_2O (g) on the dolomite decomposition in high CO_2 partial pressure regime has to be investigated. In previous papers [5–7] it has been pointed out that the water vapor enhances the sintering of MgO. One of authors [8] has proved that at the temperature of 823 K, the specific surface area of 2 nm MgO particles is reduced by 60.5% at 345 Pa of water vapor. On this ground there are reasons to believe that the H_2O (g) is effective in changing the kinetics and the microstructure evolution paths during the dolomite half decomposition reaction, since MgO is one of the solid reaction products [1]. While the effect of the CO_2 pressure regime on the kinetics and the nature of the solid decomposed products has been largely investigated [9,10], the possible influence of the simultaneous presence of H_2O (g) and CO_2, as far as we known, is still unknown. This paper has been conceived to investigate this item. To deal with decomposition reaction where solid-state and solid–gas steps are occurring simultaneously with sintering processes among the grains of one solid product is not an easy task. In order to get insights on this complex pattern, in the following, we shall compare the obtained kinetics and microstructure data with equivalent data derived on the *same* dolomite powders decomposed under *the same experimental conditions* in high dry CO_2 pressure where no sintering between the MgO grains is occurring [1]. From the comparison of the data it is possible to explain the effects of H_2O (g) on the decomposition rate temperature dependence, on the rate-limiting step, on the nature of the solid products and on the shear-mechanism that accounts for the formation microstructure of the product [1]. The results that we shall give in this paper may help also in obtaining a scientific explanation of the reasons behind the empirical expertise used to carry out the thermal decomposition of dolomite in ancient ovens [4,11].

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. For the sake of clarity let us recall that the dolomite powders are characterized by an XRD diffraction pattern formed by dolomite and the most important peaks of $CaCO_3$.

2.2. Techniques

Fig. 1 illustrates the general scheme used to decompose the dolomite natural powders through the TG-DSC technique under H_2O (g) and CO_2 (g) gaseous environment conditions. An amount of 55 ± 2 mg of dolomite powders were placed in the alumina Knudsen crucible with an orifice diameter equal to 0.1 mm. This amount of material filled the crucible completely. Calcinated kaolin powders were used as reference material in the other crucible. The crucibles were placed inside the TG-oven. The thermobalance was prepared with an atmosphere of CO_2, following the procedure already described elsewhere [1]. Under these conditions a flux of wet CO_2 was admitted just at the top of the crucible orifice at the temperature of $50\,^{\circ}$C to avoid water condensation. The wet CO_2 gas was prepared by letting dry CO_2 (g) bubble through liquid distilled water at $50\,^{\circ}$C with a flow of $35.10 \pm 0.05\,\mathrm{ml\,min^{-1}}$. The percentage of H_2O (g) in the CO_2 (g) flux has been measured to amount to 4.0 ± 0.1% in volume. No deviation from this value was observed during the entire period of the experiment. After a fluxing of about 15 min, the samples have been heated to 823 K for 30 min. No weight loss was observed during this period of time. Then the temperature was rapidly arisen to the isothermal decomposition temperatures in the range 913–973 K at a speed of $50\,^{\circ}\mathrm{C\,min^{-1}}$. In the temperature range 913–973 K, the fraction of dolomite weight lost in non-isothermal conditions is practically negligible, but it became significant for isothermal temperatures

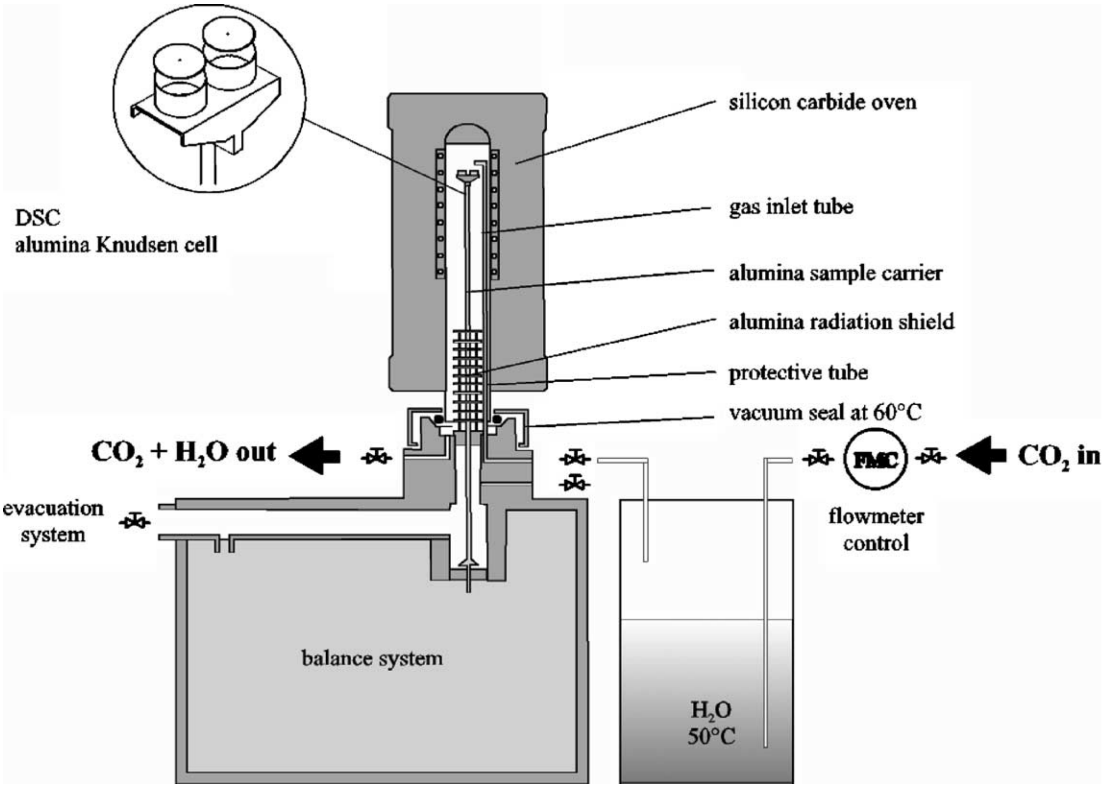

Fig. 1. TG-DSC apparatus used to decompose the dolomite natural powders in H–C experiment.

higher and/or equal to 993 K. The wet CO_2 flux was kept flowing during all steps concerning the complete decomposition cycle. At the end of the dolomite half decomposition a flux of N_2 was introduced into the TG-oven, at the rate of $52.90 \pm 0.05\,\mathrm{ml\,min^{-1}}$, to avoid any reaction during the cooling step. Three decomposition experiments were done on different fresh samples at each selected decomposition temperature. Taking into account all sources of experimental errors, the three decompositions gave TG data that are all included in a band of maximum width equal to the 10% of the reported weight loss. It has been observed that this value is higher than the one corresponding to the experiments carried out in dry CO_2 (g) environment, for which the accuracy was as high as 98% [1].

XRD powders patterns on dolomite and products obtained after thermal treatments were taken using the same apparatus and conditions already described elsewhere [1]. Scanning electron microscopy (SEM) observations on samples coated with a 20 nm thin film-layer of gold [1] were done with special attention to the high temperature cracking mechanism using an accelerating voltage of 10 kV and magnification up to 20,000×. Mercury porosimeter intrusion–extrusion technique was used in the range up to 180 MPa. To obtain information on the intergranular porosity fraction, blank runs were done on non-porous dolomite powder as it has been described elsewhere [1].

3. Results and discussion

Before starting to illustrate the results that compare the data obtained from the thermal half decomposition of powders of natural dolomite in presence of H_2O (g) and CO_2 (g) with the ones derived under the *same experimental conditions* in dry CO_2 (g) atmosphere, let us name from here on, “H–C” the results in H_2O (g) and CO_2 (g), and “C” the ones obtained in CO_2 (g) and already discussed elsewhere [1]. Fig. 2 shows

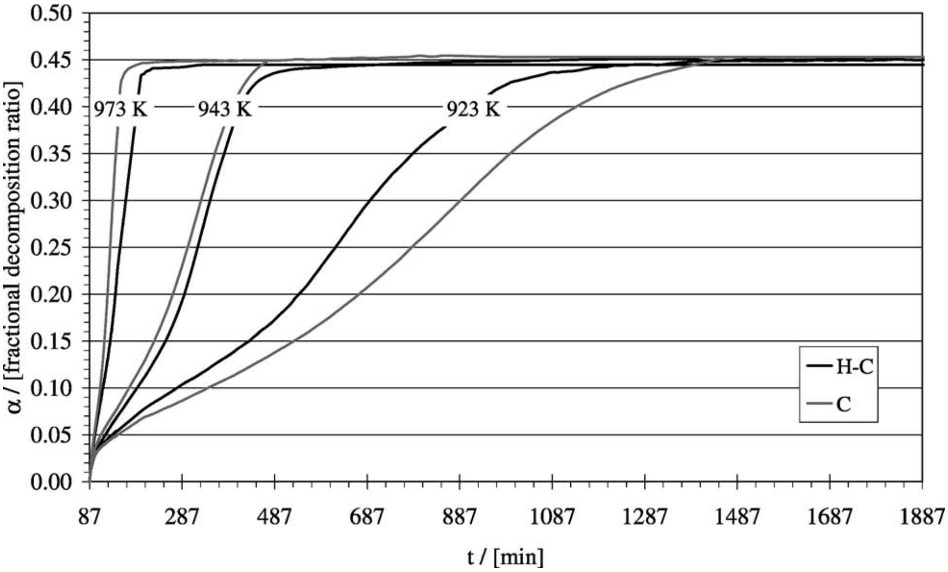

Fig. 2. Decomposed fraction of dolomite (α) vs. time in temperature range 923–973 K. Dark curves concern H–C experiment, gray curves concern C experiment.

typical thermogravimetric traces concerning H–C runs and C experiments at the temperatures of 923, 943 and 973 K. As it is possible to observe for any decomposition temperature, the dolomite decomposes to the expected theoretical degree of conversion α (47.7%) during the first step of its decomposition without being influenced by the nature of the gaseous environments in the furnace. The impurity level of $CaCO_3$, which is not decomposing during the first half decomposition process, can explain the slight difference in the final degree of conversion. However, at lower decomposition temperatures the time, τ_f, required to reach the complete half decomposition of the dolomite in H–C environments is shorter than the one concerning the C experiments. At higher decomposition temperature, the τ_f in C environment and in H–C one become practically coincident. Thus the global rate of the first dolomite half decomposition is influenced by the presence of H_2O (g) in the environment.

Fig. 3 gives the temperature dependence of the net flux J_n of CO_2 from the orifice of the Knudsen cell [1] both for the H–C and the C experiments in the temperature range 913–973 K. From the slope of these lines the total apparent enthalpy of the first dolomite half decomposition is equal to $440 \pm 10\,\mathrm{kJ\,mol^{-1}}$ in the C experiments [1], and to $345 \pm 10\,\mathrm{kJ\,mol^{-1}}$ in the H–C runs. Taking into account that in the C runs the total apparent enthalpy of the reaction is due to the transport of CO_2 across the reacting interface [1], this result strongly suggests that the presence of water vapor molecules enhances the CO_2 transport rate through some mechanism which is unknown. In our previous researches [12,13] on the adsorption of H_2O (g) and of CO_2 (g) on the surface of the magnesium oxide crystallites at high temperature, we stated a number of points that are helpful in understanding the above reported enthalpy values. To clarify this important item let us recall and comment our previous finding in the new perspective. Below the temperature of 898 K H_2O (g) adsorbs chemically on the O^{2-} sites to form $2OH^-$ ions with an enthalpy of adsorption of $-189 \pm 3\,\mathrm{kJ\,mol^{-1}}$. At temperatures higher than 898 K the water can dissolve rapidly in the MgO crystallites with a heat of solubility equal to $-84\,\mathrm{kJ\,mol^{-1}}$ [12]. When this happens, the adsorbed gas is changing the vacancies concentration of the diffusing species and the sintering steps among the oxide grains are enhanced [8,12]. Thus the presence of H_2O (g) at the interface of dolomite products promotes sintering of the MgO nanometric formed crystallites. How this step can influence the CO_2 transport from the interface, can be understood taking into account the peculiar way

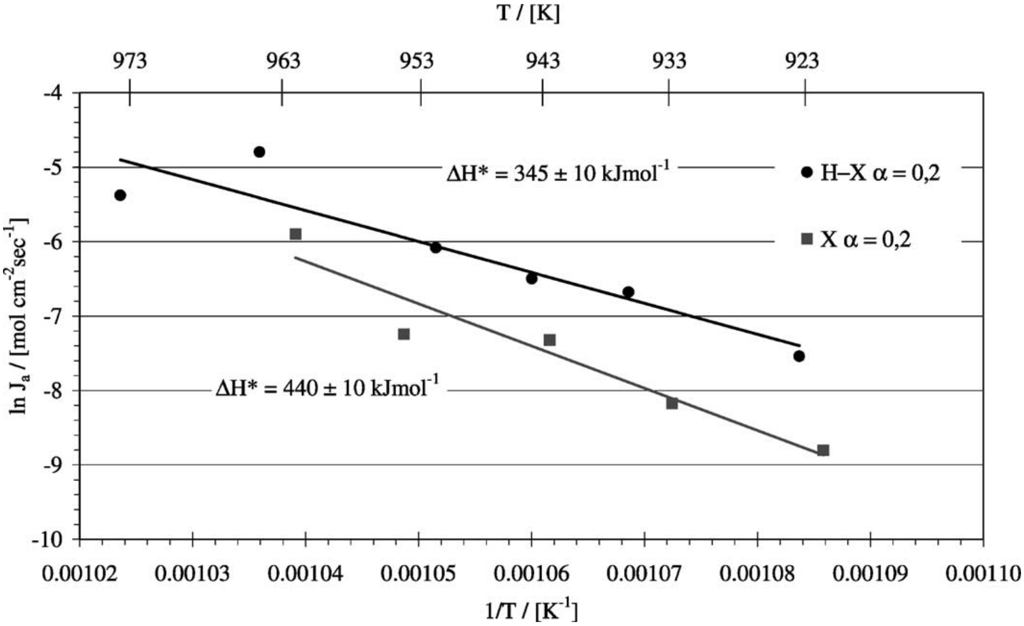

Fig. 3. Arrhenius plot related to dolomite half decomposition, $\ln J_a$ vs. $1/T$, being J_a the CO_2 flux originating from dolomite half decomposition.

according to which CO_2 (g) adsorbs on the MgO surfaces. We have proved [13] that in the temperature range 880–950 K, i.e. equal to that of dolomite decomposition, the CO_2 can be chemically adsorbed on the MgO surface according to two regimes that depend upon its degree of coverage. No dissolution of CO_2 into MgO was observed. At low coverage (I regime) the enthalpy of chemisorption is $-207 \pm 2\,\mathrm{kJ\,mol^{-1}}$, while becoming $-156 \pm 3\,\mathrm{kJ\,mol^{-1}}$ at high coverage (II regime) [13]. The difference in the total apparent enthalpies for the C runs and for the H–C experiments, ΔH^*, is equal to $47 \pm 10\,\mathrm{kJ\,mol^{-1}}$, while the difference between the desorption enthalpies, ΔH_d, of the strong bonded adsorbed CO_2 molecules and of the weaker ones is $51 \pm 2\,\mathrm{kJ\,mol^{-1}}$. This close agreement is striking and it suggests that the effect of H_2O (g) on the kinetics of the first dolomite half decomposition is that of changing the CO_2 adsorption regimes on the MgO surfaces from a strong bonded way into a weaker one. Thus, the rate of the release of CO_2 from the MgO surface in presence of H_2O (g), should be enhanced. The presence of other solid phases beside the MgO in the reacting surface might have some influence on the results derived from the above reported analysis, but any further discussion requires the knowledge of the adsorption and the dissolution of H_2O (g) and CO_2 (g) on the solid products at high temperature. As far as we know this kind of information is very scanty.

The XRD traces concerning the solid phase products obtained at the end of the first half of the dolomite decomposition in H–C and C gaseous environment at 943 K are illustrated in Fig. 4. As it is possible to observe there is no difference between the position of the peaks in the H–C pattern and in the C pattern. Changing the decomposition temperature does not change the result [3]. In agreement with the previous finding [1] it can be concluded that the nature of the solid products is formed by MgO, $CaCO_3$ and a solid solution of MgO in $CaCO_3$. Thus the general reaction that described the first half of the dolomite decomposition in H_2O (g) and CO_2 (g) is still (1):

$$\begin{aligned}&\mathrm{CaMg(CO_3)_2\,(s)}\\&\quad = (1-x)\mathrm{CaCO_3}(1-y)\mathrm{MgO\,(s)}\\&\qquad + x\mathrm{CaCO_3\,(s)} + y\mathrm{MgO\,(s)} + \mathrm{CO_2\,(g)} \qquad (1)\end{aligned}$$

As illustrated in Fig. 5(a) and (b), the block-like shape of the initial dolomite particles (Fig. 5(a)) does not change during the decomposition in H_2O (g) and in CO_2 (g) gaseous environment (Fig. 5(b)). In particu-

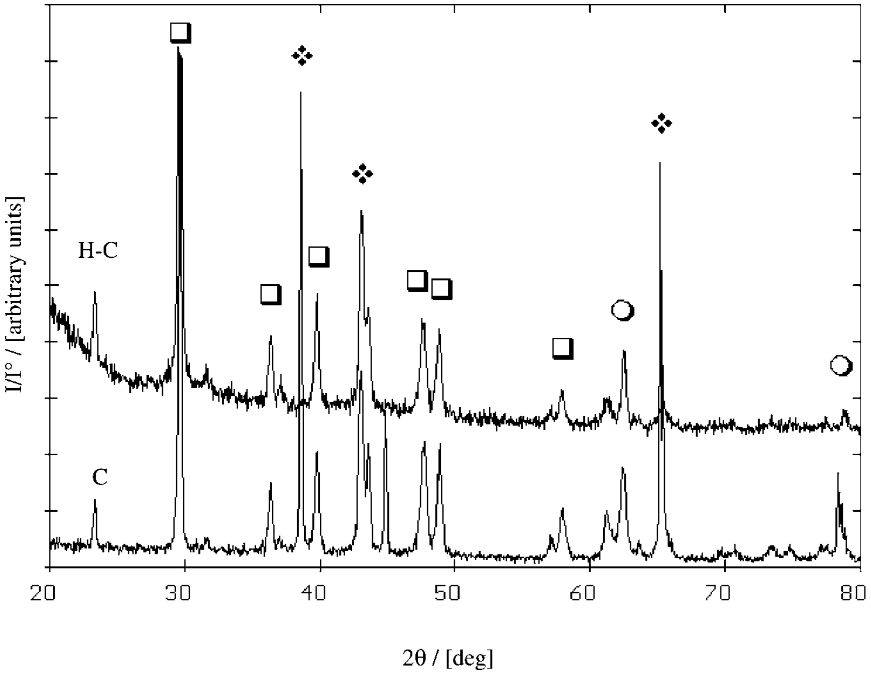

Fig. 4. XRD patterns of the solid products obtained in C and H–C experiments (the symbols showing the expected position of the XRD peaks: calcite (❑), periclase (❍) and solid solution $CaCO_3$–MgO (❖)).

lar, the edges of the decomposed particles do not seem to be rounded. This evidence strongly suggests that long distance diffusion steps are not occurring during this decomposition. Thus the microstructure of the decomposed particles is due to a shear-mechanism as it has been proved for the C decomposition [1].

Fig. 6 shows the mercury porosimeter intrusion curves concerning the final solid products for the C half decomposition (gray curve) and for the H–C ones at 943 K (dark curve). The contribution of the porosity due to the intergranular voids has been subtracted (see Section 2 and [1]), thus the curves account only for the cavities inside the decomposed particles. As it is possible to observe, the total porosity of the H–C samples, $0.164\,cm^3\,g^{-1}$, is larger than that of the C ones, $0.115\,cm^3\,g^{-1}$. Since the calculated total theoretical porosity of the particles obtained from the half decomposition of the dolomite is equal to $0.12\,cm^3\,g^{-1}$ [1], and since the shape of the H–C particles is fairly equal to that of the initial dolomite, the evidence that the porosity of the H–C grains is larger than the theoretical one, leads to the conclusion that the H–C decomposed particles must be cracked. In agreement with this observation while the C samples are characterized by a monomodal pore size distribution with average diameter of about 0.05 μm, the H–C samples have a bimodal pore size distribution where the greatest average diameter is around 1 μm. Evidence for these large cavities have been observed on the external surface of decomposed particles (Fig. 7). In the same figure, one long crack about 0.2 μm width and 8 μm long can be observed. The average size of these defects does not change significantly as the decomposition temperature is increasing, but their number does, as it is proved by the value of the total porosity that becomes $0.222\,cm^3\,g^{-1}$ at 973 K [3]. Since the change from a monomodal pore size distribution to the bimodal cracked configuration one, reported in Fig. 6, is concerning C and H–C samples that undergo the same cooling treatment, the formation of the cracks has to be considered an high-temperature process, due to the development of residual stress inside the porous matrix of the solid decomposed products. If so, the effect of H_2O (g) during the dolomite decomposition consists in increasing the level of these mechanical stress and, therefore, in enhancing the

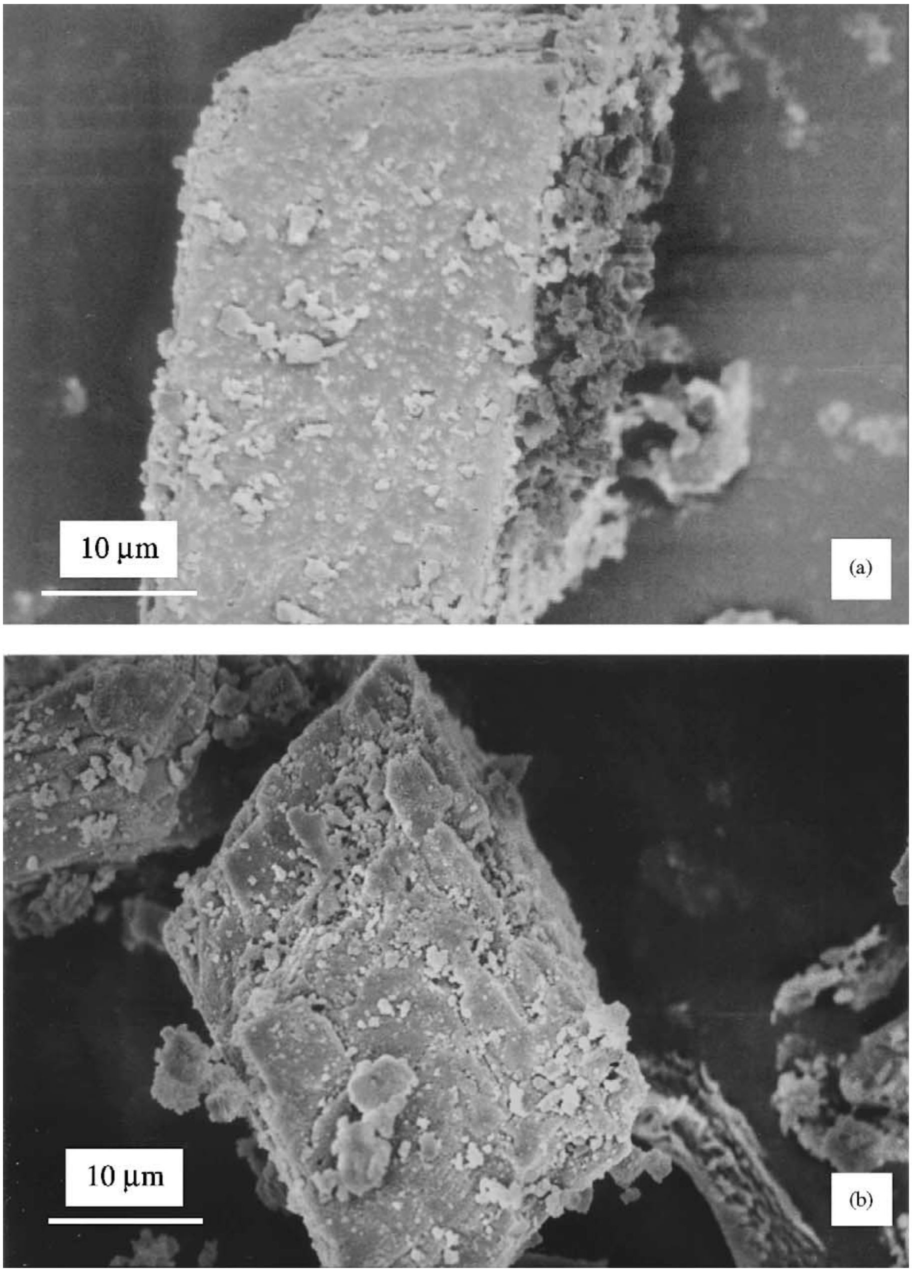

Fig. 5. SEM micrographs of: (a) undecomposed dolomite; and (b) half decomposed dolomite, at 943 K, in H–C experiment.

rate of the shear-transformation mechanism. The experimental fact on which we might account is that the grain growth of the MgO particles inside the porous network is enhanced by the presence of H_2O (g). In our previous papers [14,15] we worked out a model from which it is possible to infer that if a spherical particle inside a number of other homogenous and equal sintering particles is increasing its radius, the stress can be raised to levels capable of breaking of the bonds with the neighboring particles. This

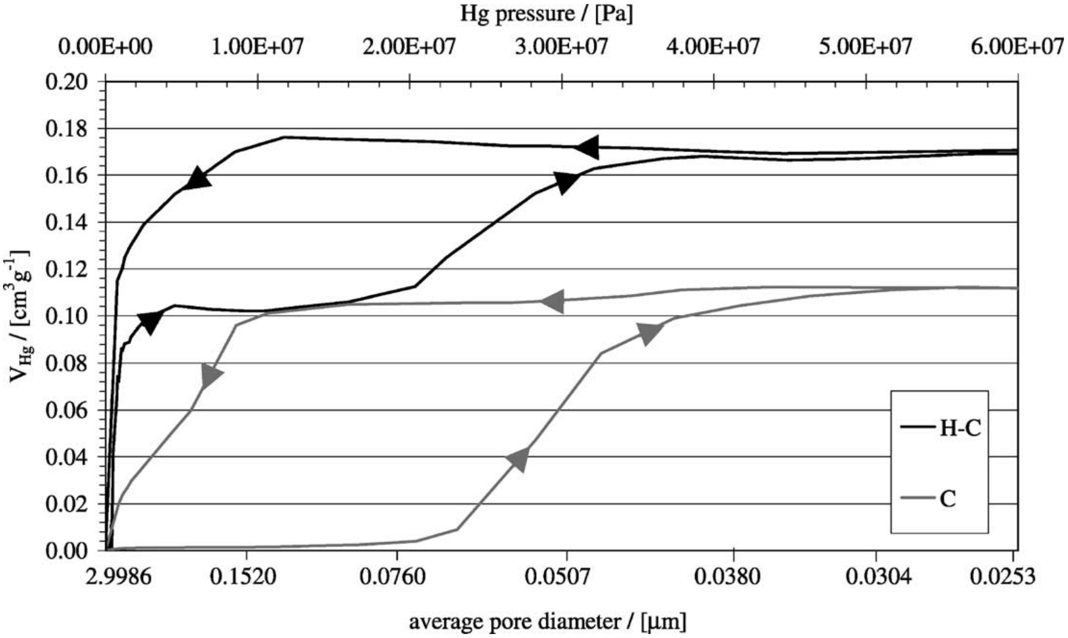

Fig. 6. Comparison of cumulative pore volume curves (intrusion and extrusion) vs. pressure for the solid products obtained from dolomite half decomposition at 943 K, in C experiment (gray curve) and in H–C experiment (dark curve).

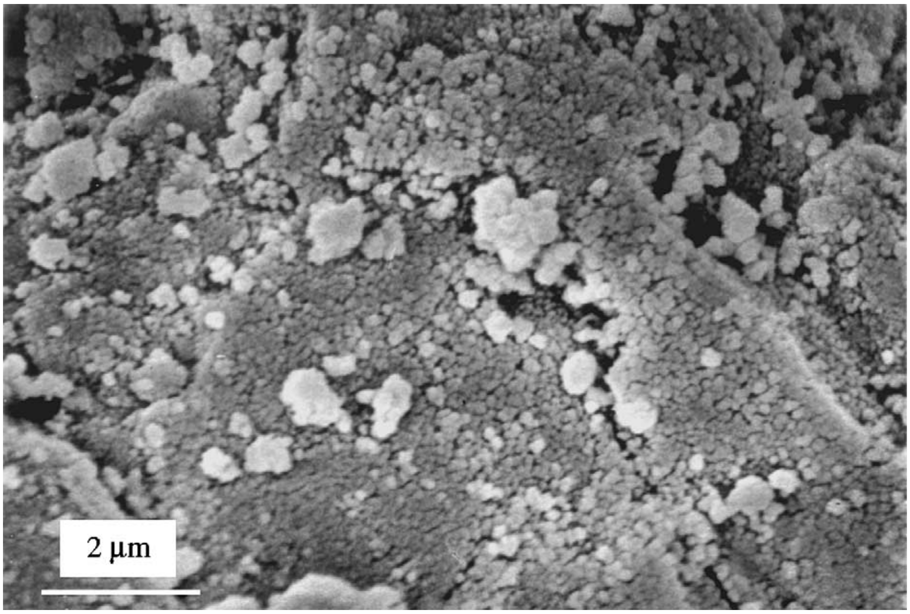

Fig. 7. SEM micrographs of half decomposed dolomite particles, at 943 K, in H–C experiment.

breaking mechanism has been experimentally observed during the sintering of ceramic oxides in presence of heterogeneity [16,17]. There are no reasons to believe that the same mechanism may not happen also during a more complex process like the one described here. If so, in the H–C decomposition, the increasing of the MgO average grain size leads, as a consequence, to an increase of the stress around the next neighboring particles. When this stress exceeds a critical one the cracked microstructure is formed.

It is interesting to observe that all findings reported in this paper are the mere consequence of the catalytic effect of H_2O (g) on the sintering of nanometric MgO crystallites [8,12]. From a practical point of view these effects tend to reduce the total time of the first dolomite half decomposition. The people that were adding extra-sources of water vapor into the ancient ovens [4,11], probably might have already observed these effects by experience.

4. Conclusions

1. The presence of H_2O (g) during the first half decomposition of the dolomite in CO_2 changes the CO_2 adsorption mode on the MgO surfaces from a strong bonded regime to a weaker one, due to the catalytic effect of the H_2O (g) on the sintering of nanometric MgO crystallites.
2. In presence of H_2O (g) and high CO_2 (g) pressure, the rate-limiting step of the first half decomposition of dolomite is still the transport of CO_2 across the reacting interface, as it has been proved for the C decompositions.
3. In the temperature range explored and in the H–C gaseous conditions, the solid products are formed by MgO, $CaCO_3$ and a solid solution of MgO into $CaCO_3$, as it has been found for the C decompositions.
4. H_2O (g) increases the shear-transformation mechanism rates yielding cracked decomposed particles at decomposition temperature lower than the ones observed in the C experiments. Also this effect is due to the catalytic action of H_2O (g) on the sintering of nanometric MgO crystallites.

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