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INFLUENCE OF GRINDING ON BOTH THE STABILITY AND THERMAL DECOMPOSITION MECHANISM OF SIDERITE

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ABSTRACT

It has been studied the influence of the comminution on the stability of a sample of siderite of the following composition: $(Fe_{0.692}Mg_{0.308})CO_3$.

Both TG and XRD data seem to show that the above sample is decomposed by ball milling at room temperature with segregation of Fe_3O_4.

On the other hand, it has been observed that the thermal decomposition under vacuum of the as received sample of siderite takes place in a single step giving FeO and MgO as final products. However two steps are observed in the thermal decomposition of the ground sample, the first one producing MgO and the second one MgO, FeO and Fe_3O_4. The ratio FeO/Fe_3O_4 decreases by increasing the grinding time of the precursor until reaching the ratio $FeO/Fe_3O_4 = 0$ after 8 hours of ball-milling. These results would be interpreted by assuming that the reactivity of the FeO and the CO_2 generated in the thermal decomposition of siderite yielding Fe_3O_4, increase by increasing the grinding time of siderite.

INTRODUCTION

It has been reported in the literature (1-4) that the comminution of materials can induce dramatic changes on their texture, structure and chemical reactivity. Therefore, it would be interesting to study the influence of grinding on the structure and thermal stability of minerals of industrial interest for producing metal or metal oxides by means of processes which involve thermal decomposition of the precursors. The scope of the present paper is to analyse the influence of the ball milling of a sample of siderite on the structure and stability of both the mineral and the products obtained from its thermal decomposition.

EXPERIMENTAL

It has been used a sample of siderite from Cala (Spain) with the following composition: Fe_2O_3,44.6%; MgO,10.8%; Mn_2O_3,3.7%; SiO_2,4.9%; CaO,1.1%; other oxide,0.9%; ignition loss, 34.0%. The analytical results obtained from both atomic absorption and X-ray fluorescence show a very good agreement. Taking into account these results and the X-ray diffraction profile of the as received sample (Fig. 1), the

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formula $(Fe_{0.692}Mg_{0.308})CO_3$ has been proposed for the mineral.

A planetary ball mill, Colerecord 20 A, with a speed of 450 r.p.m. has been used. The mill is equipped with a Corindon jar containing 10 balls of the same material, 18 mm in diameter. Sample weights about 5 g were comminuted.

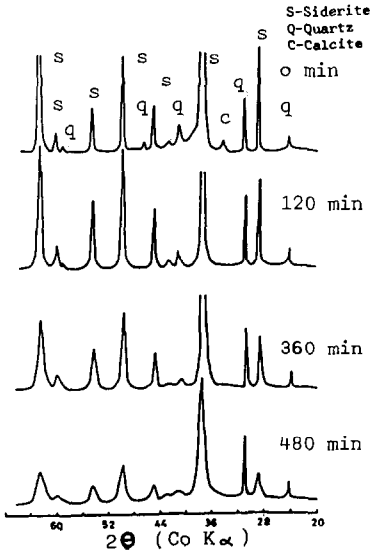

Fig. 1. X-ray profiles of both as received and ground samples of siderite.

The DTG traces of the sample have been obtained with a Cahn electrobalance under a pressure lower than 10^{-3} torr.

The powder X-ray diffraction spectra of the sample have been obtained with a Philips PW 1060 instrument using Co K_α radiation and a iron filter.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction profile of both the as received siderite and the sample obtained by ball milling the mineral up to 480 min. The results obtained from the analysis of the samples by X-ray fluorescence are included in table 1 together with the ignition loss at 1000 ºC under air atmosphere. These data point out that a mecanochemical decomposition of siderite takes place during the grinding yielding an amorphous product, provided that only siderite peaks are observed on the XRD profiles of the ground samples. Moreover, these samples are attracted by a magnet which means that a ferromagnetic oxide has been produced during

TABLE 1

Analytical results of the siderite samples as a function of the grinding time

Grinding time ⟶	0-HOURS	2-HOURS	6-HOURS	8-HOURS
Fe_2O_3 %	44.6	44.1	46.7	51.8
MgO %	10.8	11.0	11.6	13.2
Mn_2O_3 %	3.7	3.8	3.8	4.2
SiO_2 %	4.9	5.7	6.1	8.8
CaO %	1.1	0.9	0.9	0.9
Other oxide %	0.9	1.0	1.0	2.0
Ignition loss %	34.0	33.3	29.8	19.1
Values of x (equation 1)	0.0	0.037	0.189	0.569

the comminution of the mineral. If we consider that magnetite is the unique ferromagnetic oxide observed on the XRD profiles of the products obtained from the thermal decomposition of ground siderite (Fig. 3), and we bear in mind the data of table 1 we can suggest that the decomposition of siderite by ball milling at room temperature implies the segregation of Fe_3O_4 according to:

$$(Fe_{0.692}Mg_{0.308})CO_3 \longrightarrow x/2\ Fe_3O_4 + 2x/3\ CO_2 + x/3\ CO + (Fe_{0.692-x}Mg_{0.308})\ CO_{3(1-x)} \qquad (1)$$

the values of x as a function of the grinding time are included in table 1.

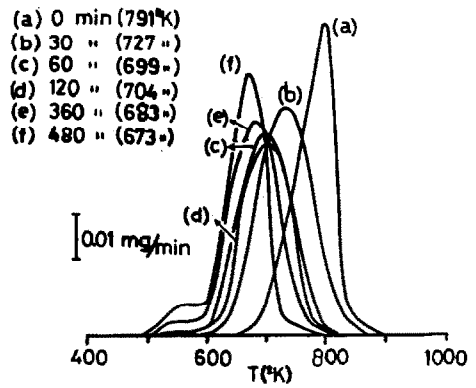

Fig. 2. DTG traces of both as received and ground samples of siderite. The peak temperature is shown into the bracket.

Fig. 2 shows the DTG traces of both the as received and ground samples of siderite. The XRD profiles of the final products of the thermal decomposition of these samples are shown in Fig. 3. These results show that the DTG traces of siderite moves at lower temperatures by increasing the grinding time. On the other hand, it can be observed that the thermal decomposition under vacuum of the unground siderite takes place in a single step, according to literature (5,6), yielding FeO and MgO. However, two steps are observed in the thermal decomposition of the ball milled samples.

Fig. 4 shows, by way of example, the X-ray diffraction profiles of the products yielded along the thermal decomposition of a sample of siderite ball milled during 480 min. These results seem to suggest that MgO is partially segregated during the first step of the reaction according to:

$$(Fe_{0.692-x}Mg_{0.308})CO_{3(1-x)} \longrightarrow (Fe_{0.692-x}Mg_{0308-y})CO_{3(1-x-y)} + y\ MgO + y\ CO_2 \qquad (2)$$

In order to determine the value of y it would be required to separate the two overlapping steps on the DTG curves of ground siderite.

The above results would be interpreted by assuming that the mechanical treat-

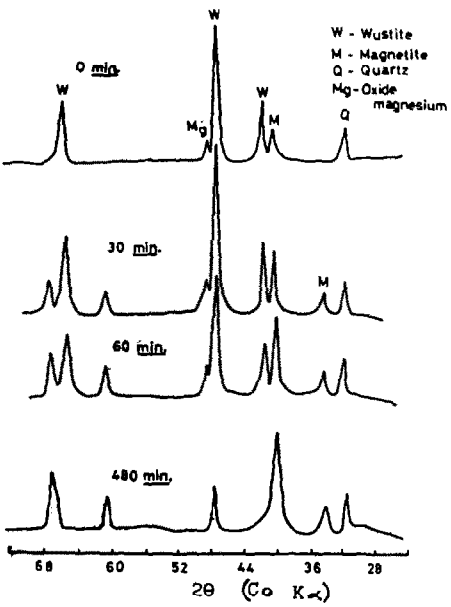

Fig. 3. X-ray diffraction patterns of the final products yielded in the decomposi - tion of siderite ground of different time.

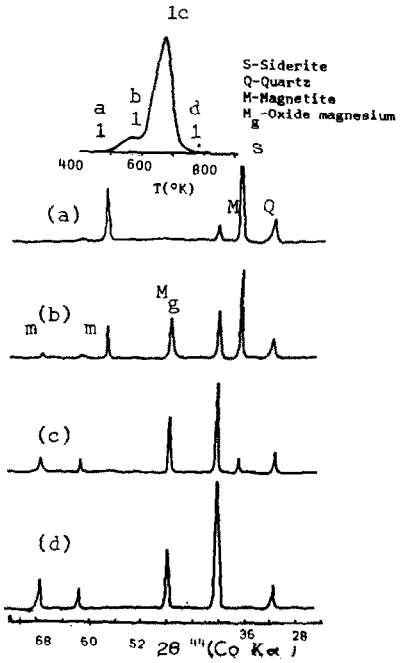

Fig. 4. X-ray diffraction patterns of the products yielded at different point of the DTG diagram of samples of siderite ball-milled 480 min.

ment of siderite leads to a redistribution of Mg^{++} and Fe^{++} ions yielding patches of magnesite dispersed into the lattice of substituted siderite. A similar behaviour has been previously reported by Brandley (7) studying the lattice distorsion of dolomite induced by grinding.

On the other hand, it can be concluded from the results included in Figs. 3 and 4 that the products yielded in the second step of the thermal decomposition of comminuted samples of siderite are MgO, FeO and Fe_3O_4. Moreover, the ratio FeO/Fe_3O_4 decrease by increasing the grinding time of the precursor until reaching the ratio $FeO/Fe_3O_4 = 0$ after 480 min. of ball milling. These results would be interpreted by assuming that the reactivity of the FeO and CO_2 generated in the thermal decomposition of the siderite towards the reaction:

$$3\ FeO + CO_2 \longrightarrow Fe_3O_4 + CO \qquad (3)$$

increase by increasing the grinding time of siderite.

REFERENCES

(1).- V.V. Boldyrev; 1. World Congress Particle Technology, Part II. (6. Euro - pean Symposium Comminution), Nurnberg (1986).

(2).- A.F. Yeremin and E.L. Goldberg; Izv. SO AN SSSR, 6, (1985).

(3).- S. Nadiv and I.J. Lin; Reactivity of Solids. Part B, (P. Barret and L.C. Dufour, Eds.), Elsevier, Amsterdam, 731 (1985).

(4).- M. Senna and Y. Iguchi; Reactivity of Solids. Part B, (P. Barret and L.C. Dufour, Eds.),Elsevier, Amsterdam, 755 (1985).

(5).- Z. Kubas and M. Szalkowicz; Thermal Analysis, Vol. 2, Proceeding 3rd ICTA, Davos, 447 (1971).

(6).- P.K. Gallagher and S.St.J. Warne; Thermochim. Acta, 43 (1981) 253.

(7).- W.F. Bradley,J.F. Burst and D.L. Graf; Crystal Chemistry and Differential Thermal effect of Dolomite, Amer. Min., 38 (1953) 207.