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Thermochimica Acta 277 (1996) 75–84

thermochimica
acta

Stimulating the thermal decomposition of magnesite

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Received 23 March 1995; accepted 23 September 1995

Abstract

This paper deals with the influence of mechanical activation and decrepitation on the process of formation of active MgO in the course of the thermal decomposition of magnesite. It has been confirmed that the activation has a favourable influence on the formation of the porous oxidic product with specific surface area $S_A > 100\ \mathrm{m^2\ g^{-1}}$ which comes into existence in the active zone of the decomposition of magnesium carbonate. The effect of decrepitation with secondary fragmentation on the reactant takes place at temperatures above 923 K. The process of forming active MgO was described by the KEKAM equation with a changing exponential factor.

Keywords: Decomposition; Decrepitation; KEKAM equation; Magnesite; Mechanical activation

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1. Introduction

In the chemical processing of magnesite, thermal processes are used for preparing active magnesium oxide [1–4]. From the view-point of stimulating the process of thermal decomposition, the possibility of influencing the properties of the products by modifying the reactivity of the carbonate raw materials by mechanical preactivation or decrepitation is important [5, 6].

It has been confirmed by many studies [1, 7–11] that the temperature of thermal decomposition decreases following mechanical activation. It is generally known that the changes induced in the process of prolonged grinding are classified as changes in granularity, surface properties, amorphization and recrystallization, polymorphous transformations and mechanochemical reactions [1, 5, 12–16].

In the case of carbonates, these particular phenomena have been widely discussed. The systematic study of the thermal decomposition of carbonates is the subject of

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SSDI 0040-6031(95)02762-9

a number of excellent works [17, 18]. However, the influence of the granularity of a material on the process of thermal decomposition is directly connected with decrepitation, which takes place predominantly in the middle range of grain dimensions, i.e. 106–1180 μm [19]. McCauley and Johnsom [19] and Dollimore et al. [20] have found the maximum (about 80%) decrepitation of dolomite to be in the 150–250 μm [19] or 180–250 μm [20] ranges of granularity. The cause of decrepitation was suggested [19] as being the result of water trapped in the dolomite structure, which at the temperature of decrepitation would produce a water vapour pressure that was similar to the pressure required to break bars of dolomite. Decrepitation is a complex physical phenomenon which may have various manifestations during the thermal treatment of grainy materials, such as increased activity, sonic emission during explosion of the material, and disintegration during selective concentration of mineral components. The thermal decomposition of dolomites is not affected by decrepitation [19]. However, the positive effect of lowering the temperature of an endothermic $MgCO_3$ peak in coarser samples of dolomites ($T_{MgCO_3} = 740°C$ for 2 μm grain size and $T_{MgCO_3} = 718°C$ for 400 and 20 μm grain size) was observed by Ozao et al. [21]. According to the literature [19, 22–25], decrepitation is brought about by the action of stress that has accumulated in the lattice of minerals resulting from the presence of gas and liquid inclusions, lattice defects, cleveage of the minerals, and cracks; and last, but not least, it is a function of the strength characteristics of the mineral.

Decrepitation is more important in mineral processing. The selective decomposition and self-comminution of active magnesia caused by decrepitation and stressing during manipulation, can be conveniently used as a simple way of magnesite dressing by screening [26]. Magnesia accumulates in the undersized fraction, whereas undecomposed calcium carbonates and quartz remain in the oversized fraction. In the decrepitation treatment of magnesite, a fine-grained highly active charge for hydrometallurgical treatment is prepared, even from lower grade magnesites [5, 6, 26–28]. The thermal decomposition of Slovak magnesites was studied very thoroughly. In Refs. [1, 29–31], the influence of mechanical activation on the process of thermal decomposition and the activity of the oxidic product was investigated. The influence of mechanically induced changes in the structure and enthalpy on the dissociation of magnesite was specified [31]. Due to mechanical activation, the temperature at which individual products of the thermal decomposition reach optimum reactivity decreases at a constant degree of conversion, $\alpha = 0.8 \pm 0.02$, is characterized by a maximum value of the specific surface. Considering the application of this information in preparation processes, the kinetic aspects of the formation of an active MgO during the thermal decomposition of magnesite are also important. Therefore, this work was undertaken to provide a kinetic analysis of the formation of active MgO during the thermal decomposition of both the mechanically activated magnesite and the fine-grained material.

2. Materials and methods

The investigations were carried out with natural Slovak magnesite of calcareous type from Jelsfiava. Its chemical composition was: 42.33% MgO; 3.28% CaO; 3.72%

Fe_2O_3; 0.68% SiO_2, and there was a 49.26% loss on ignition. The sample, of initial granularity 0.1–1 mm, was ground in a vibrating ball mill (constructed by the Mining Institute, Kosfiice) for a constant time under the following conditions: filling with grinding steel balls, 75%; ratio of the mass of charge to grinding load, 1/10; revolutions of the mill, 1220 min^{-1}; and grinding time, 4 h. This time was chosen because it was the optimum time of grinding according to Ref. [4]. By varying the amplitute of the mill ($A_m = 2.5$–6.6 mm), the power input was changed in the range 42–273 W kg^{-1}. The standard sample was prepared by 7.5 min grinding at the lowest amplitute of the mill.

The fineness of the samples was determined by dry granulometric analysis on standard screens and the specific surface area, S_A, was determined on the Gemini 2 360 apparatus (USA). The granulometric specific surface area, S_G, was calculated statistically from particle size distribution data measured on a Sartorius sedimentation balance (Germany).

The change in amorphous phase of the carbonate reactant during mechanical activation was investigated by X-ray phase analysis on a diffractometer DRON 2.0 (Russia) with the following conditions: radiation, Cu Kα; 30 kV; 20 mA; time constant, 1 s; limit of measurement, 10 impulses s^{-1}; rate of detector, 2° min^{-1}, paper drive, 2.4 m h^{-1}. The degree of structural disorder was evaluated from the change in amorphization, X_A, of the magnesite structure as defined by the equation [32]

$$X_A = 1 - \frac{I^X}{I_0} \tag{1}$$

where I^X and I_0 are the integrated intensities of the peaks of the activated sample and non-activated standard (40 μm), respectively. The calculation of amorphization according to Eq. (1) was performed for the (104) diffraction peak of magnesite corresponding to the value $d = 0.2742$ nm.

In conformity with the results of preliminary experiments, the kinetics of thermal decomposition of the samples characterized in Table 1 were investigated.

The thermal decomposition was investigated in a dynamic reactor with a static bed in argon flow. The weight of magnesite was 100 mg and the rate of argon flow was 0.303×10^{-6} m^3 s^{-1}. The reaction conditions were chosen so that the influence of CO_2 on the reaction rate was minimized. The decomposition took place at temperatures of 773, 813, 873, 923 and 973 K. The effect of decrepitation was evaluated quantitatively by the quantity of flue dust, ϵ_D, released from the static bed into the free space of the reactor.

Table 1
Grinding parameters

Sample	N	A1	A2	A3	D
τ_m/h	0.125	4.00	4.00	4.00	0
A_m/mm	2.60	2.60	5.70	6.60	0
A/kJ kg^{-1}	19.30	617.76	1582.56	3638.40	0

τ_m is the grinding time, A_m is the mill amplitude, and A is the specific grinding energy for the investigated magnesite samples.

The process of formation of active MgO in the course of the thermal decomposition of magnesite was described by the KEKAM equation [33] in a modified form

$$-\ln\left(1-\frac{\alpha}{\alpha_m}\right)=k'\tau^n \tag{2}$$

where α is degree of thermal decomposition at time τ, α_m is the maximal degree of thermal decomposition, τ is the time of heating in min, and n is an exponential factor. The apparent rate constant of the process, k, was calculated [34] from the relation

$$k=nk'^{1/n} \tag{3}$$

3. Results and discussion

The experimental results of the kinetic study of the process of formation of active MgO in the course of thermal decomposition are presented in Fig. 1. The effect of decrepitation was observed in the course of thermal decomposition of the standard sample N and the fine-grained sample D.

The character of the dependence of the specific surface of the oxidic product on the time of thermal decomposition (solid lines in Fig. 1), shows that the process of formation of active MgO may be significantly affected by mechanical preactivation. For the non-activated sample (Fig. 1b) in the investigated temperature range, no apparent maximum of the specific surface was obtained. A decomposition lasting for 10–20 min at temperatures ranging from 873 to 973 K gave rise to an oxidic product with a specific surface area of about 50 $\mathrm{m^2\,g^{-1}}$. A prolongation of the reaction time did not result in any increase in the specific surface area of the oxidic product.

The activation of the carbonate reactant has significant influence on the increase in the specific surface area of the intermediates of thermal decomposition (Fig. 1a). For such samples, a two-fold increase in the values of the specific surface area was observed and in the optimum case an oxidic product with specific surface area, $S_A \approx 100\ \mathrm{m^2\,g^{-1}}$ was formed. The decrepitation of the fine-grained sample D at 923 K may also be a factor influencing the increase of the specific surface area, $S_A \approx 65\ \mathrm{m^2\,g^{-1}}$ (curve 5).

The course of the dependence of the degree of conversion of magnesium carbonate (dashed lines in Fig. 1) on temperature showed that the process of formation of active MgO is accelerated by mechanical preactivation. The process of formation of active MgO due to thermal decomposition is characterized by maxima of the specific surface, which are situated mainly in the active zone of conversion of magnesium carbonate. With increasing temperature of thermal decomposition ($T > 873$ K) of mechanically activated magnesite, the maximum is shifted into the active zone of thermal decomposition. By decrepitation of the mineral, the process of formation of an active MgO is accelerated and it also reaches its maximum in the active zone of thermal decomposition. The height of these maxima is a function of the temperature and activity of the carbonate reactant.

The origin of the maxima can be explained by formation of the pseudomorphous structure (and fragmentation, respectively), while the fall in maxima was caused by

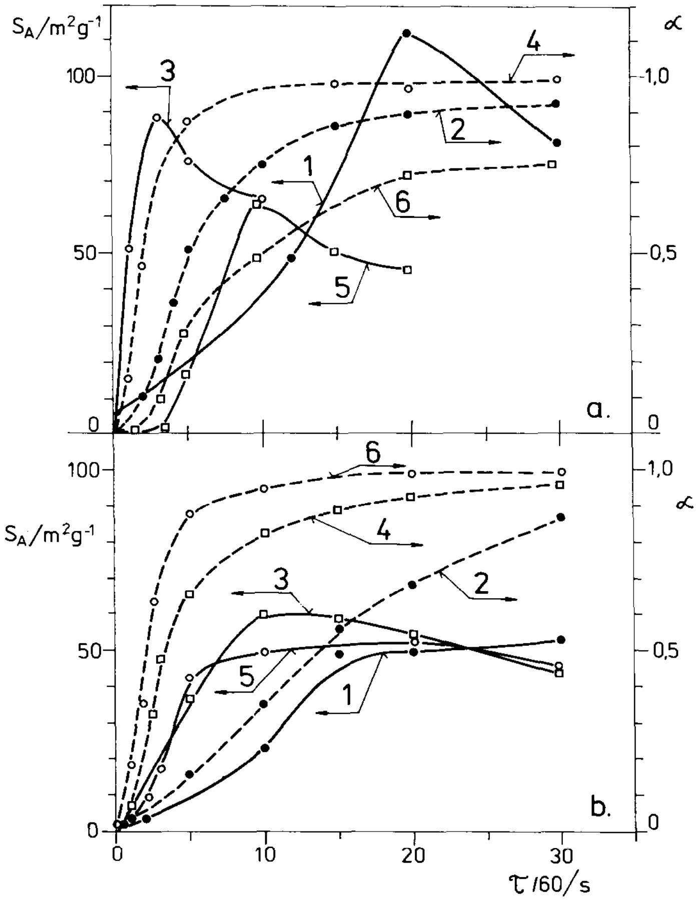

Fig. 1. Changes in specific surface area S_A and degree of $MgCO_3$ decomposition α or magnesite at different temperatures of isothermal decomposition with time τ. a. Mechanically activated sample A3: curve 1, S_A at 873 K; curve 2, α at 873 K; curve 3, S_A at 973 K; curve 4, α at 973 K. Fine-grained sample D: curve 5, S_A at 923 K; curve 6, α at 923 K.b. Non-activated sample of magnesite N: curve 1, S_A at 873 K; curve 2, α at 873 K; curve 3, S_A at 923 K; curve 4, α at 923 K; curve 5, S_A at 973 K; curve 6, α at 973 K.

collapse of the pseudomorphous structure of the product. It is known from the literature [1] that an oxidic product with a very large internal surface area is defined as an active, energetically unbalanced and structurally disordered system.

The course of thermal decomposition in the active zone of formation of the porous oxidic product can be formally described with greater probability by the KEKAM kinetic equations (2) and (3) [33, 34]. If the kinetic characteristics of differently activated samples (Table 2) are compared with each other, significant differences in the kinetics of the process giving rise to active MgO can be seen, which indicates the significance of the phenomena involved, i.e. mechanical activation and decrepitation in the thermal decomposition of carbonates.

Table 2
Kinetic parameters of decomposition (KEKAM equations 2 and 3 [33, 34])

Sample	T/K	n	k × 10^{-4}/s^{-1}	α_m
N	793	1.1033	5.575	0.550
Al		1.2354	5.834	0.747
A2		1.3030	5.936	0.758
A3		1.4739	12.010	0.790
N	813	1.1742	7.703	0.652
A1		1.5961	14.313	0.820
A2		1.6715	15.137	0.849
A3		1.6787	17.726	0.859
N	873	1.1246	12.394	0.900
A1		1.9525	45.364	0.901
A2		2.1679	58.970	0.963
A3		2.2074	63.308	0.965
D		1.3350	8.540	0.773
N	923	1.0651	32.731	0.959
Al		2.3214	102.020	0.918
A2		2.4024	117.246	0.926
A3		2.4997	123.375	0.970
D		1.4814	23.520	0.779
N	973	1.0980	42.430	0.975
A1		2.0895	114.030	0.985
A2		2.4141	155.070	0.968
A3		2.4622	164.610	0.990
D		1.7373	77.710	0.847

The exponential factor found for the non-activated sample varied about the limit of 1.1 and did not significantly change with increasing temperature. For the mechanically activated samples, this factor changed with temperature and activity of the carbonate reactant and reached values differing by one decimal order from the values found for the non-activated sample. For the fine-grained sample D, in which the effect of decrepitation ($\epsilon_D \approx 40\%$) was more important than in sample N ($\epsilon_D \approx 4\%$), the exponential factor varied in the range 1.33–1.74.

Comparing the values of the apparent rate constant (Table 2), it is seen that this constant increases with the activity (N → A3) and with the temperature of thermal decomposition. Fig. 2a shows the changes in the apparent rate constant of the thermal decomposition reaction of magnesite with changes in S_A and x_A during grinding. It is evident that the rate of the thermal decomposition reaction is changed with both variables.

The determining influence of S_A and x_A may be expressed by a hypothetical surface-structural factor in the form $S_A \cdot x_A$ of the values of the products during grinding (see Fig. 2b), representing the amount of the specific surface that was amorphized in the process of grinding. It is evident from this figure that the increase in the rate constant is

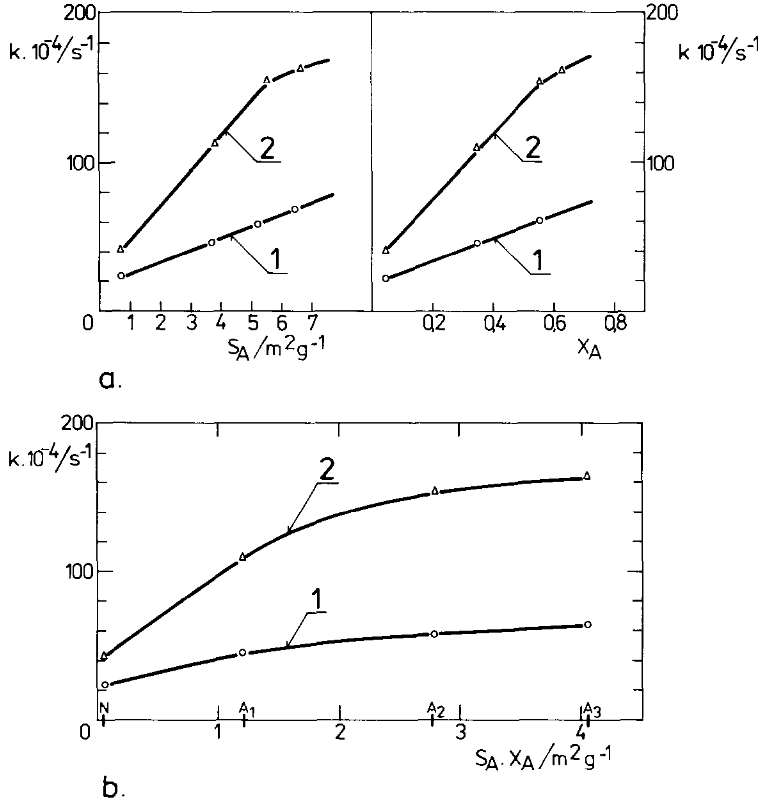

Fig. 2. Apparent rate constant k versus specific surface area S_A (a) and amorphous phase content x_A (a), and hypothetical surface-structural factor $S_A \cdot x_A$ (b) for mechanically activated magnesite at various temperatures of isothermal decomposition: curve 1, 873 K; curve 2, 973 K.

most apparent in the region of intensive disintegration (compare S_G and d in samples N, A1 and A2, respectively, in Table 3). In A3, the sample with the most apparent surface-structural changes, stagnation of the rate constant of the process was observed. This influence was more important at the higher temperature of thermal decomposi-

Table 3
Surface and structural parameters

Sample	N	A1	A2	A3	D
$S_A/\mathrm{m^2\,g^{-1}}$	0.63	3.58	5.10	6.49	0.049
$S_G/\mathrm{m^2\,g^{-1}}$	0.057	0.430	0.440	0.606	0.0326
X_A	0.04	0.34	0.55	0.62	0
$d/\mu\mathrm{m}$	77.09	15.93	7.83	6.45	443.47

S_A is the specific surface area, S_G is the "granulometric" specific surface area, X_A is the X-ray of the amorphous phase content, and d is the average grain dimension for the investigated magnesite samples.

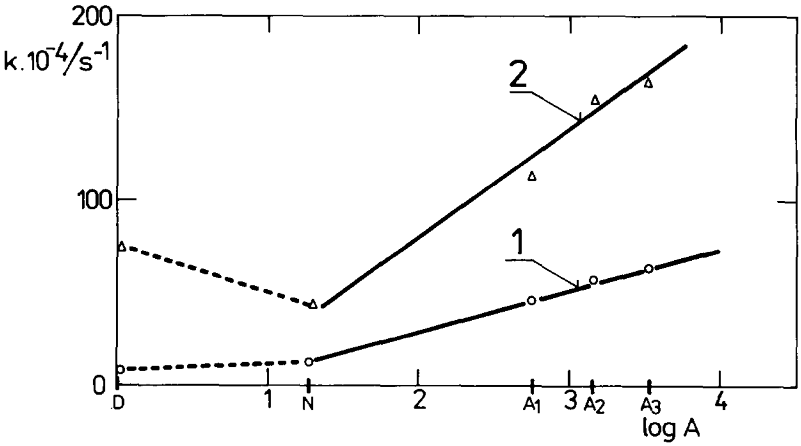

Fig. 3. Apparent rate constant k versus log of the specific grinding energy, log A for mechanically activated magnesite at various temperatures of isothermal decomposition: curve 1, 873 K; curve 2, 973 K.

tion, $T = 973$ K. The influence of structural defects on the process of thermal decomposition was less important at higher temperatures, because these were annealed out.

Fig. 3 shows the dependence of the apparent rate constant on the specific grinding energy introduced into the system in the process of mechanical activation. The results obtained confirm a favourable influence of the stimulation of the process of thermal decomposition by means of mechanical activation. This figure presents an approximation (dashed line) to the values of a fine-grained decrepitating sample D. In this sample, the increase in the rate constant was more important (in comparison with sample N) at a temperature of 973 K, when the effect of decrepitation with secondary fragmentation was largest. It is seen in Fig. 4 that the relative frequency of occurrence of the newly formed granularity classes, namely, 100–71, 71–40, and 40–0 μm, for this sample is maximum at a temperature of decomposition of 973 K [5].

4. Conclusions

Results of the kinetic study of the formation of active MgO during the thermal decomposition of magnesite have confirmed the importance of specifying the stimulation factors of this process, i.e. mechanical activation and decrepitation.

Mechanical preactivation has an important influence on the process of formation of active MgO with favourable surface-structural properties ($S_A \approx 100\,\mathrm{m}^2\,\mathrm{g}^{-1}$) during the thermal decomposition of magnesite. The effect of decrepitation with secondary fragmentation of the reactant takes place at temperatures above 923 K.

The process of forming active MgO taking place in the active zone of the thermal decomposition of $MgCO_3$ was described by the KEKAM equations (2) and (3) with a changing exponential factor [33, 34]. The method used enables us to specify only the trend of stimulation of the kinetics of formation of active MgO. Both the apparent rate

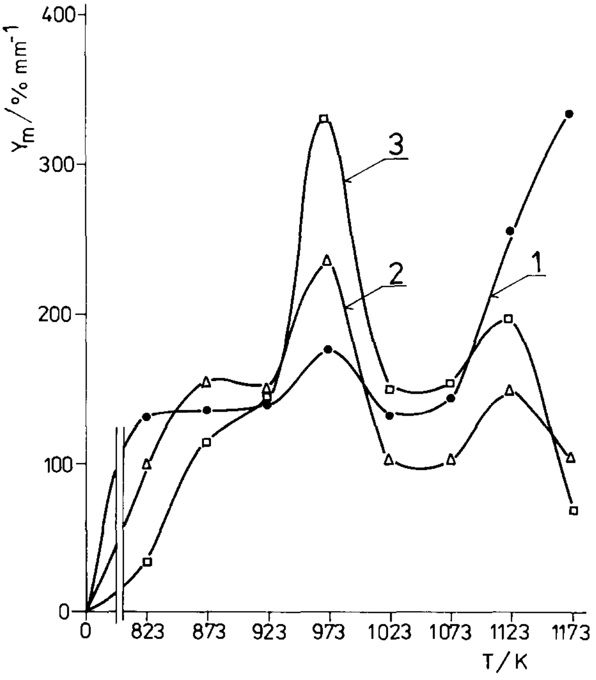

Fig. 4. The relative frequency of occurrence Y_m of the new granularity classes formed by thermal decomposition versus the temperature of the isothermal decomposition T of magnesite sample D. Curves (granularity classes): 1, 0.1–0.071 mm; 2, 0.071–0.04 mm; 3, 0.040–0.0 mm.

constant and the exponential factor of the process of thermal decomposition increased with activation in the grinding process. In the case of minerals decrepitating at thermal decomposition, in addition to secondary fragmentation a number of other factors may have influences that have not yet been unambiguously specified. Such an investigation will be the subject of future work.

Acknowledgements

This work was supported, in part, by the Slovak Grant Agency for science (Grant Nos. 117 and 1368).

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