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Determination of the mechanosynthesis conditions of the Mg – MgO reaction region

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ABSTRACT

This study deals with the prediction, by a mathematical model, and the corresponding experimental confirmation of the mechanochemical synthesis conditions of MgO. The ball milling process is a easy to implement in industry process but that involves several parameters which make it very complex to identify the optimum operating conditions. It was established that the reaction zone of MgO is between accumulative energies of 41 to 64 MJ/mol regardless of the grinding material or the conditions used. Above this region only MgO is obtained. It is necessary to have energies between 24 and 48 Wh/g and to have energies of impact greater than 0.025 J/hit to trigger the mechanochemical synthesis of MgO.

KEYWORDS

Mechanosynthesis conditions;
High energy ball milling;
Magnesium;
MgO;
Accumulated energy.

INTRODUCTION

The use of porous oxides has recently attracted great interest due to their potential technological applications in the chemical and electronics industries. This interest in nanoparticulate oxides is not only due to its high surface area, but also to the high concentration of defects on its surface's[1]. One of the most used oxides in industry is magnesium oxide (MgO) due to its physical and chemical properties. MgO has been used as a refractory material, catalyst, gas sensors, carriers for controlled drug delivery, hydrogen storage material, optically transparent ceramic window, or as a superconductor; among other applications[2-10].

Several methods have been used to produce MgO, but the particle size and the microstructure obtained depends of the method used. For instance, there are a variety of synthesis methods to produce nanocrystalline particles of MgO like: combustion synthesis, sol-gel, hydrothermal, surfactant, spray pyrolysis, laser vapor-

izing or mechanochemical synthesis[11-16]. However, mechanochemical synthesis is not only a way of producing nanocrystalline materials with a high concentration of defects, but also it is a simple, cheap and easy to implement at industrial scales synthesis method.

The mechanochemical synthesis is performed in high energy ball mills where the continuous mixing of reactants, the high structure disorder and high vacancy concentration generated by the mechanical process allows the gradual progress of solid state reactions[17-20]. The mechanochemical processes start with an activation period during which the particle size in the mixture is reduced and the formation of defects is initiated. After this period, the reaction occurs if the accumulative energy supplied by the collisions overcome the activation energy of the system; but if this energy is not achieved then only a continuous amorphizations occurs. Therefore, the study of reactive milling processes is of fundamental importance, as they can provide valuable information about the energy supplied by the devices during mechanical milling operations and it can be established the operating conditions during the reaction[21]. However, the main difficulties in establishing the operating conditions during mechanochemical synthesis is the large number of variables involved in the process such as the density of the grinding material, the number and the size of the balls, the grinding speed, the grinding time, the balls/powder weight ratio, the atmosphere used, etc. In order to simplify the system and to study the effects of different components in terms of accumulative energy several mathematical models have been implemented. However, almost nothing is known about operation conditions during the mechanochemical synthesis of MgO. Therefore, this study is focused on the microstructural evolution of Mg and $Mg(OH)_2$ induced by high-energy ball milling and on the prediction of the mechanochemical synthesis conditions of MgO using a mathematical model. This study will serve as a reference for further studies on the microstructural evolution and mechanochemical synthesis of MgO.

MATHEMATICAL MODEL

The mechanical milling process in a high energy ball mill has many variables, for example: the density of the grinding material, the number and the size of the balls, the grinding speed, the grinding time, the balls/powder weight ratio, the atmosphere used, etc. Therefore, high energy ball milling optimization required a large number of experiments.

Many mathematical models have been reported to describe the high energy ball milling process. Schwarz & Koch[22] and Davis et al.[23] propose a model to evaluate the temperature during balls collision. Maurice & Courtney[24] proposed a model to evaluate the impact time, temperature increment and powder strain, between other operation parameters. Magini & Iasonna[25] proposed a model to quantify the energy transferred per impact and per unit of mass in a planetary mill assuming that collision is the dominant energy transfer event. They assume that the energy transferred is related with the milling operating conditions. A similar model was proposed by Abdellaoui & Gaffet[26]; their model calculates the energy transferred through kinematic equations considering the speed and the acceleration of the balls. Also this model calculated the balls impact frequency and the injected shock power.

A relative simpler model was reported by Burgio et al.[27]; they propose a kinematic equation to describe the speed and acceleration of a ball in a planetary ball-mill vial. They propose a theoretical-empirical approach to evaluate the energy transfer from the mill to the system constituted by the sample, the balls and the vial. Also they reported that the end products strongly depend on the operative milling conditions and they reported a clear correlation between the operative milling conditions with the input energy. The model considers mill and vial geometry parameters as rotatory disk, vial and ball diameter, height and diameter ratio of the vial, and diameters ratio between the main disk and the vial, between others.

There are four assumptions in the model. i) The movement of one ball in the vial is static with the peripheral point (without rolling or sliding on the inner wall) until it is launched at a given moment against the opposite wall. Then, after a short succession of hits with the inner wall, the ball becomes static again with the wall itself and it is newly accelerated by the vial for the next launch. ii) Energy is only released by collisions between balls and the wall of the vial. iii) The energy is transferred from the balls to the sample trapped during collisions, which is obviously only a fraction of the total

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energy released. iv) The energy transferred is correlated to the degree of vial filling.

The energy transferred is calculated with the total energy released by the balls during the collision. This energy is given by the kinetic energy of the balls during the launch and the energy after the impact. The energy released generates deformation of the sample and instantaneous rise of temperature of: the ball, the surrounding region of the hit wall point, and the powder trapped between the ball and the wall. The energy transferred for one ball in one impact (ΔE_b) is calculated as a function of the ball and the vial density (ρ_b); the diameter of the ball (d_b) and the vial (D_v); the distance between the center of the main disk and the center of the vial (R_d); and the speed of the vial (W_v) and the main disk (W_d). This energy is calculated with:

$$\Delta E_b = \frac{1}{2}\left(\rho_b \frac{\pi d_b^3}{6}\right) W_d^2 \left[\left(\frac{W_v}{W_d}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2 \left(1 - 2\frac{W_v}{W_d}\right) - R_d \left(\frac{W_v}{W_d}\right)\left(\frac{D_v - d_b}{2}\right) - \left(\frac{W_v}{W_d}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2\right]$$

The energy transferred for one ball in one impact (ΔE_b) depends of the free space into the vial; therefore, it is used a factor (ϕ_b) to describe the degree of filling. When the vial is completely filled with balls, no movement is possible and ϕ_b=0; on the opposite, for one or few balls ϕ_b=1. Considering this factor, the corrected equation to calculate the energy transferred is:

$$\Delta E_b^* = \phi_b \Delta E_b$$

The total energy transferred from the mill to the system during collisions is the energy cumulated during the several impacts to the sample. Therefore, in order to calculate de total energy it is necessary to calculate the frequency of impact (ν_t):

$$\nu_t = N_b K (W_d - W_v)$$

N_b is the number of balls used and K is a factor related to the time necessary to dissipate the energy ΔE_b^*. K depends of the main disk and the ball geometry. Thus, the accumulated energy transferred can be calculated with the next equation, where t is the milling time and m_p is the powder mass.

$$E_{cum} = \frac{\Delta E_b^* \nu_t t}{m_p}$$

In the present study, the model proposed for Burgio et al.[27] was used to predict the operating conditions of a planetary ball mill pulverisette 7 premium line (Fritsch) for the mechanochemical synthesis of MgO. The parameters of the mill are: R_d = 6.985 cm; D_v = 4.62 cm; vial height H_v = 4.62 cm; W_v/W_d ratio = -2; N_b= 15; D_v =1 cm and K=1.5. Using these parameters and considering the vial speed, the material density, the milling time and the powder mass as variables the accumulated energy can be calculated with:

$$E_{cum} = 1322.821 \frac{W_d^3 \rho_b t}{m_p}$$

Using this equation, the cumulated energy during the mechanochemical synthesis of MgO was calculated. With this energy and the mathematical model, a new set of milling parameters were proposed and they were tested experimentally. Also an energy map of accumulative energy at different milling conditions was constructed.

EXPERIMENTAL CONDITIONS

In order to obtain the operating parameters of the high energy ball milling for the mechanochemical synthesis of MgO several millings were done. A mixture of magnesium (Mg) and magnesium hydroxide ($Mg(OH)_2$) was used as starting material. The high-energy ball milling treatment was carried out in air (in hermetically sealed vials) in a planetary ball mill (pulverisette 7 premium line, Fritsch). Vials (80 ml) and balls (15 of 1 cm (d_b)) of tungstene grinding materials were used. Different rotation rate and milling time were used, TABLE 1. The temperature during milling was not measured, but the vials could be touched directly after milling.

X-ray powder diffraction (XRPD) patterns were collected in air and at ambient temperature in a Bruker D-8 Advance diffractometer with the Bragg-Brentano θ-θ geometry and Cu K_α radiation. The 2θ-range explored was 10–80° with 0.05° step size, 10s counting time, in a continuous mode and spinning of 15 rpm.

TABLE 1: Milling conditions

Milling time (min)	Disk speed (rpm)	Density of milling materials (g/cm^3)
5, 10, 20, 40, 80, 160, 320, 640	200, 400, 600	14.7

RESULTS AND DISCUSSION

A typical powder diffraction pattern obtained from the starting material before any mechanical milling is shown in Figure 1. This powder diffraction pattern can be completely indexed by assigning peaks to either Mg or $Mg(OH)_2$.

The structural evolution of the initial powder mixture at different milling conditions and as a function of milling time can be followed by the X-ray diffraction patterns in Figure 2. It can be seen from Figure 2 that using silicon nitride as a grinding material does not have a noticeable effect on the structure of the starting material even after 640 min of grinding. However, changing the grinding material to tempered steel, it can be detected the amorphization of $Mg(OH)_2$ after 320 min and 400 rpm. The reaction and formation of MgO is observed at 640 min of milling. The same reaction is observed at 180 min of milling using tungsten carbide as a milling material. From this figure it is clear that in order get the mechanochemical synthesis of MgO certain accumulative energy must be achieved. Therefore, it is clear the complexity of the milling process and the difficulty to obtain the operation conditions experimentally. Thus the use of the mathematical model and the calculation of the accumulative energy (E_{cum}) become a powerful tool.

To get an idea of the values of accumulative energy (E_{cum}) involved during the high energy ball milling of the mixture of Mg and $Mg(OH)_2$ in TABLE 2 are shown some values using tungsten carbide (WC) as a milling material.

From TABLE 2 it can be seen that similar cumulated energies can be obtained using different milling parameters. For example, the formation of MgO was observed at 600 rpm after 180 min of milling (Figure 2), which correspond to an accumulative energy of around 42 MJ/mol (TABLE 2). Thus, to achieve the same amount of accumulative energy and get the formation of MgO at 400 rpm it is necessary to mill the mixture during 640 min (TABLE 2). In Figure 3 is shown a complete energy map of accumulative energy considering different speeds and different milling materials.

An estimate of the energy supplied to the system is given in Figure 3. This accumulative energy can be used to predict the optimum operating conditions during high energy ball milling operation.

Using the calculated energies and the experimental phase analysis, it was possible to identify the operating conditions of the mechanochemical synthesis of MgO, Figure 4. According to these results, at 200 rpm it is not possible to obtain MgO because the accumulative

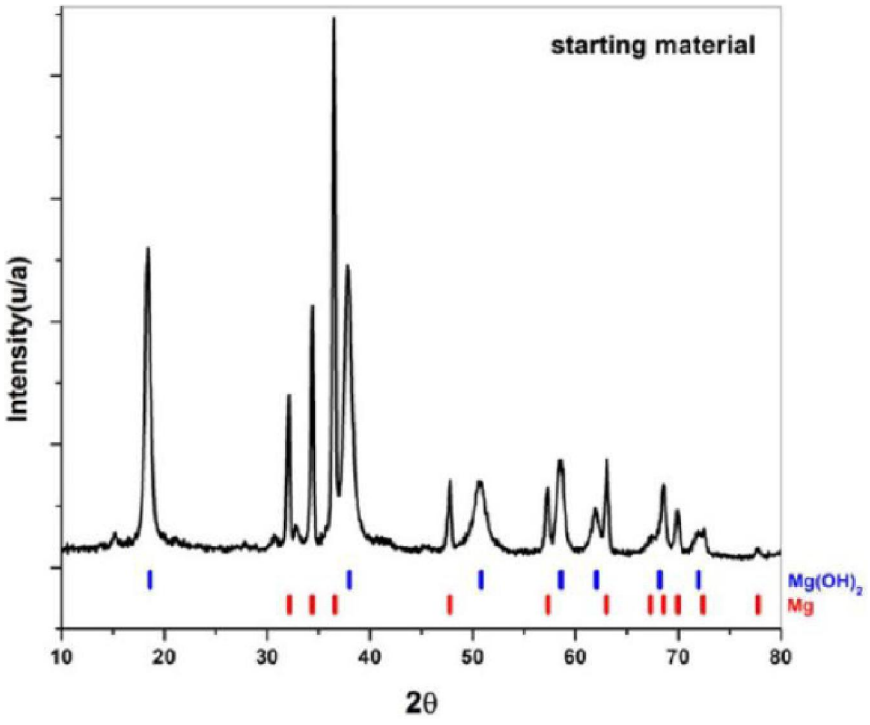

Figure 1: Powder diffraction pattern of the starting material before any mechanical milling.

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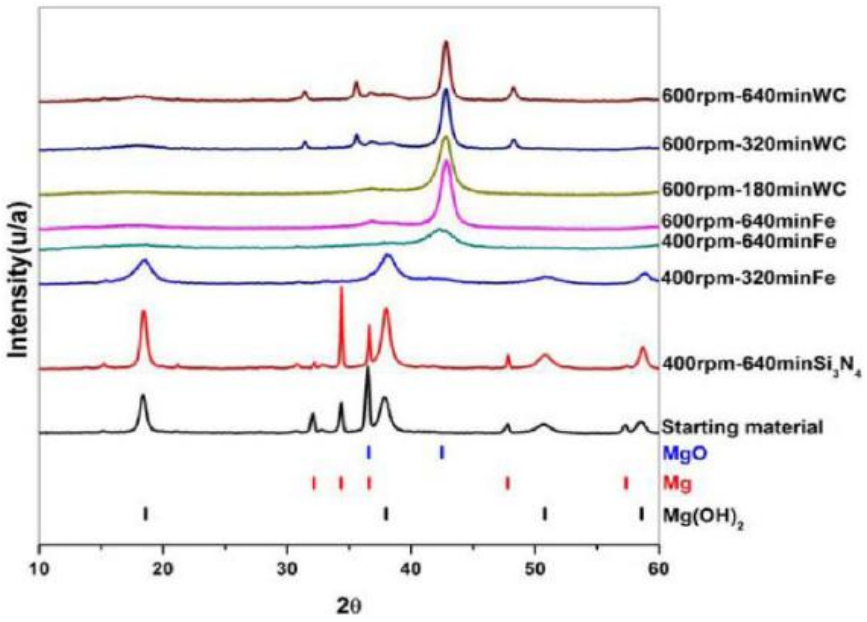

Figure 2 : X-ray diffraction patterns showing the effect of different milling conditions in the structural evolution of starting material

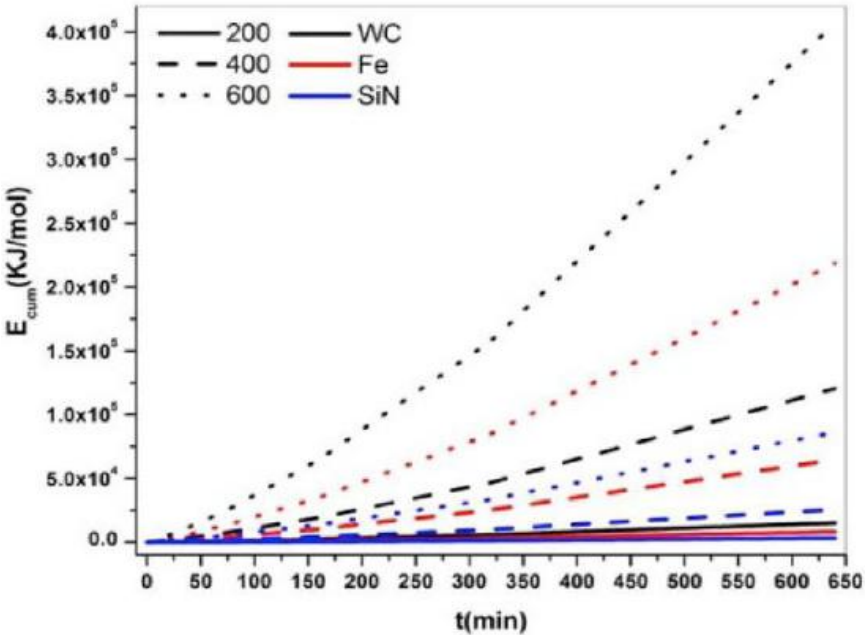

Figure 3: Energy map of accumulative energy at different milling conditions using Burgio *et al*. model[27]

energy does not overpass the activation energy that according to our results is of around 40 MJ/mol. At 400 rpm the mechanochemical synthesis of MgO is achieved only using Fe and WC as milling materials; while at 600 rpm the reaction is observed in all the cases.

Using the energy maps of Figure 4, the experimental results showed in Figure 2 can be explained completely. For example, using Fe as a reference, at 400 rpm and 320 min of milling no MgO was observed (E_{cum} = 30 MJ/mol), while at 640 min of milling the reaction

TABLE 2 : Accumulated energy using WC as a milling material

Main disk speed (rpm)	Milling time (min)	Accumulated energy (KJ/mol)
400	320	22097.23
400	640	44194.47
600	180	41950.23
600	320	74578.18
600	640	149156.36

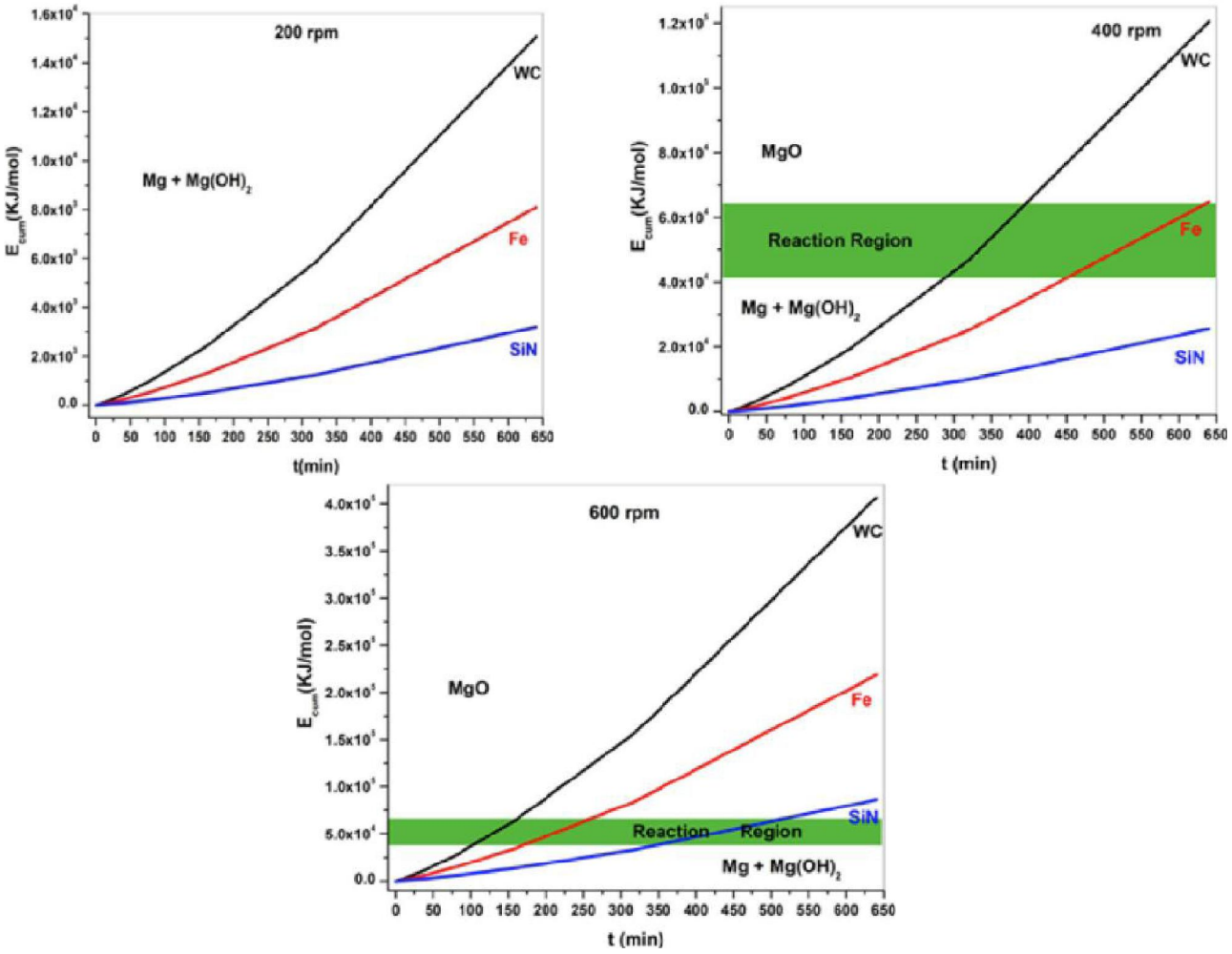

Figure 4: Energy maps of accumulative energy obtained using Burgio et al. model[27] showing the mechanochemical synthesis conditions of MgO

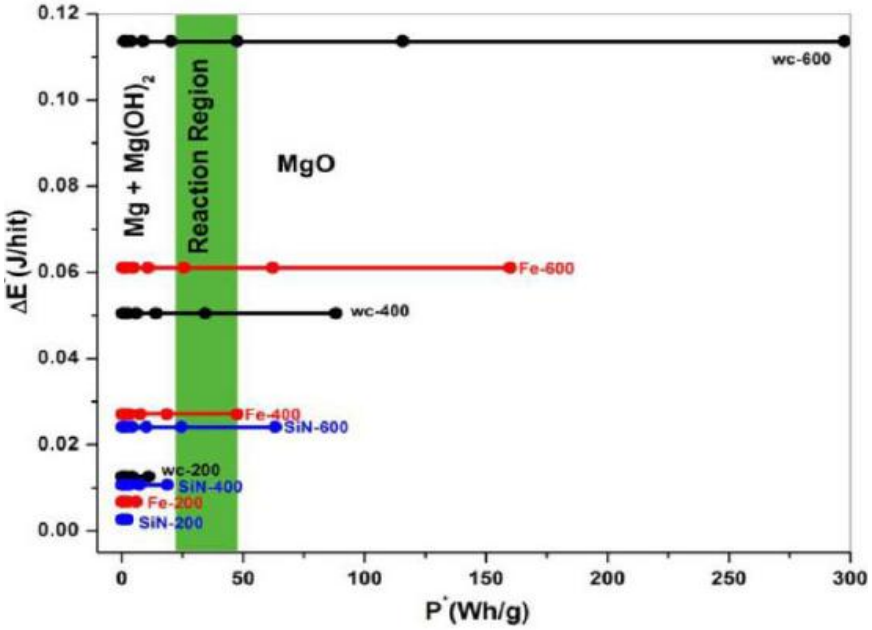

Figure 5: Correlation between the ball - impact energy (ΔE*) with the normalized weight-accumulative kinetic energy (P*)

occurs (E_{cum} = 59 MJ/mol). The intensity of the main reflection of MgO (2θ = 42.5°, Figure 2) is more intense in the sample milled at Fe-600rpm-640min than at Fe-400rpm-640min. That is because the excess of energy at 600 rpm (E_{cum} = 80 MJ/mol) promotes recrystallization. Several milling experiments were done to validate the theoretical results with success.

With this study it can be established that the reaction zone of MgO is between accumulative energies of 41 to 64 MJ/mol regardless of the grinding material or the conditions used. Below this region no reaction occurs; within this region a mixture of Mg + $Mg(OH)_2$ + MgO is found; and above the region only MgO is obtained.

The milling energy map shown in Figure 5 was constructed by correlating the balls impact energy with the normalized accumulated kinetic energy. Using this plot it is identified that the critical or minimum energy to trigger the mechanochemical synthesis of MgO is between 24 and 48 Wh/g and it is necessary to have an energy of impact greater than 0.025 J/hit.

CONCLUSIONS

Using a mathematical model was possible to predict the mechanochemical synthesis conditions to obtain MgO. It was established that the reaction zone of MgO is between accumulative energies of 41 to 64 MJ/mol regardless of the grinding material or the conditions used. Above this region only MgO is obtained. The higher the accumulative energy the better the crystallinity of the product. It is necessary to have energies between 24 and 48 Wh/g and to have energies of impact greater than 0.025 J/hit to trigger the mechanochemical synthesis of MgO.

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