

Received:
10 October 2018
Revised:
9 January 2019
Accepted:
11 February 2019

Cite as: C. Real,
F. J. Gotor. Effects of the
speed ratio on the efficiency of
planetary mills.
Heliyon 5 (2019) e01227.
doi: [10.1016/j.heliyon.2019.e01227](https://doi.org/10.1016/j.heliyon.2019.e01227)



Effects of the speed ratio on the efficiency of planetary mills

C. Real, F. J. Gotor*

Instituto de Ciencia de Materiales de Sevilla (US-CSIC), Américo Vespucio 49, 41092 Sevilla, Spain

* Corresponding author.

E-mail address: fgotor@cica.es (F.J. Gotor).

Abstract

The ignition time (t_{ig}) of the mechanically induced self-sustaining reaction (MSR) process involving the formation of TiB_2 from $Ti/2B$ elemental mixtures was used to study the influence of the ratio ($k = \omega_v/\omega_d$) between the rotational speed of the supporting disc (ω_d) and vials (ω_v) on the milling efficiency of a Pulverisette 4 planetary mill. The variation of the inverse of the ignition time ($1/t_{ig}$), which is directly related to the milling power provided by the planetary mill, with the process conditions has shown that it is not possible to find a single k value as optimal independently of the experimental conditions used (ω_d and the ball-to-powder ratio, BPR). Moreover, it was observed that the lowest milling efficiency (longer t_{ig} values) was found for $k = 1$, which is the usual value employed in routine laboratory works. The best efficiencies were found for the larger k values (2.5 or 3). At lower ω_d , the shortest t_{ig} was obtained for $k = 2.5$ and at higher ω_d for $k = 3$, independently of BPR.

Keyword: Materials science

1. Introduction

Planetary ball mills provide high energy density due to the superimposed effect of two centrifugal fields produced by the rotation of the supporting disc and the rotation of the vials around its own axis in the opposite direction [1]. During operation, the grinding balls execute motion paths that result in frictional and impact effects. These high-energy ball mills are suitable to induce mechanochemical reactions and develop

a wide range of new technological materials from powder mixtures [2]. Due to their scientific relevance, an increasing number of works are trying to model their operational mechanism, i.e., how the mechanical energy is transferred to powders and its quantification and dependence on the operating parameters. This is essential to propose the optimal milling conditions and compare the results obtained from different experimental devices.

Early models were based on kinematic equations describing the trajectory and velocity of balls inside the vial. For these models, the impacts between the balls and the inner walls of vials were the primary event in the energy transfer [3, 4, 5, 6]. However, in-situ observations have not shown signs of balls leaving the vial surface to make clear single collisions; the actual situation is much more complex with multiple types of ball-ball and ball-vial interactions [7, 8, 9]. Nowadays, most of the studies use numerical simulations of the collective three-dimensional ball motion based on the Discrete Element Model (DEM) [10, 11, 12], since it is possible to quantify in a more precise way the effects of successive small collisions between balls, the lack of single ball-wall collisions and the slipping and rolling of balls, situations that occur in real milling conditions [11, 13].

In all these studies, the key role played by the rotational speed of the planetary mill and the number and nature of balls (and indirectly the ball-to-powder ratio, BPR) have always been highlighted since these parameters determine greatly the rate of the energy transfer to the powder material. Nevertheless, the influence of the ratio (k) between the rotational speed of the supporting disc (ω_d) and vials (ω_v), ($k = \omega_v/\omega_d$), on the milling efficiency has not been frequently addressed [5, 6, 7, 8, 9, 10, 11, 14, 15, 16, 17]. The main reason is that most commercial planetary mills, especially at a laboratory scale, are characterised by a fixed transmission ratio that sets this k parameter to a value of approximately 1. However, it has been shown that the motion path of balls is greatly influenced by k and, therefore, this parameter also has a significant influence on the energy transferred to the powders.

Based on kinematic models, Le Brun et al [7] determined three different types of ball trajectories in function of k that can be defined as cascading, cataracting and rolling. The critical k values defining the cataracting domain, the optimum regime, were approximately between 1.3 and 3.1. Chattopadhyay et al [5] calculated that the effectiveness of impacts was enhanced for $k \geq 1$ and that the total impact power increased with increasing k , but not any optimal value was proposed. Kakuk et al [6] determined that the greatest impact energy is achieved at approximately $k = 2.5$, but the greatest milling power (that includes also the impact frequency) is reached around $k = 2.96$.

Based on DEM simulation, Mio et al [10] also distinguished between the three abovementioned ball movement regimes, but with really close transitional k values. They determined that the specific impact energy of balls increases with increasing k up to a critical value, which depends on the size of the planetary mill, from which the

energy began to fall. Zhang et al [14] determined also by DEM that the highest energy utilisation in a horizontal planetary mill was acquired for $k = 1.5$. However, Rosenkranz et al [8] showed by both DEM and in situ-observations that k had no considerable influence on the ball motion pattern in the range $1 < k < 3$. A cascading motion pattern was always observed in the absence of mill feed and with a typical ball filling ratio of 0.3. Nevertheless, by increasing the ball filling ratio or the friction conditions, due to the presence of the mill feed, the dynamics of balls changed to a cataracting regime.

Finally, by in-situ observations and using an image processing program, Rogachev et al [9] observed different types of ball movement depending on k . At $k < 1.7$, the rolling of the balls primarily took place and some free fly trajectories were detected. An important proportion of stagnant balls (making small oscillations around a steady position) were also observed. At $k = 1.8$ – 1.9 , the free fly type of ball motion became dominant and at $k \geq 2.0$, a circular motion of balls formed a rotating layer on the wall of the vial.

Some other works have also tried to study the effects of k on the milling efficiency from experimental observations. For example, Le Brun et al [7] observed based on microhardness values that a higher milling efficiency was achieved during milling Cu powders for a k value of 1. However, Schilz et al [15] found during the formation of the Si-Ge solid solution and the Mg_2Si intermetallic that the shortest alloying time (based on X-ray diffraction (XRD) results) was observed for $k = 2.5$ and 3, respectively. Ghayour et al [16], using the ignition time (t_{ig}) of the mechanically induced self-sustaining reaction (MSR) process involving Al, B_2O_3 and TiO_2 , determined that the optimum k value was between 1.2 and 1.4 depending on the BPR value. Rogachev et al [9] determined from the increase of the reactivity of highly exothermic mixtures (Ni-Al, Ti-Si and Si-C) that the most efficient milling regime was achieved when $k = 1.5$. Boytsov et al [17], studying the microstructure evolution of Cu powders by XRD, claimed that it is rather difficult to select an optimal value due to a non-linear dependence of the milling parameters with k .

The contradictory results of these experimental studies, which often also contradict the theoretical predictions, can originate from the way of measuring the milling efficiency, which is carried out indirectly from changes in composition, morphology, structure or crystallinity in the powder charge at increasing milling time. Frequently, it is difficult to correlate the sample property analysed with the mechanical energy involved in the process and its dependence on the milling conditions. However, in MSR processes, a direct relationship between $1/t_{\text{ig}}$ and the mechanical dose rate provided by a mill has been established [18], since ignition occurs when the milling device has provided a specific amount of energy (per unit mass) to the reactant mixture. Several studies have already shown that variations of t_{ig} with different milling parameters can be used as a fingerprint of the milling efficiency [18, 19, 20, 21, 22,

23, 24, 25,25,26]. Moreover, t_{ig} is a reproducible parameter that can be measured in real-time during milling by recording the temperature and/or the pressure inside the vial, since both signals show a sudden increase at ignition due to the heat released by the highly exothermic reaction. It has been observed in solid-solid reactions, in which no gaseous reactants or products are involved, that the pressure signal is more sensitive to self-sustaining processes than temperature [27].

In this work, the MSR process involving the formation of TiB_2 from the stoichiometric elemental mixture was selected as a model system to study the influence of k on t_{ig} and, therefore, on the milling efficiency. TiB_2 is a stoichiometric compound with high adiabatic temperature (T_{ad}), which has already been obtained by MSR [28]. The high T_{ad} ensures the occurrence of the MSR process in a wide range of different milling conditions without the interference of competitive side reactions. With this study, we tried to shed some light on the contradictory results found in the literature, both from experimental and theoretical approaches.

2. Experimental

Titanium powder (99% purity, < 325 mesh, Strem Chemicals), boron powder (95–97% purity, amorphous, Fluka) and high-purity argon gas (H_2O and O_2 < 3 ppm, Linde) were used in this work. All milling experiments were conducted under an Ar atmosphere using a Ti/B mixture with an atomic ratio of 1/2, a 60 mL tempered steel vial (inner diameter = 45 mm) and WC-Co ($d = 15$ mm and $m = 26.4$ g) balls. The powder mixtures were ball-milled in a modified Pulverisette 4 (Fritsch) planetary mill able to detect t_{ig} in MSR processes by measuring the pressure inside the vial during milling. This was possible by means of a vial with a special lid that was continuously connected to the gas cylinder at a pressure of 5 bar by a rotating union (model 1005-163-038, Deublin) and a semi-rigid polyamide tube (Legris). During milling, the gas pressure was monitored by a pressure transducer (AKS, Danfoss) connected to a paperless recorder (Ecograph T RSG35, Endress + Hauser). When ignition occurred, the heat released produced a sharp peak in the pressure-time record, from which t_{ig} was accurately determined.

To explore the dependence of t_{ig} on the milling conditions, different milling experiments were carried out by modifying the following parameters: ω_d from 250 to 400 rpm, k from 1 to 3 and BPR from 24 to 46. These values were within the range normally used by the milling practitioners and in the studies mentioned in the introduction section. In this work, the absolute k ratio ($k = -\omega_v/\omega_d$) was employed, i.e., if the supporting disc rotates at 400 rpm and the vial rotates around its own axis at the same speed but in the opposite direction (-400 rpm), the k value is 1. Note that some manufacturers use the relative speed ratio in their technical data. For the example mentioned, the relative ratio would be -2. Moreover, the BPR value was adjusted by changing both the powder charge and/or the number of balls to ensure the correct

filling of the vial. A BPR value of 46 was achieved with 7 WC-Co balls and 4 g of charge, a value of 33 with 5 WC-Co balls and 4 g of charge and, finally, a value of 24 with 5 WC-Co balls and 5.5 g of charge. The conversion of the elemental mixtures into TiB_2 after the MSR process was ascertained by XRD. The XRD patterns were obtained on a X'Pert Pro MPD diffractometer (PANalytical) equipped with a graphite-diffracted beam monochromator and a solid-state detector (X'Cellerator) using $\text{Cu K}\alpha$ radiation over a 2θ -range of 20° to 80° with a step size of 0.05° and a counting time of 300 s/step.

3. Results and discussion

Fig. 1 shows as an example the pressure-time record corresponding to a milling experiment performed using the following experimental conditions: $\omega_d = 250$ rpm, $k = 1.5$ and $\text{BPR} = 24$, from which a t_{ig} value of 110 min and 22 s was determined. As can be seen, the pressure spike at ignition is very intense and the t_{ig} value can be determined accurately. Similar records were always obtained for the different milling experiments performed in this work. Each milling experiment was repeated at least three times and the t_{ig} value obtained was always found within a range of $\pm 5\%$. Fig. 2 presents the XRD pattern of this sample collected a few minutes after ignition that clearly demonstrates the conversion of reactants into TiB_2 during the MSR process. In this same figure, the XRD pattern corresponding to another milling experiment with a significantly shorter t_{ig} value is also shown (experimental conditions: $\omega_d = 350$ rpm, $k = 1$ and $\text{BPR} = 46$). For all milling experiments, the final phase obtained after ignition was always TiB_2 regardless of the experimental conditions used and t_{ig} values found. These results confirmed that the $\text{Ti}/2\text{B}$ system chosen is appropriate to study the influence of milling parameters on the energy supplied by the planetary mill.

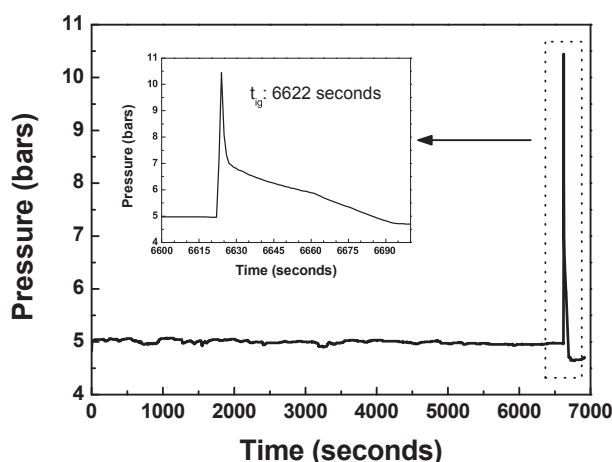


Fig. 1. A plot of the pressure-time record during the MSR process, from which t_{ig} can be properly determined. Milling experimental conditions: $\omega_d = 250$ rpm, $k = 1.5$ and $\text{BPR} = 24$.

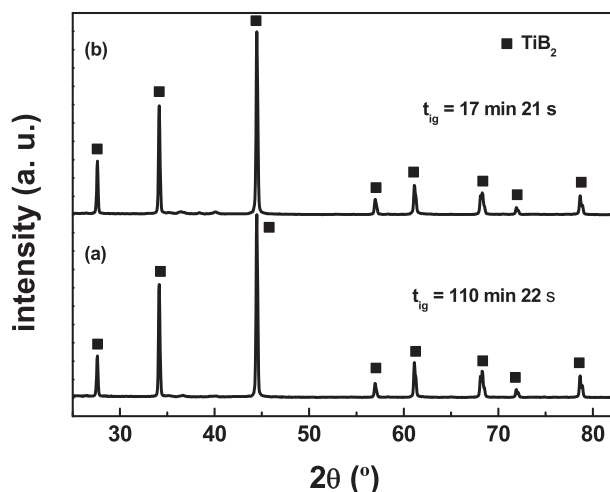


Fig. 2. XRD patterns of products after two MSR processes with significant different t_{ig} values, showing the formation of TiB_2 . Milling experimental conditions: (a) $\omega_d = 250$ rpm, $k = 1.5$ and BPR = 24; (b) $\omega_d = 350$ rpm, $k = 1$ and BPR = 46.

Fig. 3 shows the results of the full set of experiments from which the dependence of t_{ig} on k can be inferred for different ω_d and BPR values. For a given k value, Fig. 3 shows the expected behaviour (frequently observed in the literature) of an increase in the milling efficiency, i.e., reduction of t_{ig} , as ω_d and BPR increase. It is clear that when ω_d is larger, both the frequency and the energy of impacts increase, which produce the shortening of t_{ig} . On the other hand, for the milling experiments with a BPR of 46, seven balls were employed instead of five and, hence, the number of collisions per unit of time was greater, inducing a shorter t_{ig} . In the case of the milling experiments with a BPR of 24, the amount of powder sample was larger (5.5 g instead of 4 g) and, therefore, the energy transferred per gram of powder and unit of time due to collisions and friction was lower, which reduces the activation of the reactant mixture and induces a longer t_{ig} .

Nevertheless, Fig. 3 suggests that the exact evolution of t_{ig} with ω_d and BPR also depends on k . Note that at 400 rpm and independently of the BPR value, t_{ig} was progressively reduced as k increased. The shortest t_{ig} was observed for $k = 3$. However, for the other ω_d values, the same order of reducing t_{ig} with k was not followed and this order was also dependent on BPR. This fact should be related to how the frequency and the energy of impacts depend on ω_d and BPR for the different k values. Besides, the proportion of friction effects associated with the time spent by the balls sliding on the vial wall should be also considered, especially at the lower ω_d values.

Although results in Fig. 3 do not allow finding a single optimal k value independently of the experimental conditions, some clear trends can be extracted from this figure. First, the lowest milling efficiency (longer t_{ig} values) was always found for $k = 1$, which is the usual value employed in routine milling works and also the

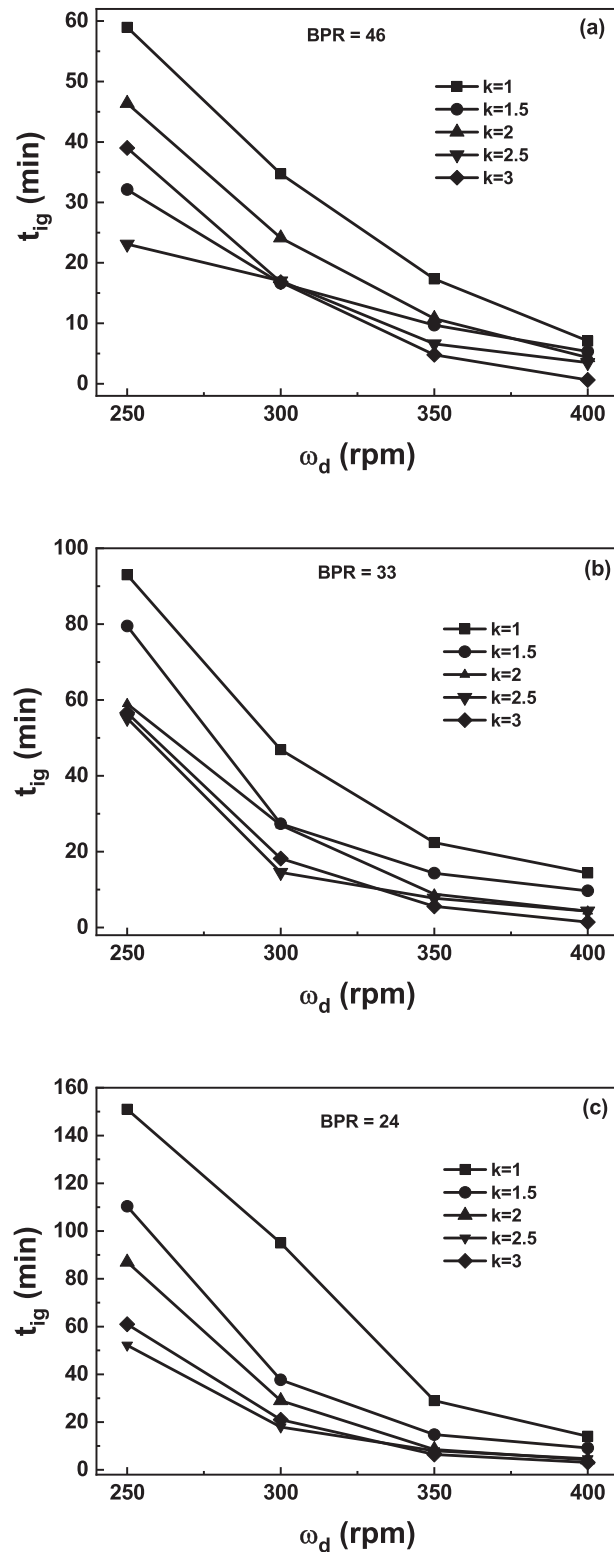


Fig. 3. Dependence of t_{ig} on k for different ω_d and BPR values: (a) BPR = 46, (b) BPR = 33 and (c) BPR = 24.

only available in many commercial planetary mills with a fixed gear ratio between the disc and vial movements. Second, differences in t_{ig} for different k values are reduced as ω_d increases. And third, best efficiencies were found for the larger k values (2.5 or 3). In this sense, at lower ω_d , the shortest t_{ig} was obtained for $k = 2.5$ and at higher ω_d for $k = 3$, independently of BPR.

These results are only in agreement with the predictions of Kakuk et al [6] based on kinematic equations and the experimental observations of Schilz et al [15] based on XRD measurements. Note that Kakuk et al [6] considered in their calculations the characteristic geometrical parameters of a Pulverisette 4 planetary mill, as employed in the present work, and Schilz et al [15] used a Retsch PM400 planetary mill with a similar geometry as the Pulverisette 4 mill. These considerations outline the fact that the optimal k value should be dependent on the size of the planetary mill. In this sense, Schilz [29] determined on the basis of classical mechanics that the impact power exhibits a maximum value for a certain k for every mill geometry, characterised by the ratio between the vial (r) and the revolution (R) radii. He claimed that for a typical planetary mill with r/R ratio between 0.1 and 0.3, the optimal k is between 3.25 and 2.25. For our set of experiments, the r/R ratio was 0.18 and the optimal k value should be approximately 2.5 in agreement with our results. This good accord is observed despite the fact that in their calculations, the balls were considered as single mass point, without any interaction or influence between them. Also no rolling or slip was taken into account that is responsible for the friction effects in real milling experiments and can have more influence as ω_d is reduced. Nevertheless, as observed in Fig. 3, the optimal k value is not only dependent on the planetary mill geometry, but also on the specific milling conditions (ω_d and BPR).

In contrast, our results surprisingly do not agree with any of the few works that exist in the literature dealing with k based on DEM simulations. For example, Zhang et al [14] determined an optimal k value of 1.5. Although Mio et al [10] determined on the basis of DEM simulation that the optimal k value was dependent on the revolution radius of the mill, they estimated for a revolution radius of 200 mm a low optimal k value of 1.8. Note that the Pulverisette 4 mill has a radius of 120 mm and the optimal k value should be even smaller according to their calculations. Moreover, Rosenkranz et al [8] claimed that their results contradicted prior considerations and theoretical calculations that identified k as a key influencing parameter on the grinding ball motion pattern.

As indicated earlier in the introduction section, it has previously been shown that $1/t_{ig}$ and the energy milling power provided by a mill are directly linked [18]. In Fig. 4, $1/t_{ig}$ is plotted as a function of k for the different ω_d and BPR, from which the multi dependence of k , ω_d and BPR on the milling efficiency can be observed. In this figure, it is more clearly visible as the best milling efficiency was obtained for $k = 3$ at the highest ω_d , and it is highly enhanced when BPR is increased. As

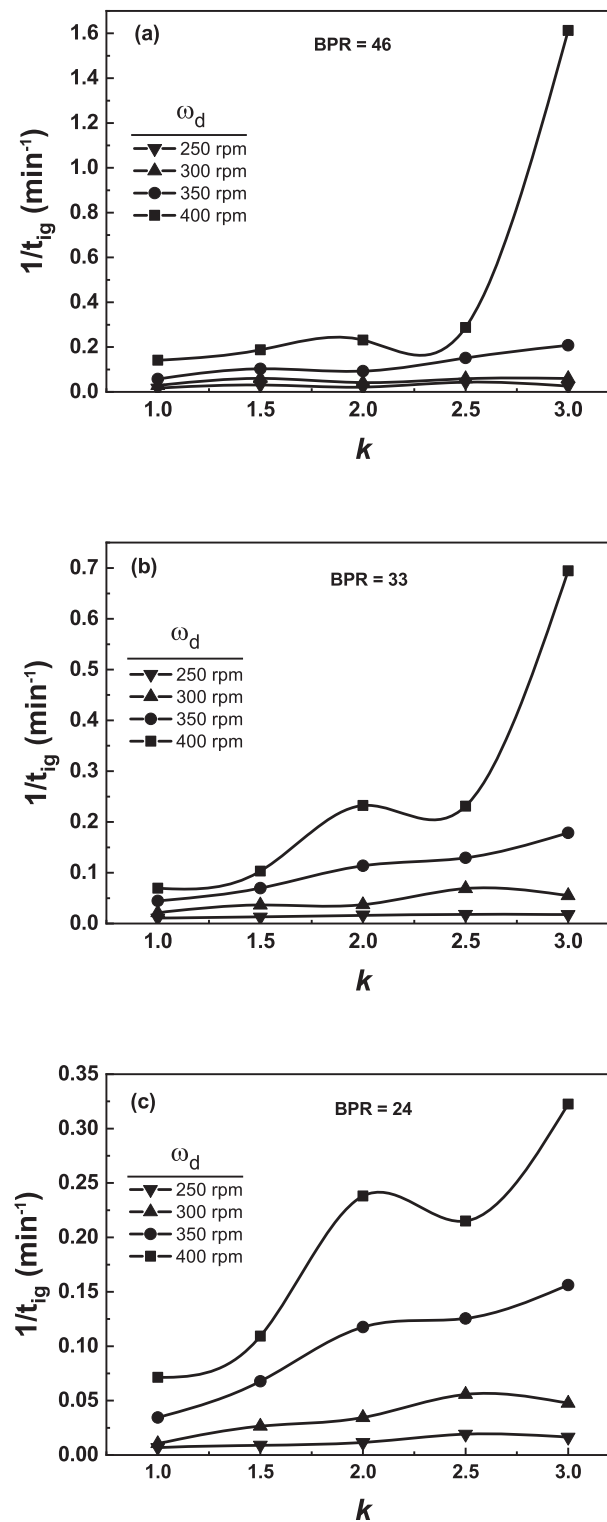


Fig. 4. Dependence of $1/t_{ig}$ on ω_d for different k and BPR values: (a) BPR = 46, (b) BPR = 33 and (c) BPR = 24.

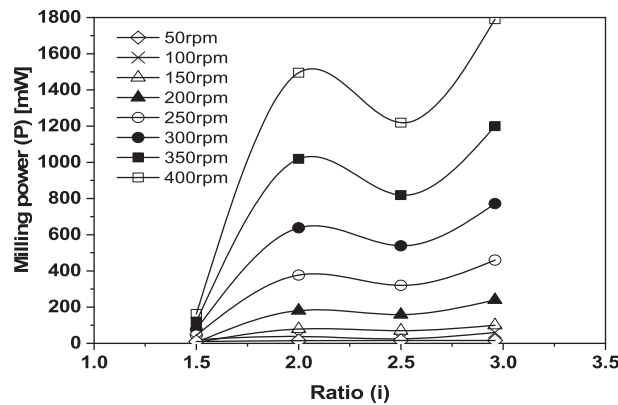


Fig. 5. Changes of the milling power (P) as a function of the ratio ($i \equiv k$) at different ω_d , reprinted from reference [6]. This figure was obtained from kinematic equations using the geometrical parameters of a Pulverisette 4 planetary mill.

ω_d is reduced, differences are less important, but milling efficiency is always better for large k values. The reason for the fall in efficiency at $k = 2.5$ that increases again at $k = 3$ is related to the fact that the milling efficiency is dependent on the product of the impact energy multiplied by the frequency of impacts, and both parameters do not correlate with k in the same way. It has been shown in [6] that at $k = 2.5$ the impact energy (of a single ball) is greater than at $k = 3$, but the impact frequency is lower. Therefore, the higher impact frequency at $k = 3$ induces the best milling efficiency only for high ω_d values. Note that the impact frequency increases with ω_d .

A great resemblance was observed between Fig. 4, especially that with a BPR of 24, and Fig. 5 (taken from reference 6) that corresponds to the calculations by Kakuk et al [6] (based on kinematic equations) for the milling power provided by the Pulverisette 4 mill as a function of k , at different ω_d values. The similarity between both figures confirms the direct relationship between $1/t_{ig}$ and the milling power and, therefore, t_{ig} of MSR processes can be a valuable milling parameter that could be used to validate the models developed to describe the operation of planetary mills.

4. Conclusions

The influence of the ratio (k) between the rotational speed of the supporting disc (ω_d) and vials (ω_v) at different ω_d and BPR on the milling efficiency of a Pulverisette 4 planetary mill was studied. The milling efficiency was determined indirectly by measuring the ignition time (t_{ig}) for the formation of TiB_2 from its elemental mixture via a mechanically induced self-sustaining reaction (MSR); longer t_{ig} values imply lower milling efficiencies. Results showed that the optimal k value is not only dependent on the geometric characteristics of the planetary mill (size of the supporting disc and vials), but also on the specific milling conditions (ω_d and BPR), which can explain the differing optimal values that can be found in the bibliography for this

parameter. For the Pulverisette 4 mill, the lowest milling efficiency was always found for $k = 1$. The best efficiencies were found for the larger k values (2.5 or 3). At lower ω_d , the shortest t_{ig} was obtained for $k = 2.5$ and at higher ω_d for $k = 3$. Surprisingly, a better agreement was found with predictions made on the basis of kinematic equations than on DEM, which in principle must be able to reproduce in a more realistic way the ball trajectories and the forces involved during a milling process.

Declarations

Author contribution statement

Concepcion Real, Francisco J. Gotor: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This work was supported by the Secretaría de Estado de Universidades, Investigación, Desarrollo e Innovación, Spain, under Grant MAT2014-52407-R, financed, in part, by the European Regional Development Fund.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- [1] C.F. Burmeister, A. Kwade, Process engineering with planetary ball mills, *Chem. Soc. Rev.* 42 (2013) 7660–7667.
- [2] P. Balaz, M. Achimovicova, M. Balaz, P. Billik, Z. Cherkezova-Zheleva, J.M. Criado, F. Delogu, E. Dutkova, E. Gaffet, F.J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wieczorek-Ciurowa, Hallmarks of mechanochemistry: from nanoparticles to technology, *Chem. Soc. Rev.* 42 (2013) 7571–7637.
- [3] M. Abdellaoui, E. Gaffet, The physics of mechanical alloying in a planetary ball mill: mathematical treatment, *Acta Metall. Mater.* 43 (1995) 1087–1098.

- [4] M. Magini, A. Iasonna, Energy-transfer in mechanical alloying, *Mater. Trans. JIM* 36 (1995) 123–133.
- [5] P.P. Chattopadhyay, I. Manna, S. Talapatra, S.K. Pabi, A mathematical analysis of milling mechanics in a planetary ball mill, *Mater. Chem. Phys.* 68 (2001) 85–94.
- [6] Gy. Kakuk, I. Zsoldos, Á. Csanády, I. Oldal, Contributions to the modelling of the milling process in a planetary ball mill, *Rev. Adv. Mater. Sci.* 22 (2009) 21–38.
- [7] P. Le Brun, L. Froyen, L. Delaey, The modelling of the mechanical alloying process in a planetary ball mill: comparison between theory and in-situ observations, *Mat. Sci. Eng. A* 161 (1993) 75–82.
- [8] S. Rosenkranz, S. Breitung-Faes, A. Kwade, Experimental investigations and modelling of the ball motion in planetary ball mills, *Powder Technol.* 212 (2011) 224–230.
- [9] A.S. Rogachev, D.O. Moskovskikh, A.A. Nepapushev, T.A. Sviridova, S.G. Vadchenko, S.A. Rogachev, A.S. Mukasyan, Experimental investigation of milling regimes in planetary ball mill and their influence on structure and reactivity of glassless powder, *Powder Technol.* 274 (2015) 44–52.
- [10] H. Mio, J. Kano, F. Saito, K. Kaneko, Effects of rotational direction and rotation-to-revolution speed ratio in planetary ball milling, *Mat. Sci. Eng. A* 332 (2002) 75–80.
- [11] C. Burmeister, L. Titscher, S. Breitung-Faes, A. Kwade, Dry grinding in planetary ball mills: evaluation of a stressing model, *Adv. Powder Technol.* 29 (2018) 191–201.
- [12] H. Ashrafizadeh, M. Ashrafizaadeh, Influence of processing parameters on grinding mechanism in planetary mill by employing discrete element method, *Adv. Powder Technol.* 23 (2012) 708–716.
- [13] X. Jiang, M.A. Trunov, M. Schoenitz, R.N. Dave, E.L. Dreizin, Mechanical alloying and reactive milling in a high energy planetary mill, *J. Alloy. Comp.* 478 (2009) 246–251.
- [14] J. Zhang, Y. Bai, H. Dong, Q. Wu, X. Ye, Influence of ball size distribution on grinding effect in horizontal planetary ball mill, *Adv. Powder Technol.* 25 (2014) 983–990.
- [15] J. Schilz, M. Riffel, K. Pixius, H.J. Meyer, Synthesis of thermoelectric materials by mechanical alloying in planetary ball mills, *Powder Technol.* 105 (1999) 149–154.

- [16] H. Ghayour, M. Abdellahi, M. Bahmanpour, Optimization of the high energy ball-milling: modelling and parametric study, *Powder Technol.* 291 (2016) 7–13.
- [17] O. Boytsov, A.I. Ustinov, E. Gaffet, F. Bernard, Correlation between milling parameters and microstructure characteristics of nanocrystalline copper powder prepared via a high energy planetary ball mill, *J. Alloy. Comp.* 432 (2007) 103–110.
- [18] F.J. Gotor, M. Achimovicova, C. Real, P. Balaz, Influence of the milling parameters on the mechanical work intensity in planetary mills, *Powder Technol.* 233 (2013) 1–7.
- [19] G.B. Schaffer, J.S. Forrester, The influence of collision energy and strain accumulation on the kinetics of mechanical alloying, *J. Mater. Sci.* 32 (1997) 3157–3162.
- [20] A. Bakhshai, V. Soika, M.A. Susol, L. Takacs, Mechanochemical reactions in the Sn-Zn-S system: further studies, *J. Solid State Chem.* 153 (2000) 371–380.
- [21] C. Deidda, F. Delogu, F. Maglia, U. Anselmi-Tamburini, G. Cocco, Mechanical processing and self-sustaining high-temperature synthesis of TiC powders, *Mater. Sci. Eng. A* 375 (2004) 800–803.
- [22] L. Takacs, V. Sepelak, Quantitative comparison of the efficiency of mechanochemical reactors, *J. Mater. Sci.* 39 (2004) 5487–5489.
- [23] T.S. Ward, W. Chen, M. Schoenitz, R.N. Dave, E.L. Dreizin, A study of mechanical alloying processes using reactive milling and discrete element modeling, *Acta Mater.* 53 (2005) 2909–2918.
- [24] J. Trapp, B. Kieback, Solid-state reactions during high-energy milling of mixed powders, *Acta Mater.* 61 (2013) 310–320.
- [25] E. Chicardi, F.J. Gotor, M.D. Alcalá, J.M. Córdoba, Influence of milling parameters on the solid-gas synthesis of $\text{TiC}_x\text{N}_{1-x}$ by mechanically induced self-sustaining reaction, *Powder Technol.* 319 (2017) 12–18.
- [26] M. Balaz, A. Zorkovska, J.S. Blazquez, N. Daneu, P. Balaz, Mechanochemistry of copper sulphides: phase interchanges during milling, *J. Mater. Sci.* 52 (2017) 11947–11961.
- [27] J.F. Li, T. Matsuki, R. Watanabe, Combustion reaction during mechanical alloying synthesis of Ti_3SiC_2 ceramics from 3Ti/Si/2C powder mixture, *J. Am. Ceram. Soc.* 88 (2005) 1318–1320.

- [28] D.D. Radev, D. Klissurski, Mechanochemical synthesis and SHS of diborides of titanium and zirconium, *J. Mater. Synth. Process.* 9 (2001) 131–136.
- [29] J. Schilz, Internal kinematics of tumbler and planetary ball mills: a mathematical model for the parameter setting, *Mater. Trans. JIM* 39 (1998) 1152–1157.