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Mechanochemical Synthesis in the Nutating Centrifugal Ball Mill

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Abstract

Mechanochemical synthesis of TiO₂ by using the simple laboratory scale nutating centrifugal ball mill was demonstrated for the first time. In our prototype, the nutation angle in the range of 0–20 deg, besides the speed of rotation of central axes up to 1400 rpm, can be adjusted independently. In order to compare the milling efficiency between Nutator and high-energy planetary ball mill TB-2, the soft mechanochemical reaction between TiOSO₄ · 2H₂O and Na₂CO₃ has been studied. In the case of nutating mill the intensity of diffractions corresponding to TiOSO₄ · 2H₂O and Na₂CO₃ completely disappeared after 5 min milling. In case of the planetary ball mill TB-2, due to the large difference in the centrifugal forces (60g vs 20g), mechanochemical treatment for 1 min leads to similar results and after 10 min, the sample contains mainly rutile TiO₂ with trace of TiO₂-II.

Key words: nutation, mechanochemical synthesis, TiO₂, powders

INTRODUCTION

Up to now, different ball mills are most commonly used for mechanochemical synthesis (MCS) as well as the major techniques for producing powders with unique properties [1, 2]. The purpose of a ball mill is to treat the material in order to generate the maximum surface area at the minimum energy consumption for the grinding process. In contrast, the purpose of an ideal device for MCS is to insert the maximum amount of energy into the treated solid to enable the accumulation of the input energy as defects mostly affecting chemical reactivity. This requires high-energy inputs to be transferred from the working medium to the treated solid during the mechanochemical reaction, which cannot be achieved with normal disintegrators. Unfortunately, such processes can lead to another problem related to the possible contamination of the final product sub-

jected to MCS with materials composing the working medium and the reactor body [1, 2].

MCS can be performed effectively and simply in traditional milling equipments such as shaker mills, planetary mill, attritors, or vibratory mills [3]. In the laboratory scale, SPEX 8000 Mixer Mill, a high-energy shaker mill (manufactured by Spex CertiPrep, Inc., the USA), is traditionally used as a mechanochemical reactor for synthesis [2, 3]. Another popular mill for MCS is a planetary ball mill, manufactured for example by Fritsch and Retsch GmbH, in Germany. The disk and the vial rotation speeds can be independently controlled in the modern versions [4]. Other examples of a laboratory planetary ball mill, such as AGO-2, developed in Russia, and TB-2 (developed in Slovakia, only as a prototype) has also been used in many cases [5, 6]. An advantage of these types of mills consists in their elegant construction principle, free of a

complicated driving mechanism, and bearings in the most loaded part of the mill, well-known from traditional planetary mills [5].

Industrial planetary mills of continuous action, characterized by productivity of up to 3–5 t/h, are now commercially available. The energy density in these mills is 100–1000 times higher than the energy density used earlier in conventional milling equipment [7]. A new concept of vibration mills working in an “eccentric” mode has been introduced by Gock *et al.* [8]. Unlike conventional vibratory mills with circular vibrations, this machine performs elliptical, circular, and linear vibrations [8].

In order to further enhance the performance, deliver energy efficiency and significantly reduce high operational costs typically associated with comminution circuits, a high-intensity ball mill based on the unusual mechanical principle “nutating mode” has been commercially implemented [9, 12]. For example, the Hicom nutating mill (Ludowici Ltd., Australia) is an adaptation of the concept of the centrifugal or planetary mill, in an arrangement which overcomes the mechanical limitations and feeding and discharging difficulties of past experience with centrifugal mills [10].

Hicom mill is a high-intensity mill which uses a nutating action to generate acceleration fields up to 50 times stronger than gravity, producing rapid and intense breakage of ores and other materials. The power density of this type of the machine is up to 2500 kW/m³, which is considerably higher than most grinding and attrition machines [12]. A specially developed rolling bearing and mechanical drive arrangement cause the mill axis to nutate about a fixed point at the nutation angle of 4.75 deg. The motion is similar to the swirling of a conical flask in a wrist: the top wobbles and the bottom moves in a circular motion. The eccentricity (e) is the radius of this circle, and increases linearly from the top down to the base of the grinding chamber. Both, the mill chamber diameter (D) and the eccentricity increase down the mill axis. Therefore, the centrifugal acceleration also increases down the nutation axis [11]. The magnitude of the centrifugal acceleration (A) in which the mill contents tumble is equal to the product of the eccentricity and the square of the mill speed:

$$A = \omega^2 e \quad (1)$$

where ω is the mill speed (rad/s) and e is the eccentricity or the radius of nutation at any point along the axis [9, 10]. The small physical size and intense grinding action of these mills make them suitable for a wide range of industrial applications. Unfortunately, the smallest version of the Hicom mill has a five-litre grinding chamber and power input of 15 kW [12] that is too robust for the small scale MCS laboratory study.

We have decided to construct a laboratory scale nutating mill Nutator with a 0.3 dm³ inner volume reactor. In contrast to the commercial nutating mill, in our prototype, the nutating angle in the range of 0–20 deg, besides the speed of rotation up to 1400 rpm, can be adjusted independently. In order to compare the milling efficiency between Nutator and the high-energy planetary ball mill TB-2, the acid-base mechanochemical reaction between TiOSO₄ · 2H₂O and Na₂CO₃ has been studied

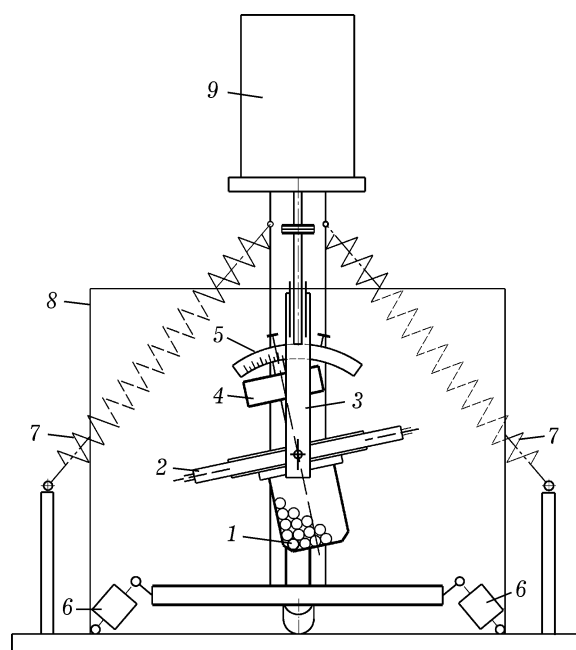


Fig. 1. Design and description of Nutator high-energy ball mill: 1 – stainless steel reactor with ceramic balls, 2 – reactor support disc, 3 – guiding rim, 4 – reactor counterweight, 5 – adjustable angle of nutation (12 deg in this study), 6 – silent blocks, 7 – spring dampers, 8 – safety box, 9 – 2.0 kW AC motor drive with frequency converters; the diameter of the reactor is 73 mm, the working volume is 200–300 cm³, ball mass is 200 g and the sample mass under treatment is usually up to 10 g.

[6, 17]. By selecting suitable conditions such as chemical reaction paths, stoichiometry of starting materials and milling conditions, this type of MCS can be used to synthesize nanoparticles dispersed in a water-soluble salt matrix. Recovery of crystallinity in samples or control the crystallite size is possible by thermal treatment [5, 6, 13–15, 17, 18].

To the best of our knowledge, this is the first study where the nutating ball mill has been used for acid-base MCS.

EXPERIMENTAL

The MCS experiments were performed in Nutator, as well in the high-energy planetary ball mill TB-2 (for technical details of TB-2, see ref. [6]). The milling speed of central axes in rpm was adjusted to 900 by a frequency converter. The centrifugal force at the bottom of the reactor in Nutator was calculated according to the eq. (1) as $20g$. The scheme and design of Nutator is depicted in Fig. 1. The starting powders were anhydrous Na_2CO_3 (Lachema) and $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ (Riedel de Haën). Ten grams of the starting powder corresponding to a Ti/Na atomic ratio of 1 : 2 was loaded to a stainless steel jar of the 0.3 dm^3 inner volume. ZrO_2 stabilized with Y (Tosoh, Japan) ceramic balls with

a 10 mm diameter were used as milling media in both cases. In case of TB-2, the corundum jar was used and the milling speed was fixed at 900 rpm. The centrifugal force was calculated according to the equations in ref. [16] as $60g$. The ball to powder mass ratio in both cases was 20 : 1. The mechanical milling was interrupted after 1, 3, 5 and 10 min. After the interruption of the milling process, a small amount of a powder was then taken for an XRD analysis. In order to obtain pure titania, a simple washing procedure was applied. Structural evolution of the powders during the processing was studied by an X-ray powder diffraction using a Philips PW 1050 diffractometer with $\text{CuK}\alpha$ radiation. The scheme of MCS of TiO_2 is depicted in Fig. 2.

RESULTS AND DISCUSSION

Figure 3 shows XRD patterns of $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ powder mixtures that were milled in the Nutator for up to 10 min. It is evident that the intensity of diffractions corresponding to $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ completely disappeared after 5 min milling and the peaks associated with the Na_2SO_4 salt matrix appeared, indicating that the acid-base reaction between $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ and Na_2CO_3 took

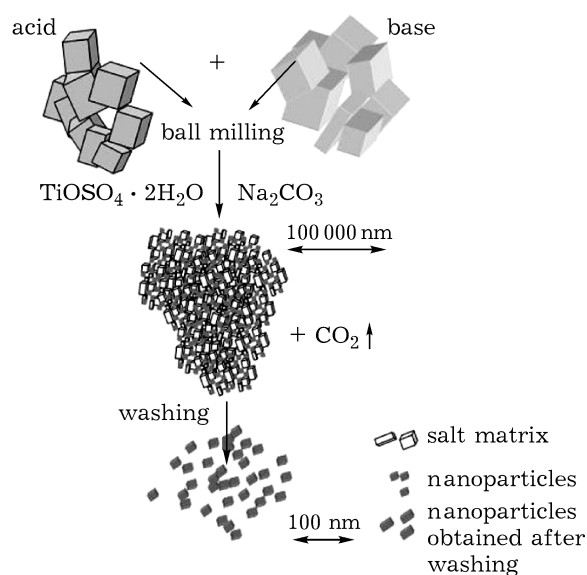


Fig. 2. Schematic view of the synthesis of TiO_2 nanoparticles in the Na_2SO_4 salt matrix.

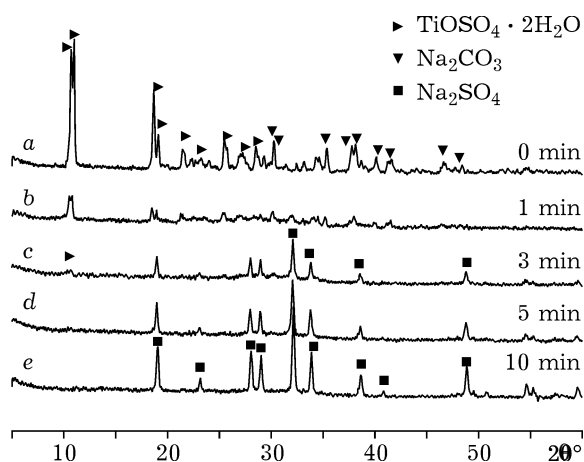


Fig. 3. XRD patterns of $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ powder mixture milled for different times by using Nutator.

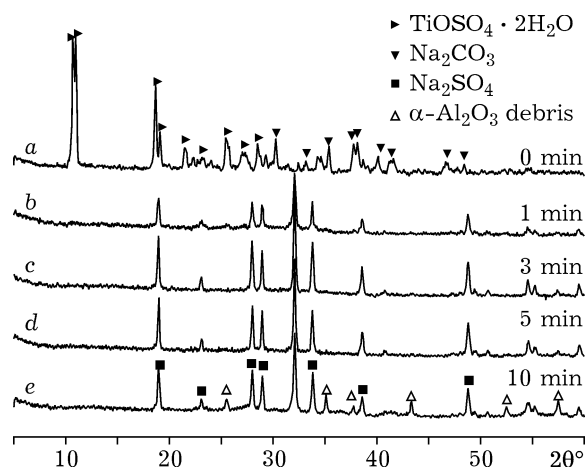


Fig. 4. XRD patterns of $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ powder mixture milled for different times by using the high-energy planetary ball mill TB-2.

place during milling. The very short reaction time can be explained by a strong acid-base interaction in the system [5]. Another very important factor for explaining the short reaction time is the free water presented during the milling process as a by-product. This water acts as a solvent for $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ or Na_2CO_3 and substantially enhances the reaction rate. For example, in case of the SPEX 8000 milling of an anhydrous $\text{TiOSO}_4 + \text{Na}_2\text{CO}_3$ mixture, a mechanochemical reaction of the precursors has not occurred to any measurable extent during the milling for up to 8 h, although the Na_2SO_4 product phase formation can provide a strong driving force for a chemical reaction between TiOSO_4 and Na_2CO_3 [18].

In case of the TB-2 milling, an XRD study showed that the diffractions corresponding to $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ have completely disappeared even up to 1 min milling (Fig. 4, b), because of the high centrifugal force ($60g$ vs $20g$). It means that the milling intensity of TB-2 (at 900 rpm) is higher than that of Nutator. On the other hand, the contamination of the powder with corundum debris from the reactor body after 10 min milling indicates that the milling intensity in the TB-2 mill at 900 rpm is too high.

Figure 5 shows XRD patterns of titania obtained after 10 min milling and washing procedure. In case of Nutator (Fig. 5, a), it is remarkable that after 10 min milling, the most intensive and very broad diffraction line 110 of rutile was observed. This indicates that a low crystalline rutile TiO_2 was formed by me-

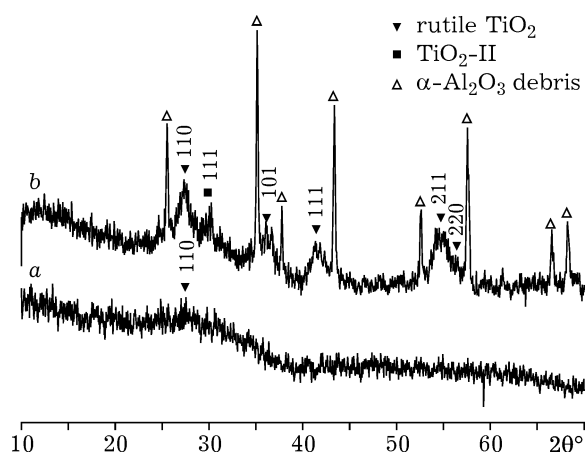


Fig. 5. XRD patterns of titania obtained after 10 min milling and washing procedure: a – Nutator, b – planetary ball mill TB-2.

chanically induced crystallization. In case of TB-2, (see Fig. 5, b), a significant rutilization was observed. Moreover, the most intensive diffraction line 111 of high-pressure orthorhombic TiO_2 -II was also observed.

Upon ball milling, high-pressure and temperature conditions, dominant at the particle surface of amorphous titania due to collisions, favoured crystallization of the high-pressure phase TiO_2 -II followed by their rutilization [19, 20].

According to an XRD study, it can be concluded that the formation of the Na_2SO_4 and TiO_2 phase can be described by the following reaction:

$$\text{TiOSO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \rightarrow \text{TiO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{CO}_2 \quad (2)$$

CONCLUSION

Laboratory scale nutating ball mill can be used for the MCS of TiO_2 . Five minutes mechanochemical treatment between $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ and Na_2CO_3 leads to interaction in mixture. In case of the planetary ball mill TB-2, because of the large difference in the centrifugal forces ($60g$ vs $20g$), mechanochemical treatment even for 1 min leads to similar results. We believe that the laboratory prototype nutating ball mill can be used also in other MCS. Further MCS studies and novel reactor designs are in development.

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