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(54) **MECHANOCHEMICAL DEVICE FOR MIXING AND/OR REACTING AT LEAST ONE CHEMICAL COMPOUND TO AT LEAST ONE REACTION PRODUCT**

(57) It is an objective of the present invention to provide a mechanomechanical device improving the quality of the analytical measurements done by diffraction or other analytical techniques (e.g. spectroscopic ones) during ball milling processes.

This objective is achieved according to the present invention by a mechanomechanical device (2) for mixing and/or reacting at least one chemical compound to at least one reaction product (4), comprising:

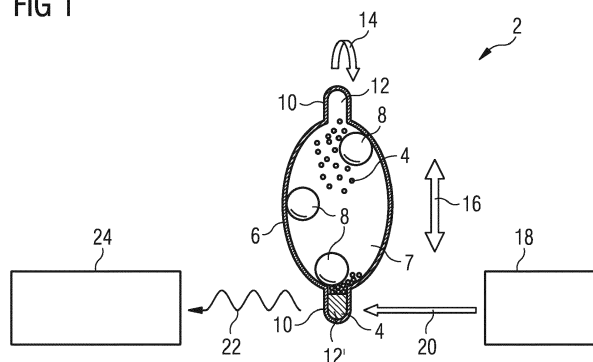
a) a grinding container (6) having a milling chamber (7), milling elements (8) and at least one probing chamber (10) wherein the at least one probing chamber (10) is realized as a recess volume (12) of said milling chamber (7) and wherein the recess volume (12) has a cross-sectional opening towards the milling chamber (7) that is smaller than the dimensions of the milling elements (8) preventing the milling elements (8) from entering into the

recess volume (12); and

b) a motor (14, 16) coupled to the grinding container (6) in order to rotate the grinding container (6) thereby bringing the recess volume (12) at least temporarily into a position allowing a gravitation driven release of the at least one compound and/or the at least one reaction product (4) that entered the recess volume (12) back into the milling chamber.

This device enables measurements done in a small part called probe chamber being specifically designed for analytical techniques. The features of the present invention make sure that the reaction product and/or its precursors (the ration strongly depends on the progress of the reaction of the precursors) is quasi-permanently present in the probe chamber which allows for an quasi-permanent analysis on the progress/evolution of the desired mechanomechanical-induced reaction.

FIG 1



Description

[0001] The present invention relates to a mechanochemical device for mixing and/or reacting at least one chemical compound to at least one reaction product.

[0002] Nowadays, *in situ* materials characterization techniques are more and more used as they give an accurate description of the sample in a particular state without disturbing the system and adding supplemental parameters/errors in the measurement. Further, there is a strong interest on *in situ* real-time measurements, where not only a particular state but the evolution of a particular process is probed. This is possible due to the recent technological progresses of analytical machinery giving more reliable measurements in a very short time-lapse.

[0003] One category of such processes, where *in situ* and real-time monitoring is important, is that of mechanochemical reactions. Mechanochemistry has attracted a special attention as a promising alternative synthetic strategy to traditional "wet chemistry" methods. The last years have witnessed a renewed interest by the rise of novel grinding methods paving the way to once impossible reactions or improving the yield of a particular final product.

[0004] Ball milling is one of the ways to induce mechanochemical reactions: it involves 'shaking' a container with powder reagents and steel balls, which implies a transfer of kinetic energy from the container to the balls and from the balls to the powder mix, resulting in reactivity. A large body of work exists on *ex situ* studies, where the materials are reacted and then analyzed.

[0005] The latest state of the art analytical technique is the real-time monitoring of mechanochemical reactions by X-ray diffraction. For the first time, a mechanochemical reaction was real-time monitored by a probe beam, giving direct information on the sample state inside the vessel and not only an indirect one as by probing the vessel temperature or pressure. Combinations with other solid-state techniques such as Raman spectroscopy are considered in order to have a clear understanding of the mechanisms in milling reactions.

[0006] However quick, efficient and good the analytical instrument could be, the container design is often neglected and present work is done with radiation passing through its entire body, leading to increased background and lower resolution. The container design and functionality has to address two main points:

- An improvement in the quality of the experimental data: good signal-to noise ratio enhanced by the path of the incident and outgoing beam probe through the vessel.
- a good mixing of the powder inside the milling chamber: efficient and fast exchange between the milling chamber and the collection area, which is important for obtaining the most representative picture possible of the process happening while collecting data.

[0007] It is therefore an objective of the present invention to provide a mechanomechanical device improving the quality of the analytical measurements done by diffraction or other analytical techniques (e.g. spectroscopic ones) during ball milling processes.

[0008] This objective is achieved according to the present invention by a mechanochemical device for mixing and/or reacting at least one chemical compound to at least one reaction product, comprising:

a) a grinding container having a milling chamber, milling elements and at least one probing chamber wherein the at least one probing chamber is realized as a recess volume of said milling chamber and wherein the recess volume has a cross-sectional opening towards the milling chamber that is smaller than the dimensions of the milling elements preventing the milling elements from entering into the recess volume; and

b) a motor coupled to the grinding container in order to rotate the grinding container thereby bringing the recess volume at least temporarily into a position allowing a gravitation driven release of the at least two compounds and/or the reaction product that entered the recess volume back into the milling chamber.

[0009] This device enables measurements done in a small part called probe chamber being specifically designed for analytical techniques. The features of the present invention make sure that the reaction product and/or its precursor(s) (the ration strongly depends on the progress of the reaction of the precursor(s)) is quasi-permanently present in the probe chamber which allows for an quasi-permanent analysis on the progress/evolution of the desired mechanochemical-induced reaction.

[0010] A preferred embodiment of the present invention can be achieved when designing the recess volume as a continuous ring-like groove having a width smaller than the smallest dimension of the mixing elements.

[0011] Suitable mixing and grinding elements can be provided if they are designed as steel balls.

[0012] For a beneficial support of the desired *in situ* analysis of the evolution of the mechanochemical reaction, the wall of the recess volume can be permeable to light beams, such as X-rays, and/or particle beams, such as protons, neutrons and/or electrons. Suitable materials could be for example mylar® or kapton®.

[0013] Preferably, the wall of the recess volume can be made from a material different from the material used for the wall of the milling chamber. Therefore, the material for the wall of the milling chamber can be optimized for the goal of milling while the material for the wall of the probe chamber can be optimized for the analysis method applied to the material trapped in the recess volume.

[0014] Preferred embodiments of the present invention are hereinafter described in detail with reference to the attached drawings which depict in:

Figure 1 schematically the general function principle of a mechanochemical device during analytical acquisitions; and

Figure 2 schematically the design of a milling chamber.

[0015] Figure 1 shows a schematic drawing of the general function principle of a mechanochemical device 2 during analytical acquisitions, through a vertical cut of the mechanochemical device 2 itself. Figure 1 illustrates the motion of the mechanochemical device 2 during a vertical ball milling process.

[0016] The mechanochemical device 2 for mixing and/or reacting at least one chemical compound to at least one reaction product 4 comprises a grinding container 6 having a milling chamber 7, milling elements 8, e.g. steel balls, and a probing chamber 10. The probing chamber 10 is realized as a recess volume 12 of said milling chamber 7. This recess volume 12 has a cross-sectional opening towards the milling chamber 7 that is smaller than the dimensions of the milling elements 8 preventing the milling elements 8 from entering into the recess volume. Further, the mechanochemical device 2 comprises two motors (represented by arrows 14 and 16) coupled to the grinding container 6 in order to shake (arrow 16) and rotate (arrow 14) the grinding container 6. Arrow 14 indicates this rotation. By this rotation, the recess volume 12 is at least temporarily brought into a position allowing a gravitation driven release of the at least one compound and/or the at least one reaction product 4 that entered the recess volume 12 back into the milling chamber 7. In Figure 1, this situation is shown for the upper recess area 12 which released all its content back into the milling chamber 7 while the lower recess area 12' is filled with the at least one reaction product 4 and/or the at least one precursor compound of the at least one reaction product 4 which do not have yet reacted to the at least one reaction product 4.

[0017] The grinding container 6 is driven by a general motion here in a direction up and down which is represented by the arrow 16, preferably at a frequency above 10 Hz. This movement is coupled with the slow rotation of the grinding container 6 that is represented by the arrow 14, preferably with a frequency of less than 0.5 Hz with a rotation axis coaxial to the probing chamber 10. By this dual motion, the probe indicated by the dashed area in the probe chamber 12' is immediately re-injected in the milling chamber 7 by combined vertical motion and gravity. As a result a fresh portion (always available in the recess volume 12') of the at least one reaction product 4 (the grinding mixture) is continuously examined by an X-ray source 18 emitting an X-ray beam 20 through the recess volume 12'. The transmission of the X-ray beam 20 is not affected by the milling elements 8 due to the design of the cross-sectional opening of the recess volume 12, 12' to the milling chamber 7, where the milling elements 8 can not enter in due to the larger dimensions

as compared to the dimensions of the cross-sectional opening. After the penetration of the recess volume 12', a diffracted beam 22 (diffracted by the probe in the recess volume 12') is detected by a detector 24. Since the milling elements 8 cannot access into the recess volume 12, 12', the path of the probing X-ray beam 20 and the transmission of the outgoing diffracted beam 22 and thus the quality of data acquisitions is tremendously improved as compared to prior art grinding devices.

[0018] Figure 2 shows a three-dimensional technical draw of a mechanochemical device 2, with the different elements composing it. The mechanochemical device 2 comprises two half-containers 25a, 25b, each composed by a hollow half-spherical central part 26a, 26b devoted for the pure milling and a circular ring 28a, 28b with several curved apertures 30a to 30d where the analysis may take place. Ring disks 32a, 32b act as walls and spacer ring 34 acts as a spacer defining the thickness of the apertures 30a to 30d. All the parts are kept together by a compression nut 36. The complete assembly is held by a pin 38 included on the center of each half-container 25a, 26b. These pins 38 define the axle around of which the mechanochemical device 2 can rotate.

[0019] In a standard apparatus the mixing of solids is done by the motion of the milling elements 8 which ensures the homogeneous mixing of powders, important for reactivity. Where a recess volume 12, 12' exists the solid can get stuck into it.

[0020] The specific aspect of the invention is to have a milling chamber 7 with a separated probe chamber 10 for the analysis where the milling elements 8 cannot access. The probe chamber 10 can therefore have walls of a desired material, e.g. less resistant, harder, shockproof as compared to the wall of the milling chamber 7 that should withstand the impact of the milling elements 8. Coincidentally, a vigorous mixing of the precursor compounds is ensured between the probe chamber 10 and the milling chamber 7. The technical solution is achieved by having a mixing force driven not only by the motion induced into the milling elements 8 but also by gravity, as obtained by providing an additional rotation motion (arrow 14 in Figures 1 and 2) in the case of the present examples.

Claims

1. Mechanochemical device (2) for mixing and/or reacting at least one chemical compound to at least one reaction product (4), comprising:

a) a grinding container (6) having a milling chamber (7), milling elements (8) and at least one probing chamber (10) wherein the at least one probing chamber (10) is realized as a recess volume (12) of said milling chamber (7) and wherein the recess volume (12) has a cross-sectional opening towards the milling chamber (7)

- that is smaller than the dimensions of the milling elements (8) preventing the milling elements (8) from entering into the recess volume (12); and
b) a motor (14, 16) coupled to the grinding container (6) in order to rotate the grinding container (6) thereby bringing the recess volume (12) at least temporarily into a position allowing a gravitation driven release of the at least one compounds and/or the at least one reaction product (4) that entered the recess volume (12) back into the milling chamber (7).
2. Mechanochemical device (2) according to claims 1 wherein the recess volume (12) is designed as a continuous ring-like groove (10) having a width smaller than the smallest dimension of the mixing elements (8).
3. Mechanochemical device (2) according to claim 1 or 2, wherein the mixing elements (8) are steel balls.
4. Mechanochemical device (2) according to any of the preceding claims, wherein the wall of the recess volume (12) is permeable to light beams (20), such as X-rays, and/or particle beams, such as protons, neutrons and/or electrons.
5. Mechanochemical device (2) according to any of the preceding claims, wherein the wall of the recess volume (12) is made from a material different from the material used for the wall of the milling chamber (7).

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FIG 1

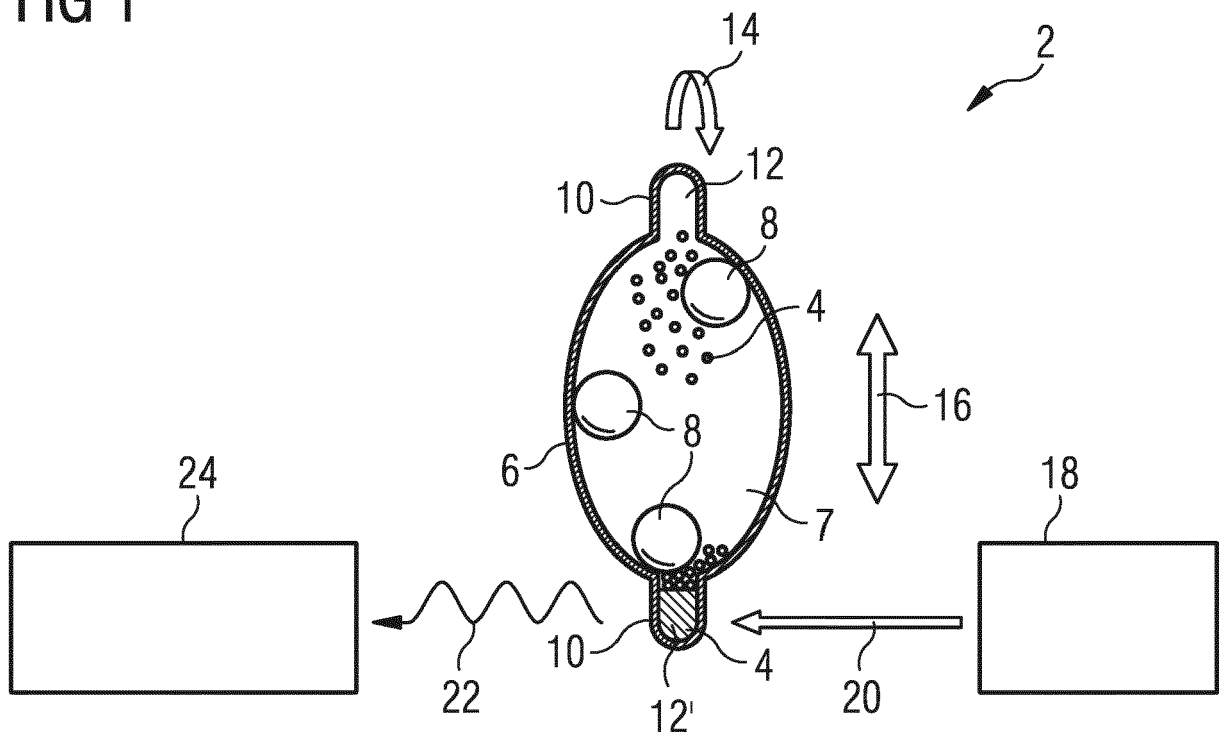
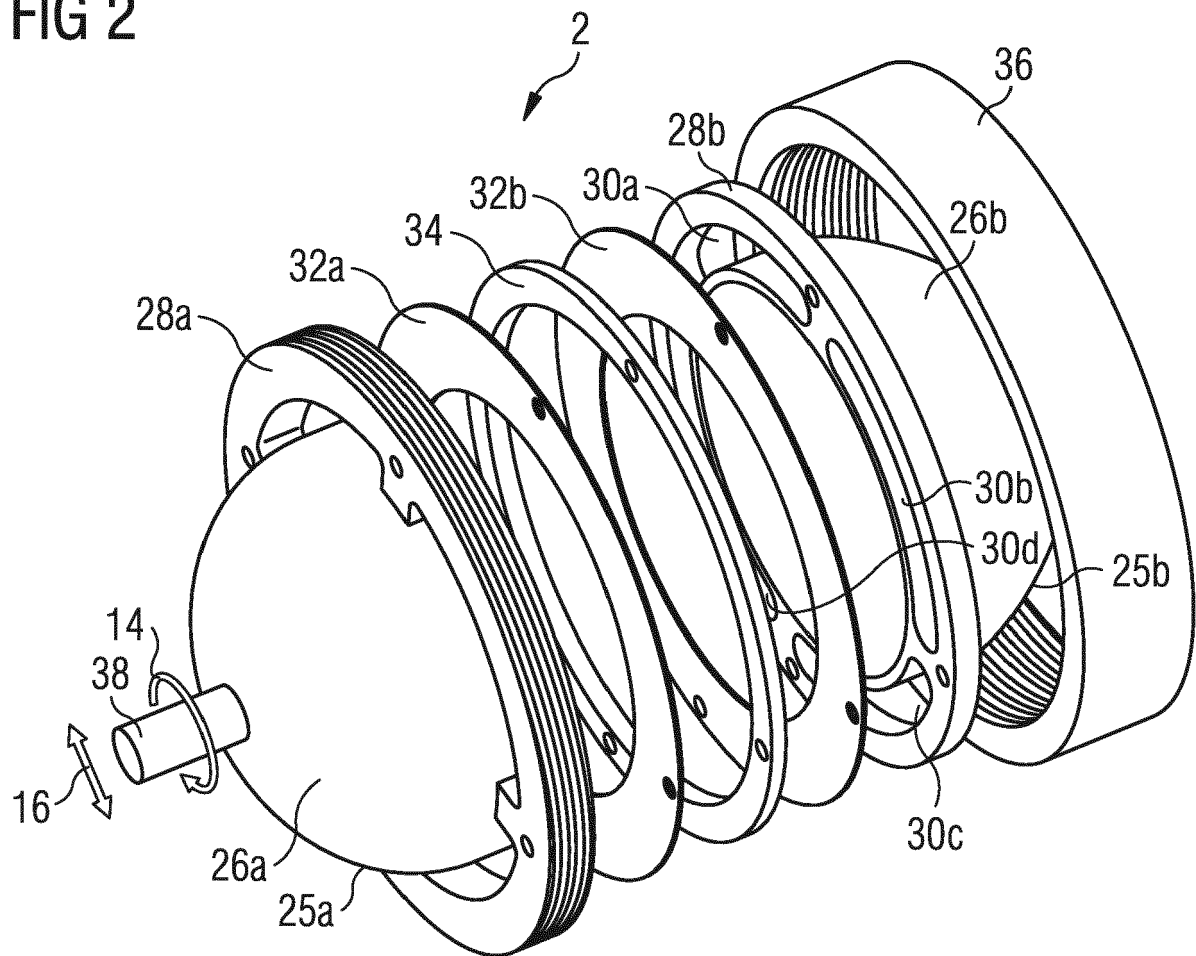


FIG 2





EUROPEAN SEARCH REPORT

Application Number
EP 15 19 7992

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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X	US 2011/100928 A1 (ZHANG WEI-XIAN [US]) 5 May 2011 (2011-05-05) * the whole document *	1-5	ADD. B02C17/14 B02C17/10 B02C17/16 B02C17/18
			TECHNICAL FIELDS SEARCHED (IPC)
			B01J B02C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 12 May 2016	Examiner Serra, Renato
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 15 19 7992

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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