PLANETARY MILL

Rev. 7/21/11

Description

The mill operates by rotation of four milling vials in a planetary motion pattern. Adjustable milling parameters are the operating speed (rpm), milling duration (minutes), and duration of the periodic reversal of the sense of rotation. Two types of milling vials are used: standard hardened steel vials and custom-made high pressure vials. Temperature in the milling compartment is controlled by an air conditioner equipped with customized timer. Additional cooling fins can be mounted onto standard milling vials.

Before starting:

1) Ensure that the work area is clear of dust, debris, material samples, and any lab components not directly used for the experiment. Use cleaning solution to prepare the countertop surface prior to start.
2) Determine the type of milling experiment desired. Identify milling parameters for your specific experiment. Select among the following milling parameter options:
    a. *Use of Process Control Agent (PCA)*: PCA inhibits formation of agglomerates and/or cold-welding. Some PCAs used are stearic acid and hexane.
    b. *Wet or Dry Milling:* "Wet" milling requires the use of liquid process control agent during the milling.
    c. *Vial Atmosphere:* Inert atmosphere requires loading vials inside the glove box which contains argon. See glove box instructions for details. For standard vials, alternatively, inert gas can be filled using customized vial lids equipped with valves.
    d. *Milling media*: Varied ball sizes are available for use as well as other milling media.
    e. *Charge ratio*: Mass ratio of the milling media to the powder sample
    f. *Milling time*: Needs to be determined before the experiment
    g. *Use of ring clamps* on standard steel vials. If a spontaneous reaction can be triggered during milling, and if standard vials are used, the lids must be secured with ring clamps.
    h. *Use of cooling fins* on standard steel vials. Some materials benefit from lower milling temperatures, and the respective cooling fins can be used. Note that one can not use cooling fins and ring clamps at the same time (they don't fit together). Therefore, cooling fins can not be used for materials where a reaction can be triggered during milling. The cooling fins add substantial weight to the milling vials, so make sure to arrange the vials so that the mill is balanced.
3) Locate the necessary tools for opening, closing, loading, and mounting milling vials. Clean the tools before use.
4) Locate materials to be used as starting components

Loading milling vials:

1) Place the vials inside a fume hood.
2) Weigh the milling balls and the powders in separate weighing cups, one cup for each type of powder, and transfer them into the vials.
    Note: when loading powders, ensure no cross-contamination between samples and stock material.
3) For wet milling measure the necessary amounts of process control agent in separate jars.

4) For *inert atmosphere* milling, PCA should be preloaded into the sealable jars, one jar for each vial. The sealed jars, the vials with starting material and milling media, vial lids and respective bolts or clamps, and the wrench should be placed inside the evacuation chamber of the glovebox. Make sure that all the vials are partially open during the evacuation of the chamber; otherwise, the vials will be evacuated and will be difficult to open inside the glovebox. If no inert atmosphere milling is required, pour the prepared PCA into the vials placed inside the fume hood and immediately secure lids. Continue to step 7.
5) Inside the glovebox, pour the process control agent into the vials and immediately secure lids.
6) Important: **double check that the vials are tightly sealed**.
7) Important: **double check that the jars that contained PCA are empty** which means that PCA was poured into the vials. It is important to ensure that materials requiring wet milling are not milled without PCA.
8) If loading was done in the glovebox, remove the vials and all the accessories (the wrench, the empty jars etc.) from the glovebox.
9) Install the vials on the sun table of the ball mill. Align the vials ensuring that the bottom notch matches up with the cavity found at the bottom of each vial.
   Note: the mill must be balanced. This means that two vials mounted opposite to each other on the sun disk must be of the same weight. This is especially important when cooling fins are used.
10) Secure the vials in the ball mill. Verify that they are held securely by clamps. It is important that no vials become loose during milling.
11) If temperature sensors are used, secure sensors to each vial and verify transmission of the temperature signal to the data acquisition system.

During the milling run:

1) Monitor milling operation at least once every hour
2) It is possible to set up "after hour" runs for preparing samples using an established protocol
3) If temperature sensors are used, monitor the milling temperature

Adding liquid during a milling run:

Some materials are initially prepared dry, but should be milled in a liquid (hexane, heptane, others) before extraction. Some materials are milled with a small, measured amount of a liquid, but should be recovered as a slurry. In either case, use the following procedure.

For standard vials with vented lids:

1) Keep the vials secured in the mill.
2) Make sure that the graduated glass reservoir (wall-mounted, to the right of the mill) has enough of the desired liquid in it). Make sure the valve below the reservoir is closed, and turn on the pump. There should be a few audible clicks from the pump.
3) Open the vent on one vial.
4) Insert the nozzle in the vent, hold it down, and open the valve below the reservoir.
5) Watch the liquid level in the reservoir and close the valve when the desired amount has been pumped.
6) Remove the nozzle, and be sure to close the vent.

7) On removing the nozzle, a short burst of gas will flow out of the vent. This is normal. If this does not happen, or if liquid spills over and does not properly enter the vial, then the vent is blocked. Treat that vial as unrecoverable and prepare to discard the material from that vial after the run. For now, close the vent, and leave the vial in its place. *Clean up any spilled liquid*.
8) Proceed to the next vial and repeat steps 3-7 until liquid has been injected in all vials.
9) Turn off the pump.
10) Continue to mill.

For high-pressure vials, or standard vials without vented lids:

1) Remove the vials from the mill, and loosen the bolts on the lids (1/4 turn) but leave the vials closed otherwise
2) Transfer the unopened vials to the glove box. Also take an appropriate wrench and a container with the desired liquid in the glove box. If specific liquid amounts are required, one small closed jar with a pre-measured amount per vial is recommended. If only "excess liquid" is required, one larger container suffices. Refer to the glove box instructions for details.
3) In the glove box, open one vial at a time, and transfer the liquid inside. Close the vial and secure the lid.
4) Repeat for the remaining vials.
5) Remove all materials and equipment from the glove box.
6) Tighten the bolts on the vial lids before putting the vials back in the mill.
7) Mount the vials in the mill, and continue milling.

Extraction of the prepared samples:

After completion of the ball-milling run, clean surface of the lab bench and make sure there is a clean open area inside the fume hood. Verify that no flammable chemicals or samples are placed on the bench and inside the fume hood to be used to recover the newly prepared material.

NOTE: The material prepared may be reactive in air, it is important that the protocol is followed. Make sure to wear goggles, lab coat, and gloves.

If a new, unknown material is formed, determine if the material is pyrophoric.

a. Load an UNOPENED vial inside the glove box
b. Slowly loosen the bolts or sealing clamps. Note: *High pressure vials* require slight loosening the bolts before loading into the glove box (1/4 turn only).
c. Crack the lid open
d. Carefully remove a small powder sample with a spatula
e. Place the spatula with this small sample inside the airlock and expose it to air for at least 3 minutes to determine the material's pyrophoricity.
f. If the material is pyrophoric, leave it inside the glovebox inside the milling vial with the lid cracked open for 24 hours. Check whether the material is passivated. If it is not passivated, store it inside the glovebox.

The extraction procedure depends on the specific material. There are four main cases:

- dry milled, sample is not sensitive to air (e.g., mechanical alloying, Al-Ti)

- dry milled, sample is sensitive to air (e.g., mechanical alloying: Al-Li)
- wet milled, to be collected dry (e.g., Zr-$NaNO_3$)
- wet milled, to be collected as slurry (e.g. Ti-B composites)

A: dry milled, sample is not sensitive to air

1) Transfer the vials from the mill to the fume hood next to it.
2) Open one vial at a time, and dump the contents into a large, coarse sieve to separate balls from powder.
3) Collect powder from sieve bottom pan, and balls from sieve.
4) Repeat for remaining vials.
5) Proceed to *Vial Cleanup* below.

B: dry milled, sample is sensitive to air

1) Transfer the milling vials in the glove box. Also transfer sieve, sieve pan, and tools as needed.
2) Continue as in case A, steps 2-4, only inside the glove box.
3) Proceed to *Vial Cleanup* below.

C: wet milled, to be collected dry

1) Transfer the milling vials in the glove box. Also transfer sieve, sieve pan, container for sample, and tools as needed.
2) Open one vial at the time, and transfer the wet powder onto the sieve.
3) Either leave the powder sitting until liquid is evaporated, or dry powder using the vacuum airlock.
4) Collect powder from sieve bottom pan, and balls from sieve. Replace balls in vials and close vials.
5) Repeat for remaining vials.
6) Place empty vials (containing only balls) in airlock. Remove vials from airlock and immediately move vials to fume hood.
7) The vials may contain traces of material that is sensitive to air. Be careful to open one at a time, and leave open in fume hood for an hour.
8) Remove any other equipment you used from the glove box.
9) Proceed to *Vial Cleanup* below.

D: wet milled, to be collected as slurry

1) Transfer milling vials to a fume hood.
2) Open one vial at the time.
3) Remove materials from the vials by washing them out with hexane. A suction assembly (found in the fume hood) can be used to collect the slurry.
2) Upon collection completion, transfer the material from the suction assembly to a suitable storage container.
3) For most materials, it is recommended to store them under hexane.
4) Repeat for all remaining vials.
5) Proceed to *Vial Cleanup* below.

Vial Cleanup

NOTE: When milling materials that have the potential for spontaneous reaction during milling, you **must** clean up the vials and balls after each milling run. Milling the next

batch with traces of the previous batch left in the vials makes accidental reaction during milling much more likely.

1) To clean leftover sample from the milling vials and balls, load the milling vials with the balls, some amount of a solvent (hexane or other hydrocarbon, approx. 50 mL. **Do not use alcohols or acetone**), and some sand (approx. 5 g), and mill this for 5-10 minutes.
2) Collect the balls and the sand according to Case A in Sample Extraction above.
3) Wipe out the vials, and inspect the inside. If there is still caked sample in the vial, repeat the short milling with sand until the vials are clean.

NOTE: While cleaning vials with samples that are sensitive to air, you **must not** use hammer and chisel, steel brushes or other sparking tools. Material stuck to the vial must be treated as potentially pyrophoric. Prying stuck material from the vial wall will expose fresh surface which can react with air and ignite the material. Therefore, **do not pry air-sensitive material from the vial walls**. Instead, repeat the short cleanup milling step if sample remains stuck in the vial.

4) Clean up your working area. Clean all tools used and wipe down the surfaces with solvent. Dispose waste in properly labeled containers. Treat paper towels that were used to wipe the vials as flammable solid waste.