BALL MILLING IN THE PRESENCE OF A FLUID: RESULTS AND PERSPECTIVES

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Abstract. By milling powders within a fluid (water, dodecane or hydrogen) together with stainless steel balls in a steel vial placed on a planetary mill it is possible to synthesize materials as diverse as well crystallized and highly anisometric graphite (HAG); graphite-lithium intercalation compounds, in particular the superdense phase LiC_3; pure maghemite as well as its composites with graphite ; several transition metal oxides; alkali metal hydrides (especially RbH and CsH, not available on the market). This paper is related to those syntheses and the observations during the process in order to enlarge this field to the synthesis of new compounds.

1. INTRODUCTION

The attempts of milling in the presence of a liquid were firstly done in the 1960's [1,2] in order to prevent the agglomeration of the particles during the grinding, especially for ductile materials. This point is particularly interesting when working with graphite that is a fragile and very soft material with a large tendency to agglomerate. The graphite is easy to cleave and a planetary mill that favors the friction mode is the best apparatus for this purpose.

The vials, tighten by a rubber gasket, are made of a special hard steel: Z200C12 whereas the balls are in stainless steel.

2. EXPERIMENTAL

2.1. Graphite

When dry ground, the graphite (mean size: 40 μm) is broken and the size of the particles decreases, but as the milling duration and/or the rotation rate is increased, part of the powder becomes amorphous. This is the reason why the milling was done in the presence of a liquid in order to decrease the violence of the shocks. The easier liquid to deal with is water and the first experiments lead to very thin and well crystallized graphite particles. However, the magnetic behavior of this powder reveals the presence of impurities other than the simple contamination resulting of the abrasion of the milling tools. This is particularly true if one takes into account the softness of graphite and the moderator role towards the violence of the shocks plaid by the water. In fact those impurities are iron oxides (mostly maghemite g Fe_2O_3) coming from the oxidation by water of the iron contained in the milling tools [3] according to the equation:

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2. \qquad (1)$$
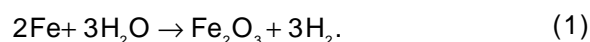
This result was turned to account for the synthesis of maghemite described somewhere else [4].

The preparation of pure graphite nanoparticles was actually obtained by substituting water by dodecane, a liquid inert towards steel. The milling conditions are as follows: 5 g of natural Ceylon type graphite (Alfa) and 50 cm³ of dodecane are milled together with 200 g of stainless steel balls (diameter 5 mm) for 12 hours. The graphite particles,

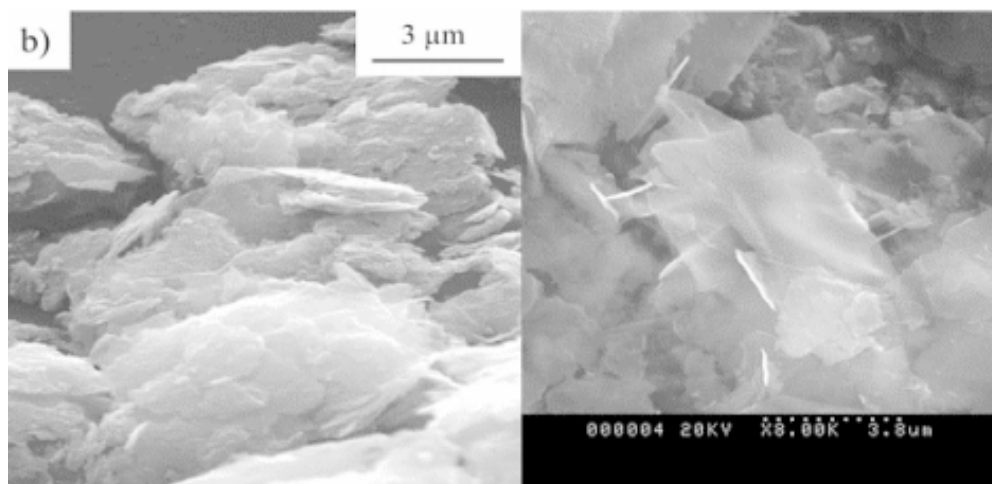Corresponding author: Daniel Guérard, e-mail: daniel.guerard@laposte.net

Fig. 1. Graphite powders dry milled (left) and milled within water (right).
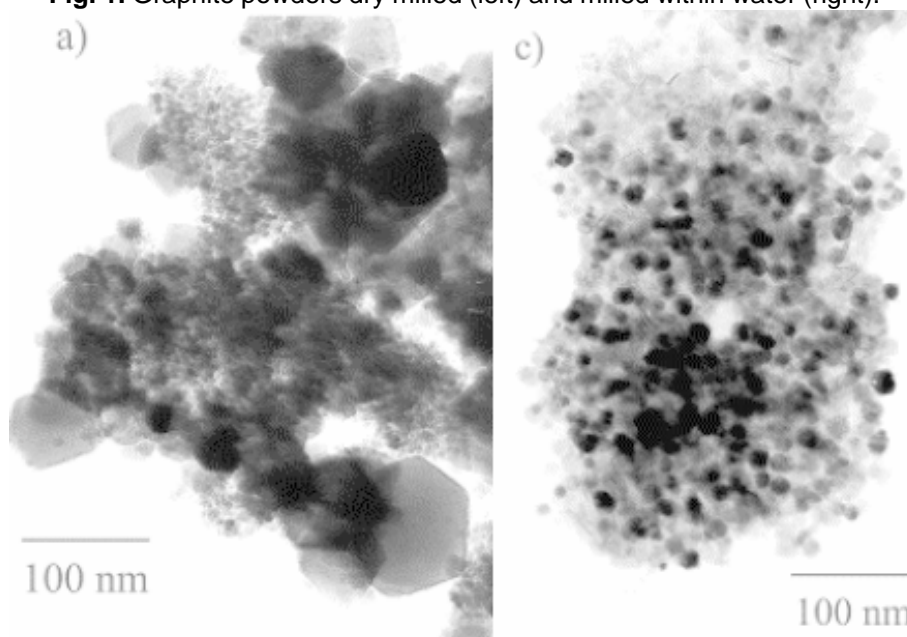

Fig. 2. Influence of the milling time on the synthesis of maghemite after 12 h (left) and 48 h (right).

well crystallized, present a high anisometry, typically several μm in diameter for 20 nm in thickness, as shown in Fig. 1, are mostly single crystals. Moreover, used as anodes in lithium-ion batteries, this milled graphite presents a smaller irreversible capacity than the starting powder, in spite of a much larger (by a factor greater than 100) specific area, generally considered as responsible for this irreversibility. The explanation is as follows: the surface increase is mainly due to the cleavage of graphite (the mean diameter is divided by a factor of 2 to 10, the thickness by 200 to 500) occuring

preferentially at the defects ; thus the ball milling leads to a better crystallinity and can be considered, in this case, really as a soft method.

2.2. Maghemite and graphite-maghemite composites

The synthesis is done by milling of 5 g of iron powder, 50 cm³ of water and 200 g of balls (diameter 5 and 10 mm in the weight ratio 1:1, the mixture of two different diameters increases the violence of the shocks that is necessary to reach to pure

maghemite) at 200 rpm for 48 hours. Such a duration of milling is made necessary since, after 12 hours, the powder is a mixture of maghemite and magnetite. The decrease of the particles size is tightly connected to the oxidation of magnetite as seen in Fig. 2: the large magnetite particles become smaller by oxidation into maghemite.

Since the structures of maghemite and magnetite are quite similar: cubic with close *a* parameters: 8.35 and 8.39 Å respectively and since the chemical formula of maghemite and hematite (a Fe_2O_3) are identical. Therefore, many analyses were necessary to determine the exact nature of the resulting powder: XRD, SEM, TEM, chemical analysis, Mössbauer spectroscopy, magnetic susceptibility measurements. This synthesis method is very easy compared to the classical ones [5,6].

The synthesis of graphite-maghemite composites can be done either by separate synthesis of each component and light mixing with dodecane for 12 hours at 200 rpm or by successive syntheses in the same vial: the maghemite is prepared firstly as described above, then the desired quantity of graphite powder is added in the vial for an other 12 hours of milling [7].

2.3. LiC_3, a superdense graphite intercalation compound

Pure LiC_6, synthesized for the first time in 1972 [8,9], constitutes the metal reservoir of the anode in lithium-ion batteries. It corresponds to a specific capacity of 372 mAh/g of graphite and many researches are done to increase this capacity, mostly by using other carbon varieties but, in this case the global capacity is increased but the part of irreversibility is such that the true reversible part is close to 372 mAh/g. Moreover, the potential for intercalation-deintercalation into graphite is much higher than with graphite, much less interesting. An other possibility is to increase the capacity is to use a "superdense" Li-graphite compound: LiC_2 whose first deintercalation leads to a capacity much higher (close to 1 Ah/g) at a very low potential vs. lithium: a few tens of mV [10]. Unfortunately, the electrochemical intercalation of lithium is limited to LiC_6 and the capacity of the following cycles is limited to 372 mAh/g. The synthesis of LiC_2 requires a high pressure: 50 kbars and a temperature of 300 °C for several days [11]. By ball milling it is possible to reach locally and instantly such conditions [12,13] and the synthesized compound LiC_3 was obtained under the following conditions: 5 g of lithium and graphite powders (Li + 2C), 1 cm³ of dodecane and

200 g of balls (5mm in diameter) are milled at 200 rpm for 12 hours. The dodecane is added in order to avoid the sticking of lithium on the milling tools, an other role plaid by the presence of a liquid. The electrochemical behavior of the resulting powder is unfortunately the same as that of the compound obtained under high pressure [14].

2.4. Alkali metal hydrides

Rubidium and cesium hydrides are not commercially available. For their intercalation into graphite, it was necessary to synthesize them and for that, a method was set up 20 years ago [15] but its efficiency was quite low. By milling 2 g of metal and 100 g of balls under 7 bars of hydrogen (the vial volume is 250 cm³) at 250 rpm for 12 hours, one obtains a grayish powder containing small quantities of free metal, divided enough to transform in pure hydride by heating the vial (outside of the mill) for 1 hour at 120 °C [16]. In this case, the fluid (hydrogen) reacts directly with the metal.

2.5. Discussion, other experiments

From the previous results, it appears that the ball milling in the presence of a fluid is a powerful, very efficient method for new syntheses easy to transfer at the industrial scale. Other experiments were done in particular for the synthesis of transition metal oxides, especially CrO_2 for its applications for magnetic memories. According to previous results it appears that there is no systematic behavior as a function of the electronegativity, hardness as shown in Table 1.

In order to increase the number and violence of the shocks, the rotation rate and duration are increased, the water volume being decreased, but, despite of those changes, the results are not completely successful.

Since chromium with a smaller electronegativity or nickel despite of a lower redox potential than iron are not oxidized by water, it was also tried to relate the ability for the oxidation to compare the respective hardness of the metals to that of iron. This factor is probably an explanation of the results: chromium and nickel particles are hard and therefore are not broken by milling. The surface of the large Cr and Ni particles reacts with the iron coming from the milling tools to form an alloy, which is easier to oxidize than the metal powder itself. Small particles of binary oxide are thus formed at the surface of Cr (or Ni).

On the opposite side, copper particles are not broken upon milling due to the high ductility of cop-

Table 1. Some properties of the metals and results as a function of the experimental conditions.

Metal	Electro <0 (Pauling)	Redox potential [V]	Hardness			Experimental conditions			Resulting powder [17]
			Brinell	Mohs	Vickers	Water [cm³]	Rotation [rpm]	Duration [hours]	
Cr	1.6	- 0.91		9.0	130-220	50	200-300	48	No reaction
						5	300	48	Cr and traces of Cr_3FeO_6
Mn	1.5	- 1.18		5.0		50	200	48	Mn_3O_4, traces of
						50		72	Mn, λ MnO_2
Fe	1.8	- 0.44	82-100	4-50		50	200	18	Pure maghemite ($\gamma\, Fe_2O_3$)
Co	1.8	- 0.28	125		170-320	50	200	48	CoOOH and Co
						50	200	72	Mixture of CoOOH,
						5	200	120	$Co(OH)_2$, Co $Co(OH)_2$, traces of Co
Ni	1.9	- 0.25	100-190			50	200	48	No reaction
						50	250-300	48	Ni, traces of NiO, Ni_2O_3, NiO_2,
Cu	1.9	+ 0.34		2.5-3	49-87	3-50	up to 300	48-120	Surface reaction, Cu deposition on the milling tools

per. The Cu particles are only deformed by the shocks as pointed out by the particular shape of particles: both cylindrical and spherical shapes are easily explained by the friction mode generated by a planetary mill. The surface is oxidized leading to Cu_2O oxide. As this oxide much more fragile than the underneath copper is removed upon milling to form small particles [17].

Another attempt to be more efficient was to substitute water by hydrogen peroxide. This was firstly done for the synthesis of maghemite, not for this purpose, but in order to decrease the pressure inside the vial at the end of the synthesis: according to Eq. (1) and taking into account the vial internal volume the final pressure is around 12 bars.

The amount of hydrogen peroxide was below the stoichiometric amount corresponding to the following reaction:

$$2Fe + 3H_2O_2 \rightarrow Fe_2O_3 + 3H_2O. \qquad (2)$$
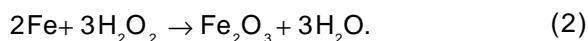
The gas pressure should have decrease. In fact, it increases and an explosion, accompanied by a flame, occurs at the opening of the vial. This points out that the gas in the vial is a mixture of hydrogen and oxygen, this last coming from the decomposition of H_2O_2, whereas hydrogen comes from the water reduction by iron. The addition of hydrogen peroxide is, thus, not interesting. By the way, this result proves that the iron is oxidized by the reduction of water, not by the oxygen freed by the decomposition of hydrogen peroxide [17].

3. CONCLUSION AND PERSPECTIVES

The ball milling within a fluid is an easy and rapid synthesis method that is possible to transfer at the industrial scale. Using only one type of mill (planetary), three different fluids (water, dodecane and hydrogen), various types of materials were synthesized:

- transition metal oxides and composites with graphite with interesting electrochemical properties [7,14],
- alkali metal hydrides MH [15]
- a superdense graphite-lithium compound: LiC_3 [14],
- highly anisometric graphite [14,18] whose electrochemical properties should be deepen.

Despite those results, this work has to be considered as a preliminary one. For instance, the transition metal oxides can probably be better prepared using a spex or cannon-ball types of mill: the shocks will be more efficient to crush the powders. Several new ways should be interesting to investigate:

- intercalation of sodium powder into graphite. The classical method based on the reaction of sodium vapor on graphite powder is limited by the low stability of low stage (rich in sodium) compounds, which limits the formation of a pure 6th stage ($NaC4_8$) synthesized at 175 °C (stage 8, NaC_{64} is prepared at 400 °C). At that temperature, the vapor pressure of sodium is too low to expect the intercalation at lower temperatures [19]. Probably, by ball milling one can expect the formation of a first stage compound that could be used as anode in cheap sodium-ion batteries, taking into account the respective prices of lithium and sodium.
- The amount of the liquid plays a role on the violence of the shocks as seen with the synthesis of transition metal oxides. Its role for the synthesis of the lithium superdense graphite intercalation compound LiC_3 is different: without dodecane, the lithium powder sticks on the milling tools and the graphite turns mainly to amorphous carbon, 1 cm^3 of dodecane for 5 g of powders is enough. Above 3 cm^3, the resulting powder is LiC_6 [14,18]. Other compounds involving soft materials with a tendency to stick, e.g. barium could probably be intercalated into graphite at room temperature. There are many other systems to investigate e.g. alloys like lithium-aluminum, lithium-magnesium. Their hydrides, actually interesting for the hydrogen storage, will be easy to synthesize in the same vial as for the alloying: hydrogen can be introduced after the preparation of the alloy powder.

- Lithium also might be intercalated into boron nitride as well as into graphite and with similar synthesis conditions. In fact, I was working on the intercalation of lithium vapor into boron nitride, but the side formation of lithium nitride or boride (due to the temperature: 400 °C) was too large to detect the intercalation into BN [20]. Those side reactions will probably be avoided by ball milling, the intercalation occurring at room temperature

Finally, by using other mill systems, materials for the vial and balls (tungsten carbide, zirconia), liquids… there is a lot of work to do. One condition is to use only powders, except for the heavy alkali metals that melt during the milling.

REFERENCES

[1] B. Clarke and J.A. Kitchener // *Br. Chem. Eng.* **13** (1968) 991.

[2] P.C. Kapur, A.L. Mular and D.W. Fuerstenau // *Can. J. Chem. Eng.* **43** (1965) 119.

[3] R. Janot and D. Guérard // *Carbon* **40** (2002) 2887.

[4] R. Janot and D. Guérard // *J. All. Comp.* **333** (2002) 302.

[5] R. Massart // *C.R. Acad. Sc. Paris* **291** (1980) 1.

[6] N. Randrianantoandro, A.M. Mercier, M. Hervieu and J.M. Grenèche // *Mat. Let.* **47** (2001) 150.

[7] R. Janot and D. Guérard // *Carbon 2002,* Pékin, 15-20/9/2002, H062.

[8] D. Guérard and A. Hérold // *C. R. Acad. Sc. Paris* **275C** (1972) 571.

[9] D. Guérard and A. Hérold // *Carbon* **13** (1975) 337.

[10] V. V. Avdeev, V. A. Nalimova and K. N. Semnenko // *High Press. Res.* **6** (1990) 11; *ibid.,* **145** (1998) 2377.

[11] V. A. Nalimova, C. Bindra and J. E. Fisher // *Solid State Commun.* **97** (1996) 583.

[12] D.R. Maurice and T.H. Courtney // *Met. Trans.* **21A** (1990) 289.

[13] R.M. Davis, B. Mc Dermott and C.C. Koch // *Met. Trans.* **19A** (1988) 2867.

[14] R. Janot and D. Guérard // *Prog. Mat. Sc.* **50** (2005) 1.

[15] D. Guérard, N. E. Elalem, S. El Hadigui, L. Elansari, F. Rousseaux, H. Estrade-Szwarckopf, J. Conard and P. Lauginie // *J . Less Com. Met.* **131** (1987) 173.

[16] L. Elansari, L. Antoine, R. Janot, J.C. Gachon, J-J. Kuntz and D. Guérard // *J. All. Comp.* **329** (2001) L5.

[17] D. Guérard and R. Janot // *J. Met. Nanostr. Mat.* **24-25** (2005) 275.

[18] R. Janot and D. Guérard // *Carbon* **40** (2002) 2887.

[19] A. Métrot, D. Guérard, D. Billaud and A. Hérold // *Synthetic Metals* **1** (1980) 363.

[20] D. Guérard, unpublished results (1967)