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Ball-milling with a fluid: A powerful means for new syntheses

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Abstract

By reactive ball-milling in the presence of a fluid (either liquid as dodecane or gaseous as hydrogen), it is possible to synthesize nanomaterials as diverse as: alkali metal hydrides; well-crystallized highly anisometric graphite (HAG) whose typical particle size is a thickness of 40 nm for a mean diameter of several micrometers; a superdense lithium–graphite intercalation compound: LiC_3; maghemite (γFe_2O_3) and its composites with graphite. Most of those compounds present interesting electrochemical properties and can be used as anodes in lithium-ion batteries. Depending on the system, the role of the fluid can be either a shock moderator, avoiding the amorphization of the material (e.g. graphite), or a reagent (e.g. hydrogen forms alkali metal hydride, water oxidizes transition metal powders). Some reaction mechanisms are described in this paper with a particular attention to the oxidation by water of chromium, nickel and copper.

Keywords: Electrode materials; Nanostructures; Mechanochemical synthesis; X-ray diffraction

1. Introduction

The efficiency of materials used as anodes in lithium-ion batteries supposes a high rate for the charge–discharge process and a high capacity. Numerous attempts in this direction [1,2] were made by milling graphite or other carbon materials, which decreases the size of the particles and can form porosity where extra lithium can be inserted (compared to LiC_6 the well known graphite intercalation compound [3]). However, dry milling leads to a partly amorphous powder [2] and, if larger lithium amounts can be intercalated, the irreversible capacity is largely increased and the overall reversible capacity remains close to that obtained by large graphite particles. Moreover, the potential for desinsertion (versus Li^0) is also increased, which reduces the interest of the small gain in capacity.

By adding a liquid as moderator in the vial together with graphite powders and milling balls, one decreases the intensity of the shocks, thus the degradation of fragile materials such as, for instance, graphite. Moreover, the use of a planetary mill favors the tangential shocks and the cleavage of graphite and the presence of a liquid prevent the sticking of the graphite particles, which remain very thin. The resulting powder is completely different of that prepared by dry milling, which leads always to a partly amorphous material. Dodecane is used as liquid: $C_{12}H_{26}$ (melting point: −9.6 °C, boiling point: 216.3 °C, vapor pressure at 25 °C: 16 Pa), which is inert towards metals, including the alkali metals.

For the synthesis of transition metal oxides, we have added water rather than ethyl alcohol, often used in ball-milling for several purposes, e.g. for the activation of materials for hydrogen storage, oxidizing material, enrichment in one metal in alloys . . . Numerous papers are related to its use [4–7]. Our choice of water for the oxidation of transition metals due to the fairly high vapor pressure – highly inflammable of ethyl alcohol – around room temperature. Moreover, it seems that H_2O and EtOH present oxidizing properties close to each other [8].

2. Experimental

2.1. Milling tools

The mill is a planetary one: Retsch PM400. It favors the friction mode, which is very interesting in the case of lamellar materials as graphite. The home made vials (Fig. 1) are in a special hard treated steel: Z200C12, 12% of chromium, 2% of carbon in weight, they are tightened by a rubber gasket and present an internal volume of 270 cm^3, the balls are in stainless steel (diameters: 5, 10 and 20 mm). A special cover is designed to introduce pure hydrogen under 15 bar.

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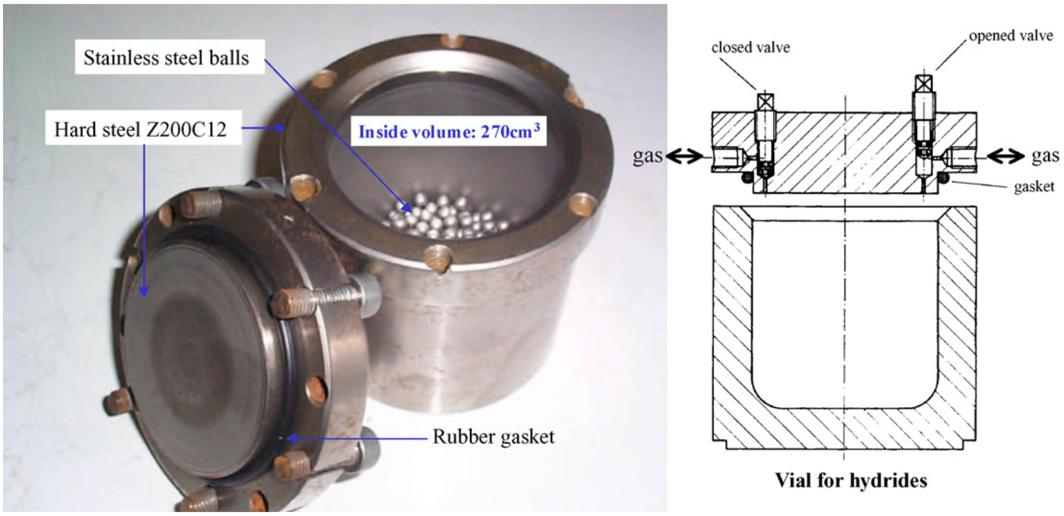

Fig. 1. Vial for the syntheses. The right part shows the special cover used for hydride synthesis.

2.2. *Preparation of graphite nanocrystals [9]*

When graphite powder is milled together with water, the resulting powder, consisting mainly of well-organized graphite nanoparticles, presents a magnetic behavior more important than that predicted for metallic particles coming from the abrasion of milling tools. In fact, the magnetic impurities come from the oxidation by water of the milling tools resulting in maghemite (γFe_2O_3) formation. One has to note here that only maghemite is formed under those conditions, there is no formation of chromium and/or nickel oxides. This gives an interesting trend that chromium and nickel are much more difficult to oxidize than iron. To avoid such a side reaction, we have used dodecane as shock moderator.

The milling conditions are: 5 g of Ceylon type graphite powder commercialized by Alfa (mean diameter: 40 μm) are milled with 50 cm^3 of dodecane, 200 g of stainless steel balls (5 mm) for 12 h at 200 rpm. The resulting powder is made of very well-crystallized graphite nanocrystals (often single crystals) whose typical dimensions are: 40 nm in thickness for a diameter of several micrometers, which makes them highly anisometric graphite (HAG) particles. They are characterized by a small irreversible capacity (half that of the pristine powder) when used as anode material in lithium-ion batteries. The reason is due to the milling mechanism itself: the planetary mill favors the friction mode, thus the cleavage of graphite. This cleavage occurs preferentially at the grain defects, which are mainly responsible of irreversible capacity because grain defects lead to a strong electrolyte decomposition. In other words, a large part of defects in graphite vanishes by wet ball-milling, which is unforeseen with a milling method.

2.3. *Synthesis of LiC_3 a superdense graphite lithium compound*

The electrochemical capacity corresponding to the formation of LiC_6 from graphite is 372 mAh/g. By applying a pressure of 50 kbar, at 300 °C, on a mixture of Li and graphite powders (initial composition Li + 2C), it is possible to synthesize a superdense compound LiC_2. This compound is named superdense since its lithium content is three times higher than that in LiC_6, for the same unit cell volume. Unfortunately, this compound is unstable when the pressure applied for the synthesis is released and decomposes slightly (in 1 year) into LiC_6 and free lithium. Locally and instantly, the ball-milling involves pressure and temperature close to those required for LiC_2 synthesis. A superdense phase LiC_3 can be formed by ball-milling and the capacity at the first deintercalation is close to the theoretical value (1000 mAh/g), but, unfortunately the superdense compound is not formed back during the electrochemical intercalation and the following capacity is that corresponding to the formation of LiC_6 [10]. The synthesis conditions are as follows: 5 g of Li + C powders are milled with 1 cm^3 of dodecane and 200 g of balls (5 mm) for 12 h at 200 rpm. The quantity of dodecane may appear as negligible; in fact, its role is somehow special: it avoids a simple sticking of lithium on the milling tools and, allows lithium to act as a shock moderator. Without dodecane, balls and vial are covered by lithium and the graphite, containing only traces of lithium, becomes amorphous upon milling [11].

2.4. *Synthesis of alkali metal hydrides*

The rubidium and cesium hydrides are not commercially available. Their synthesis is difficult, due to the low permeation of hydrogen through the hydride layer formed at the alkali metal surface. The milling technique, allowing a continuous renewal of the particle surface, appears therefore as a promising technique for the synthesis of alkali metal hydrides. The milling of alkali metals under hydrogen pressure allows the synthesis at ones of 5–30 g of MH (from NaH to CsH).

The milling is done in two steps: the rotation rate is slowly increased up to 250 rpm in order to avoid a large dispersion of metal, which becomes rapidly liquid due to the low melting points of alkali metals. Moreover, the formation of MH during that period modifies the surface tension of the liquid, decreases the dispersion and acts as a catalyst. The second step consists in keeping the rotation rate of 250 rpm for 12 h. At that time, the powder is grayish, due to the presence of a low amount of highly divided free metal, which is easily transformed into MH after heating the vial at 100 °C for a few hours [12].

2.5. *Synthesis of maghemite*

This synthesis is described elsewhere [11,13], but some aspects are reminded here since it acts as a model for the oxidation of other transition metals. Maghemite is obtained using the following synthesis conditions: iron powder (5 g), water (50 cm^3), stainless steel balls (200 g of balls with 5 and 10 mm in diameter in the weight ratio 1:1), 48 h of milling at 200 rpm.

In order to determine the exact nature of the iron oxide resulting of the synthesis, XRD is efficient to distinguish hematite (αFe_2O_3) from magnetite (Fe_3O_4) or maghemite (γFe_2O_3): their structure differ largely. On the other hand, magnetic susceptibility measurements indicate clearly that we have got maghemite: an irreversible transformation appears around 650 °C from maghemite to hematite ($\gamma Fe_2O_3 \rightarrow \alpha Fe_2O_3$). Maghemite and magnetite whose XRD patterns are very similar, can be distinguished by chemical analysis at different milling duration [11].

It turns out that two different steps take place during the synthesis reaction (cf. Fig. 2):

- After 12 h of milling, the particle size is quite disperse (10–100 nm) and EDX spectra reveal that the larger particles are magnetite (Fe_3O_4), whereas, the smaller are maghemite (γFe_2O_3). This is confirmed by chemical analysis, since the Fe^{2+} atomic content is about 12% (24% for pure magnetite).

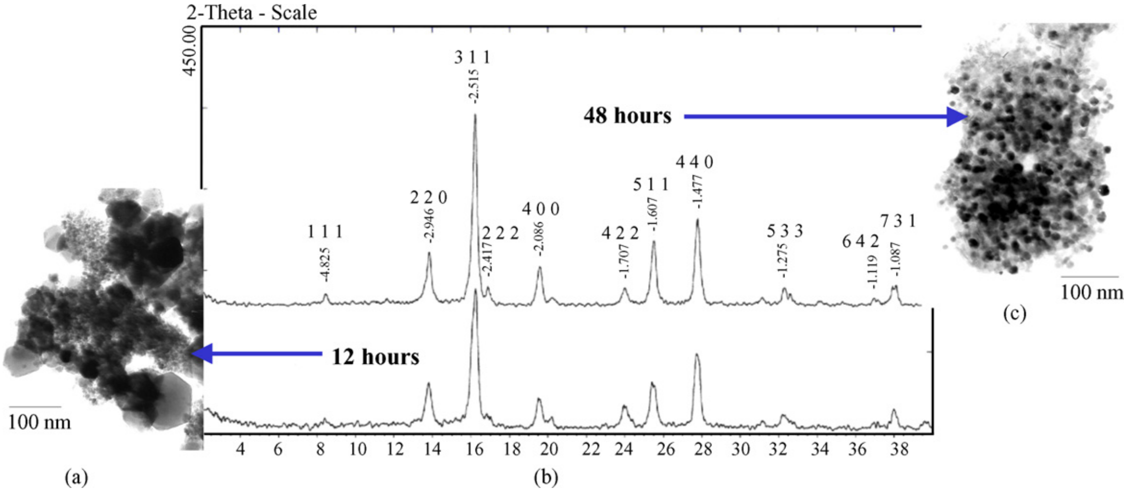

Fig. 2. XRD and TEM of iron powder milled within water at 200 rpm for 12 h (bottom) and 48 h (top).

- After a milling of 48 h, the Fe^{2+} content is reduced to less than 1%, which emphasizes the γFe_2O_3 formation. The particle size is monodisperse: 15 ± 5 nm, which is in good agreement with the disappearance of magnetite.

The TEM observations point out the large difference between the 12 and 48 h ball-milled powders. Manganese and cobalt behave similarly but the reaction requires a larger efficiency of the shocks: the rotation rate is increased up to 300 rpm [14], the volume of water is decreased down to 5 cm^3 (quantity large enough to oxidize 5 g of a transition metal) and the balls are of three different sizes (5, 10 and 20 mm, in the ratios 1:1:1). The mixture of different sizes for the balls involves an increase of the shock intensity: the small balls are projected with a high speed by the shocks with the large balls and the milling becomes more efficient. On the other hand, the 1:1:1 ratio corresponds to the best experimental results.

2.6. Oxidation of chromium, nickel and copper

The above milling conditions are also used for the oxidation of Cr, Ni and Cu powders, but the milling duration is however increased up to 72 h. Chromium and nickel lead to large particles and the corresponding XRD diagrams reveal a mixture of un-reacted metals and binary oxides (cf. Fig. 3). These oxides contain iron, which comes from the milling tools, and their stoichiometry is

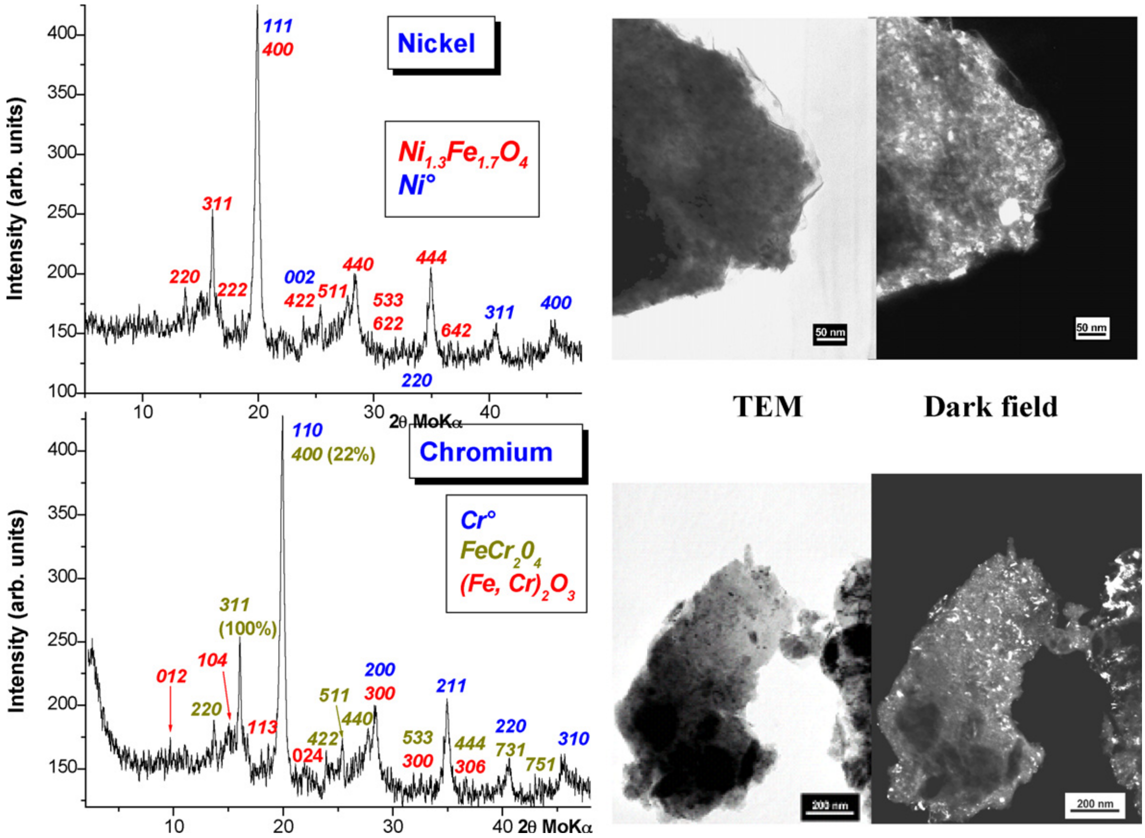

Fig. 3. XRD diagram and TEM pattern of Cr and Ni powders milled with 5 cm^3 of water at 300 rpm, 48 h.

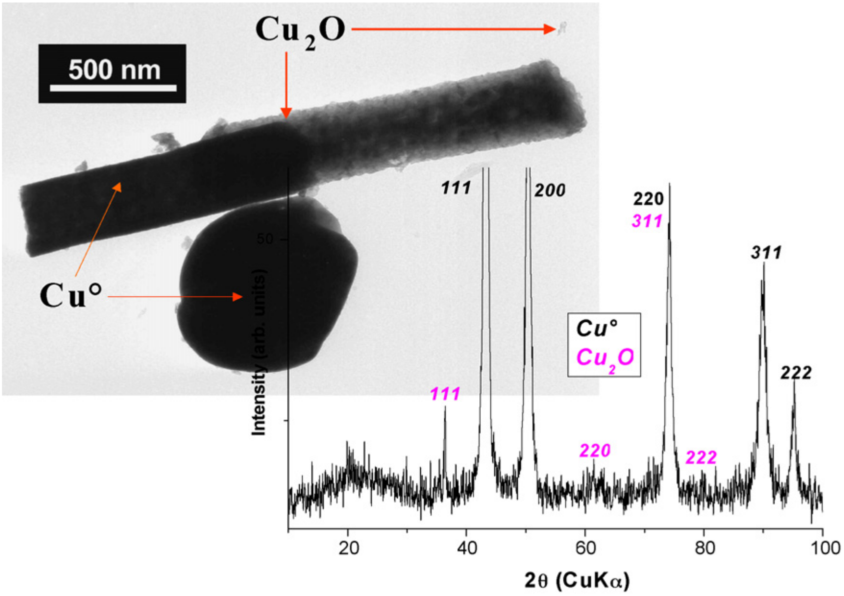

Fig. 4. XRD diagram and TEM micrograph of copper powder milled with 5 cm^3 of water at 300 rpm, 48 h.

mainly M_3O_4 with a variable Fe/Cr or Fe/Ni ratio. The shape of the particles differs largely from that of maghemite, the latter exhibiting particle size less than 100 nm after 12 h of milling and around 15 nm after 48 h (cf. Fig. 2). In the case of Cr and Ni, the particles are several hundreds of nm large. The dark field image points out the presence of small structural domains and shows that the oxidation remains superficial and that the underneath metal remains not oxidized.

The oxidation mechanism leading to binary oxides containing iron and nickel (or chromium) is probably as follows: the iron coming from the milling tools forms an alloy at the metal (Cr or Ni) surface. Then, iron, which is easily oxidized, acts as a catalyst for the formation of binary oxides. Nevertheless, the oxidation remains largely incomplete, even after 72 h of milling. This experiment seems to point out the role played by iron for chromium oxidation and the following question arises: *is the presence of iron necessary or not for the oxidation of chromium by water?*

In order to answer to this question and try to synthesize pure chromium oxides, the milling was done with iron free milling tools. The use of milling tools made of tungsten carbide was avoided, since cobalt is often used for the sintering of WC powders. Therefore, vial and balls in zirconia were used, but chromium seems not oxidized at all after 72 h of milling, which confirms the role of iron in the enhancement of Cr oxidation when ball-milled within water.

Another experiment was performed with a chromium–iron alloy (∼Cr_3Fe) milled with the same zirconia milling tools. The alloy reacts with water and leads to the formation of $FeCr_2O_4$ according to the following equation:

$$FeCr_3 + 4H_2O \rightarrow FeCr_2O_4 + Cr + 4H_2 \quad (1)$$

This confirms that the presence of iron is necessary for chromium oxidation.

The behavior of copper is particular: its oxidation occurs only at the particle surface. The formed layer is peeled by the shocks and leads to small Cu_2O particles (Fig. 4) as shown also by EDXS.

3. Discussion

The metals whose oxidations are described in this paper behave quite differently. Chromium alone is not oxidized by water, but it can however lead to the formation of a binary oxide together with iron coming from the milling tools. On the other hand, copper is only oxidized into Cu_2O at the particle surface. Those metals are characterized by their hardness, which decreases from Cr to Ni and finally Cu. This parameter could explain the difference of behavior towards the oxidation by water: chromium and nickel particles are hard and therefore are not broken by milling. The surface of the large Cr and Ni particles reacts with 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). This agrees well with the TEM observations: the particles remain quite large, but the dark field image points out small oxide particles at the surface (Fig. 3). The formation of oxide particles differs completely with iron milled within water (Fig. 2), for which aggregates of very small (15 nm) maghemite particles are obtained.

On the other hand, copper particles are not broken upon milling due to high Cu ductility. The Cu particles are only deformed by the shocks as pointed out by the particular shape of particles shown in Fig. 4: 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 is much more fragile than the underneath copper, it is removed upon milling to form small particles.

4. Conclusions

The reactive ball-milling in the presence of a fluid, easy to deal with, is a powerful mean for the synthesis of various compounds, crystals and composites. The nature of the fluid is a key point: depending on the system, the role of the fluid can be either a shock moderator, avoiding the amorphization (e.g. graphite), a lubricant, which avoids the lithium sticking on the milling tools (LiC_3) or a reagent (e.g. hydrogen forms alkali metal hydride, water oxidizes transition metal powders). Some reaction mechanisms can be described, especially for the oxidation by water of some transition metals.

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