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The influence of the composition of atmosphere on the mechanisms of degradation of graphite in planetary ball millers

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ABSTRACT

This study focuses on the degradation process of graphite in a planetary ball miller. It is shown that this degradation is only related to the milling mode. The sliding mode is very gentle toward the graphite structure whereas the shock milling mode leads to the quick degradation of the graphite structure producing poorly organized nanoparticles. Nevertheless, the milling mode is not determined by the ball miller rotation speed but by the ability of graphite to form a lubricating layer. The development of this lubricating layer in only possible in presence of oxygen which annihilates the reactive sites created during milling by forming oxygen groups. In this case, the sliding mode predominates. When the oxygen disappears or under inert atmosphere, the reactive sites stick to the ball surface, destroying the graphite lubricating layer and resulting in shock milling mode. This explains the link between the milling atmosphere and the graphite structure evolution in planetary ball millers. This also explains why the sliding milling mode is not possible.

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In the case of carbon materials, mechanical grinding can be used to produce a material with specific properties or it can be used as a model experiment for processes taking place during their use in industrial applications. For this latter case, we can mentioned the example of carbon-based materials which are used as friction materials for industrial applications going from brushes in fuel pump motors to brakes in aircrafts and racing cars. The rubbing behavior of these carbon materials depends on the friction conditions (load, sliding speed, temperature) [1,2] but also on the environment. First demonstrated by Savage and Campbell on graphite brushes [3,4], the influence of water, oxygen and all lubricating vapor on wear, friction and friction film morphology were widely studied, especially on pin-on-disc and disc-on-disc dynamometers [5-7]. Beside the film morphology study, several papers focused also on the analysis of the chemical, physical and textural properties of the debris generated during the rubbing of the carbon materials [8-10]. The similarity between the characteristics of the debris and of the carbon materials resulting from milling underlines that there is an analogy between the two processes. Therefore, studying the milling mechanism can be also useful to obtain a better knowledge of the evolution of carbon materials submitted to highly energetic mechanical stresses similar to what encountered during friction.

Mechanical grinding has been widely used to modify the structure or the surface chemistry of carbon materials [11-14]. Milling of graphite enables to obtain high surface area graphite (HSAG) with unusual nanostructures like nanoonions, graphite nanoplatelets with a low number of stacked graphene layers, etc. [15-17]. Graphite milling in inert or hydrogen atmosphere is also a promising technique to prepare anodic materials for lithium-ion batteries [18,19] or hydrogen storage systems [21,20], respectively. The strong influence of the gas atmosphere on carbon structure evolution under planetary ball milling was reported by several authors [22]. Under hydrogen, the structure of a graphitic material is quickly transformed into poorly organized nanoparticles that chemisorb large amounts of hydrogen chemically bonded to the carbon. The presence of C-H bonds shows that the highly reactive sites created during milling which are able to decompose gaseous hydrogen. Under inert atmospheres, the graphite structure is also strongly affected and the reactive sites created during the milling react when exposed to air, leading to the formation of surface oxygen groups by oxygen chemisorption. Moreover, the milling also strongly modify the specific surface area of the graphite and values as high as $400 \,\mathrm{m}^2/\mathrm{g}$ can be reached.

On the contrary, the graphite structure is preserved and a low surface area is maintained under oxygen milling in the same apparent mechanical conditions as shown by Ong and Yang by XRD analysis [22]. This phenomenon is attributed to the reaction between the reactive sites and the oxygen during milling. Ong et al. proposed that oxygen suppresses the fracture rate by forming

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Fig. 1. Sound intensity emitted by the miller recorded during 3 min at 300 rpm (a) without graphite under oxygen, (b) with graphite under argon, and (c) with graphite under oxygen.

oxides on the active centres. However the influence of the gas atmosphere is far less sensitive in vibratory milling devices. Indeed, in the case of vibratory milling the milling mode is mainly a very energetic shock type interaction whereas in a planetary ball mill, two different milling modes may occur. The first one is a gentle sliding of the balls along the material while the second one is shock type interaction similar to the one observed in vibratory milling. In the latter mode, the energy transferred to the material is far higher than in the former one, leading to an important degradation of the graphite material. The two modes can therefore lead to different materials [23]. The milling mode is generally thought to be controlled by the ball miller rotation speed. A low rotation speed should lead to a sliding mode whereas high planetary ball miller speed should lead to an impact mode.

The milling mode in which the planetary ball miller is running can be easily detected by the analysis of the sound emitted by the experimental setup: the sound intensity during the shock mode is significantly higher than in sliding mode. Therefore, the objective of this study is to show how the milling mode is controlled by the gas atmosphere during a planetary ball milling of graphite and how this milling mode can lead to different degradation states of graphite. The understanding of the influence of the milling mode on the carbon degradation is a necessary prerequisite before studying the influence of the gas environment during milling.

To reach this objective, a graphite (SLX-50 from Timcal SA -Bodio - Switzerland) was milled in a planetary ball miller with five balls and a jar in stainless steel (Fritsch Pulverisette 6). The rotation speed of the planetary ball miller was chosen at 300 rpm. The jar was equipped with two taps enabling to fulfill the jar with the desired gas but also to follow up the gas phase composition and pressure. The gas phase composition was measured by calibrated mass spectrometry (Inficon Transpector 2) and the pressure by a pressure gauge (1000 Torr MKS Baratron). The specific surface area of the milled carbon materials was obtain by applying the BET model on the nitrogen adsorption isotherm at 77 K in the relative pressure range [0.05–0.3]. The XRD spectra were measured for the milled materials (spectrometer Philips X'pert 2000, monochromatised wavelength Cu k α at 1.5405 Å, range 10–60°, count time 5 s per 0.05° step). The mean thickness of the graphite crystallites L_c was obtained by applying Scherrer's equation on the $d_{0.02}$ peak of the carbon material.

When the miller operates without any carbon material in an oxygen atmosphere, the shock mode is observed as shown by the high mean sound intensity recorded (Fig. 1a). If graphite is added in the jar with an argon atmosphere, the sound intensity recorded is exactly the same as the one measured with an empty jar, showing



Fig. 2. Evolution of the mechanism of milling inside the ball miller in correlation with the oxygen concentration inside the jar.

that the milling mode is again the shock mode (Fig. 1b). This shock milling mode persists during the whole experience of the graphite milling. After 2 h of milling at 300 rpm under argon atmosphere the specific surface area reaches $400 \text{ m}^2/\text{g}$ (see Fig. 3b). This increase of the surface area is also related to a strong degradation of the structure of the material. The Fig. 3a shows that the mean crystallite thickness L_c decreases from 210 Å down to 60 Å during these first 2 h. On the contrary, when the milling atmosphere is oxygen, the milling behavior changes (Fig. 1c). During the first 15 s of milling, the intensity emitted by the experimental setup is high, roughly similar to the one observed during milling under argon. This shows that the beginning of the milling occurs in the shock mode. After this transition phase, the sound intensity quickly decreases to a level which is typical of a sliding mode of milling. As this transition occurs



Fig. 3. Influence of the atmosphere in the jar on the evolution of the structural and textural parameters of the milled material. (a) Average crystallite thickness L_c and (b) BET surface area S_{BET} .



Fig. 4. MEB images of the surface of the balls after a milling of graphite during 3 min. (a and b) Under argon and (c and d) under oxygen.

after only 15 s, it cannot be related to some structural modification of the graphite material.

At 300 rpm, the sound recording presented in Fig. 2 shows that this sliding mode phase persists during 1 h 30 min. Then, an intermediate step which have a duration of around 1 h is observed in which the miller operates alternatively in sliding and shock modes. This is shown on the sound record by the fast switch between high and low sound intensity (see Fig. 2). This change of the milling mode can be related to the evolution of the gas phase composition in the milling jar. In fact, the oxygen content in the jar atmosphere decreases during the milling. After 1 h 30 min, about 70% of the initial amount of oxygen is consumed by chemisorption on the graphite reactive sites. A small part of the oxygen chemisorbed groups are then released as CO₂. The duration of this intermediate step in which the miller operates alternatively in sliding and shock modes is 1 h with our experimental conditions. When the oxygen and the CO₂ are almost consumed, that is after 2 h 30 min, the milling continue under vacuum conditions and the mechanism changes to the shock mode. As it was mentioned in the introduction. the modification of the milling mechanism has a great influence on the evolution of the properties of the carbon material. Fig. 3a and b shows the evolution with the milling duration of the specific surface area and of the average thickness of the crystallites L_c of the carbon material, respectively. Under argon, the graphite is quickly degraded and its surface area increases up to $500 \text{ m}^2/\text{g}$. At the same time, the L_c value decreases down to 50 Å. This shows that the milling quickly leads to the formation of carbon nanoparticles with a low structural order compared to the pristine graphite. Under oxygen, the degradation of the structure of the carbon material is significantly lower than under an inert atmosphere, this behavior was already observed by Ong and Yang [22]. In our experiments, the

sliding mode is observed during the first 2 h of milling, the rate of degradation of the graphite material is low and the increase of the TSA value is not significant. During this phase, the level of structural order is not modified and the mean L_c value is close to the pristine one.

Then, between 1 h 30 and 2 h 30 min of milling, a period alternating sliding and shock modes takes place. This step is also characterized by a decrease of the oxygen concentration in the jar. The modification of the milling mode leads to a significant increase of the TSA of the graphite which is the indication of an increase of the rate of degradation of the carbon material. As a consequence, the rate of creation of active sites on the carbon surface increases. This phenomenon induces an increased consumption of the oxygen and enhance the transition to the shock mode. Therefore, a feed-back loop is created which leads to a quick change from sliding mode to shock mode. The XRD analysis of the milled materials shows that during this transition phase, the global structural ordering of the material is mainly kept. Therefore, this change in milling mode is not directly related to a strong modification of the bulk material.

After 2 h 30 min, the milling mode transits in a pure shock type mode as shown by the sound intensity (Fig. 2). The oxygen disappears from the gas atmosphere after 3 h of milling. Although less reactive toward the surface of the carbon material than O_2 , the CO_2 resulting from the carbon–oxygen reaction, is also consumed by the active sites after 4 h. The jar atmosphere can then be assimilated to vacuum. In such conditions, the shock mode is the predominant one leading to a quick destruction of the graphite structure and to an increase of the surface area as it is observed under argon atmosphere. This is confirmed by the strong decrease of the value of the L_c parameter from 210 Å to 90 Å in less than 1 h of milling. Therefore, our results clearly point out that the degradation pro-



Fig. 5. MEB images of the surface of the balls after a milling of graphite during 6 min, the balls have been cleaned by compressed air. (a) Under argon and (b) under oxygen.

cess in the planetary ball miller are strongly linked to the change of the milling mode which is itself controlled by the gas atmosphere present during the milling of graphite.

To explain this behavior, a SEM analysis of the surface of the balls was performed after 3 min of milling under argon and oxygen. The Fig. 4a and b shows the surface of the ball after 3 min of milling under argon. The graphite particles are randomly distributed on the ball surface. On the contrary, under oxygen the graphite particles lie parallel to the ball surface forming a lubricating graphite layer (see Fig. 4c and d).

The surface of the balls was then cleaned by compressed air (Fig. 5). For the ball used during the milling under argon, a carbon layer remains at the surface indicating that an adhesive carbon layer was formed during the milling (Fig. 5a). On the contrary, in the case of milling under oxygen, the graphite layer is completely removed from the ball surface after cleaning and the stainless steel surface is apparent (Fig. 5b). Therefore the oxygen seems to inhibit the adhesion of graphite on the steel ball. Under inert atmosphere (argon, vacuum), the impacts of the ball creates highly reactive sites on graphite which cannot be stabilized by reactions with the jar atmosphere since O_2 and CO_2 are not present. As a consequence, the existence of these sites promotes the strong stick of the graphite on the steal ball surface. On the contrary, in the case of milling under oxygen, the oxygen and the carbon dioxide from the atmosphere react with the reactive sites and hence prevent the adhesion of graphite on the ball surface. The particles are adsorbed on the surface through low energy interactions along basal planes. The orientation of the graphite particles is parallel to the sliding direction and a lubricating layer is formed. This lubricating layer prevents the ball to be carried by the jar motion. Thus, the planetary ball milling of graphite under oxygen operates under a sliding gentle milling mode. Under argon, the lubricating layer is not formed. The graphite particles are randomly distributed creating roughness. As the ball is rough, it is carried by the jar motion and centrifugal forces take the ball down the jar wall. Then, the ball is projected on the opposite jar wall leading to a shock mode milling.

In summary, the influence of the gas atmosphere on the evolution of the carbon properties in a planetary ball miller must be studied by taking into account the milling mode (sliding or shock mode). Our work clearly highlights that this milling mode is not directly controlled by the operating conditions, and that it can change during the milling depending on the evolution of the composition of the atmosphere inside the jar. This change in milling mode has then a great influence on the evolution of the properties and on the nature of the milled material.

The sliding mode is very gentle toward the graphite structure whereas the shock milling mode leads to a quick degradation of the graphite structure characterized by a strong evolution of its texture and of its structure. As a consequence nanoparticles with a low structural organization are produced. Nevertheless, the milling mode is not determined by the ball miller rotation speed but by the ability of the graphite to form a lubricating layer or not. This layer prevents the existence of the shock mode. The development of a graphite lubricating layer in only possible in presence of oxygen (or some other reactive molecule) which annihilates the reactive sites created during milling by forming functional groups. In this case, the sliding mode predominates. When the oxygen is consumed or under inert atmosphere, the reactive sites can not react anymore with the jar atmosphere; the milled graphite sticks to the ball surface and the graphite lubricating layer disappear, promoting a shock milling mode. Hence, the link between the milling atmosphere and the graphite structure evolution in planetary ball milling can be explained. This also explains why the graphite structure evolution is far less sensitive toward environment in a vibratory ball miller in which the sliding milling mode is not possible [22].

Our work underlines that the study of the influence of the milling atmosphere on the evolution of the graphite characteristics requires to carefully determine the type of milling mode existing during the milling. In other words, it is not possible to establish a correlation between the carbon degradation during milling and the gas atmosphere without taking into account the different milling modes which can occur in planetary ball millers.

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