Strain-free graphite nanoparticle synthesis by mechanical milling

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A B S T R A C T
Graphite nanoparticles are synthesized by comminution of coarse graphite particles over an extended period in a ball mill. The size reduction is modelled using artificial neural network to develop a predictive tool to minimize contamination due to attrition in the ball mill. The particle size analysis and microstructural characterization were carried out using X-ray diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy. It was found that the strain stored in the graphite lattice reaches a saturation value and remains constant during extended milling. Thermal annealing at 600 °C for 1 h effectively relieves the residual stresses so that the nano-sized graphite particles are stress free. This paper demonstrates that mechanical milling can be an effective tool to synthesize stress free nanosized graphite particles in bulk.

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1. Introduction

Pure graphite nanoparticle synthesis using top down approach is still a significant challenge. Due to the difficulties of synthesizing pure graphite nanoparticles several researchers have modified their approach to synthesis of graphite nanoparticle with reduced contamination, which is well discussed in the literature [1–4]. Graphite in various forms is of research and industrial interest due to its unique properties. Some of the popular applications include solid lubricant, arc lamp electrode, refractories, batteries, brake linings and foundry facings. In the last decade several applications involving graphite nanoparticles, such as flexible and conductive support of anode materials for lithium ion batteries, highly conductive enzyme biosensor for electrochemical glucose detection, reinforcement of electrospray polycrylonitrile nanofibres, conductive additives in composite or coating materials, and the raw materials for preparing industrial diamond have seen the light of day [5–10]. The most popular approach for synthesizing graphite nanoparticles in large quantities is by mechanical grinding in a ball mill [11–13]. However, crystalline graphite has a layered structure with strong in-plane covalent bonds and weak Van der Waal bonds across layers. Such a structure is not amenable to fracture and makes grinding extremely difficult, especially to obtain submicron particle sizes [14]. In the present work a modelling effort is undertaken to understand the graphite particle size reduction until nanoparticle formation during mechanical milling. Such an exercise is useful to optimize the particle size reduction process such that cumbersome intermediate particle size sampling and over-milling is avoided. Though graphite is categorized as a brittle material, it still undergoes deformation with a small amount of strain before fracture, which is discussed in this work.

2. Material and methods

Graphite powder with average particle size ~28 μm (purity 99.85%) was used as the starting material. The milling was carried out with a Planetary Ball Mill (Retsch PM100). A Stainless steel grinding jar of 50 ml capacity and 20 stainless steel balls of 8 mm diameter were used as a milling medium. In all runs, the ball-to-powder weight ratio (BPR) was 10:1 and the jar rotation speed was either 200 rpm or 250 rpm. A fresh sample was used for each ball milling run to maintain BPR and to prevent sample mixing. X-ray diffraction (XRD – D8 Advance, Bruker) studies were carried out on samples taken at regular intervals using Cu Kα (λ = 0.15406 nm) radiation to follow the progress of mechanical milling on the graphite powder. The Scanning Electron Microscope (SEM – Quanta 200 FEG, FEI) operating at 30 kV equipped with Energy Dispersive X-Ray Spectroscopy (EDS – EDAX) was used to get information on the particle size distribution, fragmentation mode and impurity analysis. The Soft Imaging System of Dewinter Material Plus (version 4.1) for professional and industrial microscopic imaging solution was utilized for measuring the mean particle size of graphite powders based on SEM images. Artificial neural network (ANN) was used to determine the average particle size dependence on milling time and to forecast the milling time for nanoparticle formation. The milled powder was analysed under the Transmission Electron Microscope (TEM – Tecnai G², FEI) operating at 200 kV for imaging and diffraction pattern analysis.
### 3. Experimentation and modelling

The milling experiment was conducted at two different speeds 200 rpm and 250 rpm for various hours of run (1 h, 2 h, 3 h, 5 h, 8 h, 10 h, 12 h, 15 h, 20 h, and 25 h) with same initial particle size of graphite. Each run was distinct with no repetition. Dewinter Material Plus is utilized for measuring the mean particle size of graphite particles from the SEM images. Based on observations of graphite particle size under SEM for all the experimental runs, database prepared with 280 input–output experimental observations and the ranges for which data was available is given in Table 1. These data are used to develop an ANN model to predict the average particle size as a function of milling time. A brief overview of the ANN approach is described here.

ANN is a modelling technique frequently used to capture the specific output variation due to influence of multiple input parameters [15–17]. ANN usually consists of at least three layers, namely, an input layer, hidden layer(s) and an output layer as shown in Fig. 1a. In ANN similar to linear regression, linear functions of the inputs $x_i$ are operated by an activation/transfer function (Eq. (1)) so that each input contributes to every hidden unit. Mathematically we can describe neural network by writing the following pair of equations:

$$u_k = \psi\left(\sum_{j=1}^{m} w_{kj} x_j + b_k\right)$$  \hspace{1cm} (1)

where $\psi$ is hyperbolic tangent transfer function; $x_1, x_2, \ldots, x_m$ are the input signals; $w_{k1}, w_{k2}, \ldots, w_{km}$ are the synaptic weights of neuron $k$; $u_k$ is the linear combiner output due to the input signals; $b_k$ are the biases, and $y_i$ is the network output signal and defined as a linear function of hidden nodes and the constant (Eq. (2)).

The data base spread used for modelling is shown in Table 1. In the present work, data were normalised according to:

$$p_n = 2\left(\frac{p_o - p_{\min}}{p_{\max} - p_{\min}}\right) - 1$$  \hspace{1cm} (3)

where, $p_n$ is the normalised particle size which lies within the range of $+0.5$ to $-0.5$. The ANN model was developed in a MATLAB environment (version 8). In developing the model, 70% of the randomly chosen data was used for training, 15% for validation and 15% for testing. Gradient Descent algorithm has been used to train the network, which apply a function minimization routine and back propagate error into the network layers as a means of improving the calculated output. The best performance of training was found with a single hidden layer comprising of 12 nodes and overall behaviour of the model is illustrated in Fig. 1b.

<table>
<thead>
<tr>
<th>Input/output</th>
<th>Parameters</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input</td>
<td>Milling speed (rpm)</td>
<td>200</td>
<td>250</td>
<td>211.9</td>
<td>21.36</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>1</td>
<td>25</td>
<td>13</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Initial particle size (μm)</td>
<td>16.71</td>
<td>47.30</td>
<td>28.25</td>
<td>7.71</td>
<td></td>
</tr>
<tr>
<td>Output</td>
<td>Particle size (μm)</td>
<td>0.39</td>
<td>1.63</td>
<td>0.88</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 1

Data base spread used for ANN modelling.

![Fig. 1.](image-url) (a) Schematic of feed forward ANN with single hidden layer, (b) shows overall behaviour of ANN model, (c) EDS results of graphite powder milled at 200 and 250 rpm, and (d) shows the mean graphite powder particle size decreases with progression of milling and arrow indicates ANN prediction which was verified experimentally.
EDS analysis was done for the milled powder after 10 h of milling at different jar rotation speeds of 200 rpm and 250 rpm, which shows that the contamination is inevitable at higher rotational speed (Fig. 1c). Based on EDS results we opted for a lower jar rotation speed of 200 rpm for graphite nanoparticle synthesis with consideration of relatively lower amount of contamination that will incur during milling. So ANN was used for particle size prediction after various hours of milling at constant milling speed of 200 rpm. The model output for the mentioned input data is shown in Fig. 1d, where dots represent the mean particle size after milling for specified time intervals. The statistical fitting curve is generated for the particle size evolution predicted from ANN model. Based on prediction made by ANN, trial runs were carried out for 70 h of milling at jar rotation speed of 200 rpm for synthesis of graphite nanoparticle with less contamination. Higher contamination is expected on continuous milling at higher rotational speed. To counter this lower rotational speeds are chosen to minimize contamination due to disintegration of the grinding media on repeated impact with each other and the jar walls. Contamination level can be further reduced by interrupting the milling at frequent intervals.

4. Results and discussion

4.1. XRD analysis

X-ray diffraction patterns of milled graphite powder samples taken at several time intervals are shown in Fig. 2a. The diffraction pattern was used to follow the structural evolution during milling. Williamson–Hall method was used to determine the grain size and lattice strain using Eq. (4) [11] which is based on peak broadening of the diffraction pattern due to the internal strain \( \varepsilon_{\text{strain}} \) and grain size \( \varepsilon_{\text{size}} \).

\[
\beta \cos \theta = 0.9 \lambda / d + 2\varepsilon \sin \theta
\]  

(4)

where \( \beta \) is FWHM (full-width at half maximum) of diffraction peak (rad), \( \theta \) is the position of peak in the pattern, \( d \) is the average crystal size, \( \varepsilon \) is the residual strain in the lattice. A standard defect-free silicon sample was used to correct for instrumental broadening \( \varepsilon_{\text{bulk}} \). A Gaussian peak profile analysis approach is applied to estimate the broadening effect due to size reduction and induced strain according to Eq. (5) where \( \varepsilon_{\text{bulk}} \) is the FWHM of observed peak.

\[
\beta = \beta_{\text{size}} + \beta_{\text{strain}} = \sqrt{\beta_{\text{size}}^2 - \beta_{\text{bulk}}^2}
\]  

(5)

Using Williamson–Hall method, the XRD pattern of graphite powder milled for different time intervals was analysed (Fig. 2b) and fitted to a linear equation where the slope represents the lattice strain and the y-intercept is a constant.

From the XRD analysis it is evident that the graphite particles have not lost its crystallinity even after prolonged milling. Graphite has a layered structure with strong covalent bonds in plane in a hexagonal structure and weak Van der Waals bonding between layers. The weak bond between layers is the reason for the excellent lubricating property of graphite. The strong bonds in-plane does not allow it to fragment in a finer scale, whereas, it does fracture in a brittle manner in the macro-scale with negligible strain inducement. The result obtained from XRD shows that the reduction in average particle size reaches saturation and subsequent size reduction is rather low with longer milling duration. Significantly, the lattice strain is nearly constant for all the milled samples. The milled graphite powder was heated at 600 °C for 1 h to relieve stresses (Fig. 2c).

4.1.1. Induced strain evaluation in graphite during milling

The mechanical milling of graphite causes a measurable permanent strain in the lattice. Deviation in interplanar spacing is an indirect indication of dimensional variation in the lattice structure. Based on observations inferred from XRD pattern (refer Table 2) it is clear that basal

<table>
<thead>
<tr>
<th>Condition</th>
<th>2θ (°)</th>
<th>Relative intensity</th>
<th>Plane index</th>
<th>Interplanar spacing ( d_{\text{hl}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite (0 h milling)</td>
<td>26.42</td>
<td>100</td>
<td>(002)</td>
<td>0.3369</td>
</tr>
<tr>
<td></td>
<td>54.42</td>
<td>5.2</td>
<td>(004)</td>
<td>0.1683</td>
</tr>
<tr>
<td></td>
<td>77.44</td>
<td>2.4</td>
<td>(110)</td>
<td>0.12308</td>
</tr>
<tr>
<td>Graphite (10 h milling)</td>
<td>26.47</td>
<td>100</td>
<td>(002)</td>
<td>0.3363</td>
</tr>
<tr>
<td></td>
<td>54.45</td>
<td>4.67</td>
<td>(004)</td>
<td>0.1683</td>
</tr>
<tr>
<td></td>
<td>77.47</td>
<td>1.83</td>
<td>(110)</td>
<td>0.12305</td>
</tr>
<tr>
<td>Graphite (20 h milling)</td>
<td>26.34</td>
<td>100</td>
<td>(002)</td>
<td>0.3379</td>
</tr>
<tr>
<td></td>
<td>54.28</td>
<td>4.89</td>
<td>(004)</td>
<td>0.1687</td>
</tr>
<tr>
<td></td>
<td>77.40</td>
<td>2.71</td>
<td>(110)</td>
<td>0.12308</td>
</tr>
<tr>
<td>Graphite (70 h milling)</td>
<td>26.51</td>
<td>100</td>
<td>(002)</td>
<td>0.3357</td>
</tr>
<tr>
<td></td>
<td>54.43</td>
<td>5.18</td>
<td>(004)</td>
<td>0.1683</td>
</tr>
<tr>
<td></td>
<td>77.46</td>
<td>4.66</td>
<td>(110)</td>
<td>0.12307</td>
</tr>
</tbody>
</table>

Fig. 2. (a) XRD pattern of graphite powder after various milling times, (b) shows Williamson–Hall plot for milled graphite powder with a linear fit for each sample, (c) shows Williamson–Hall plot for heat treated milled graphite powder at 600 °C for 1 h.
planes undergo less deviation in their internal dimensions due to strong covalent bond between atoms whereas, the dimensional difference is comparatively higher in the direction normal to the basal plane. This is because the layers of sp² hybridized covalently bonded layers are bound together by weak Van der Walls bonds. Three planes, namely, (002), (004) and (110) are considered for study and the strain behaviour in graphite using Williamson Hall plot. The plane (002) is half of the basal plane contributing main peak in XRD pattern of graphite while (004) plane is the second order reflection plane of the same plane which is the second major peak in the XRD pattern. The structure of graphite is detailed elsewhere in the literature [18]. From XRD results and Bragg’s law the calculations made for interplanar spacing of above considered planes are furnished in Table 2.

The strain computation for milled powder and heat treated powder after milling was done using Williamson–Hall method and the error in strain for a set of data points is calculated using following equation:

\[
\text{Error} = \frac{1}{n} \sum_{i=1}^{n} |y_i - x_i|
\]

where, \(y_i\) is estimated strain, \(x_i\) is the strain value estimated by considering pairs of strain data. There are \(n\) such pairs. Table 3 contains the summary of the strain data and the estimated error in strain measurement. It is clear that the error in strain measurement is small compared to the strain stored in the lattice due to mechanical milling. Therefore, the measured strain is not due to any instrumental error. After milling for 10 h the strain reaches saturation and further milling does not change the lattice distortion. Nevertheless, the error associated with the measure is slightly different though its small amount authenticating the measured value. On heat-treating the milled graphite powder for 1 h at 600 °C the lattice is free from strain. The measurement confirms this as the difference in the strain measured after annealing is within the measured error of the strain data.

4.2. SEM and TEM analyses

SEM images provide information of surface morphologies and the agglomerated condition of the graphite particles. Fig. 3a shows the unit cell of graphite structure while Fig. 3b shows the SEM image of initial graphite powder where the average particle size is about 28 μm. The substantial particle size reduction and its distribution after 10 h of milling is shown in Fig. 3c which indicates that milling is an effective fragmentation process for graphite. Fig. 3(d and e) shows the TEM image and selected area electron diffraction pattern of the final milled graphite powder.

TEM image appears translucent showing polycrystalline graphite structure which indicates that mechanically milled graphite powder particles have retained its crystallinity at the nanoscale with an average particle size of 67 nm which is fairly close to the ANN model predicted value of 86 nm. Using the same method Chen et al. [13] earlier reported that particle size of graphite powder reaches nanoscale with continuous porous structure, while most work reported on ball milling of graphite leads to mixture of amorphous and crystalline phases [13,19,20]. TEM image of graphite nanoparticles confirmed the formation of nanoparticles. Most of the particles are semi-transparent which indicates that

---

Table 3

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Milling time (hrs)</th>
<th>Annealing time (hrs)</th>
<th>Strain</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial graphite</td>
<td>0</td>
<td>0</td>
<td>0.0013</td>
<td>0.0006</td>
</tr>
<tr>
<td>Milled graphite</td>
<td>10</td>
<td>0</td>
<td>0.0054</td>
<td>0.0018</td>
</tr>
<tr>
<td>Milled graphite</td>
<td>20</td>
<td>0</td>
<td>0.0054</td>
<td>0.0002</td>
</tr>
<tr>
<td>Milled graphite</td>
<td>70</td>
<td>0</td>
<td>0.0054</td>
<td>0.0012</td>
</tr>
<tr>
<td>Milled graphite</td>
<td>10</td>
<td>1</td>
<td>0.0013</td>
<td>0.0007</td>
</tr>
<tr>
<td>Milled graphite</td>
<td>20</td>
<td>1</td>
<td>0.0009</td>
<td>0.0003</td>
</tr>
<tr>
<td>Milled graphite</td>
<td>70</td>
<td>1</td>
<td>0.0004</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

---

Fig. 3. (a) Unit cell of graphite structure, (b) SEM image of initial graphite powder, (c) SEM image of 10 h milled graphite powder, (d and e) show the TEM image and selected area electron diffraction pattern of the 70 h milled graphite powder, (f) distribution of particle size for 70 h milled graphite powder.
there are very few grain boundaries in a particle and their thickness is of the order of a few nanometers. Fig. 3f shows a monotonic distribution of particle size with a very narrow size range. At this size, graphite particles are endowed with the large surface area. This is most desirable as it lends to enhanced electrical conductivity within the composite and/or coating materials even with very low graphite contents [21,22].

5. Conclusions

Mechanical milling method with modelling technique was successfully applied to raw graphite of macro size for the preparation of graphite nanopowder. Milling was done at 200 rpm as it was found that milling at a lower rpm reduced contamination. An ANN model is used as a predictive tool to follow the comminution process to optimize the milling duration to achieve a certain average particle size. The TEM result confirms that model prediction for particle size of milled graphite powder is in good agreement with experimental results. It is reported that the milled graphite powder, irrespective of the milling duration has a strain value of 0.54%. The residual strains were fully relieved when heat treated at 600 °C for 1 h. This work affirms that mechanical milling can be an economical approach to process stress-free and contamination-free graphite nanopowder in bulk.

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References


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