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Strain-free graphite nanoparticle synthesis by mechanical milling

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ABSTRACT

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 nanosized 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.

1. Introduction

Pure graphite nanoparticle synthesis using top to 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 electrospun polyacrylonitrile 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 K_α ($\lambda = 0.15406$ 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 G^2, FEI) operating at 200 kV for imaging and diffraction pattern analysis.

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Table 1
Data base spread used for ANN modelling.

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

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_j 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:

$$u_k = \varphi\left(\sum_{j=1}^{m} w_{kj}x_j + b_{kj}\right) \quad (1)$$

$$y_i = \varphi\left(\sum_{k=1}^{l} w_k u_k + b_k\right) \quad (2)$$

where φ is hyperbolic tangent transfer function; $x_1, x_2,...x_m$ are the input signals; $w_{k1}, w_{k2},...w_{km}$ are the synaptic weights of neuron k; u_k is the linear combiner output due to the input signals; b_{kj} and 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:

$$p_n = 2\left(\frac{p_0 - p_{\min}}{p_{\max} - p_{\min}}\right) - 1 \quad (3)$$

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.

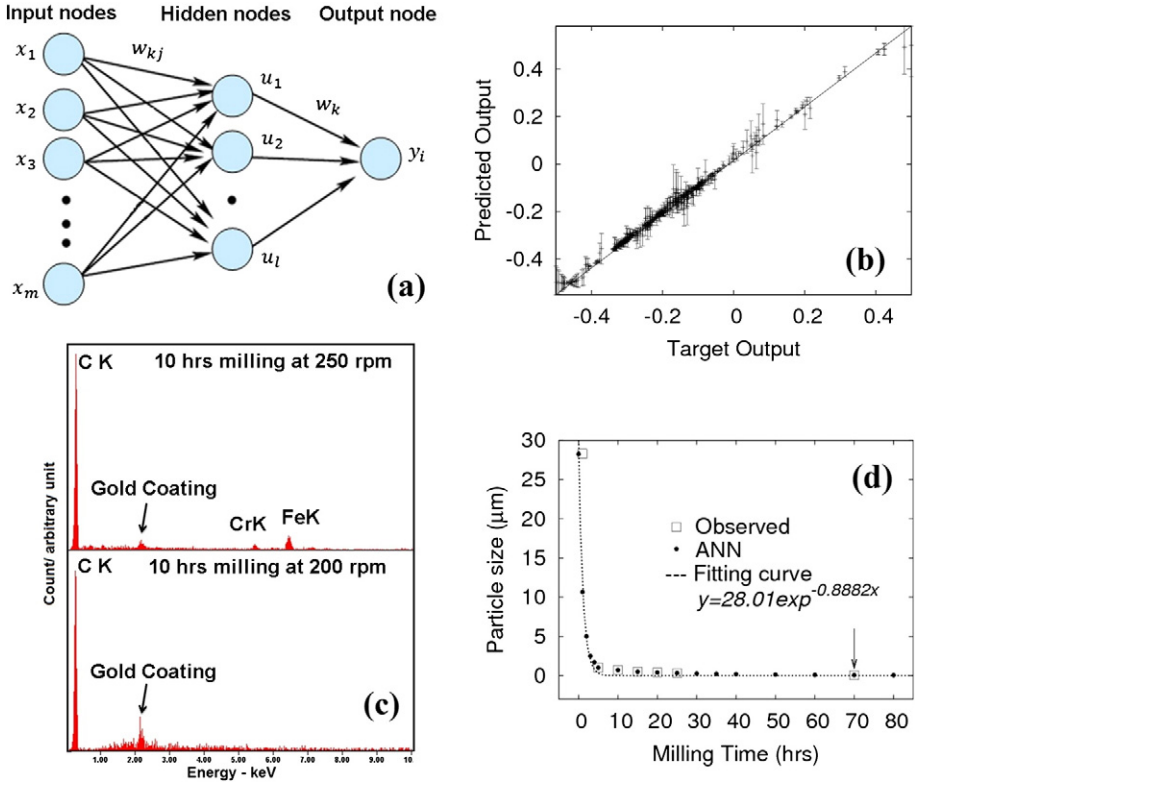

Fig. 1. (a) Schematic of feed forward ANN with single hidden layer, (b) shows overall behaviour of ANN model, (c) EDS results of graphite powder milled at 200 and 250 rpm, and (d) shows the mean graphite powder particle size decreases with progression of milling and arrow indicates ANN prediction which was verified experimentally.