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Synthesis of nanopowders under high frequency electric discharge assisted mechanical milling

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Abstract

Electric discharge assisted mechanical milling can be applied to the synthesis of a range of fine powder products, including nanocrystalline agglomerates and individual nanoparticles and nanofragments. Processing variables include: starting powder sample size; electric arc parameters such as arc length and arc voltage/current; mechanical milling parameters; gas atmosphere and ionized gas species present. We describe results of an initial experimental program underway to investigate phase transformations and/or particle fragmentation during discharge milling using a new pulsed power supply working at frequencies in the kHz range. The aims were to determine processing parameters required for the synthesis of potentially useful high surface area particles, nanostructural powders and nanoparticles and to compare products with those synthesised by Hz frequency discharge milling.

Microstructural, morphological and phase changes induced by kHz discharge milling were characterised by X-ray diffractommetry and transmission electron microscopy. Results were found to depend on the often competing processes of fragmentation into nanoparticles, agglomeration of powder particles, particle melting and/or sintering and chemical reaction induced by mechano-processing in the presence of a particular type of plasma. Discharge milling of graphite under Ar/4% H_2 resulted in a range of products including: graphite nanostructures, carbon nanotubes and other exotic nanofragments. It was found that, compared with processing at 50 Hz, high frequency (kHz) electric discharge assisted mechanical milling of graphite resulted in higher yields of carbon nanofragments. Discharge milling of hematite resulted in partial reduction to magnetite and FeO and the formation of nanostructural oxide nanorods and nanorod clusters. Discharge milling of Co–WC resulted in products including: micron and submicron fracture products, nanostructural regions of Co and WC and carbon rich nanorods.

Keywords: Nanostructured materials; Mechanochemical processing; Transmission electron microscopy; Nanofabrications

1. Introduction

Electric discharges have been extensively used in many materials processing techniques; including plasma coating, plasma synthesis of fine powders, waste processing, sintering of powders, metallurgy and, recently, for the synthesis of nanomaterials [1]. Present research efforts concentrate on new approaches for the synthesis of nanometre size structures the future growth of this technology will depend on development of new processing methods with better control of the particle size, size distribution, reproducibility and better process efficiency. Therefore, novel reactor designs are of great interest.

In previous publications we have described application of novel electric discharge assisted mechanical milling materials processing method [2–7]. This new technique involves application of high voltage, low current electrical discharges during materials synthesis and processing. Within the mill, the electrical discharges cause molecular breakdown of the controlled atmosphere, the formation of monatomic gases and, depending on the species present and discharge conditions, formation of specific types of plasma in the proximity of powder particles.

The power supplies employed for this work allowed high voltage 50 Hz discharges to occur each time physical and electrical contact was made and broken during each milling cycle, the contact being between the conducting chamber, powder particles and conducting rod or balls, depending on the device used. In the current series of experiments a high voltage high frequency (kHz range), pulsed ac power supply was used instead of the 50 Hz ac power supples employed in previous investigations. Preliminary investigations were performed involving discharge milling of small samples under an Ar/4% H atmosphere. Starting powder samples investigated included: (i) high purity graphite, known to transform under 50 Hz discharge processing, into a

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range of products, with minor fractions of nanofragments and nanotubes [6], (ii) high purity hematite, also known to transform under 50 Hz discharge processing into reduced oxide species and pure iron [7] and (iii) Co–WC hardmetal composite, crushed into powder form.

2. Experimental details

2.1. Device description

A vibrational laboratory rod mill was modified in order to a produce milling mode involving repeated impact of a hardened curved rod end on particles placed on a vibrating stainless steel hemispherical container under a controlled electrical discharge in a controlled atmosphere. During milling, gaps, of up to ∼3 mm, between the vibrating mill base, the powder particles and the loosely suspended conducting plunger occur, as illustrated in Fig. 1a. A particular type of electrical discharge was generated within those gaps. The experiments were performed using a custom built power supply, designed to generate kHz frequency range pulsed arc discharges, of variable energy and duration, superimposed on an athermal or glow discharge. The aim of the arc discharge is to locally heat up powders which are subsequently subjected to complex ac plasma treatment (Fig. 1a). The pulse current and pulse duration time (in the 20–100 ms range) can be manually adjusted to create a range of electrical conditions, as illustrated in Fig. 1b. The main electric parameters varied in this study are the current (10–800 mA range) and impulse duration time, as shown in Fig. 1b. The power supply used in this study was connected through an ac high voltage transformer, generating typically up to 3 kV and 10–800 mA impulses within the kHz range. A digital camera image of discharge in the vicinity of milled particles is shown in Fig. 1c.

2.2. Sample preparation

The following powders were processed; high purity hematite; high purity graphite and cemented WC–10 wt.% Co, crushed under liquid nitrogen into starting powder (<300 mesh). Samples were placed in the milling cell and subjected to mechanical milling with electrical impulses. Milling was performed with and without gas flow (Ar4% H_2). The small amount of hydrogen was included in the gas mixture, both to increase arcing temperature thus improving efficiency of the process, and to ensure a partially reducing environment. Throughout all experiments the Ar/H_2 gas pressure with no gas flow was maintained at near atmospheric pressure. In flow mode the flow rate at 1 atm was maintained at about 2 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. Nanoparticles formed by the processing combination of local arc heating of the powder target and plasma treatment were collected from milling cell after completion of the milling process or, in the case of flow mode, samples were immediately introduced with flow of the gas into plastic bags connected to the milling cell gas outlet. Milling times used in these experiments were within the range, 1–15 min. Powders were first analysed by X-ray diffraction (XRD), using Cu Kα radiation and graphite monochrometer. The shape and size of nanostructural particles was investigated by transmission electron microscopy (TEM) using a JEOL 2011, 200 keV analytical instrument with JEOL EDS (energy dispersive X-ray spectroscopy) analysis system. For bright field TEM examination, powders were dispersed on carbon or lacy carbon support films.

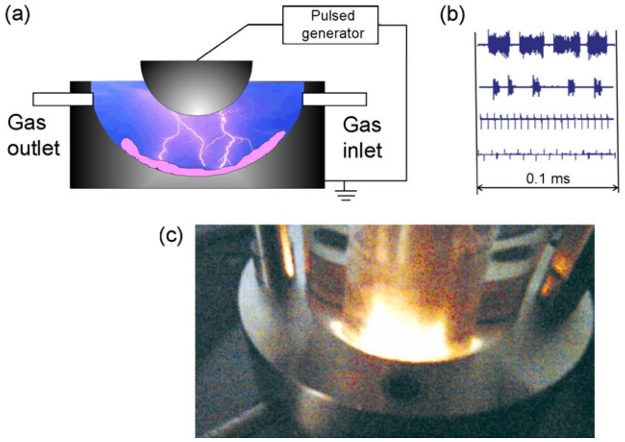

Fig. 1. Schematic of (a) electrical discharge milling cell, (b) spectra of pulsed discharges used in this work and (c) photograph of plunger base, perspex shield and mill base during discharge milling.

3. Results and discussion

In the past few years there has been a growing interest in a new class of materials called nanocrystalline, nanophase, nanostructured or ultrafine-grained materials [8–10], consisting of nanoscale particles or grains (1–100 nm). These materials, which have a very high surface or interfacial areas, exhibit exiting properties that can be utilized in many applications [11–13]. In the following we describe milling results involving the synthesis of nanopowders in graphite, hematite and cemented WC.

3.1. Graphite

XRD examination of graphite, discharge milled in Ar/H_2 revealed peaks corresponding to amorphous carbon, graphite and additional peaks which corresponded to carbon nanofragments. TEM examination confirmed the presence of graphite and amorphous carbon, and revealed a significant fraction of carbon nanofragments, some of which are believed to be carbon nanotubes, as indicated in Fig. 2 which shows low magnification image of a region containing tube-like features and high magnification inset showing what appears to be the end of a hollow tube, with outer diameter less than 2.5 nm. High resolution imaging is currently underway to determine the nature of the nanofragments formed; however, they appear to include (i) thin ribbons of graphite sheets and (ii) multi-walled nanotubes, often associated with the presence of small remelted particles of stainless steel. For example, the dark round particles, such as those marked P, were confirmed by EDS analysis to be rich in Fe, and containing Ni and Cr. Whether these Fe-rich particles play a role in nanotube formation within the discharge mill is yet

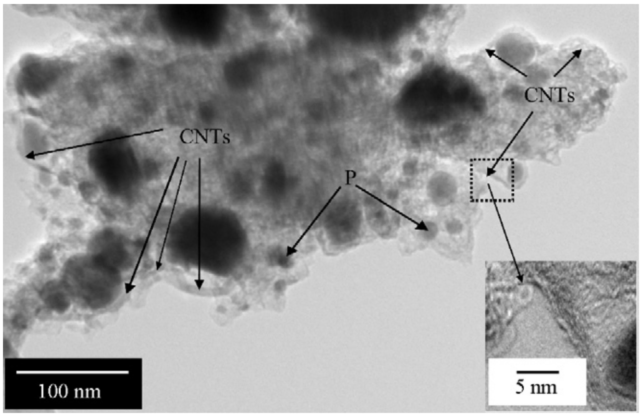

Fig. 2. Bright field TEM image of graphite discharge milling products. Spherical particles, such as those marked P, were confirmed by EDS analysis to contain Fe, Ni and Cr. Regions believed to be multi-walled carbon nanotubes are also marked, including the possible end-on nanotube in the high magnification inset.

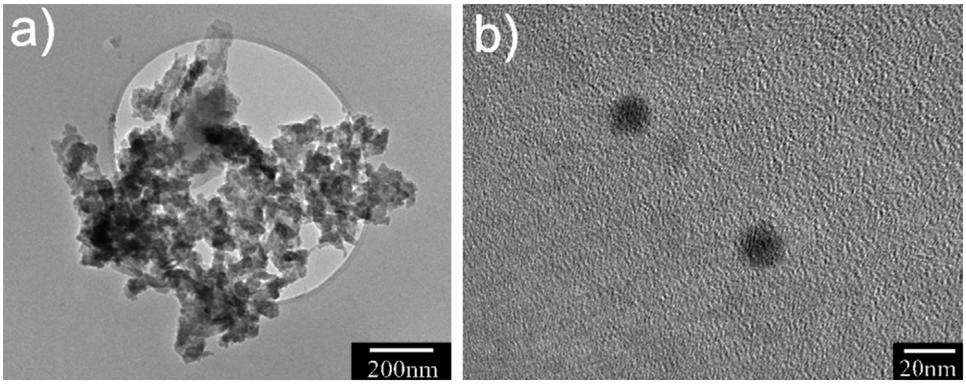

Fig. 3. (a) Nanoparticle clusters and (b) individual, isolated nanoparticles, observed in bright field TEM images of hematite, discharge milled in Ar/H_2.

to be determined. The yield of nanofragments and/or nanotubes appeared much higher than in graphite or activated carbon discharge milled using a 50 Hz power supply [6].

3.2. Hematite

XRD analysis of hematite discharge milled under high frequency for 5 min in Ar/H_2 indicated partial reduction of the starting powder, with the major product, magnetite and minor product, FeO. This result was consistent with a previous investigation, where the product of extended discharge milling (15 min in Ar/H_2) at 50 Hz frequency was magnetite, FeO and pure iron [7]. TEM examination of the product the kHz discharge milling experiments revealed a range of morphologies. Fig. 3 shows TEM micrographs of hematite milled for 5 min in ArH_2, using the electric condition; 250 mA, 0.50 kV and impulse duration time 0.02 ms. This milling condition was found to produce predominantly particles ∼20 nm in size (Fig. 3a and b).

These results, and those obtained for milled graphite, indicate that during milling a thermal plasma condition is created which is a source of very high temperatures and steep temperature gradients, which leads to the synthesis of fine powders down to the nanometer size range. The condensation of supersaturated vapor is believed to provide the driving force for particle condensation leading to the formation of nanoparticles by homogenous nucleation. Thermal plasmas suitable for the synthesis of fine powders are primarily produced by means of high-intensity arcs (ac or dc) and high-frequency discharges (RF and microwave).

Fig. 4 shows the results kHz frequency milling of hematite with relatively low electric discharge energy: 100 mA and 0.17 kV. This condition led to the formation of particles believed to be magnetite nanorods. By varying the current under these low energy milling conditions, both the length of nanorods, and the number of joined nanorods were observed to increase with increasing current. The tendency for formation of clusters of larger, parallel-joined nanorods (Fig. 4b) also increased with increasing current. However, above around 200 mA current, no nanorods were detected in the product. There is much interest in the synthesis of magnetic iron oxide nanorods [14] and other magnetic nanoparticles, as these have great potential for several applications in range of areas including: magnetic recording material, pigments, catalysts, sensors and biomedical tracing particles. A more detailed TEM investigation of oxide nanorod formation during discharge milling is currently underway.

3.3. WC–Co

Sintered WC–Co based hardmetals have formed a major basis of metal cutting, wire drawing, fitting and turning, and rock drilling industries for the past century. Unfortunately, this material is difficult to recycle directly by crushing and re-sintering due to chemical reaction during initial processing, leading to dissolution of carbon in the Co binder and decarburisation of the WC particles. It was decided to investigate fragmentation of this material under kHz discharge assisted milling. Preliminary TEM investigations (Fig. 5) revealed mixed

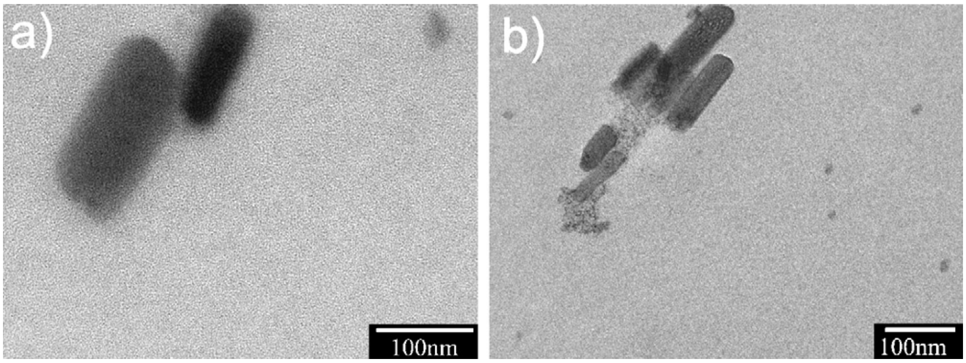

Fig. 4. Iron oxide nanorods observed in hematite, discharge milled in Ar/H_2.

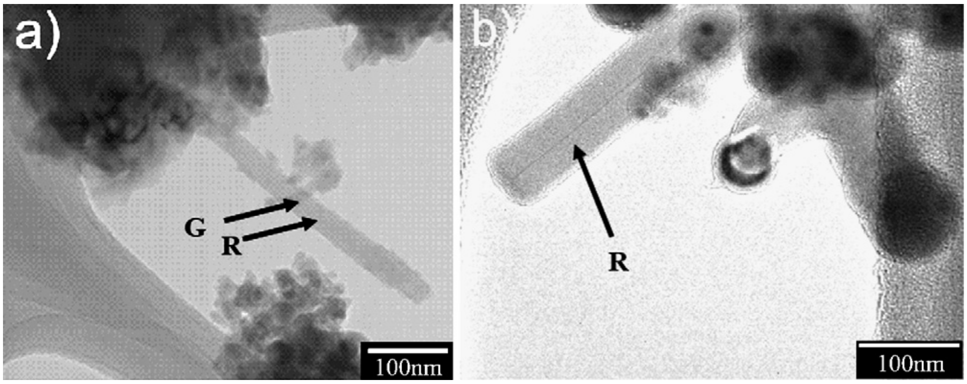

Fig. 5. (a) Carbon rich nanofragments observed in Co–WC hardmetal, first pulverised under liquid nitrogen and then discharge milled in Ar/H_2, features marked R in (a) and (b) are believed to be carbon nanorods while the object marked G in (a) is either graphite or carbon nanorods.

product, including large particles of WC and Co, regions of ultrafine and/or nanostructural product comprising a mixture of Co and WC and, surprisingly, a range of carbon rich nanotubes or graphite ribbons (marked G in Fig. 5a) and thicker, carbon rich nanorods (marked R in Fig. 5a and b). Further work is underway to investigate the discharge milling products, and the mechanism of formation of the carbon nanotubes and nanorods in Co–WC. However, conditions of decarburisation under the extremes of thermal plasma, in the presence of either Co or Fe catalyst (from the stainless steel milling chamber) are likely candidates to promote carbon nanotube and nanorod formation in Co–WC.

4. Conclusions

Electric discharge assisted mechanical milling of graphite in Ar/H_2, using a high frequency (kHz) pulsed power supply resulted in formation of carbon nanotubes with higher yields of carbon nanofragments than that resulting from discharge assisted milling of graphite at 50 Hz. Depending on the input current, high frequency, low current, discharge milling of hematite resulted in the synthesis of iron oxide nanorods and other nanoparticles. With increasing current discharge current the rod morphology ranged from individual nanorods and nanorod pairs, to wider, longer, joined clusters of parallel nanorods and, at higher currents, iron oxide spheroidal nanoparticles. Discharge milling of cemented Co–WC hardmetal resulted in a range of products, including micron and submicron fracture products, nanostructural regions of Co and WC, and carbon rich nanorods and nanotubes.

These results confirm that, depending on the starting powder, electric discharge mechanical milling under high frequencies (kHz) in an Ar/H_2 atmosphere can promote conditions favourable for the synthesis of a range of nanofragments, nanorods and nanotubes.

Acknowledgement

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