BALL MILLING MULTIWALL NANOTUBES TO IMPROVE ELECTRICAL CONDUCTIVITY

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ABSTRACT

Applications using nanotubes for electrical conductivity are expected to increase as material becomes available in commercial quantities at lower prices. Notably, the electrical arc process can produce low cost material and users have a choice of many aggregate sizes. Ball milling has been used to reduce the aggregates to tiny particles to improve dispersion to promote electrical conductivity. This is the first study which directly compares the electrical conductivity of ball milled multiwall nanotube materials to ground materials. DC conductivity measurements by two-probe method were determined for six aggregate sizes of multiwall nanotube materials. The samples were compressed at a pressure of 2.4 kPa, 65.9 kPa and 837 kPa in a hollow plastic cylinder using two metal plunges connected to a Flute multimeter. The conductivity of ball milled MWNT-A at room temperature was found to decrease from 10 ohm-cm when lightly pressed at 2.4 kPa to 0.3 ohm-cm at 65.9 kPa and to 0.1 ohm-cm at 837 kPa. Ball milled MWNT-A had the best conductivity of all samples at the highest pressure. Data defining the MWNT-A is presented including TEM, TGA, Raman, X-Ray diffraction and High Density

KEY WORDS: Ball Milling, Nanomaterials,

1. INTRODUCTION

NanoCraft, Inc has demonstrated high volume production of electrically conductive multiwall nanotubes. This study evaluates electrical conductivity changes of multiwall nanotubes as a result of ball milling.

Discoveries of multiwall nanotubes by Tennet in 1983 [1] and by Iijima in 1991 [2] have consistently led to the issue of dispersion. Nanotubes have the potential for wide range of applications spanning the areas of absorption, filtration, lubrication, super-capacitors, storage of methane and hydrogen, catalytic supports for methanol fuel cells, biomedical, field emission, additives for adhesives, toughing agents, electrical fillers for resins, paints and sealants, EMI shielding and many more. These applications all benefit from finer particle size, greater surface area and greater electrical conductance with lower loading factors. This paper will present data that demonstrates that ball milling improves electrical conductivity of multiwall nanotubes.

Ball milling is an established process for reducing material to a small size and several research teams have experimented with graphite and various forms of nanotubes. It has been reported that ball milling of graphite and thermal annealing can lead to formation of carbon nanotubes [3] although in minor quantity and poor quality. Another team has reported that ball milling of cup-stacked carbon nanotubes increased the number of accessible active sites and anisotropic properties at both ends [4] with some shortening due to breakage. Ball milling natural graphite fibers with alcoholic vapors has been shown to produce high electrical conductivity [5]

2. MATERIAL CONSIDERATIONS

NanoCraft, Inc provided material used in this study. Electric arc multi wall carbon nanotubes (MWNT-A) are produced in high volume and have the potential to be a low cost material. NanoCraft, Inc manufactures MWNT-A using a modified proprietary high volume electric arc process. The MWNT-A used in this study is exactly as produced with no additional processing except for grinding or ball milling.

2.1 Electron Microscope Photo, TEM

NanoCraft, Inc.'s standard multiwall nanotube product is a material consisting of nanotubes (20 to 30%), nano-onion like and nano-polygonal particles (50 to 70%), and variable fraction of graphite platelets. Electron microscope analysis TEM microphotographs reveal the nanotubes are 5 to 20 nm in diameter and 300 nm to 2000 nm long, as shown in figure 1. The nano-onion like particles are 20 to 60 nm diameter.

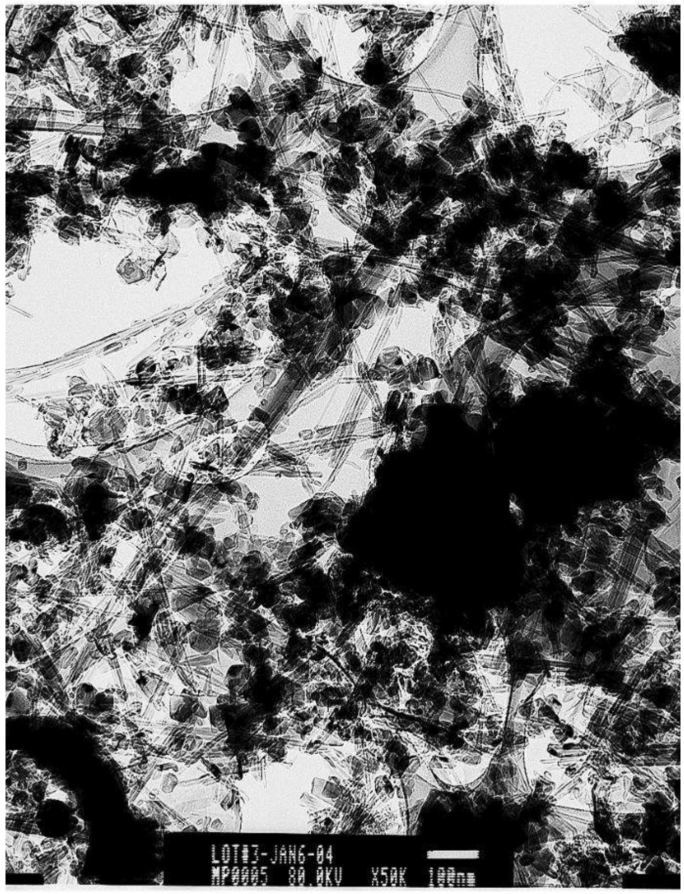

Figure 1: TEM of MWNT-A

2.3 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. MWNT-A is a high crystalline material that is resistant to temperature and oxidation. MWNT-A has the highest resistance against oxidation of all forms of multiwall nanotubes and its maximum oxidation rate is 785 degrees C as shown in Figure 2. This oxidation resistant property of MWNT-A suggests it would be very suitable material for high temperature applications.

There is little or no material loss before 600 degree C. This indicates that no measurable amorphous carbon is present in MWNT-A.

MWNT-A is produced without catalytic material. Note that there is only a small residual of less then 0.6% above 900 degree C demonstrating no metal catalyst is used in the process.

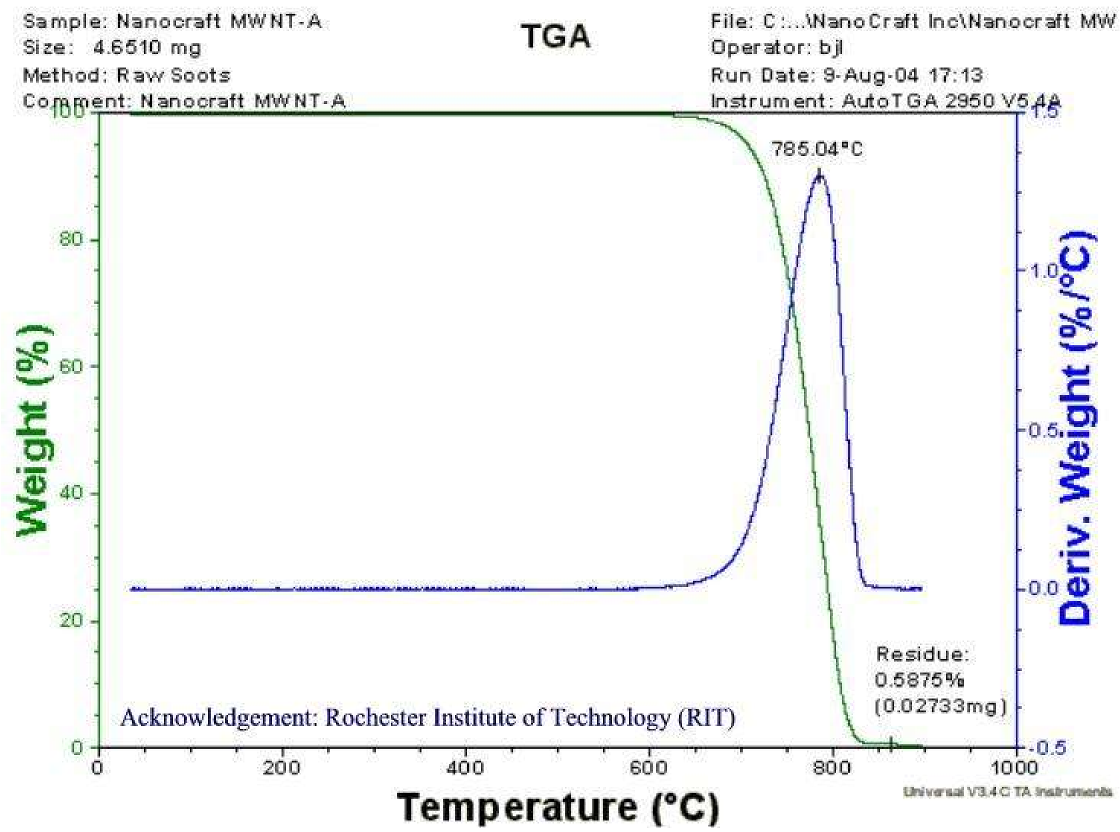

Figure 2: TGA of MWNT-A

2.4 X-ray Diffraction of MWNT-A

The MWNT-A material is further characterized by X-ray Diffraction as shown in Figure 3. Note the sharp peak at approximately 26 degree, which is characteristic of the graphite and carbon.

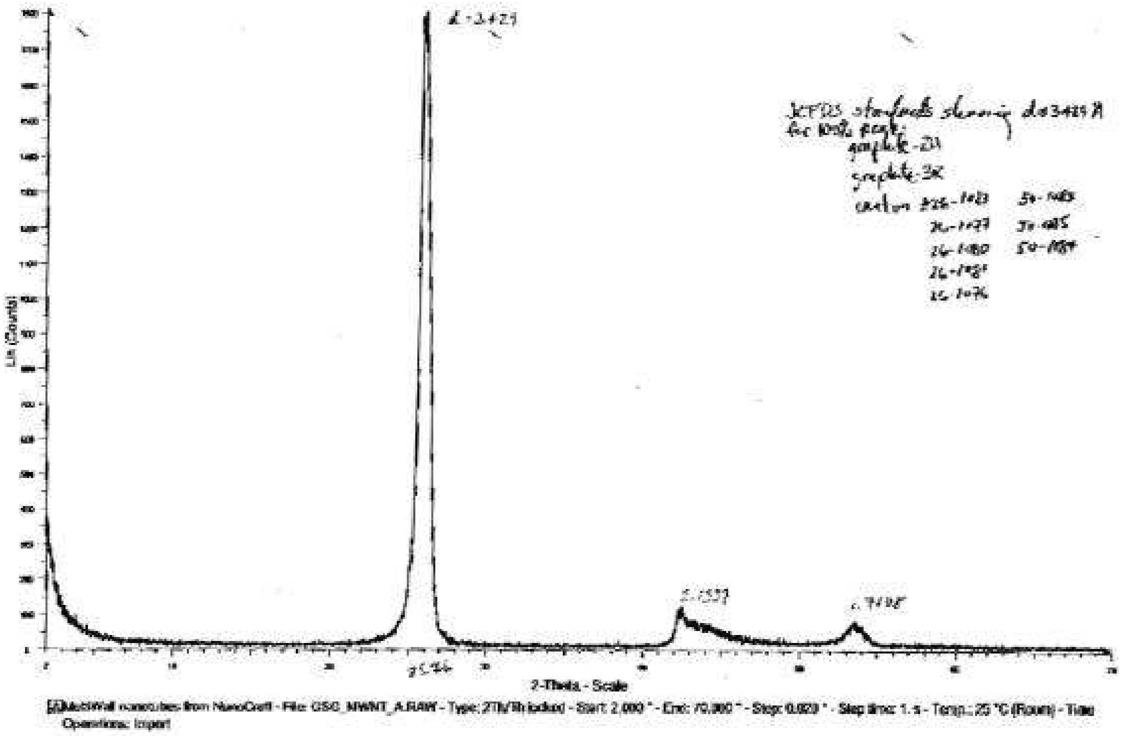

Figure 3: X-Ray Diffraction

2.5 RAMAN of MWNT-A

MWNT-A has a distinctive RAMAN signature as shown in Figure 4.

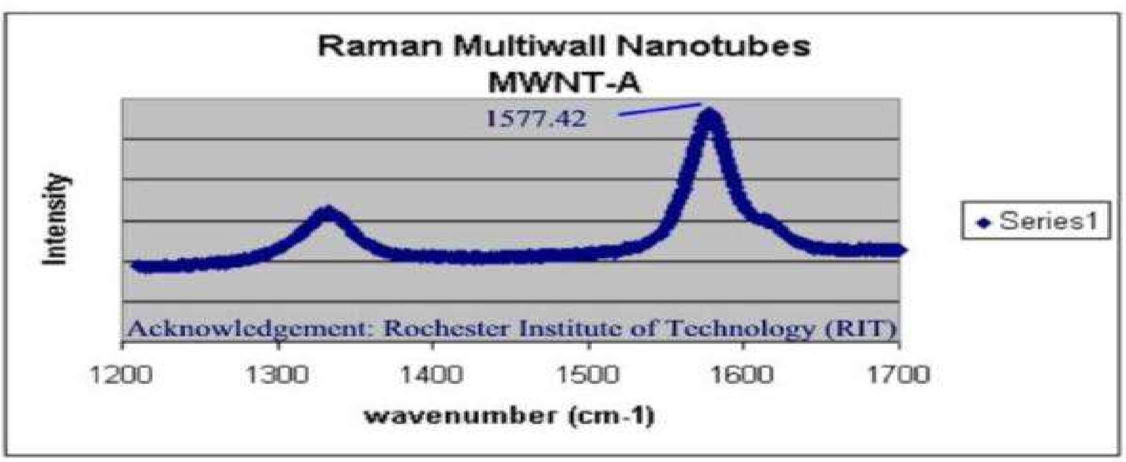

Figure 4: Raman

3. EXPERIMENTAL

3.1 **Electrical Resistance** Samples of six forms of MWNT-A were prepared and evaluated.

3.1.1 ***Sample Preparation*** Solid pieces of multiwall block formed as cathode deposit during electric arc process were processed to six forms. Materials were produced with mechanical devices and sized by screening. Ball milling was performed with a high intensity ball mill for 2 hours using 20 kg of steel balls. The forms are identified by size. 20 grams of each form were prepared. The six forms were:

- MWNT-A, NB — Solid form, 2 cm x 1 cm x 1 cm
- MWNT-A, 6 mm — 6 millimeter chips (6 mm x 1.0 mm thick)
- MWNT-A, 3 mm — 3 millimeter chips (3 mm x 0.5 mm thick)
- MWNT-A, 1 mm — 1 millimeter chips (1 mm x 0.5 mm thick))
- MWNT-A, GD — < 0.1 mm ground material (< 0.1 mm)
- MWNT-A, BM — Ball milled

3.1.2 ***Test Method*** DC conductivity measurements by two-probe method were determined for six aggregate sizes of multiwall nanotube materials. The samples were compressed at a pressure of 2.4 kPa, 65.9 kPa and 837 kPa in a hollow plastic cylinder using two metal plunges connected to a Fluke multimeter.

3.1.3 ***Test Data*** Table 1 – test data

Pressure Applied	***MWNT-A NB***	***MWNT-A 6 mm***	***MWNT-A 3 mm***	***MWNT-A 1 mm***	***MWNT-A 0.1 mm***	***MWNT-A BM***
2.4 kPa	0.1 Ohm-cm	1.5 Ohm-cm	1.6 Ohm-cm	1.8 Ohm-cm	3.8 Ohm-cm	10 Ohm-cm
65.9 kPa	< 0.1 Ohm-cm	0.5 Ohm-cm	0.5 Ohm-cm	0.5 Ohm-cm	0.4 Ohm-cm	0.3 Ohm-cm
837 kPa	< 0.1 Ohm cm	0.2 Ohm-cm	0.2 Ohm-cm	0.2 Ohm-cm	0.1 Ohm-cm	< 0.1 Ohm-cm

Table 1: Test Data

4.0 CONCLUSIONS

Ball milling solid MWNT-A bar increased the electrical resistance of MWNT-A by 100 fold from < 0.1 to 10 ohm-cm. However, when the ball milled form is compacted by light to moderate pressure the electrical resistance returns to the level of the solid form. Furthermore, the compacted ball mill form has lower resistance then all other chipped and ground forms when pressurized to 65.9 kPa and 837 kPa. This indicates that the ball milled MWNT-A can be compacted to form electrical contact of the particles with greater efficiency then the larger particle forms.

The conclusion of this study is that ball milling of MWNT-A improves the electrical conductivity and will lead to successful electrical conductivity applications of MWNT-A ball milled form.

5.0 ACKNOWLEDGEMENTS

The author wishes to thank Colin MacLean, a student of Dr. William G. Lamb, Winningstad Chair in the Physical Sciences at the Oregon Episcopal School in Portland, Oregon who assisted in collection of the resistance data during a visit to NanoCraft, Inc.

The author also wishes to acknowledge the collaboration with Professor Stephen Guggenheim of the University of Illinois at Chicago for X-Ray Diffraction and Rochester Institute of Technology (RIT) for the TGA and Raman.

6.0 REFERENCES

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