Bulk Carbon Nanotube Yarn Conductivity and Strength Enhancement Through High Temperature Annealing

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Introduction

Carbon Nanotube (CNT) yarn, CNTs collectively spun together into a bulk textile, is an emerging technology in niche electrical power transmission applications. High temperature annealing has improved CNTs in general as reported before[1], and may be a possible post processing step for improving the properties of bulk CNT yarn.

This study investigates annealing bulk CNT yarn spun directly from forest growth CNT arrays. Post processing annealing ranged from 1100 to 2700 °C in an inert environment. The high temperature treatment, resistance measurements were conducted as a function of temperature (100 – 900 °C) in high vacuum. Mechanical tensile testing, Raman spectroscopy, XRD analysis, and TEM were also used to understand the affect of annealing CNT yarn

Experimental Setup

The CNT yarn was subjected to various thermal treatment using two different annealing chambers. The first chamber, a Centaur furnace, heated the samples at 1100 °C for 1 hour, 12.4 kPa overpressure. Two atmospheres were attempted: pure argon and a 5% hydrogen argon mixture. Heat-treatments to 2000 to 2700 °C were completed in an MRF model 20x16-G-3000VG graphitization furnace with a 13.8 kPa overpressure of argon maintained during the heating and cooling.

After high temperature annealing, the CNT yarn resistance was measured as a function of temperature. The CNT yarn sample length was kept at 5.2 cm between silver painted copper leads. Contact resistance, however, was determined by measuring the open air resistance of multiple length samples. The interpolated resistance at zero length, or the contact resistance, was approximately 60 Ohms which does not exceed 5% of the total resistance.

For electrical characterization, the prepared samples were placed on top of an electric heater within a vacuum chamber. Before heating, the vacuum was maintained less than 3 µTorr. The sample heated in 100 °C increments from room temperature up to 900 °C and back down again. At every 100 degree increment, the sample remained at that temperature for 30 minutes to ensure thermal equilibrium between the sample and measuring thermocouples. With every sample run, there were two cycles to 900 °C, yielding a total of four different temperature sweeps (two up and two down). Typically, the first run had a different resistance response then the next three, most likely due to CNT out gassing. Only the data after this initial out gassing run was used for analysis. At each 100 degree increment, an Agilent 4284A Precision LCR meter measured the samples resistance at 20 Hz.

Linear density measurements were obtained by weighing the lengths of yarn after electrical testing on a Satorius Model ME36S microbalance with 1 µg resolution. Linear density and mechanical properties were measured on a Textechno Favimat tester with a built-in vibroscope linear density measurement attachment. Raman spectroscopy of the yarns was measured by a Renishaw inVia Raman Microscope. X-ray diffraction of the CNT yarns was performed using an image plate in a Statton camera at 53 mm (WAXD) and 300 mm (SAXS) using CuKα radiation at 40 kV and 150 mA.

Results and Discussion

In general, both with and without annealing treatment, the temperature dependence of the CNT yarn's resistance resembled the behavior of amorphous carbon — a semiconducting like, strictly decreasing resistance with temperature [2] – see Fig. 1.

When annealing the CNT yarn with the Centaur© furnace at 1100 °C, both the pure argon and argon hydrogen atmospheres led to a nearly identical increase in resistance. The Raman D to G ratio also remained nearly the same. A possible explanation for the degradation is that, with the Centaur furnace runs, sample heating began once the atmosphere was applied, which gave the CNT yarn little time to out gas volatile oxygen. With the graphitization furnace, samples had several hours to outgas before temperature was applied.

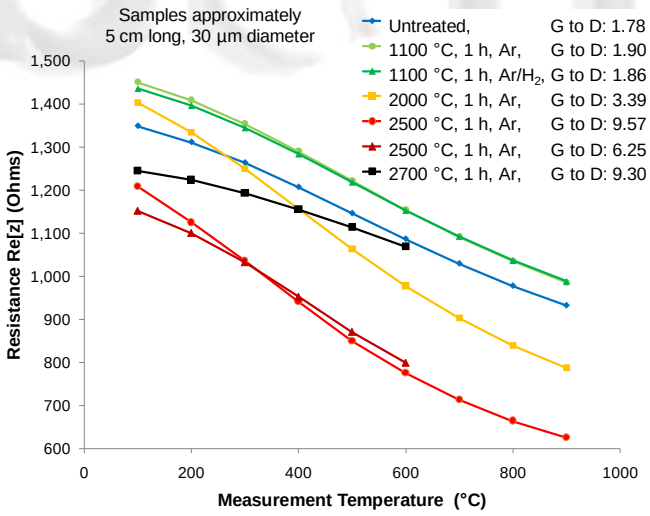

Fig. 1. Resistance versus temperature of CNT yarn previously annealed in various environments

Samples annealed with the graphitization furnace (2000 - 2700 °C) had at least a partial resistance decrease over the temperature range considered. Overall, annealing at 2500 °C, seemingly independent on dwell time, yielded the best results.

A summary of derived parameters are listed in Table 1. Note that these parameters are based on open air measurements before the temperature dependent electrical characterization. In addition, the contact resistance, measured earlier, was subtracted from the measured resistance. this produced the actual yarn resistance from which parameters, such as resistivity, were calculated.

The CNT yarn average diameter, determined by SEM, was utilized for the resistivity calculation. Derived density, used to calculate linear density, was measured by weighing and measuring the volume of the CNT yarn. The linear density measurements determined by the vibroscope and the microbalance methods agree closely. Activation energy was calculated by considering the linear portion of the Arrhenius plots, as the inverse of temperature approaches zero.

As the annealing temperature increased, resistivity decreased and activation energy increased. The G to D ratio increased, but so did the variance. As shown in the TEM images in figure 2, annealed outcroppings of CNTs are thinner, longer, and more defined. Quite possibly, the annealing not only removes amorphous carbon, but actually removes outer concentric CNT layers, which are likely more defective. . In addition, the degree of CNT graphitization increases. As a result, a more crystalline structure remains with greater conductivity.

The x-ray diffraction and Raman show few SWNTs. RBMs in the Raman spectra disappear after the 2000 °C heat-treatment. The WAXD is dominated by the graphitic (002) peak with very little lower angle diffraction typical of SWNTs. The small-angle scattering shows a peak in the scattering (not shown) for all yarns near 12-15 nm, regardless of treatment.

TEM shows the loss of amorphous carbon and thinner and straighter CNTs (Fig. 2). The widths of the CNTs in the right-hand TEM of figure 2 show the CNTs are fairly wide – typical of SWNTs that have expanded their diameter to the point where they collapse their center [3]. These types of SWNTs do not have Raman RBMs and show typical inter-planar spacing in WAXD consistent with our results. The sizes observed in Fig. 2 are also on the same order as the SAXS peak observed.

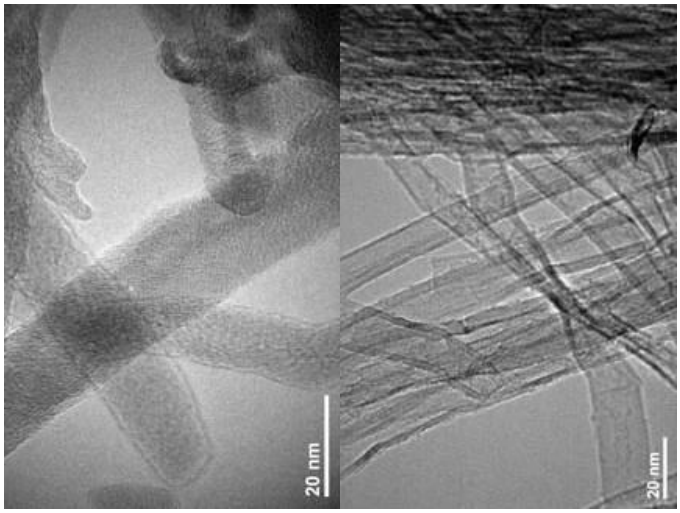

Fig. 2 Left: TEM of Untreated CNT yarn. Right: 2000 °C Annealed CNT yarn outcropping.

Conclusions

Annealing above 2000 °C improves the conductivity, Raman G to D ratio, and activation energy of the CNT yarn. TEM showed annealing produces straighter and thinner CNTs. The optimal annealing condition was 2500 °C for 1 hour in pure Argon. This condition produced a significant 70% increase in specific conductance of the yarn.

Acknowledgments DPA would like to acknowledge the support of AFRL via contract FA8650-05-D-5052 and Brian McMasters for operation of the Raman spectrometer and Tom Ekiert for operation of the balance. Also, thanks to William Lanter and Jennifer DeCerbo at AFRL/ RZPE for assistance with their vacuum chamber and LCR.

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Table 1. Parameters for the untreated and annealed CNT yarn.

Annealing conditions	Derived density	Linear Density		Modulus	Tenacity	Resistivity @RT	Conductivity per Linear Density @RT	Activation energy		G to D ratio
		Length and mass	Vibro-scope							
	(g/cm^3)	(tex or g/km)		(N/tex)	(N/tex)	(μΩ-m)	(S/g)	(kJ/mol)	(meV)	
untreated	0.95	0.60	0.64	17.1	0.39	15.2	110×10^6	4.51	46.7	1.78
1100 °C, 1 h , Ar	0.84	0.51	0.56	31.9	0.17	15.6	126×10^6	4.46	46.2	1.90
1100 °C, 1 h, Ar/H_2	1.12	0.69	0.60	30.5	0.47	15.7	92×10^6	4.36	45.2	1.86
2000 °C, 1 h, Ar	0.87	0.46	-	-	-	11.7	186×10^6	6.13	63.5	3.39
2500 °C, 1 h, Ar	0.85	0.49	0.58	28.5	0.60	10.9	187×10^6	6.08	63.0	9.57
2500 °C, 6 h, Ar	0.90	0.70	-	-	-	11.2	128×10^6	-	-	6.25
2700 °C, 1 h, Ar	-	-	-	-	-	-	-	-	-	9.30