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Ultrahigh Conductivity Umbilicals: Polymer Nanotube Umbilicals

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Abstract

It is estimated that over half of offshore Electrical Submersible Pump failures occur in the power cable string. Failures of this type cause marked increases in operating costs. The technology under development and discussed in this paper, a polymer sheathed double-walled carbon nanotube (DWNT) wire, is designed to replace copper transmission lines in the cable string and is to be demonstrated with a prototype umbilical. The difficulties with copper that lead to power string failure includes a) corrosion, particularly at wire terminations, and b) strength as ultra-deepwater, unarmored umbilicals' own weight. In addition to the high mechanical loads and extended service life requirement, offshore umbilicals deliver significant power to the sea floor. A technical solution to these difficulties that meets the requirements is a carbon-based wire with similar conductivity to copper and a fraction of the weight. To this end, the resources provided by the Research Partnership to Secure Energy for America (RPSEA), contract number 10121-4302-01, are being used to continuously produce DWNT in wire form and jacketed with a high temperature polymer. This we term polymer nanotube umbilical (PNU) cable. Since the wire is carbon-based, we anticipate minimal salt water corrosion with the conductor having 1/6th the weight of copper. Also, the DWNT conductor shall have greater tensile strength than copper and higher current carrying capacity. NanoRidge Materials, Inc., located in Houston, Texas, is the prime contractor and has subcontracted Rice University and DUCO, Inc. to participate in this endeavor. Professor Alan Windle, Cambridge University, UK, is a consultant on the contract. Representatives from Shell, Baker Hughes, Total, and DUCO, the project's cost share partners, comprise the Steering Committee and Working Project Group. Described in this paper are 1) our previous efforts, 2) the current state of the art, 3) our specific technical plan, and 4) progress as it relates to equipment and DWNT forming processes.

Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted considerable attention (O'Connell, 2006). They are comprised exclusively of *sp2*-hybridized carbon (same for graphite) in cylindrical form. Depending on the variety, these cylinders or tubes are between less than or equal to one nanometer to a few hundred nanometers. A single-walled carbon nanotube (SWNT) is a hollow cylinder with the wall being one carbon atom thick; whereas, double-walled carbon nanotubes have a tube-in-a-tube morphology. Metallic SWNTs have a reported current-carrying capacity of 10^9 A/cm^2 (Yao, 2000); this is 1,000 times greater than copper wire (10^6 A/cm^2). It is important to note, however, that bulk production of SWNTs yields a mixture of chiralities with their electronic properties being chirality-dependent (Jarosz, 2011). Therefore, as-produced SWNT consists of metals and semi-conductors; i.e., consists of a mixture of chiralities. Although progress has been made in selective production of metallic SWNT (Sundaram, 2011), the mixture of chiralities has complicated efforts to obtain 10^9 A/cm^2 in macroscopic carbon nanotube materials. DWNT have a current-carrying capacity equally as high if not higher than SWNT irrespective of chirality (Moon, 2007). This is a primary reason for the use of DWNT in this work. A plausible explanation for the higher current-carrying capacity is the mitigation of electron-phonon scattering due to intershell coupling. In addition to the noteworthy electronic properties, carbon nanotubes have exceptional mechanical properties. The tensile strength of an individual nanotube is approximately 22 GPa (Li, 2000); the tensile strength of copper is 0.25 GPa. Although translation of individual CNT measurements to bulk properites is a work in progress, Prof. Windle's group has formed carbon nanotube fibers with 6 GPa strength (Koziol, 2007). Tensile strength of fibers is a function of percent defects and voids. A key aspect of our effort is to minimize defects and densify the as-produced fiber. This is described in greater detail in the **Technical Approach** section.

Background

For some time, NanoRidge, in collaboration with Professor Enrique Barrera at Rice University, has researched the use of carbon nanotubes for electronic applications including electromagnetic induction (EMI) shielding, lightning strike mitigation, and power transmission. Due to the extraordinary electrical properties of SWNT, carbon nanotube/polymer blends were investigated. Although polymers tend to be electrical insulators, we envisioned adding SWNT at a loading greater than the percolation threshold thereby forming a conductive pathway. To maximize the electrical conductivity of a carbon nanotube/polymer composite, excellent dispersions are required. A great deal of trade secret know-how was developed in this area. We selected the widely used plastic polyethylene (PE), an insulator with electrical resistivity of 10^{15} Ω•cm. Excellent dispersions of SWNT/PE were manufactured and extruded into a wire. The electrical resistivity was improved to 10^{-2} Ω•cm. This is well within the EMI shielding regime. Attempts to decrease the resistivity beyond this were unsuccessful. For lightning strike mitigation (10^{-3} Ω•cm) and power transmission (10^{-6} Ω•cm), nanotube/polymer blends are impractical. The mechanism of electron transport in an individual carbon nanotube is ballistic conduction and has limited collisions. The transport mechanism as an electron moves from one carbon nanotube to another is hopping conduction. To decrease the resistance due to hopping, the nanotube-nanotube spacing must be minimized. An insulating polymer or macrovoid confounds attempts to promote nanotube interconnection and serves to increase the resistivity. We postulate that a wire comprised of high current-carrying capacity, sufficiently long DWNT with a minimum of voids and no contamination will have resistivity equal to copper (10^{-6} Ω•cm). A wire of this type, we believe, will also have mechanical properties rivaling the most tenacious carbon fiber (tensile strength = 6 GPa).

Technical Approach

The current RPSEA contract is a three-year, stage-gated effort with three technical deliverables and one milestone. At successful program completion, the following shall be realized:

- The carbon nanotube-based conductor has 10^{-6} Ω•cm resistivity.
- The polymer nanotube umbilical (PNU) cable is capable of operating at 5500 psig pressure.
- Formation of a prototype umbilical that uses the PNU cable for power transmission shall be completed. This is the milestone and shall be used for a demonstration program.

In order to satisfy the program objectives and meet the technical requirements of the deliverables, a DWNT conductor is the material of choice. In the previous sections, several of the key factors that led to the specification of a DWNT-based wire were described. These include high current-carrying capacity, consistent conductivity regardless of chirality, produced cleanly with minimal contamination, and free of insulating polymer and voids. An optimized DWNT conductor or wire is considered foundational to the success of this effort. Our technical approach can be broadly divided into the following technical thrusts:

- Production of DWNT
- Fiber spinning
- Post-processing
- Polymer jacketing
- Characterization and special testing
- Production of the prototype umbilical

The production of DWNT leads the way with the other tasks being initiated once DWNT is formed. Each of these is discussed separately below.

Production of DWNT.

The production method employed is a chemical vapor deposition (CVD) process conducted in a tube furnace (see section **Equipment**). The liquid feedstock is introduced to the furnace as a fine mist and a swept through the quartz tube by the hydgrogen carrier gas. The feedstock is composed of an iron precursor, promoter, and carbon source. Four thermodynamic processes must occur to form DWNT:

- The first process that occurs is the iron precursor, in which ferrocene dissociates to form iron atoms and organic fragmentation products. The iron atoms coalesce to form iron particles. Growth of the iron particles is restricted to diameters of between 5 and 10 nm. Smaller particles form SWNTs of variable chirality; larger particles form multiwalled carbon nanotubes (MWNTs). The particle diameter is controlled by temperature profile and carrier gas flow rate.
- The next major process that occurs is termed sulfur promotion. Thermal decomposition of a sulfur-containing organic compound forms sulfur. The sulfur complexes with the newly formed iron particles; this promotes nanotube growth and inhibits the further coalescence of iron.
- From here, the carbon source decomposes to form small organics such as methane.
- The final process is further decomposition of the organic compound on the molten iron surface. The carbon dissolves in the iron until satuaration is reached and then grows from the iron surface as a carbon nanotube.

To achieve the greatest possible conductivity and strength, the production conditions are controlled to restrict the iron particle diameter and inhibit growth of amorphous carbon. Amorphous carbon and residual metal are unwanted side products and are considered contaminants. Manufacture of a clean product is crucial to obtain the greatest possible conductivity and mechanical strength of the DWNT wire. This process can be conducted in batch or continuous mode.

Fiber Spinning.

The newly formed DWNT reaches the end of the reaction tube as a black elastic smoke or aerogel. In batch mode, the material coalescences on the terminal end of the quartz tube. In continuous mode, the elastic smoke is wound onto a cold member extended into the end of the production tube. The cold member is then removed from the furnace and the DWNT is strung onto a take-up spool. The spool is operated externally and at an RPM corresponding to the velocity or flow rate of the carrier gas. Professor Windle was the first to develop and describe (Li, 2004) this process. At this time, we are operating in batch mode until the take-up spool arrives (estimated delivery is January 18, 2013).

Post-Processing of DWNT Fiber.

Once the fiber is collected on a spool, several processes may be conducted off-line. These include purification, doping, drawing, twisting, weaving, and polymer jacketing. Purification and doping has been performed thus far with positive outcomes. Once the production process is optimized, purification may become unnecessary. Doping refers to treatment with iodine in order to increase the conductivity of the fiber. The initial fiber has a large volume fraction of voids. This is ideal for purification and doping but diminishes conductivity and strength. Densification by surface tension-based methods (Koziol, 2007), drawing, twisting, or wire-drawing dies shall be explored. Densification or drawing step is utilized to increase the DWNT alignment in the fiber direction and collapse the voids. This leads to improved conductivity and strength. This is the bare conductor and shall be tested extensively. The first deliverable is this conductive fiber with a resistivity of 10^{-5} **Ω•**cm. Larger gauge wires shall be necessary for the prototype umbilical. In this case, a stranded wire shall be produced from several individual fibers in a post-processing step. Polymer jacketing is described below.

Polymer Jacketing.

Once the required resistivity is achieved, the bare conductor shall be jacketed. We anticipate the use of high molecular weight polyethylene or some other high temperature polymer. The conductor shall be initially coated with polymer by a fiber-sizing step. Coextrusion shall be employed to produce the final jacketed wire. The jacketing serves to protect the conductor from abrasion. The resistivity of this material shall be determined at elevated pressure. The phase II deliverable is 10^{-5} **Ω•**cm resistivity at 5500 psig pressure.

Characterization and Special Testing.

We have specified and costed a copious amount of testing. Characterization of the bare conductor, jacketed fiber, and stranded wire are to be performed. Tests to be performed include electrical testing, tensile tests, fatigue testing, corrosion testing, temperature cylcling, thermal testing, and pressure testing. Resistance of the jacketed fiber to abrasion, crushing, and bending shall also be assessed. Strategies to terminate the wire to standard control boxes shall be developed.

Production of the Prototype Umbilical.

A demonstration project with a prototype umbilical shall be conducted in phase III. The deliverable for this phase is a wire with 10^{-6} **Ω•**cm resistivity at 5500 psig pressure. Several tasks are scheduled to achieve this performance. Production of the prototype includes forming a stranded wire with dimensions 10 mm^2 and 5 to 10 meters long. The optimized DWNT production process along with necessary post-processing steps shall be consolidated into a continuous process by this time. We anticipate a demonstration project by Q4 of year 3.

For a more thorough discussion of tasks and the project timing, please see **Appendix A – RPSEA Project Management Plan**, document number 10121-4302-01.01

Equipment

The equipment used on this project includes a tube furnace, two modified flanges, and spinning equipment. The furnace configuration and take-up spool position is shown in Figure 1.

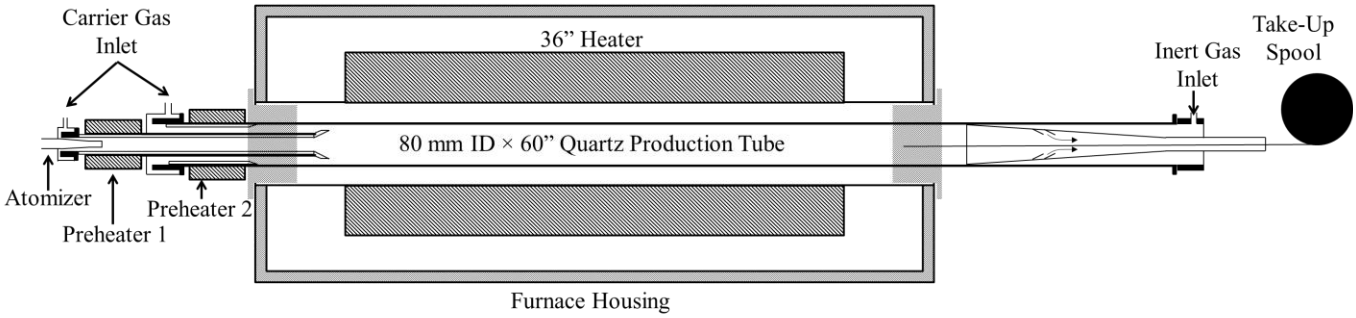

Figure 1. DWNT Production Furnace and Spinning Equipment.

The feedstock is introduced as a fine droplet mist through an atomizer. The mist is carried into a steel cylinder that is heated by the first preheater. The carrier gas is introduced at two locations. The first location is behind the atomized liquid to carrier the mist into the production furnace. The second location is between the steel cylinder and quartz tube and serves as a shroud gas. The combination of steel cylinder, gas inlets, atomizer, and the modified inlet flange, was designed by the team. The machined part is made of 316 stainless steel. High temperature gaskets are used to form gas tight connections. The quartz tube can be of variable dimensions. We are currently using a 60-inch long, 80 mm ID tube. The furnace has three heated zones that combine to form a 36-inch heater and is rated form a maximum temperature of 1200 °C. The modified exit port flange is currently under construction. The requirements of this flange include the abilities to:

- Allow the insertion and removal of a cylindrical cold member or rod
- Prevent hydrogen seapage
- Direct the hydrogen carrier gas and inert gas to a flare (not shown)
- Maintain an unobstructed port during the spinning operation

The variable rate take-up spool is a catalog item capable of constant tension and positioned external to the production furnace.

The production furnace is specifically designed to ensure selective formation of DWNT with a minimum of contamination (residual metal and amorphous carbon). Included in the design are three separate heating elements. This is to tightly control the thermal gradient because DWNT production is a series of four thermodynamic processes, as described above. The system is designed with separate flow controllers for the feedstock, gas inlet 1, gas inlet 2, and the inert gas. The heater temperatures and flow controller rates can be modified independently to obtain the optimized DWNT fiber.

Data and Results

The Rice team led by Professor Barrera with assistance from Professor Ajayan has formed DWNT fiber with 10^{-5} Ω•cm resistivity (Zhao, 2011). The fiber was doped with iodine and characterized. Improvements to this result are anticipated as the technology developed by the RPSEA project matures. Currently, we are producing DWNT at NanoRidge in batch mode. Transitioning to continuous operation is the first order of business. This is to be completed by the end of January 2013. Once fiber formed from the continuous process is in hand, assessment of post-processing steps shall be conducted. The phase I deliverable shall result from this study.

Conclusions

Double-walled carbon nanotubes are the material of choice to achieve the performance requirements of the RPSEA project. DWNT fiber shall be continuously produced by a specifically designed furnace. Post processing of the fiber shall yield the phase I deliverable. Once the resistivity is optimized, polymer jacketing of the bare conductor shall be performed. The jacketed wire shall be tested at pressure to complete the phase II deliverable performance requirement. Further optimization of the bare conductor in Years 2 and 3 shall be conducted to decrease the resistivity from 10^{-5} to 10^{-6} Ω•cm. This conductor shall be used to form a stranded cable of the requisite prototype umbilical size. A demonstration project is anticipated for Q4 in phase III.

Acknowledgements

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